Formulating Detergents and Personal Care Products

A Guide to Product Development

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Lambersart, France

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Foreword to the English Edition

When I first saw a translated version of this book, it immediately became clear to me that:

- This was a truly unique volume, and after an acceptable English text was developed,
- It would be an excellent addition to the publications by AOCS Press.

The book is unique in many ways:

- It is the most complete guide to detergent and personal care product development I have seen in 50 years of experience in the detergent area.
- It is written from the perspective of the formulator—and one with superior competence at that—who is central to the development of a product and sees it through all of the stages of conception, development, manufacture, consumer testing, and quality control.
- Beyond these, it covers relevant peripheral topics such as analysis, perfumery, packaging and laundering equipment, subjects not usually found in texts on detergents.
- It discusses as much theory as is needed to explain the "why" behind the many choices a formulator must make in the course of his activities.
- At the same time, it offers helpful and practical advice, which reflects the experience the author acquired in the course of his career.
- It represents a distillation of a lifetime of experience by a creative and respected practitioner in the field.
- It is written in an informal style, more like a series of instructive lectures rather than a dry review.

The U.S. reader should note that the book is written from a French perspective, with examples taken from the French market and French legislation. It is stronger on detergents than on personal care products—hence the sequence of these subjects in the title.

These limitations are minor compared to the scope and breadth which the book provides. The latter have inspired me to spend many hours on editing the original translation to make this book accessible to English-speaking readers.

Arno Cahn
Arno Cahn Consulting Services, Inc.
Pearl River, New York
May 2000

Foreword to the Original Edition

This book is about the essential contribution of detergent products to the development of cleanliness and hygiene in the world. The anguish caused by the last great epidemics at the beginning of the century (when Spanish flu is estimated to have killed 3 million people) is little more than a distant memory. Cleanliness and hygiene are now part of our civilization, providing both an effective barrier against the spread of disease and a large degree of comfort and even pleasure in our day-to-day lives.

This book explains the role and structure of detergents in the highly pragmatic manner that typifies its author. He provides a wealth of details on the components and how they can be put together to produce an optimum result. No matter how important the subject may be, in the same way that it is no longer necessary to know how a car works to be able to drive it, there is no obligation to read this book to be able to benefit from the cleanliness offered by detergents.

Having said that, there are many people other than the researchers, engineers, and technicians working in the detergents industry who would do well to read this work, including the following:

- Suppliers of raw materials, basic chemicals, petrochemicals, biological material, fragrances, and packaging
- Technicians in the textile, pottery, and porcelain industries
- Washing machine manufacturers
- Health authorities (dermatologists, poison-control centers)
- Government agencies (industry, hygiene, health)
- Professional and scientific organizations (chemicals, detergents, perfumery) and consumer and environmental associations
- Industrial and university libraries
- Teachers specialized in formulation, and their students . . . and all the rest of us who are not forbidden from taking an interest in these headed and tailed molecules that Coluche described as "strong small arms" ("des petits bras musclés") to hold back stains.

When Louis Ho Tan Tai asked me to comment about his book, I accepted willingly, knowing his skills and teaching abilities from the countless conferences and presentations at which I had the pleasure of observing him. We were fortunate to work together in Lever France for several decades, myself as Chairman in the later years, and Louis Ho Tan Tai as the free-floating technical electron. To better understand the author, I would like to highlight three characteristics that typify him:

1. In the family of researchers, he is one of a rare breed of "inventors" who not only observe new phenomena but are also capable of imagining how their apparently independent properties can be combined to produce innovation.

2. His acute listening skills, which allow him to understand a problem quickly and clearly and which give him the inspiration to find instantly at least half the solution. As the proverb says the rest is just trials, experiments, objective evaluation, combined with concentrated work, rigor and determination.
3. Finally, for Louis Ho Tan Tai, lonely understanding is a source of great frustration. His great skill has always been in sharing his knowledge, making complex concepts clear, and giving his listeners the comforting feeling that they have at last become intelligent.

It is doubtless in this spirit that Louis Ho Tan Tai decided to write his book, leaving some trace of a lifetime of hard work and passing on his vision of the many facets of detergency, while at the same time being conscious, as Copernicus said, that "knowledge is a living structure, never perfect" and that in the fullness of time, somebody else will come along to build our knowledge further.

J. Lier
Former Chairman of Lever France
President Prodimarques

Preface

During my career with Unilever, which lasted for about 30 years, of which 25 were spent in the Development Department of Lever France, I was fortunate enough to be personally involved in a wide variety of activities, such as basic studies, process development, product development, perfume studies, product performance evaluation, and physicochemical analyses. With such extensive professional experience, I feel a strong need to share my knowledge with others by writing this work.

Why write yet another book on detergents and personal care products? Indeed there are already many publications covering these areas, but they are sometimes purely theoretical, or they cover only limited categories of products, or they are simply out of date. The aim of this work is to cover both theory and practice, using the most recent knowledge, encompassing all of the relevant categories and products, and examining all aspects of the development of these products from concept stage to their launch onto the market.

During my professional life, I had frequent opportunities to speak at university conferences and seminars on one aspect or another of the subjects covered by this book; in all cases, my audiences were very interested in what I had to say. I was also fortunate to be able to train young managers in a pragmatic and didactic approach, and wrote a "Bible" for them in which they could find both the theory and practice of new product development. I believe that this book, which is more complete and up to date (without divulging proprietary information) should interest the universities, and students and engineers working in the industry. And why not also the less young who may wish to revise what they knew and may have forgotten with time?

In writing this book, I have had in mind my country of birth, Vietnam, and also all countries on the road to development. In a number of ways, this book should be of great help to their engineers because they may not have all of the information readily available, and obtaining it could be costly. In addition, a lack of knowledge may lead to mistakes involving technology, the environment, and the safety of workers and consumers.

If only because of the level of advertising (particularly on television), consumer products including detergents may have a poor brand image at least among certain segments of the population. Through this book, I aim to show the extent of research and development, and the industrial equipment resources that lie behind the products concerned and support the efforts by the main manufacturers to put quality products that are safe for their users and that respect the environment onto the market.

When I discussed my project to write this book with my friends, all of them encouraged me strongly, and I thank them for this and for their support. We will now offer an overview of the different parts of this book so that the reader can understand clearly which subjects are dealt with and go directly to the chapters that may be of particular interest.

The introduction to the work outlines a number of generalities one must be familiar with in order to understand the world of detergents and its evolution. These include the history, the world markets, details of the stages in the development of a product, and consumer habit surveys.

The first part deals comprehensively with the products. It seemed important to dedicate a complete chapter to surfactants, which are present in all products. The other main ingredients making up a detergent are also dealt with separately in the Chapter 2. The following chapters deal with the different categories of products, including types of problems (stains) encountered, formulation principles, and the products themselves, including examples of formulations. This is a vast area, covering the cleaning and care of textiles, dishes, and other hard surfaces (floors, kitchens) and the care of a specific surface, our bodies, with bath and shower products, shampoos, and toothpastes.

Because the range is very large, we restrict ourselves to the main products and leave aside, intentionally, the smaller products or associated product categories such as pretreatment products for clothes or cosmetic products.

The second part covers in detail subjects that are common to the whole industry of detergents and personal care products, including performance testing, manufacturing processes, perfumes, packaging, analytical methods, and consumer tests. Quality assurance and environmental safety issues are also covered.

The book would not be complete if it did not look into the future. The world of detergents evolves continuously as new molecules and new product concepts appear every day. The trends of today that give clues to the products of the third millennium are examined in the final chapter.

That summarizes in a few stages the main contents of this book. We think the book contains enough material so that all of its readers can easily find the parts that fit their needs without losing time reading what is not of interest to them or searching in numerous works that may not at times even be available.

Enjoy the reading!

Louis Ho Tan Tai
Lambersart, France

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Introduction

A Little History . . .

It is not our intention to spend much time looking at the history or to trouble the reader with useless dates. However, it did seem of interest to us to summarize briefly how detergents have evolved from their ancestor (soap) to the products we know today.

Soap is the first detergent known to our civilization. Earlier research had attributed soap to the Gauls, until the discovery of a "hypocaust," or underground chamber in which water was heated; this earliest ancestor of today's bathroom was discovered in the Indus Valley (urbanized by 2500 B.C.). From the same period, Sumerian clay tablets gave the following recipe for soap making: wood ashes heated with oil.

Our famous Gallic ancestors had therefore discovered nothing new in this area, which did not prevent a number of their descendants from leaving their names associated with significant discoveries. Honor has been saved!

A number of Egyptian papyruses also mention how to make soap, i.e., natural soda known as *Trona* (which formed a crust around the edge of certain lakes) that was mixed with fats.

Even though its manufacture was simple, soap has remained for centuries a luxury product used for washing, a cosmetic, and even a medicine!

It took the efforts of two French scientists to turn soap into an everyday product. At the end of the 18th century, Leblanc discovered that soda could be produced from sodium chloride; some years later, Chevreul explained the chemical reaction between alkalis and triglycerides. From then on, as industrial manufacturing became easier and better understood, the use of soap became general. Soap lost its image as a luxury product reserved for the privileged, becoming an everyday product to the point that with the increase in population and living standards, one of the raw materials necessary for soap making became scarce, leading in turn to the replacement of animal fat by vegetable oils. During this period, many factories started operations around the Mediterranean area, giving birth to the famous "Savon de Marseille."

Although soap has wide application, it has definite limitations when used on its own. The principal drawback is the formation of very disagreeable *calcium* (lime) soaps. An early improvement came with the addition of sodium silicate, which both softened the water and eliminated iron ions that caused textiles to yellow.

A second stage was completed with the observation that when clothes were dried in direct contact with grass in the fields they were whiter (thanks to the combined action of light and *the oxygen of the air*), giving rise to the idea of creating an ingredient capable of reproducing the phenomenon. The arrival of sodium perborate in detergent formulations was in itself a mini-revolution. It was Henkel in Germany who first

produced a product containing *per*borate and *sil*icate, and the name of the brand was ready-made: *Persil* was born. At the same time a Marseillais (inhabitant of Marseille) named Monsieur Ronchetti had registered the Persil brand name, which he subsequently sold to Unilever, the current brand owners in France and the UK. Henkel owns the brand in other countries, including Germany, Benelux, Italy, and others.

Subsequently, scientists turned their attention to replacement products that would be even more effective than soap and that could be obtained through chemical synthesis. Fritz Gunther of BASF managed to make the first synthetic detergent by the alkylation and then sulfonation of naphthalene. However, the carbon chain of the alkylnaphthalene molecule was too short to give adequate detergent properties. It took another German (Bertsch) to discover that the esterification of castor oil fatty acid, followed by sulfonation, produced a substance with excellent wetting properties (butyl ester sulfonate) but still with inadequate cleaning properties. Given that one of the main characteristics of a researcher is pugnacity, Bertsch and his colleagues succeeded some years later in producing excellent detergents by the sulfation of fatty alcohols.

Thus, fatty alcohol sulfates were born into the world of surfactants. We should mention in passing the names of two other Frenchmen, Bouveault and Blanc, who invented a process to manufacture fatty alcohols by reducing the corresponding fatty acids with sodium. Unfortunately, the production cost of fatty alcohols was too high. The real beginning of the synthetic detergent era came when another German, W. Schrauth, managed to synthesize fatty alcohols by the catalytic reduction of fatty acids with hydrogen under pressure. The fatty alcohol sulfates were then used in the manufacture of detergents for clothes laundering (general purpose and for more delicate textiles, i.e., "fine wash"), dishwashing, and cosmetics.

During the Second World War and by force of circumstances, research changed direction; animal and vegetable fats were no longer available and researchers' attention turned to petroleum derivatives. In 1946, a further important step was taken with the arrival of a new raw material that was neither too expensive nor too aggressive, alkylbenzenesulfonate (ABS), which could efficiently replace soap and the soap-based powders then used for household cleaning. Procter & Gamble was first to use it in the detergent Tide in the United States. In Europe, synthetic surfactants, especially tetrapropylenesulfonate, were introduced and progressively replaced soap in detergent products during the 1950s. Lower sensitivity than soap toward hard water, combined with excellent effectiveness at an affordable price, have made ABS the best known surfactant after soap.

Other molecules were discovered in the years that followed, notably the nonionic family such as fatty alcohol ethoxylate and nonylphenol ethoxylates. Nevertheless, ABS remained the main surfactant, and its development continued into the early 1960s when other concerns began to appear, notably ecological considerations.

Many readers will probably remember the pictures of huge quantities of foam floating on our rivers. It became necessary to do something, and ABS, with its

poor biodegradablility, was condemned—at least in its original form. The solution was found by replacing tetrapropylene with linear chains, i.e., LAS (linear alkylbenzenesulfonate) replaced ABS. Little by little, laws were introduced prohibiting the use of ABS, first in Germany, then in Italy and Japan. In other countries such as the UK, agreements were signed between industry and government limiting the use of ABS.

In parallel with this evolution of surfactants, other improvements were made in the composition of detergents, including the replacement of sodium carbonate by more effective complexing agents such as sodium diphosphates (or pyrophosphates), followed after the Second World War by sodium triphosphate [or sodium tripolyphosphate (STPP)], which is still widely used today, even though environmental constraints in some countries have made zeolites more attractive.

Gradually, formulations have become more sophisticated with the addition of antiredeposition agents, optical brighteners, and enzymes (1968).

In 1978, a further step was made in bleaching thanks to Lever France, which introduced a bleach activator, tetraacetylethylenediamine (TAED), that "boosted" perborate performance, thereby opening the door to a reduction in wash temperatures. In addition, and in random order, we can also mention the development of foam control agents, certain polymers (soil release, antiredeposition, and others), and new enzymes effective on different kinds of stains.

It is not only product formulations that have progressed; physical appearance has been transformed, so that we find concentrated powders, tablets, and liquid detergents alongside conventional powders. Packaging has followed the trends, adapting itself to new product forms and new needs (e.g., mini-boxes or eco-refills), all to meet consumer needs.

The Market of Detergents and Personal Care Products (1)

Detergents and Soaps

A distinction must be made between developed and developing countries because their needs are not the same. In developing countries, soap remains the main (and often only) detergent for almost all types of cleaning. Toilet bars without soap [nonsoap detergent bars (NSD)] are widely used in the Philippines (sometimes with the addition of perborate/TAED and enzymes) and in India. Detergent pastes also exist, particularly in Indonesia.

In developed countries, the range of products is much wider to meet specific consumer needs. For example, we find the following: (i) products to wash everyday clothes ("heavy duty" products), products for delicate articles ("delicate fabrics" products), and products for colored textiles; (ii) fabric softeners (with varied perfumes, colors, and types of packaging); (iii) household cleaners that perform better and are better adapted to the different surfaces found in homes (e.g., tile, enamel, glass, or ceramic); and (iv) new types of products for personal care (e.g., shower and bath products or non-soap toilet bars).

TABLE I.1
World Production of Detergent Products[a]

	1991	1992	1993	1994	1995	1996
Hard soap	5149	5095	5035	4995	5084	5072
%	24.4	24.5	24.3	24.1	23.8	23.7
Detergent bars	1208	1277	1289	1278	1323	1339
%	5.7	6.1	6.2	6.2	6.2	6.3
Detergent powders	12,904	12,675	12,664	12,555	12,859	13,245
%	61.3	60.9	61.2	60.7	60.1	62
Pastes/gels	210	213	222	312	341	359
%	1	1	1.1	1.5	1.6	1.7
Liquid detergents	1595	1536	1484	1544	1797	1357
%	7.6	7.4	7.2	7.5	8.4	6.3
Total	21,066	20,796	20,694	20,684	21,404	21,372

[a]Production is given in 1000 T, excluding industrial detergents.

Table I.1 summarizes world production of different categories of products. We can see that >60% of world production is in powder form. Soap is relatively stable (24.4% in 1991 and 23.7% in 1996). This is perhaps surprising for this "ancestor" from the distant past, but its dominance is explained in large part by its strength in developing countries.

These production volumes represent an average consumption of ~4.5 kg detergent/(person · y). This average figure hides enormous variations between developed and developing countries as is shown in Figure I.1 for detergents.

Figure I.2 shows the development of concentrated detergents in the world between 1991 and 1996. According to this chart, concentrated powders are increasing their market share to the detriment of conventional powders.

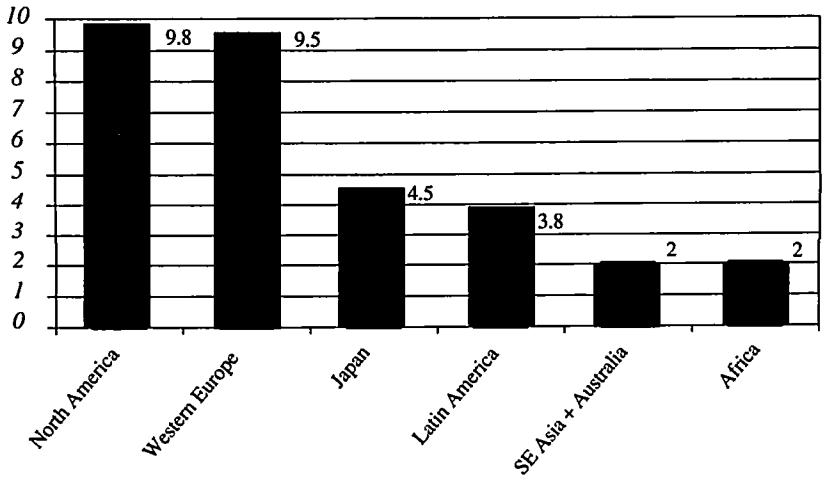


Fig. I.1. Detergent consumption [kg/(person · y)].

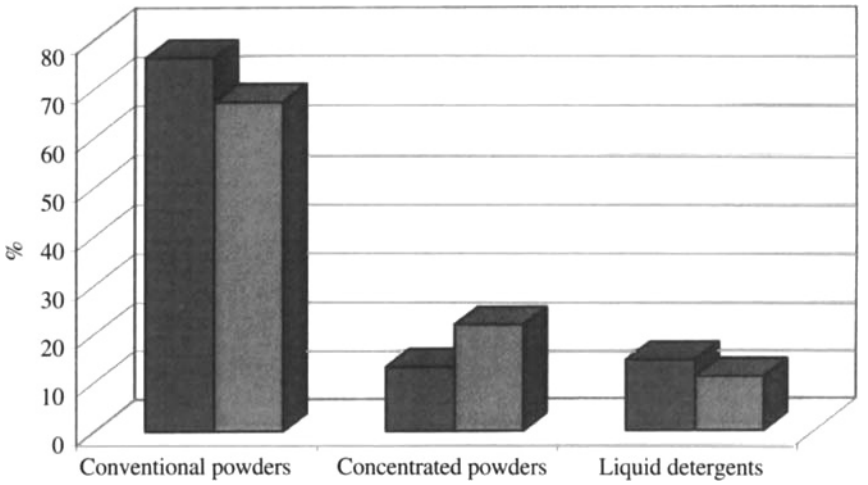


Fig. I.2. Development of concentrated detergents (by volume) in the world. , year 1991; , year 1996.

However, this trend is not the same in all countries. As we can see in Figure I.4 and Table I.2, in North America, Japan, and Germany, a large reduction in conventional powders has occurred, whereas in other countries they remain predominant. For liquid detergents, a drop in volume has occurred in Europe. This drop is

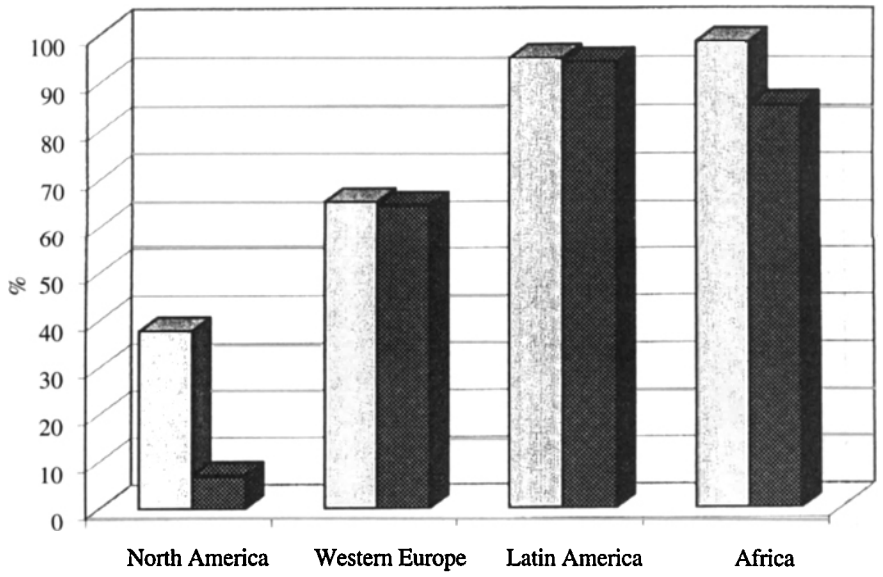


Fig. I.3. Conventional powders market. ❑, year 1991; , year 1996.

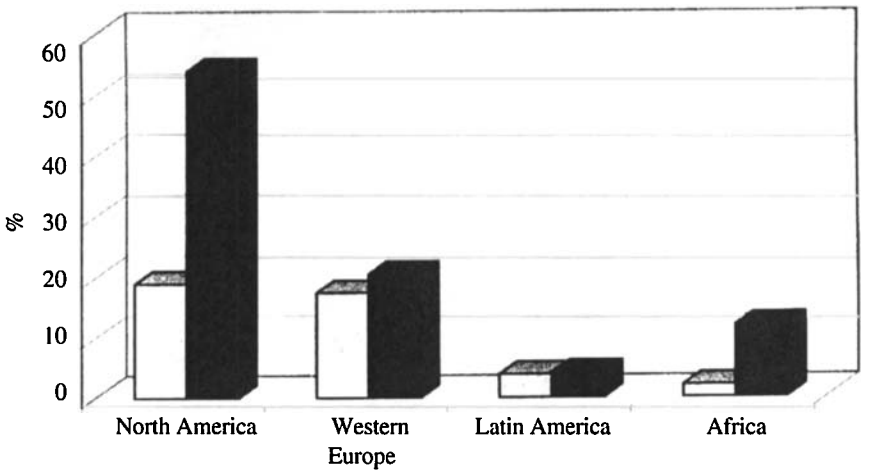


Fig. I.4. Concentrated powders market. ❑, year 1991; ■, year 1996.

not compensated by growth elsewhere because market shares remain low in developing countries compared to those for conventional powders (4.5% in Latin America, 3% in Africa).

Table I.2 gives the main detergent producing countries in 1996.

Shampoos and Toothpastes

The comparison of these product categories with detergents can be done only on the basis of monetary value. Figure I.5 gives an example for Western Europe.

TABLE I.2
Main Detergent Producing Countries in 1996[a]

	USA	China	India	France	Germany	Brazil	Japan	Mexico	Spain
Conventional powders	3.6	90.4	98.0	65.4	47.7	99.6	9.4	96.4	84.7
Concentrated powders	54.7	9.6	2.2	13.2	46.6	—	82.5	0.5	6.8
Conventional liquids	0.5	—	—	15.5	2.7	0.4	3.0	3.1	7.2
Concentrated liquids	41.2	—	—	5.9	3.7	—	5.1	—	0.1
Tablets	—	—	—	—	—	—	—	—	1.2
Tonnage (1000 T)	2453	1670	857	634	634	614	569	539	415

[a]Values are percentages.

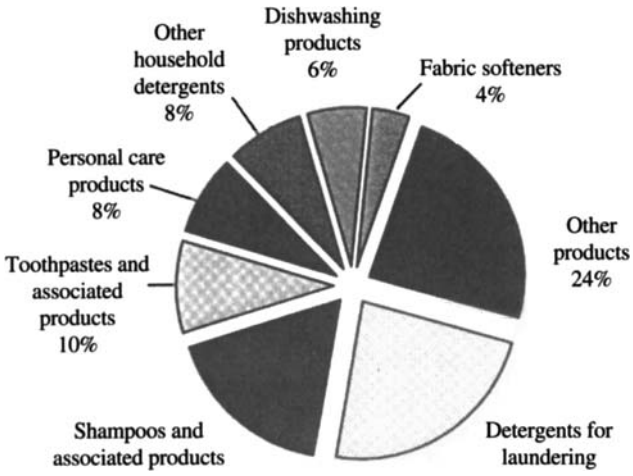


Fig. I.5. Split of the European market in 1996 (% value).

Shampoos. Figure I.6 shows the trend in worldwide production of shampoo and conditioners from 1991 to 1996. According to these figures, we can conclude that there have been no great variations in this market during the last 6 years.

Figure I.7 shows the distribution of shampoos and conditioners in different countries in 1996.

The primary production areas for shampoos and conditioners were North America, Europe, and South America. It is of interest to note that in Europe, the consumption of conditioners is smaller than in the Americas.

Figure I.8 gives the consumption of shampoo [kg/(person · y)]. Here again, we see enormous variation between developed and developing countries.

Worldwide toothpaste production. Figure I.9 shows the trends in worldwide toothpaste production between 1991 and 1996.

As is true for other products, there are great differences in consumption patterns in different countries, as illustrated in Figure I.10. As we will see in Chapter 10, these differences have a large influence on dental problems in developing countries.

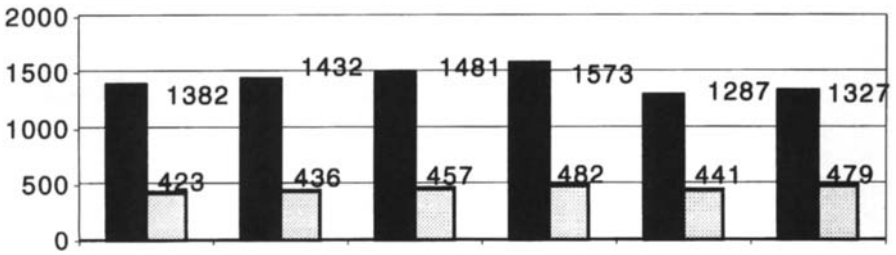


Fig. I.6. Production of shampoos (■) and conditioners (■).

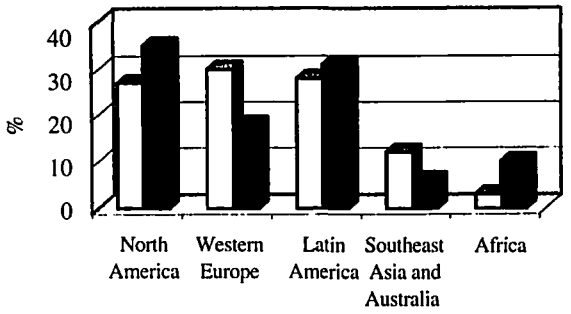


Fig. I.7. Distribution of the production of shampoos (□) and conditioners (■) in the world in 1996.

Stages in the Development of a Detergent: The Role of the Formulator

Before a new product appears on the market, it will have been the subject of many months (or even years) of investigation and testing of all sorts. For the "developer," who is really a "formulator" in the case of detergents, the key issue is to transform a consumer need into a finished product.

This means that above all, the developer must have a good knowledge of consumers, their habits, their problems, and, in particular, their needs. All of the major detergent manufacturers make extensive use of market research to obtain this information. If the developer is not in tune with consumer needs, the product will not be a success on the market, irrespective of the technical skills demonstrated. We will look at this problem in more detail later in this introduction.

Once a new concept has been clearly defined by the marketing department, the formulator can begin work. Each new product is a challenge that must be met successfully. In this race against time (in general, big financial interests are at play, particularly because the competition to be first onto the market is intense), the for-

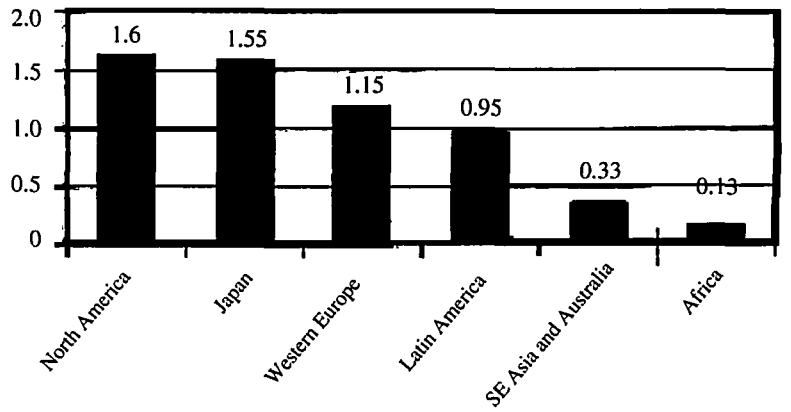


Fig. I.8. Consumption of shampoos [kg/(capita · y)] for 1996.

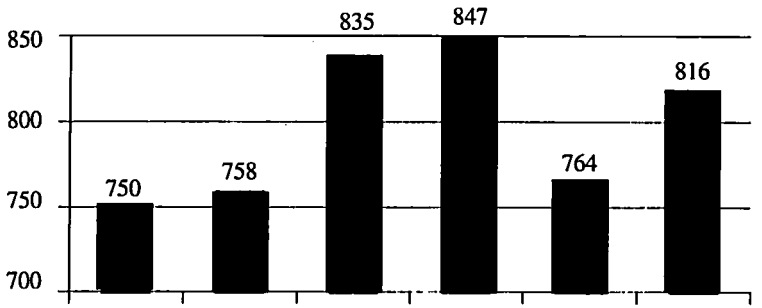


Fig. I.9. Worldwide toothpaste production.

mulator becomes the focal point of a whole organization involving almost every department in the company, as is shown in Figure I.11.

- The central research laboratories supply the formulator with the highest level of current information in the relevant area, and can also advise on the status of existing patents that could either impede product development or that can be used. They can also advise on registering a patent if there is a discovery during the development.
- Raw material suppliers must respect the specifications defined by the formulator once the choice has been made.
- The quality of the finished product depends above all on the quality of its component ingredients.
- In general, several suppliers are contacted so that the production of the new product is not only dependent on one supplier (in case there should be technical or social problems, for example). This is why all raw materials must have at least one substitute product.
- Selection criteria for the different ingredients (including purchase price) are discussed with the purchasing department of the company.

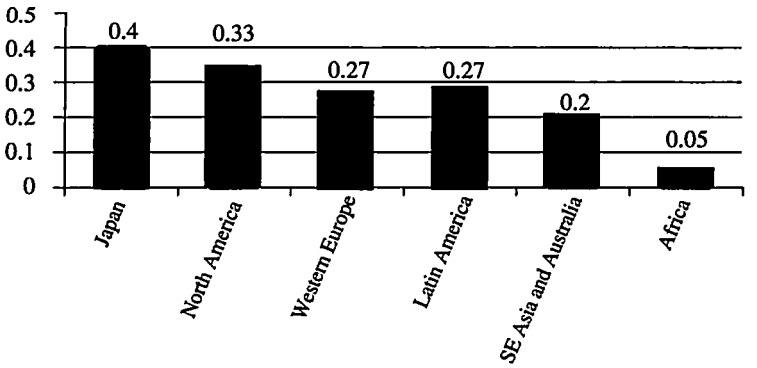


Fig. I.10. Consumption of toothpaste [kg/(capita · y)] for 1996.

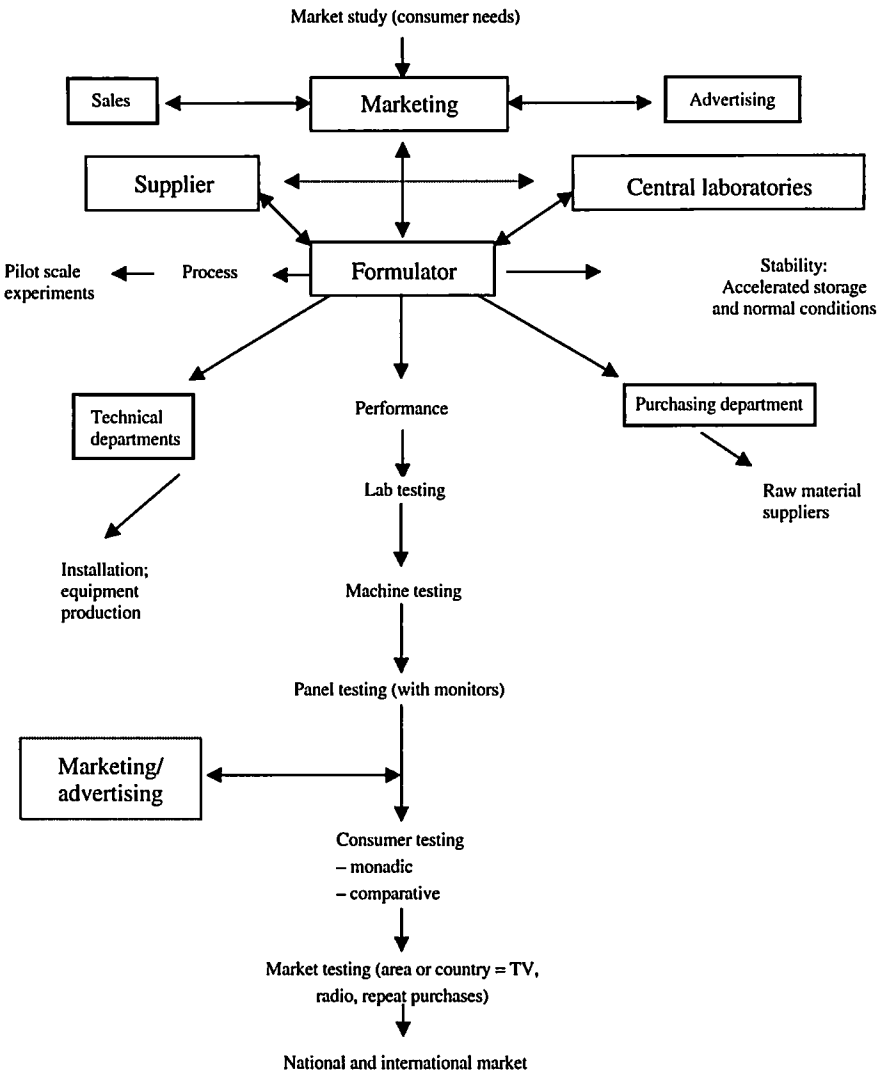


Fig. I.11. Steps in the development of a product.

- Once the formulator has developed the product in the laboratory, the person responsible for the manufacturing process decides how the product should be made, starting in a pilot plant and moving to a commercial scale operation (this concerns both the product itself and its packaging).
- The formulator will work with the technical service team to develop the new production unit, a responsibility held until such time as all of the problems have been resolved. Production of the new formulation then becomes a routine part of normal production.

- The new production unit will be subjected to accounting scrutiny to determine production costs (purchase and depreciation of machinery, raw material costs, manufacturing costs, including labor, energy, and so on). These production costs will be used subsequently to calculate the selling price of the future product.

Of course, at each stage of production (from the delivery of raw materials until the product leaves the factory gates), the department responsible for quality will ensure that the specifications are strictly followed.

Generally speaking, detergent and personal care product manufacturers are not producers of raw materials or packaging. These are manufactured by specialized chemical and packaging companies. However, there is usually very close cooperation between the two parties; for example, if the manufacturer discovers a new molecule or synthesis process, the chemical manufacturer will be asked to produce it on a commercial scale (often with an exclusivity contract). Similarly, when the product requires particular packaging features, the packaging manufacturer will be asked to produce the required specification. The entire process is dictated by investment costs and costs of production. It is sometimes more profitable to buy semifinished products. For example, the fact that the Philippines produces large amounts of coconut oil is not a sufficient reason for detergent manufacturers to put in their own production of fatty alcohols. Similarly, soap manufacturers in Southeast Asian countries that produce coconut oil, palm oil, and palm kernel oil do not necessarily have their own soap-making line because soap production costs will often be lower and quality higher when soap is sourced directly from a major fatty raw material supplier.

Thus, the creator, developer, or formulator plays the role of the conductor of an orchestra who must listen to the playing of each of the instruments!

Consumer Habit Studies

If the daily work of the formulator is to develop new products and continuously improve existing products, this can be achieved only with complete familiarity with the target audience, i.e., the consumer. It is consumer behavior that guides the formulator in continuous efforts to do better. Consumer habits and use of household detergents must be studied on a continuous basis, i.e., how consumers go about cleaning (whether laundry, dishes and hard surfaces, or personal hygiene), what problems are encountered, and what the user's expectations are. A few examples will illustrate this point.

What would be the point of including an expensive ingredient to deal with fatty stains if consumer habit surveys showed, for example, that fruit stains were *the* problem for 90% of consumers? Stains in France are ranked as follows:

- very difficult: oil, ink, grass, fruits
- difficult: tomato sauce, sauces, vinegar, blood

Why develop a formula that requires high dosage levels to be efficient when we know that only half the recommended amount will be used? Why use a large

quantity of fluorescers (fluorescent whitening agents) in a formula that will be used only for colored and synthetic articles?

These examples (of which there are many more) help us to come to the following simple conclusion: To help the formulator, it is absolutely essential that regular consumer surveys be conducted.

The speed of change is such that it is now necessary to conduct a major survey of habits every 2 y (some years ago, every 5 y was considered sufficient). These surveys are long and costly, and have to be conducted in all countries in which the same product is sold—detergent X will not be used in the same way by Mme. Dupont in France as by Sra. Sanchez in Spain.

Methodology

We will look at only one type of survey here, i.e., laundering, which is the most important.

1. Several hundred households are recruited, forming a sample that is representative of the target population.
2. A general questionnaire will provide the main information, i.e., profession, age of people in the home, brand and model of the washing machine and its age, brands and types of detergents used regularly, where they are stored, water hardness, and so on.
3. For every wash load done, whether by hand or by machine, during the duration of the research, the consumer fills in a diary with the following information, for example:
   - *Wash load:* cottons/synthetics, whites/colors, and the degree of dirt (particularly staining)
   - *Wash cycle used:* with or without prewash, temperature, economical or not, half-load or not
   - *Product used:* general purpose or specialized for whites or colors
   - *Dosage:* quantity used, whether weighed or measured into the machine, decided by the distributor or a dosing device in a machine; if a device, where this was placed—under the clothes, in the middle, or on top?
   - *After the wash*: how cleanness is judged, condition of the clothes, absence of stains.

Wash Frequency

The above information is generally completed by in-home interviews during which the researchers obtain further important information: (i) clothes sorting: how clothes are sorted (by type of fiber, color, dirtiness, or stains); (ii) pretreatment: use of stain removers, prewashing by hand, which articles are treated and where (for example, the collars and cuffs of shirts); (iii) other additives, such as anticalcium products (brand, type, dosage), chlorine bleach (quantity), fabric softener (brand, type, dosage); (iv) after washing: drying (machine or air), ironing, storage.

In total, tens of thousands of wash loads are closely observed and recorded. Figure I.12 shows the complexity of the "simple" task that is laundering; to wash clothes requires a whole series of decisions, which are often not consciously realized by the person performing the task: "Is my wash white or colored, relatively clean or very dirty; which machine program do I use; how much do I rinse; are there too many articles to use a lower water setting; should I use an all-purpose powder; how much do I add; should I add bleach and softener; can I dry the clothes in an electric dryer; How do I iron them?"

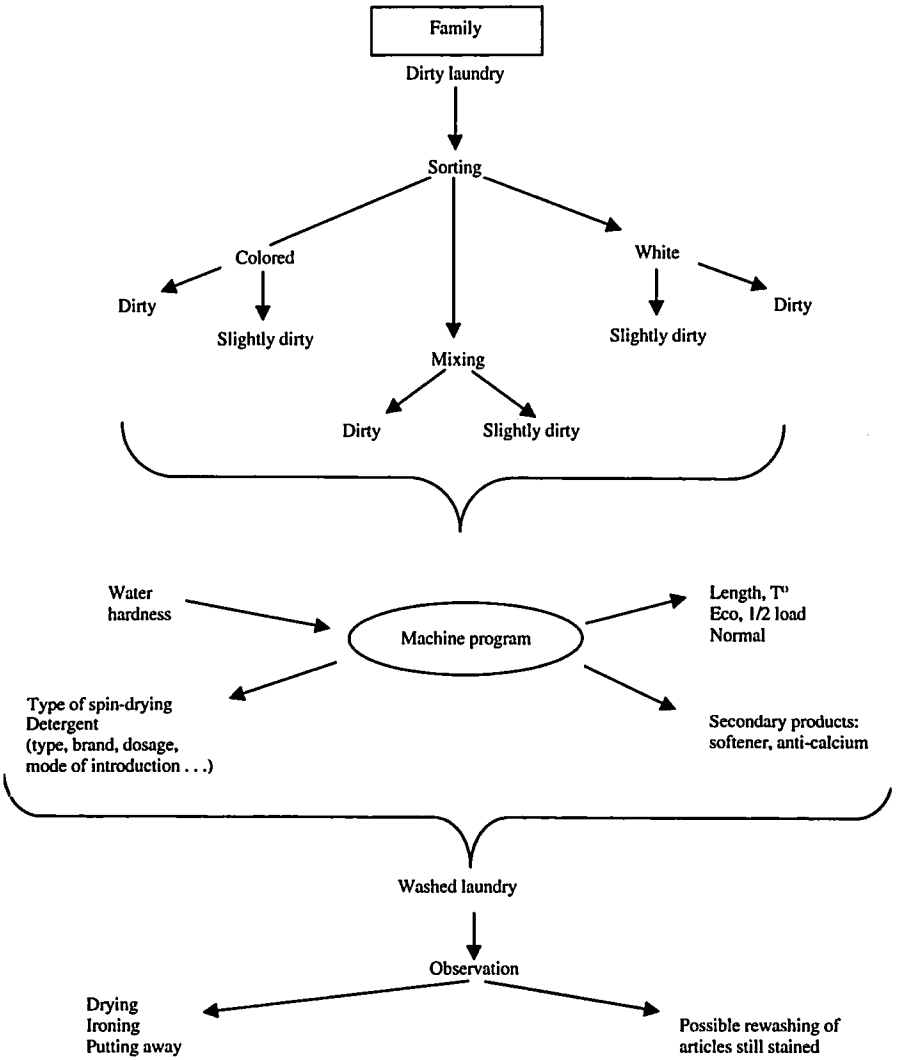


Fig. I.12. The range of tasks and decisions involved in laundering.

The research highlights the main problems encountered by consumers. Thanks to research of this type, we know that on the whole, today's consumers are satisfied with the results they obtain but that certain stains continue to cause problems (ranked from the most resistant to the least difficult).

Consumer needs are also carefully monitored, thanks to this type of study. The problems encountered and consumer demands are the two indicators that help the formulator to develop products that truly reflect current consumer needs. This example based on clothes laundering is of course applicable to all other types of detergents for which similar surveys are conducted, i.e., dishwashing (hand and machine), personal care (soap, shower and bath products, shampoo), and other surfaces (bathrooms, floors, windows, modern surfaces).

Reference

1. World Market Analysis, Unilever, September 1997.

CHAPTER 1

The Main Surfactants Used in Detergents and Personal Care Products and Theories of Detergency

Main Surfactants and Their Process of Synthesis

Classification of Surfactants

A surfactant molecule consists of two parts, a hydrophobic part (insoluble in water) and a hydrophilic part (soluble in water). These molecules are highly active in the interfaces between air and water or oil and water. They have a number of names, including surface active agents, detergents, surfactants, or simply actives. The four main classes of surfactants are: anionic, nonionic, cationic, and amphoteric.

Anionic Surfactants. When the polar group, which is linked in a covalent manner with the hydrophobic part of the surfactant, carries a negative charge ($-COO^-$, $-SO_3^-$, $-SO_4^-$) the surfactant is called anionic; soaps, alkylbenzenesulfonates, and fatty alcohol sulfates are all anionic active surface agents.

Cationic Surfactants. When the polar group carries a positive charge ($-NR_1R_2R_3^+$), the surfactant is cationic; dimethyldistearyl ammonium chloride is an example of this category.

Nonionic Surfactants. Nonionic surfactants have a polar group that cannot be ionized in an aqueous solution. The hydrophobic part consists of the fatty chain. The hydrophilic part contains nonionizable atoms of oxygen, nitrogen, or sulfur; solubility is obtained as a result of the formation of hydrogen bonds between water molecules and certain functions of the hydrophilic part, for example, the ether function of the polyoxyethylene (hydration phenomenon). In this category we find mainly derivatives of polyoxyethylene or polyoxypropylene, but sugar esters and alkanolamides can also be included.

Amphoteric Surfactants. Amphoteric surfactants are components with a molecule forming a dipolar ion. Cetylamino acetic acid, for example, produces the two following forms in an aqueous environment:

$C_{16}H_{33}-\overset{+}{N}H_2-CH_2-COOH$ **cationic**, in an acid environment

$C_{16}H_{33}-NH-CH_2-COO^-$ **anionic**, in a basic environment

In all of these molecules, the hydrophobic part is made up of an alkyl or fatty chain. This is represented by the following:

$CH_3–CH_2–CH_2–CH_2–$ or or R

The four types of surfactants are represented by the following symbols:

Anionic

Cationic

Nonionic

Amphoteric

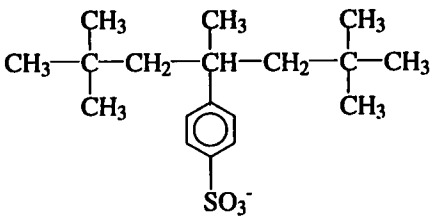
For readers who may be less familiar with these kinds of products, we say that these surfactant molecules have a "head" (the hydrophilic part) and a "tail" (the hydrophobic part).

Examples of the Main Surfactants Used in Detergent and Personal Care Products

The synthesis process of some surfactants is outlined below. For more technical details, the reader should consult the numerous specialized works available (1–5).

Anionics. This group includes alkylbenzenesulfonates, paraffin- or alkanesulfonates, primary alcohol sulfates, α-olefinsulfonates, alkyl ether sulfates, sulfosuccinates, acyl isethionates, methyl ester sulfonates, soaps, sulfoalkylamides of fatty acids, diglycolamide sulfates, *N*-acyl amino acids, and alkyl polyoxyethylene carboxylates.

Alkylbenzenesulfonate (ABS) is the most widely used surfactant. ABS can be branched, e.g., tetrapropylenebenzenesulfonate (TPS) or linear, e.g., linear alkylbenzenesulfononate (LAS). The former is used in only a very few countries because of its slow rate of breakdown by microorganisms (biodegradability). Branched ABS (TPS) has the following chemical structure:



First, propylene is subjected to an oligomerization reaction, followed by acid-catalyzed condensation with benzene, and then sulfonation according to the following equations:

$$\underset{\text{(propylene)}}{C_3H_6} \xrightarrow{\text{catalyst}} \underset{\text{(tetramer)}}{C_{12}H_{24}} + \underset{\text{(pentamer)}}{C_{15}H_{30}}$$

$$C_{12}H_{24} + C_{15}H_{30} + \bigcirc \xrightarrow[\text{or HF}]{AlCl_3} C_{12}H_{25}-\bigcirc \quad \text{or} \quad C_{15}H_{31}-\bigcirc$$

There is an alternative method to make branched ABS, i.e., alkylation of benzene with chlorinated hydrocarbons according to the following equation:

$$C_nH_{2n+2} + Cl_2 \longrightarrow C_nH_{2n+1}Cl + HCl$$

$$C_nH_{2n+1}Cl + \bigcirc \longrightarrow C_nH_{2n+1}-\bigcirc + HCl$$

Sulfonation of the above-mentioned alkylates (using SO_3^- or oleum) produces the required alkylbenzenesulfonic acids.

LAS has the following chemical structure:

$$CH_3^-(CH_2)_n-\bigcirc-SO_3H$$

Linear ABS

The two processes that produce alkylates are as follows:

(i) alkylation with chlorinated *n*-paraffins according to the following reaction:

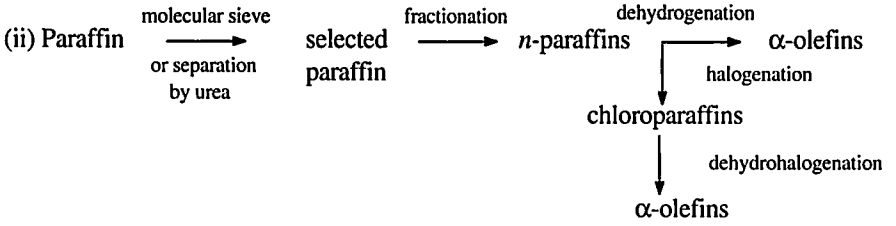
$$C_nH_{2n+1}Cl + \bigcirc \longrightarrow C_{2n}H_{2n+1}-\bigcirc + HCl$$

(ii) alkylation with linear olefins according to the following reaction:

$$C_nH_{2n} + \bigcirc \longrightarrow C_nH_{2n+1}-\bigcirc$$

It should be noted that because the double bond can be either at the end or inside the carbon chain, isomerics are obtained with the phenyl group in positions 1, 2, or 3. The processes for obtaining linear olefins are outlined below:

(i) Paraffin $\xrightarrow[\text{or separation by urea}]{\text{molecular sieve}}$ selected paraffin $\xrightarrow{\text{cracking}}$ α-olefins C_5–C_{20} $\xrightarrow{\text{fractionation}}$ α-olefins C_9–C_{15}



Paraffin- or alkanesulfonates (SAS: secondary alkanesulfonate) have not yet been used in detergents because of their relatively high cost. In view of their greater biodegradability in an aerobic environment, they represent a potential source of anionics. These components have the following chemical structure:

$$CH_3—(CH_2)_n—\underset{\displaystyle SO_3^-}{\underset{|}{CH}}—(CH_2)_m—CH_3$$

paraffinsulfonate

They are made by a photochemical process from *n*-paraffins on the following basis:

$$\underset{n\text{-paraffin}}{R—H} \xrightarrow{UV} R^\bullet$$

$$R^\bullet + SO_2 \longrightarrow R—SO_2^\bullet$$

$$R—SO_2^\bullet \xrightarrow[\textbf{oxidation}]{O_2} R—SO_2—O—O^\bullet$$

$$R—SO_2—O—O^\bullet + R—H \longrightarrow R—SO_2—O—OH + R^\bullet$$

$$R—SO_2—O—OH \longrightarrow R—SO_2—O^\bullet + HO^\bullet$$

$$HO^\bullet + R—H \longrightarrow H_2O + R^\bullet$$

$$R—SO_2—O^\bullet + R—H \longrightarrow \boxed{R—SO_2—OH} + R^\bullet$$

The reaction cycle starts again with R*. Neutralization of R—SO_2–OH yields the corresponding paraffinsulfonate.

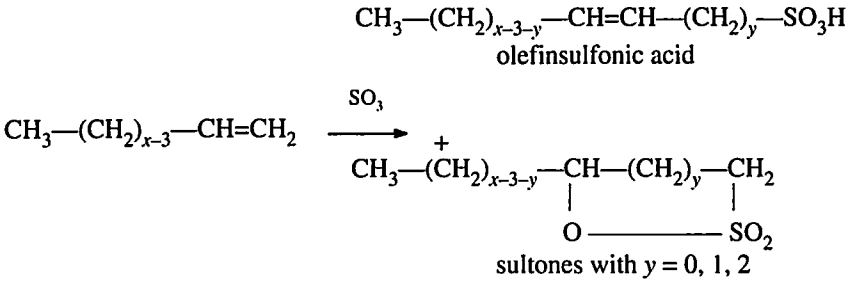
Primary alcohol sulfates (PAS) are obtained by sulfation of fatty (natural or synthetic) alcohols with a mixture of air/SO_3 according to the following reaction:

$$R—OH + SO_3 \rightarrow R—O—SO_3H$$

fatty alcohol sulfuric acid

It should be noted that continuous sulfation is widely used today, with the mixture of SO_3 /air in reactors such as Chemithon and Ballestra.

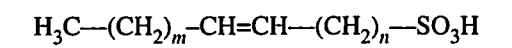
α-Olefinsulfonates (AOS) are synthesized by a reaction of SO_3 with α-olefins according to the following equation:



olefinsulfonic acid

sultones with $y = 0, 1, 2$

Hydrolysis is done to complete the reaction and transform the sultones into α-olefinsulfonic acid, with the following chemical formula:

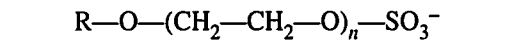


α-olefinsulfonic acid

with $m + n = 9–15$; $n = 0, 1, 2, \ldots$,; $m = 1, 2, 3, \ldots$

This gives a mixture of several α-olefinsulfonic acids. They are less sensitive to water hardness than alkylbenzenesulfonates or fatty alcohol sulfates. In the United States, laundry products do not include AOS because it can irritate the skin if used in the presence of chlorine bleach, a product much used in that country for whitening. On the other hand, AOS is used in Japan. Bleach is also used to improve the color of AOS and can lead to the formation of sensitizers.

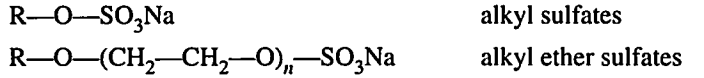
Alkyl ether sulfates (fatty alcohol ether sulfates: AES) have the following chemical formula:



alkyl ether sulfates

If R = Lauryl, we have LES or *L*auryl *E*ther *S*ulfate

This type of surfactant is used mainly in liquid formulations (e.g., for dishes, liquid detergents, and shampoos). Ether sulfates differ from alkyl sulfates by the ether glycol units between the carbon chain and the sulfate group as follows:



Ether sulfates are obtained in two stages as follows: (i) addition of ethylene oxide molecules to the fatty alcohol (see nonionics, ethoxylated fatty alcohols) and (ii) sulfation

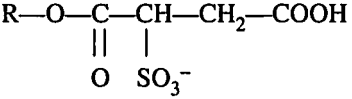
of the ethoxylated fatty alcohols by a mixture of air/SO_3 (as for alkylbenzenesulfonates), and then neutralization using different alkaline components, e.g., sodium hydroxide, ammonia, or alkylamines. The chemical reaction is as follows:

$$R{-}O{-}(CH_2{-}CH_2{-}O)_n{-}H + SO_3 \rightarrow R{-}O{-}(CH_2{-}CH_2{-}O)_n{-}SO_3H$$

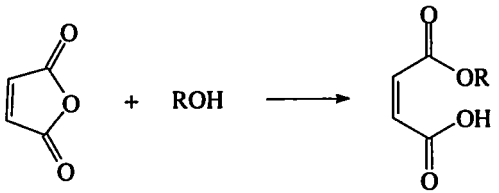
alkyl ether sulfuric acid

The most widely used ether sulfates are lauryl ether sulfates, with $n = 2$ or 3 (LES).

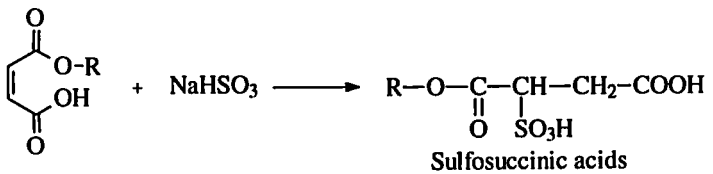
Sulfosuccinates have the following chemical formula:



These are hemiesters of succinic acid with two anionic groups, carboxylic and sulfonic. They are made by an equimolar reaction of maleic anhydride with fatty alcohol to produce first a monoester:



Sulfosuccinic acid is then obtained by a reaction of the monoester with bisulfite sodium:

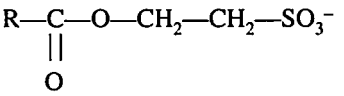


R = 12 – 14 C

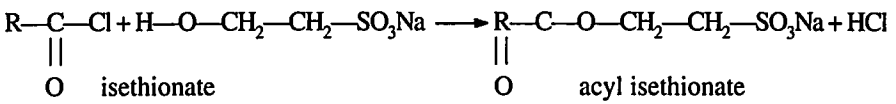
Sulfosuccinic acids

Salts of sulfosuccinic acids are gentle to skin. They are used to make dishwashing liquids or shampoos. Because they have an ester group, they are sensitive to hydrolysis, which means that they have to be formulated at a pH between 6 and 8.

Acyl isethionates have the following chemical formula:

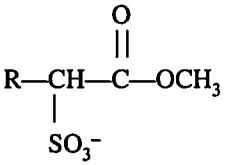


These derivatives are obtained by the reaction between sodium isethionate and fatty acid chlorides as follows:



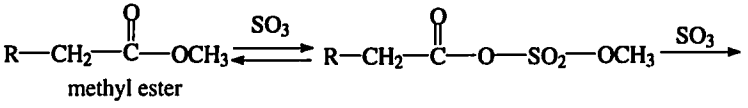
These derivatives are sold under the brand HeO S 3390-2 (Hoechst) or Fenipon AC (G.A.F.). They have the same properties as the sulfosuccinates in terms of mildness to skin and stability (hydrolysis). However, because their solubility is poor in cold water, they are used mainly in creams or thickened liquids (shampoos and foam baths) and in toilet bars.

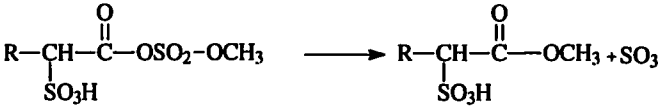
Methyl ester sulfonates (MES) have the following chemical formula:



methyl ester sulfonate

These surfactants are obtained by sulfonation of methyl ester using the following reaction:

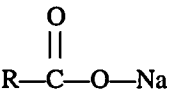




methyl ester sulfonic acid

These surfactants were looked at closely in the 1960s. At that time, costs were high because tallow was the raw material used. Today, with the availability of palm oil, prices are becoming more competitive. The best performance is obtained from C_{16}–C_{18} (6). They are used both in powder and liquid detergents, particularly in Asian countries (notably Japan).

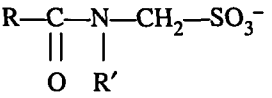
Soaps have the following chemical formula:



soap

In Europe, soap is used in detergents only as an antifoaming agent. It is also used in liquid detergents and soap-based shower gels. In developing countries, it is used for all-purpose products. Soap manufacturing processes are covered in detail in Chapter 12.

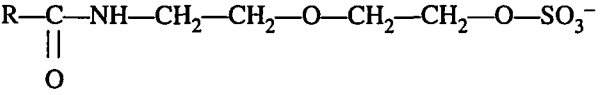
Sulfoalkylamides of fatty acid (N-*alkyl taurides)* have the following chemical formula:



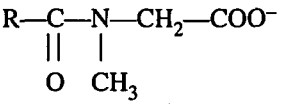
If $R' = CH_3 \rightarrow$ *N*-methyl tauride

The advantages of these products include foaming ability, lime soap-dispersing properties, and a feel similar to that of soap-based formulas.

Diglycolamide sulfates are not unstable in an aqueous solution and can be used in shampoos. The formula is as follows:



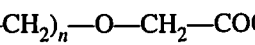
N-*Acyl amino acid*s include acylsarcosinates; the formula is as follows:



acyl sarcosinates

The salts of *N*-acyl amino acids have good foaming and detergency properties. They are more soluble in hard water than soap and are not too aggressive on skin or hair. They give a soft feeling to hair and skin.

Polyoxyethylene carboxylates have the following chemical formula:



These derivatives have satisfactory detergency properties and the ability to disperse lime soap (the same properties as the *N*-acyl amino acid salts); when *n* is high, they are compatible with cationics. They are easy to rinse off and are soluble at a low pH.

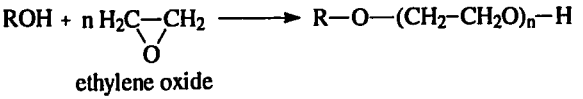
Nonionics. This group includes fatty alcohol polyethylene glycol ether or fatty alcohol ethoxylates, ethylene oxide and propylene oxide copolymers, amine oxides, alkylamines, alkanolamides, polyglycerol esters, alkyl polyglucosides, and fatty acid *N*-alkylglucosamides.

Alcohol ethoxylates (AE) have the following chemical formula:

$$R—O—(CH_2–CH_2O)_nH$$

fatty alcohol ethoxylate

Among commercial nonionics, those made from fatty alcohols with ethylene oxide are the most commonly used today. The basic chemical reaction used to change a fatty alcohol into a nonionic is the following:



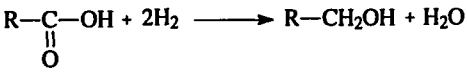
There are a number of processes for synthesizing fatty alcohol; the following are among the main ones:

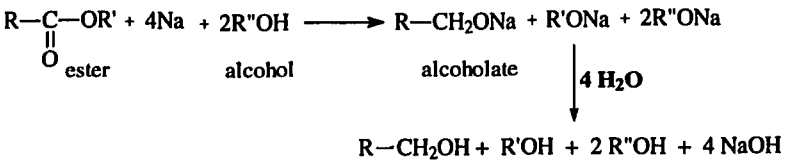
(i) Primary alcohols. The chemical formulation is as follows:

$$R—CH_2—OH$$

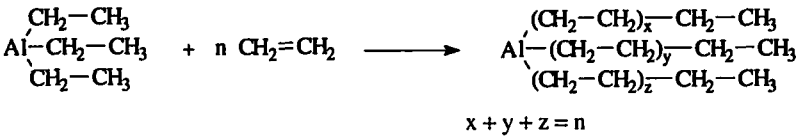
primary alcohol

(ii) Natural alcohols. Natural fatty alcohols are produced from vegetable oils and fats. Although there are many processes to produce natural fatty alcohols, the most common is the reduction of either fatty acids or fatty esters according to the following equations:

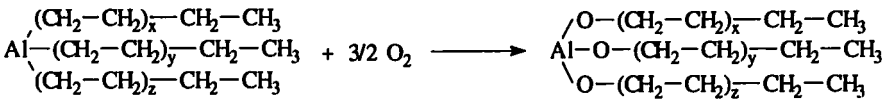




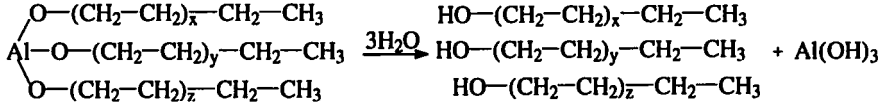
(iii) Synthetic alcohols. In the Ziegler process, the first stage is to react ethylene with a triethyl-aluminum to obtain an aluminum alkyl as follows:



The aluminum alkyl is then oxidized to give an aluminum alcoholate as follows:



The aluminum alcoholate is finally hydrolyzed in an acidic medium to produce the fatty alcohols.



A mixture of fatty alcohols is obtained with a Poisson distribution. The alcohols with a carbon chain between C_{12} and C_{20} are separated for use as detergent raw materials. It should be noted that alcohols obtained by the Ziegler method have an alkyl chain with an *even number* of carbon atoms, e.g., C_{12}-C_{14}-C_{16}-C_{18}-C_{20}.

In the OXO process, there are two main stages in the synthesis of fatty alcohols. In the first stage, a molecule of carbon monoxide and hydrogen and a molecule of olefin are combined according to the following reaction:

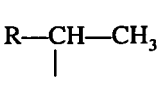
$$R—CH{=}CH_2 + CO + H_2 \rightarrow R—CH_2—CH_2—CHO$$

In the second stage, the aldehyde function is reduced to obtain fatty alcohol:

$$R—CH_2—CH_2—CHO + H_2 \rightarrow R—CH_2—CH_2—CH_2—OH$$

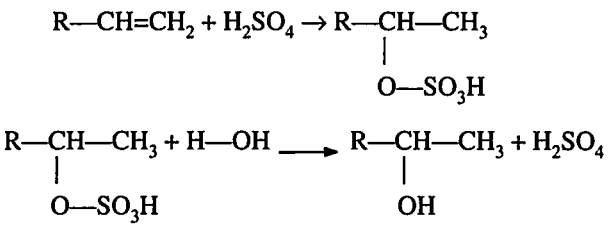
The alkyl chains of the alcohols can have an odd number or an even and odd number of carbon atoms (uneven, starting product = ethylene; even + uneven, starting product = olefin). Commercial products belonging to this class and regularly used in Europe are Dobanols (Shell), even and odd number of carbon atoms, and Synperonics (ICI), odd number of carbon atoms.

(iv) Secondary alcohols. The chemical formula is as follows:



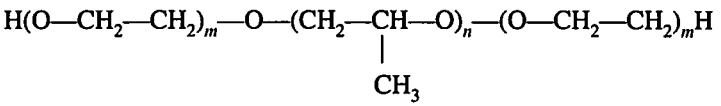
secondary alcohol

Considerable work has been reported on the preparation of secondary fatty alcohols—oxidation of paraffin, hydrogenation of paraffin and hydrolysis of halides, the addition of thioacetic acid to olefin, and hydrolysis and hydration of α-olefins. The hydration of α-olefin follows:



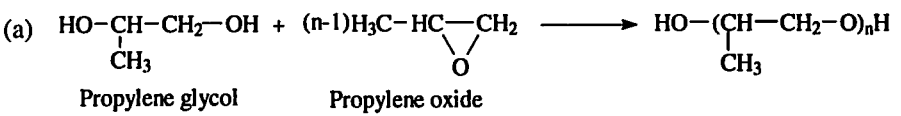
Secondary fatty alcohol ethoxylates sold in the industry are, for example, Tergitol 15-S-5 and 15-S-7 EO, respectively (Union Carbide).

Ethylene oxide (EO) and propylene oxide (PO) copolymers (EO/PO adducts) have the following chemical formula:



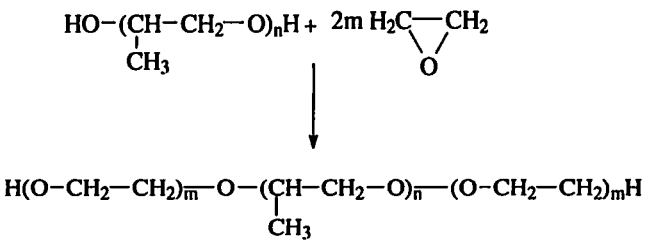
ethylene and propylene oxide copolymers

These are polyols obtained by adding propylene oxide to propylene glycol, followed by an addition of ethylene oxide, using the following scheme:



Propylene glycol Propylene oxide

(b)



In abbreviated form this is written as follows:

$$HO(OE)_m(OP)_n(OE)_mH$$

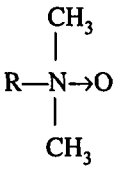
To obtain better alkaline stability, it is preferable to invert the addition as follows:

$$HO(OP)_m(OE)_n(OP)_mH$$

The ratio of EO to PO can vary between 4:1 and 9:1 with a minimum molecular weight of ~2000. These derivatives are used mainly in automatic dishwashing products

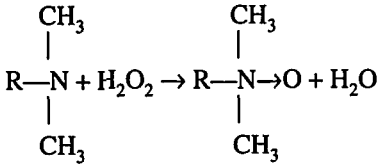
because of their low foaming profile. The main product used is one in which $m = 2$ and $n = 32$. Although these molecules are not very biodegradable, they are nevertheless used because of their low toxicity ($LC_{50} > 100$ mg/L) and their minimal effect on aquatic life.

Amine oxides have the following chemical formula:



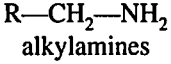
amine oxides

They are obtained by reacting alkyldimethylamine with hydrogen peroxide as follows:



Amine oxides are very stable in the presence of oxidants (oxidizing agents), including very strong ones such as chlorine bleach.

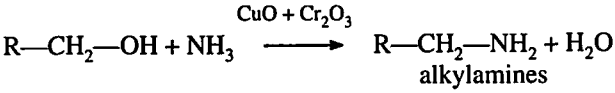
Alkylamines have the following chemical formula:



alkylamines

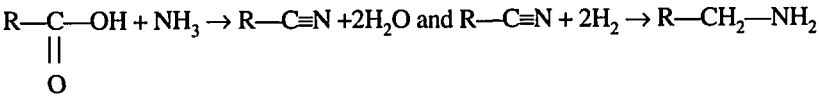
They are made using different methods; the main ones are summarized below:

(a) from fatty alcohols



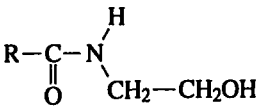
(b) from fatty acids

The reaction is in two stages, preparation of nitriles and hydrogenation of nitriles, respectively, as follows:



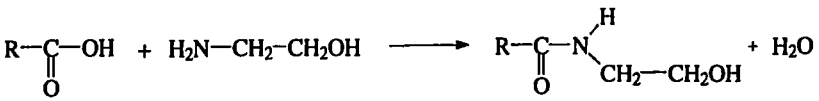
Alkylamines are used in detergents as a source of softening agents.

Alkanolamides have the following chemical formula:

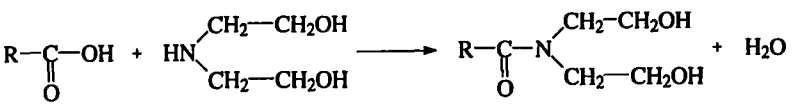


alkyl monoethanolamide

These derivatives are prepared by condensing fatty acids or esters with ethanolamine or diethanolamine as follows:



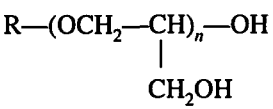
ethanolamine — alkyl monoethanolamide



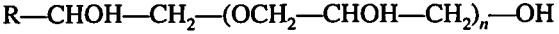
diethanolamine — alkyl diethanolamide

Monoethanolamides are used to increase or to stabilize foam in fatty alcohol ether sulfate–based formulations (dishwashing liquids and shampoos). They also have thickening, pearlizing, and softening properties depending on the carbon R chain.

Polyglycerol ethers have the following chemical formula:

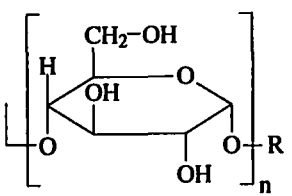


or



These derivatives are very compatible with skin and have very good foaming properties.

Alkyl polyglucosides have the following chemical formulation (7):



alkyl polyglucoside

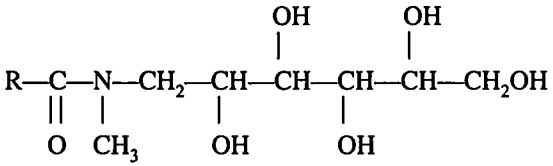
where n = 1–3, and R = C_9–C_{13}.

These products are obtained by two different methods, i.e., transglucosidation of C-3 and C-4 alcohols and direct glucosidation of fatty alcohols with acid catalysts:

$$R{-}CH_2OH \xrightarrow{\text{glucose}} \text{alkyl polyglucoside}$$

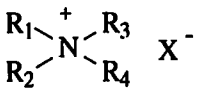
The reaction is complex, giving a mixture of alkyl polyglucosides and alcohols, which is purified by distillation. These products are used in powder formulations, and in particular in liquid detergents, dishwashing liquids, and shower gels; they are mild to the skin and are easily biodegradable. Their synthesis is done using entirely renewable products (natural alcohol and glucose).

Fatty acid N-*alkylglucosamides* are other glucose derivatives such as those obtained by the reaction with monosaccharides such as hexoses (8). They are similar to alkyl polyglucosides. In these molecules, the hydrophobic part is an acylamino group, whereas the hydrophylic part is made up of sugar, whose cyclic structure is opened by hydrogenation. The following is an example of a fatty acid *N*-glucosamide (9):



N-methylglucosamide

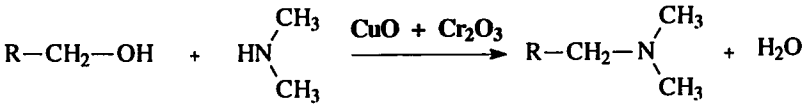
Cationics. The chemical formula is as follows:



cationic

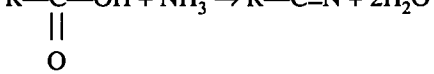
In the synthesis of compounds with a single alkyl chain, tertiary amine is prepared first, either from fatty alcohol or fatty acid as follows:

(a) fatty alcohol



tertiary amine

(b) fatty acid

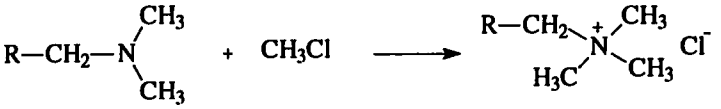


$$R—C{\equiv}N + 2H_2 \rightarrow R—CH_2—NH_2$$

$$R—CH_2—NH_2 + 2H_2C{=}O + 2HCOOH \downarrow$$

$$R—CH_2—N(CH_3)_2 + 2H_2O + 2CO_2$$

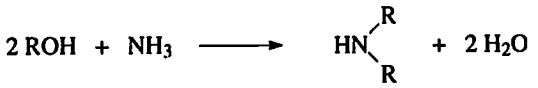
The tertiary amines then react with methyl chloride to yield quaternary ammonium chlorides as follows:



quaternary monoalkylammonium chloride

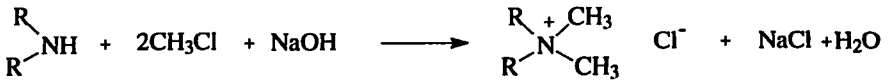
Quaternary ammonium chlorides with a benzyl group and a short carbon chain are used as antimicrobials. Those with a longer carbon chain are adsorbed on hair and can therefore be used in hair conditioner formulations.

For the components with two alkyl chains, the dialkylamines are first made from either fatty alcohol or fatty acids. With fatty alcohol we obtain the following reaction:



dialkylamine

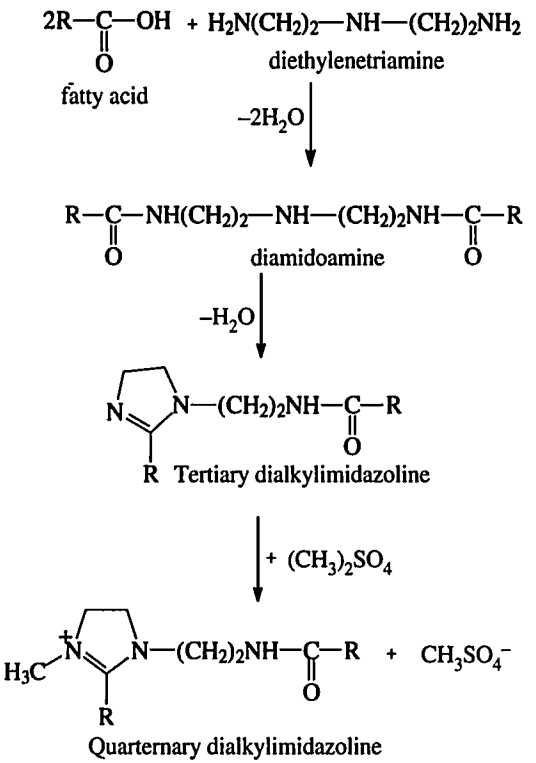
Quaternization then takes place with methyl chloride as follows in the presence of 50% sodium hydroxide to neutralize the hydrochloric acid that is formed:



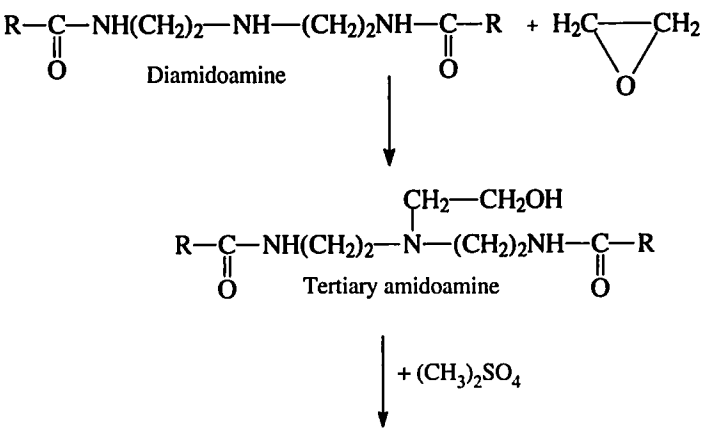
dialkyldimethylammonium chloride

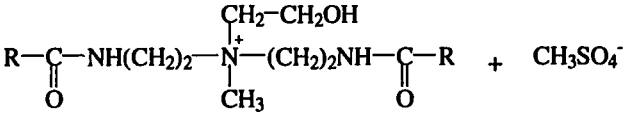
Distearyldimethylammonium chloride (DSDMAC) or dihydrogenated tallow-dimethylammonium chloride (DHTDMAC) can be used in fabric softener formulas. These are no longer used extensively in Europe because of poor biodegradability. The short carbon chains give more soluble components and act as antimicrobials.

Certain North American manufacturers use another class of cationics to make concentrated fabric softeners, i.e., derivatives of imidazoline. Methods of synthesis are as follows:

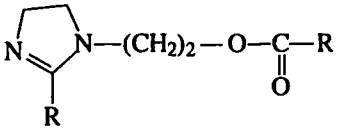


In Europe, biodegradable cationics have been developed to replace quarternary distearyldimethylammonium chloride. In the literature, we find mainly cationics with an ester function which are more biodegradable. The synthesis of a few of the many molecules studied, some of which are already in use in several European countries, is presented in the following:

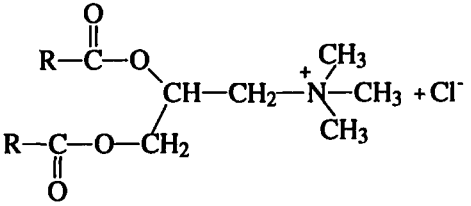




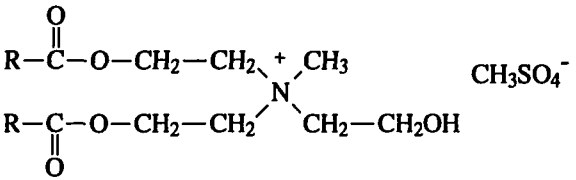
quaternary dialkylamidoamine



dialkylamidazoline ester

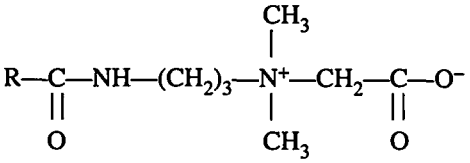


dialkyl ester quaternary of dihydroxypropylammonium chloride



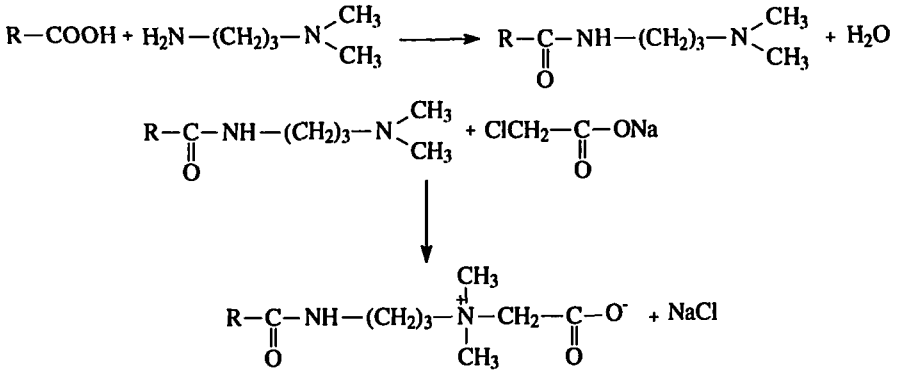
dialkyl ester quaternary of triethanolammonium methosulfate

Amphoterics. It is important to remember that amphoterics behave like cationics at low pH and like anionics at high pH. At medium pH, they carry both positive and negative charges, i.e., the structure of a bipolar ion. Unlike amphoterics, surfactants called "Zwitterionics" maintain a bipolar structure over a large range of pH. In this group of products, betaines are the most commonly used. Their chemical formula is as follows:



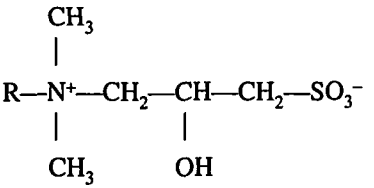
amidopropyl betaines

Often, R = lauryl; this product is used most frequently in shampoos, foam baths, and even dishwashing liquids because of its good detergency, its foaming properties, and its compatibility with skin. This product is called cocamidopropyl betaine (CAPB). Its synthesis involves the following reactions:

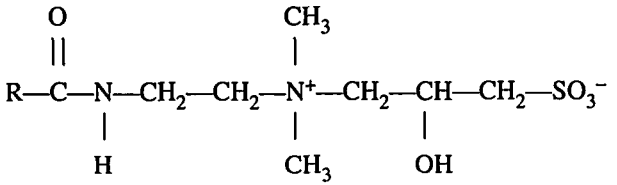


amidopropyl betaine

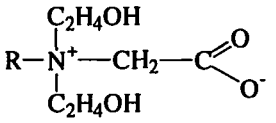
Amphoteric surfactants with a sulfonate group instead of carboxylate are called sulfobetaines or sultaines. Examples include the following:



alkyl sulfobetaines



amidopropyl sulfobetaines



ethoxylated betaines

Physiochemical Characteristics of Surfactants

Definitions. (i) *Surface tension.* Between molecules, there are forces that attract, called Van der Waals forces. In a given liquid, any one molecule will always find itself at the center of a field of attracting forces of spherical symmetry caused by neighboring molecules. The effect of the Van der Waals forces is thus nullified. But at a surface of a liquid, the situation is quite different; molecules are subjected to an asymmetrical force field. In the gaseous phase, the attracting force is almost negligible because of the widely dispersed molecules. In the liquid phase, the attracting forces from other similar molecules are as strong as those inside the liquid itself. Thus, the surface molecules are subjected to a resulting force, which tends to displace them toward the interior. On a macroscopic scale, this force acts to minimize the surface area in contact with air. For instance, a drop of water falling freely through space will be spherical. The unbalanced force field on the surface can be represented by a quantity of *surface free energy.* As we have seen, this contracts the surface. To increase the surface area, we must supply an *equivalent amount of work* to this free energy. Surface free energy is expressed in joules (J).

The surface free energy on a given surface is called *surface tension.* From a mathematical and dimensional perspective, free energy expressed in J/m^2 is equivalent to tension expressed in newton (N)/m (work, $F \times d$; surface, d^2), from which surface tension is described as follows:

$$F \times d/d^2 = F/d, \text{ i.e., N/m (newton/meter)}$$

To summarize, we can represent these different ideas as follows: Van der Waals attractive force field [free energy = work (joules) and free energy/surface unit (J/m^2) = newton/m = surface tension]. In practice, mN/m (millinewton/m) is used.

(ii) *Interfacial tension.* Let us look now at two immiscible liquids, and a solid and a liquid. The boundary that separates them, called the interface, is similar to the surface that separates a liquid and a gas. Each unit of air is associated with free energy. This free energy expressed in joules per unit of surface is called *interfacial tension.* From a mathematical perspective, it is the equivalent of a force (tension) per unit of length. It can therefore be expressed in newton/meter. It should be noted that surface tension is a special case of interfacial tension. The term "surface tension" is used to refer to the interfacial tension between a liquid and a gas (air). This notion of "thermodynamics" will be widely used in this book, particularly in the section on the mechanisms of detergency.

(iii) *Micelles and critical micelle concentration (CMC).* Surface active agents or surfactants are different from other dissolved molecules because of their specific behavior in aqueous solution. Above a certain surfactant concentration, molecules combine to produce micelles. The explanation is as follows. Because surfactant molecules contain both a hydrophobic and hydrophylic part, they are strongly adsorbed at the interfaces; it is there that the hydrophobic part finds itself in a more favorable environment than in the solution where it is surrounded by water molecules. For the same

reason, when in water, these molecules combine to form micelles because, in their agglomerated state, the hydrophobic parts are in a more favorable energy situation and the system is more stable (force of attraction hydrocarbon/water < force of attraction water/water and force of attraction hydrocarbon/hydrocarbon). The formation of micelles causes "anomalies" in the physical and electrical properties of detergent solutions (see Fig. 1.1).

Thus, when we increase the concentration of surfactants, certain properties change suddenly. For example, we obtain the curves shown in Figure 1.2. These changes are attributed to the sudden formation of micelles. The concentration that corresponds to this micellization is called the critical micelle concentration (CMC). It should be noted that these concentrations are determined by tracing the variation in a given physical property as a function of the concentration of surfactant. The point of intersection of the two linear parts of the graph gives the CMC. Surfactant solutions containing micelles can be considered as colloidal solutions.

Krafft Point or Cloud Point. One characteristic of anionic surfactants is that their solubility increases with temperature; solubility increases suddenly when the surfactant becomes sufficiently soluble to form micelles. *The Krafft point* is defined as the temperature at which solubility is equal to the CMC, or the temperature at which micelles become soluble (10). This Krafft point can be estimated by measuring the temperature at which a clear solution is obtained with a given quantity of surfactant in water. This is only an estimate because the temperature obtained will depend to some degree on the quantity of surfactant used.

For nonionics, we have already seen that their solubility results from the hydrogen bonds between water and the polyoxyethylene chain. On heating, these hydrogen bonds dissociate, dehydration results, and with it, reduced solubility. As we have seen above, this behavior is the opposite of that of anionics whose solubility increases with temperature. The *cloud point* is the temperature at which the nonionic in question becomes insoluble (which causes the cloudy solution).

HLB (Hydrophile-Lipophile Balance). Certain physicochemical properties of surfactant molecules, particularly emulsifying properties, are closely linked to the

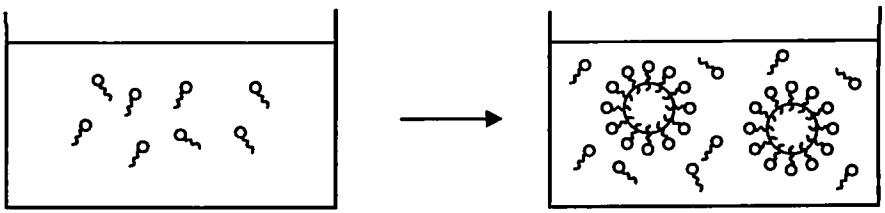


Fig. 1.1. Micelle formation.

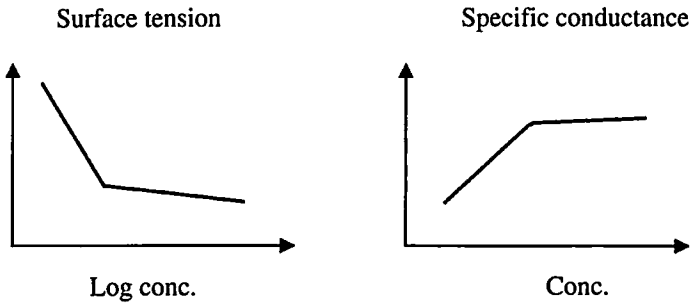


Fig. 1.2. Determination of critical micellar concentration (CMC).

polarity of their structure. Around 1950, Griffin thought that it would be possible to describe this polarity by an empirical value that he termed HLB (hydrophile-lipophile balance). It is a value on an arbitrary scale, i.e., a compound that is slightly hydrophilic (meaning difficult to dissolve in water) has a small HLB. An increase in HLB equals an increase in the hydrophilic characteristics of the molecule. HLB is therefore nothing more than a measure of the polarity of the molecule. There are several possible equations with which to calculate the HLB value. The relationships between the solubility or dispersibility of surfactants and the HLB values are indicated in Table 1.1.

For nonionics, the HLB can be adjusted as required, simply by varying the number of moles of ethylene oxide. Where anionics are concerned, we are more limited, given that the hydrophilic part (ionic group) does not change very much (sulfonate and sulfate group).

Physicochemical Properties of Surfactants. These include changes in surface and interfacial tension and micellization. An important characteristic of surfactants is their adsorption at the interface. This adsorption profoundly changes interfacial tensions. Adsorption of surfactants at the interface between water and air lowers the surface tension of water. As illustrated in Figure 1.3, the surfactant molecules have their polar groups turned toward the water phase at the interface between water and air. At the solid/liquid interface or the liquid/liquid interface (e.g., textile/water, a particular soil/water, or oil/water), the adsorption of surfactants diminishes the interfacial tension

TABLE 1.1
The Relationship Between Solubility (Dispersibility) of Surfactants and Hydrophile-Lipophile Balance (HLB) Values

Dispersibility	HLB value
Not dispersible in water	1–4
Poor dispersibility	3–6
Weak dispersion, but stable	8–10
Clear solution	13

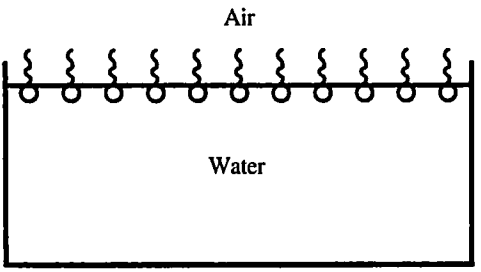


Fig. 1.3. Behavior of surfactants at the air/water interface.

of the fiber or the soil relative to the water. On the other hand, the interfacial tension between a textile and soil is increased. Figure 1.4 illustrates the phenomenon of adsorption (the polar grouping is always turned toward the aqueous phase). It should be noted that if the polar group is charged (as in the case of anionics) adsorption at the interfaces between a liquid and a solid changes their properties, for example, their electrostatic repulsion.

To summarize, the adsorption of surfactants at the interfaces has the following effects: (i) It reduces interfacial tension between air and water, called surface tension, i.e., $\gamma_{A/W} \downarrow$ where A/W = air/water. (ii) It reduces the interfacial tension between fiber and water, and soil and water, i.e., $\gamma_{F/W}$, $\gamma_{O/W}$ $\gamma_{P/W} \downarrow$ where O = oil, P = particle, and F = fiber. (iii) It increases the interfacial tension between fiber and soil, i.e., $\gamma_{F/O}$ or $\gamma_{F/P} \uparrow$.

The reduction of interfacial tension can be translated into concrete terms as the *wetting property*. To illustrate, if we place water on a fiber, the water will tend to contract because the surface tension is great. If we add a surfactant, however, we reduce the surface tension and water spreads over the fiber—we say that it has wet the fiber.

A further interesting property of surfactant solutions is their ability to increase the solubility of certain organic materials that are almost insoluble in water (such as hydrocarbons). This phenomenon, called solubilization, is due to the incorporation of organic matter into the micelles of surfactants. Solubilized molecules are incorporated into the micelles in three different ways as illustrated in Figure 1.5. Nonpolar molecules, such as heptane, are inside the micelles and have no contact with the water. Molecules with a polar group, such as heptanol, are incorporated into the micelles in the same way as the surfactant agents. Polar molecules are to be found on the outside surface of the micelles.

Solubilization is an example of the formation of mixed micelles. It can be considered as a specific example of the solubility phenomenon known as "hydrotropy"

Fig. 1.4. Adsorption of surfactants at the solid/water interface.

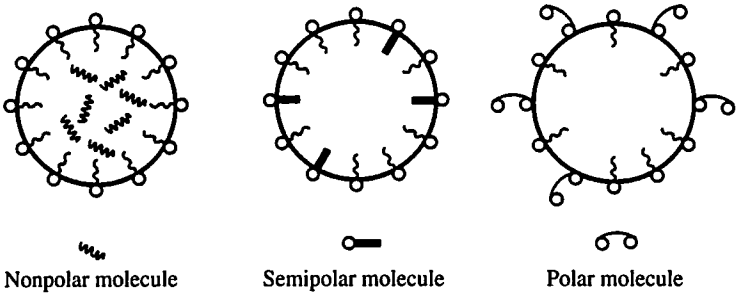


Fig. 1.5. Solubilization in micelles.

whereby the solubility of a substance (ABS, for example) in a solvent (water, for example) can be greatly increased by the addition of other compounds (sodium toluenesulfonate, for example). Solubilization differs from hydrotropy in that a very small quantity of solubilizing agents is sufficient to dissolve organic matter.

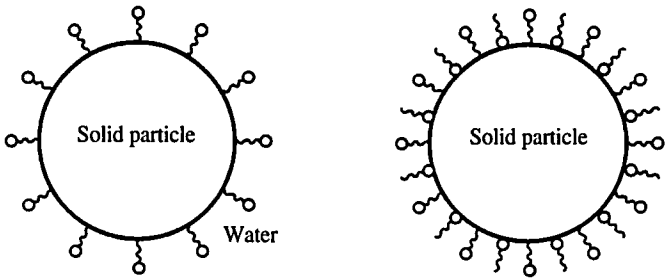
We should also distinguish among solubilization, emulsification, and peptization. An emulsion is the dispersion of liquid particles (diameter >0.5 μm) in another immiscible liquid. Peptization is the dispersion of colloidal particles. In other words, solubilization is on a molecular scale, whereas emulsion and peptization are on a microscopic scale (>1 μm). These two latter phenomena are illustrated in Figures 1.6 and 1.7.

Solubilization depends on the quantity and size of the micelles. The more micelles in solution, the greater will be the solubilization, and large micelles appear to have a greater capacity to dissolve organic matter. Finally, the cloud point of nonionics can be considered as a signal for the formation of "super large micelles." This could explain why solubilization (which is one of the mechanisms used for detergency, as we shall see below) is very active around the cloud point for nonionics.

The Influence of Different Factors on the Physicochemical Properties of Surfactants

Influence of the Type of Molecule on Interfacial or Surface Tension. Much research has been done to relate physical properties, particularly surface and interfacial tension, to the chemical makeup of surfactants. For anionics, Traube (11) showed that

Fig. 1.6. Emulsification.



Peptization (particle) Peptization with a double layer

Fig. 1.7. Peptization.

in a homogeneous series, each CH_2 group added to a fatty chain reduces by one-third the concentration necessary to obtain a given surface tension. In other words, for a given concentration, surface tension diminishes when the carbon chain is lengthened.

Hartley (12) found that if micelles are prevented from forming, surface tension drops strongly with higher concentrations than the original CMC; micelles can be prevented from forming by reducing molecular symmetry. To do this, it is necessary to branch out the hydrophobic chain or else substitute two shorter chains for one single long chain (for example, by displacing the ionic group toward the interior, but not in the center of the fatty chain). Practical tests on wetting capacity (which is related to surface tension) subsequently confirmed Hartley's hypothesis. For nonionics, measurements have shown that lowering of surface tension can be maximized with a fatty chain C_{12}–C_{14} and a degree of ethoxylation of ~3–5 (13).

Influence of the Type of Molecule on Adsorption at the Different Interfaces. In general, adsorption increases with the length of the hydrophobic chain. For nonionics, adsorption diminishes as the number of ethylene oxides (hydrophilic part) increases (14,15).

Influence of the Type of Molecule on the CMC. First, it should be noted that the CMC of nonionics is much lower than that of anionics (1/100). On the other hand, the number of micelles of nonionics (number of aggregates) is higher than for anionics. For anionics, the CMC increases with the carbon chain and does not change greatly with the type of polar group. For nonionics, the CMC diminishes as the hydrophobic chain increases and increases with the number of ethylene oxides, but the effect is less significant than for the length of the hydrophobic chain.

Influence of Temperature on Surface and Interfacial Tensions. Temperature has only a small influence on surface and interfacial tensions. In general, an increase in temperature slightly reduces surface and interfacial tensions. For nonionics, it does not change greatly beyond the cloud point.

Influence of Temperature on Adsorption. Adsorption of nonionics increases with temperature. It becomes very significant around the cloud point.

Influence of Temperature on the CMC. The effect of temperature on the CMC of anionics is weak and quite complex. A number of works have shown that the CMC *curve presents a minimum as a function of temperature* (16). With nonionics, an increase in temperature decreases the CMC. It should also be noted that the number and size of micelles increase with temperature, particularly around the cloud point (17).

Influence of Electrolytes on Adsorption. The addition of electrolytes diminishes the solubility of surfactants (the salt effect), which increases adsorption at the interfaces.

Influence of Electrolytes on the CMC. With anionics, addition of electrolytes reduces their CMC according to the following relation (18):

$$\log \text{CMC} = A - B \cdot \log C^{+}$$

where C^{+} is the concentration of counterions. If we add a large amount of polar organic matter (e.g., urea or ethanol), we prevent the formation of anionic micelles. These are *hydrotropes*, which are used particularly in liquid detergents (dishwashing liquids, shampoos). On the other hand, the addition of a small quantity of these materials diminishes the CMC. For nonionics, the addition of electrolytes produces the salt effect, and therefore reduces the CMC. However, it should be noted that the effect of electrolytes on the formation of micelles operates only with nonionics with <15 ethylene oxides (19).

To summarize, we can say that solubilization is very closely linked to the number and size of micelles, i.e., everything that can reduce the CMC (hydrophobic chain, electrolytes) increases the number and size of micelles and for that same reason increases solubilization. Adsorption has the effect of changing properties at the interface, particularly a reduction of interfacial tension, which translates into an increase in the wetting properties of the surfactant solution.

Various Theories of Detergency

Detergency is defined as "*cleaning* the surface of a *solid* object, using a solution in which a specific agent, the detergent, acts by a *physicochemical* process other than simple dissolution" (1). In cleaning, the detergent removes soil from textiles and keeps soil in suspension in water to prevent redeposition on clothes present in the solution. Redeposition is dealt with in a subsequent chapter; thus this discussion will deal only with removal of soil and, in particular, with an examination of the mechanisms of detergents in dealing with two kinds of soil, i.e., fatty soil and particulate soil.

On household articles we find mainly greasy soil (grease or oil) and particulate soil (finely divided particles). These greasy and particulate types of soil are found independently or mixed in largely varying degrees. Fatty soil can come from human sebum or from contact with greasy articles in the environment (e.g., food, cosmetics, or motor oil) or from soap residues deposited on towels. Particulate soil includes metallic oxides, clay, or carbon composites such as soot. Surfacants are concerned principally with fatty and particulate soil. The mechanism by which they remove soil is very complex, particularly if we try to look at both types of soil at the same time. The explanation of the cleaning process is simplified if we consider that these two types of soil are removed independently of each other. To simplify things, we will therefore deal separately with the removal of fatty and particulate soils.

The Removal of Fatty Soil

Thermodynamic Theory: The Lanza Process. Let us consider a fatty matter *O* (oil) and a solid surface *F* (fiber). How *O* dirties *F* is shown in Figure 1.8. When a drop of oil *O* (condition I) is in contact with fiber *F* (condition II), it spreads until it reaches equilibrium with a contact angle θ, defined by the surface of the fiber and the tangent of the oil/air interface. Free energy in condition II can be written according to the following equation:

$$E_{FA} = E_{FO} + E_{OA} \cos \theta \tag{1}$$

where E_{FA} is the free energy of the fiber/air interface, E_{FO} is the free energy fiber/oil interface, and E_{OA} is the free energy of the oil/air interface. As we have already seen, free energy per unit of surface is equal to the interfacial or surface tension. Equation (1) becomes the following:

$$\gamma_{FA} = \gamma_{FO} + \gamma_{OA} \cos \theta \tag{2}$$

In addition, the adhesion of liquid *O* to the substrate *F* is given in the Dupré equation:

$$W_{FO} = \gamma_{FA} + \gamma_{OA} - \gamma_{OF} \tag{3}$$

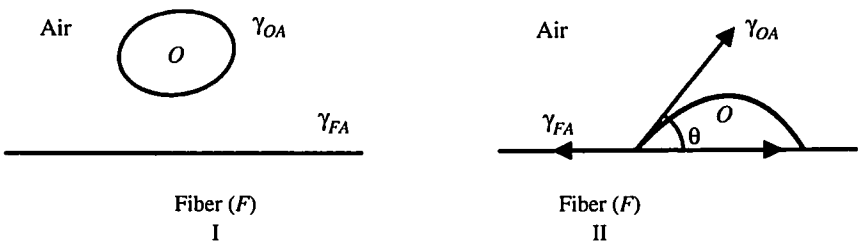


Fig. 1.8. Formation of fatty soil.

Using this equation, we can see that soiling an object becomes progressively easier because the work to obtain adhesion W_{FO} is small. For this to be the case, the surface tension of F (γ_{FA}) or of O (γ_{OA}) should be low. Nonpolar surfaces (e.g., oil or polyester) have low surface tension. Therefore, fatty matter sticks easily to polyester fibers. Cotton, on the other hand, is polar and thus has greater surface tension and is soiled less easily with oil.

The removal of fatty stain O from surface F in a wash solution is shown in Figure 1.9. It involves moving from condition II to condition III. Let us calculate the work necessary to achieve this change. At the initial stage II, free energy is given by the following equation:

$$E_{II} = \gamma_{OF} + \gamma_{OW}$$

When the soil is detached from F, as in condition III, free energy is given by the following:

$$E_{III} = \gamma_{FW} + 2\gamma_{OW}$$

(We find $2\gamma_{OW}$ because in condition III, we have created one extra interface between O and W.) The work necessary to go from II to III is equal to the following:

$$W_A = E_{III} - E_{II} = \gamma_{FW} + 2\gamma_{HW} - (\gamma_{OF} + \gamma_{OW})$$

or

$$W_A = \gamma_{FW} + \gamma_{OW} - \gamma_{OF} \tag{4}$$

According to this equation, the work required is less (and the removal easier) when the first two terms γ_{FW} and γ_{OW} are smaller and the third term γ_{OF} is larger. The addition of a surfactant does exactly this, i.e., it reduces the surface tension (reducing γ_{FW} and γ_{OW}) and increases interfacial tension γ_{OF} by its adsorption at the interfaces F, W, and O/W.

It can also be observed that in the case of (nonpolar) polyester fiber, which has been soiled by a (nonpolar) fatty matter, the interfacial tension γ_{OF} is low; the removal of this soil is therefore more difficult than for cotton where γ_{OF} is larger

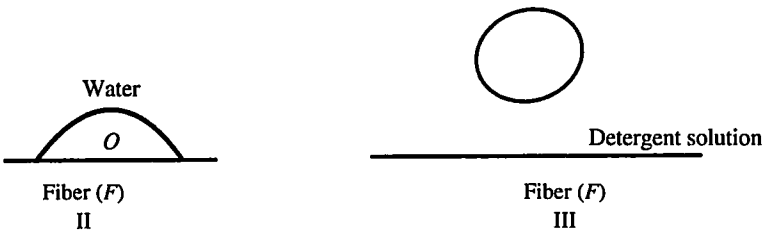


Fig. 1.9. Removal of fatty soil.

because cotton is polar. Using thermodynamics, we can determine the conditions necessary for *spontaneous cleaning* of fatty soil. For soil to remove itself spontaneously, it would be necessary for the free energy in the final condition (clean) to be less than in the original condition (dirty), which means that the following is true:

$$E_{III} < E_{II}$$

or

$$\gamma_{FW} + 2\,\gamma_{OW} < \gamma_{OF} + \gamma_{OW}$$

or

$$\gamma_{FW} + \gamma_{OW} < \gamma_{OF}$$

Therefore, if the surfactant, through its adsorption on the fiber and the soil, manages to lower the interfacial tension (relative to the water) in such a way that the sum becomes lower than the interfacial tension between the fiber and the soil, the soil will remove itself spontaneously. This mechanism is known as the *Lanza process.*

The "Rolling-Up" Mechanism. The removal of fatty soils can also be explained by the "rolling-up" theory pointed out by Stevenson (20) in 1953 and illustrated in Figure 1.10. The removal of soil is accomplished by going from condition II to condition IV, *via* intermediate condition III. At equilibrium, the resulting three vectors γ_{OW}, γ_{OF}, γ_{FW} are given by the following equation:

$$\gamma_{FW} = \gamma_{OF} + \gamma_{OW} \cos\theta \tag{5}$$

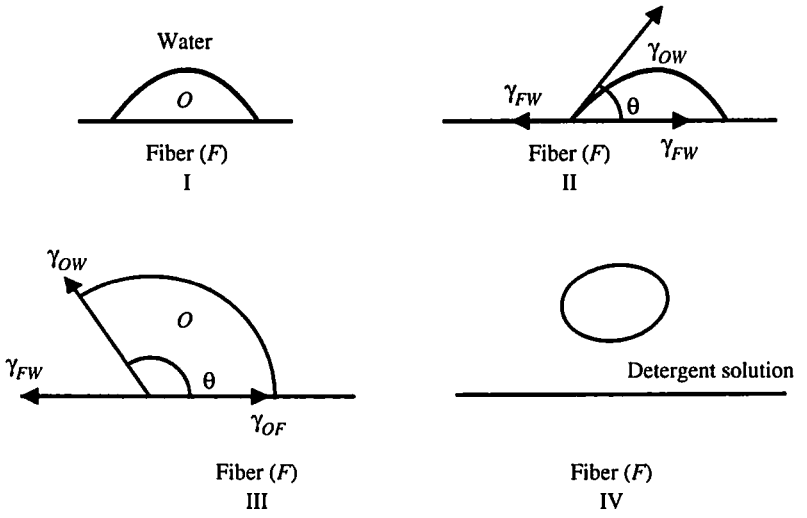


Fig. 1.10. "Rolling-up" process.

thus

$$\cos \theta = \frac{\gamma_{FW} - \gamma_{OF}}{\gamma_{OW}} \tag{6}$$

For the soil to be removed, it is necessary that θ be equal to 180° or $\cos \theta = -1$, in which case the equation becomes the following:

$$-1 = \frac{\gamma_{FW} - \gamma_{OF}}{\gamma_{OW}}$$

thus

$$\gamma_{OF} = \gamma_{FW} + \gamma_{OW} \tag{7}$$

Through adsorption on fiber and soil, surfactants lower interfacial tensions γ_{FW} and γ_{OW} in such a way that Equation (7) is confirmed. The fatty film (fatty soil) will then roll up and detach itself from the fiber through agitation (hand or machine washing). This is what is known as the rolling-up mechanism.

Solubilization. Rolling up is applicable only to liquid fatty soil and relies essentially on the lowering of interfacial tension by surfactants. Once the critical micelle concentration is reached, there is no further lowering of interfacial tension, and the rolling-up effect no longer increases above this level of concentration. However, because an increase in detergency beyond the CMC is observed, we have to introduce a further mechanism, namely, solubilization. This theory was first advanced by McBain (21) in 1942, and was subsequently taken up by Ginn *et al.* in 1961 (22).

We discussed above the solubilization phenomenon (physicochemical properties of surfactants, micellization, and the influence of different factors on the CMC), whereby surfactant molecules combine in dilute solutions to form "micelles" at a certain level of concentration called the "critical micelle concentration." In micelles, the hydrophobic part of the surfactant molecule faces the interior, whereas the hydrophilic part (ionized group or polyoxyethylene) is turned toward the water. A large number of compounds that are insoluble in water such as fatty acids, fatty alcohols, triglycerides, and hydrocarbons are dissolved in the interior of the micelles. If the solubilized molecules have polar groups (e.g., hydroxyls or carboxyls), they are generally to be found in the hydrophilic part of the micelles. Finally, solubilization can occur only when the concentration of surfactants is above the CMC.

To summarize, to obtain good detergency, it is necessary not only to have the surface tension lowered (Lanza process, rolling-up mechanism), but also to increase the concentration of surfactants to form micelles (solubilization) and to have a sufficient quantity of actives (e.g., anionics, nonionics), depending on the amount of fatty soil present in the wash solution.

Removal of Particulate Soil

Thermodynamic and Electric Theory. The phenomena of adhesion and removal of particulate soil are based on the theories of electricity and adsorption. The latter has already been dealt with in the context of fatty soil. We will look here at the electrical theory, based essentially on the theory of Dujaguin, Landau, Verwey, and Overbeck (DLVO) (23). Consider a flat surface F and a particle P. At a given distance δ, F and P are subject to attractive forces (Van der Waals) or to repulsive forces (electrostatic). The curves shown in Figure 1.11 show the repulsive and attractive energies of F and P as a function of their distance from each other.

Figure 1.12 shows the potential energy resulting from the superposition of attractive and repulsive energies. When P and F are in contact ($\delta = 0$), there is adhesion by attraction. The removal of particle P from surface F is illustrated in Figure 1.13.

The removal of particle P from surface F consists of moving from I to II, and then to III. In the first stage, we need to *supply* work W_1 to separate particle P from surface F by a given distance. In the second stage, the liquid penetrates between particle P and surface F, and a sum of work equal to J is obtained. The total amount of work is given by the following equation:

$$A_W = W_1 - J \tag{8}$$

where W_1 is the work supplied and J is the work created.

But $J = \gamma_{FP} - \gamma_{FW} - \gamma_{PW}$ where γ_{FP} is the interfacial tension between F and P in condition I, and γ_{FW} and γ_{PW} are the interfacial tensions of P and F with the detergent solution in condition III. As work A_W becomes smaller, the removal of soil or stain becomes easier. The addition of surfactants reduces γ_{FW} and γ_{PW} and therefore increases J. In this case, A_W decreases and the work to remove P is easy. This is the contribution of thermodynamics to the removal of particulate soil. Let us now look at the part played by electricity.

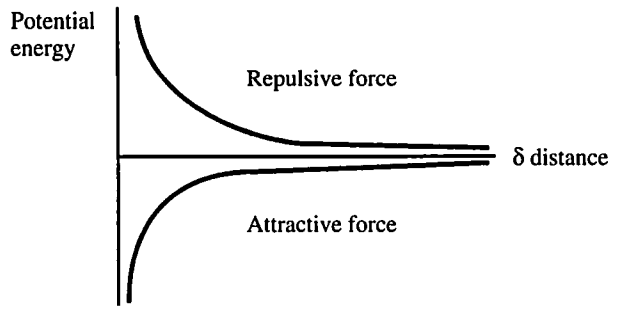


Fig. 1.11. Attractive and repulsive forces.

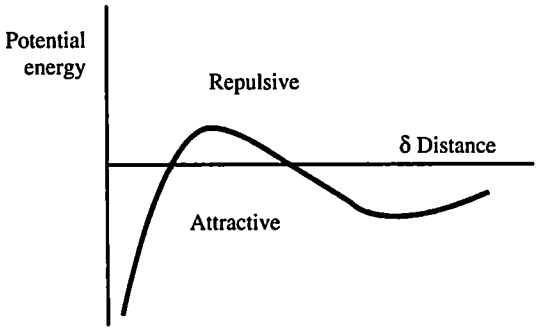


Fig. 1.12. Curve resulting from attractive and repulsive forces.

In Equation (8), A_W is low when W_1 is low. This happens if the repulsive force is strong or the attractive force is weak. In other words, we must have potential attractive forces that are as weak as possible. Figure 1.14 shows the two different repulsive forces. These figures show that in the first case, the work necessary to separate particle P from surface F by a distance δ is less because the repulsive energy is greater. This is the case, for example, for a particle and a polar surface, and this is precisely why surfactants in solution adsorb on particles and surfaces, resulting in an increase in their repulsive energy and making cleaning easier.

The Lanza Process. As for fatty stains, and still using thermodynamics, we can say that particulate soil will detach itself spontaneously from the fiber when the free energy at the final clean stage is lower than at the original (dirty) stage, according to the following equation:

$$\gamma_{PW} + \gamma_{FW} < \gamma_{FP}$$

Surfactants lower the interfacial tensions γ_{PW} and γ_{FW} until the situation illustrated below is achieved, and there is spontaneous detachment of the particle from the fiber with agitation, as illustrated in Figure 1.15. Using the same reasoning, if the

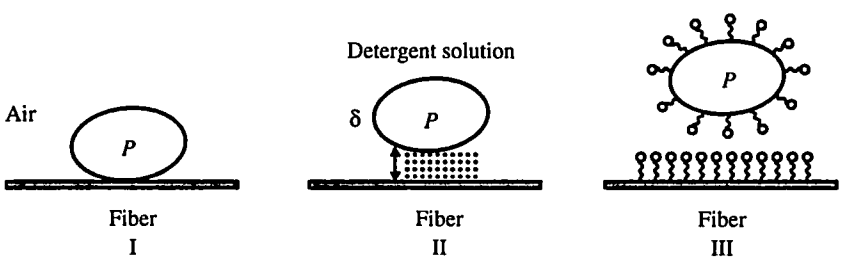


Fig. 1.13. Particulate soil removal.

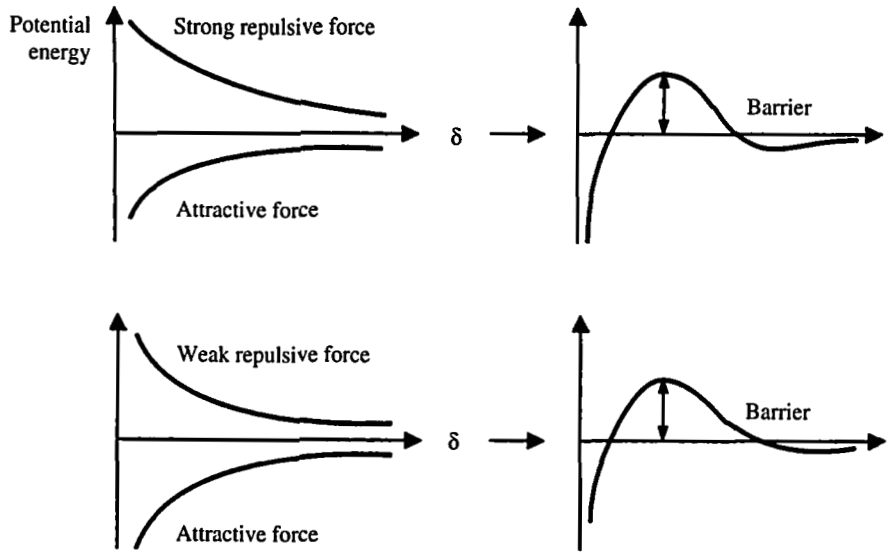


Fig. 1.14. Illustration of strong and weak repulsive forces.

soil is a mixture of fatty liquid and particles, there will be spontaneous separation of the liquid and the particles when the following relationship is achieved:

$$\gamma_{OP} > \gamma_{OW} + \gamma_{PW}$$

As noted above, spontaneous separation of oil/fiber, particle/fiber, and oil/particle is known as the Lanza process.

Other Detergency Mechanisms

Formation of Mesomorphic Phases. Micelles formed in a dilute solution are small and approximately spherical. If we increase the surfactant concentration, the micelles become larger and asymmetrical. Finally, a new phase called the "mesomorphic phase" is reached. This is a highly viscous, or even gelatinous liquid, made up of micelles organized in a specific way. It is birefringent, and diffracts X-rays. For this reason, it is also called a "crystalline liquid" (24). At the

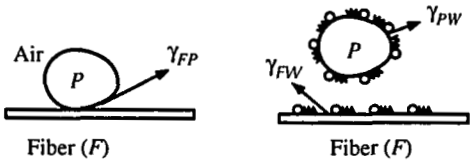


Fig. 1.15. The Lanza process.

interface between oil and water, there is adsorption of surfactants, which gives rise to a compact monolayer of molecules. Locally, we can consider that the concentration of surfactants is sufficient for a viscoelastic phase to form between the soil and the detergent solution, in the form of a crystalline liquid or the "mesomorphic phase." Subsequently, this mesomorphic phase is "swollen" and then "broken" by the rush of water. The soil is then dispersed into the detergent solution in the form of an emulsion or is "solubilized" in the micelles.

It should be noted that the "mesophase" can be formed only with more or less polar fatty matter, such as fatty acids or fatty alcohols. This particular detergency mechanism can be used only on polar soil. In addition, the mesophase layer constitutes a very viscous membrane, which prevents a new detergent solution from penetrating the soil, thus delaying considerably the break-up and dispersion processes. For these reasons, this mechanism is not of great significance in the laundering process.

Formation of Soaps. Some mineral compounds in detergent formulations such as tripolyphosphate, silicate, and perborate confer an alkaline pH on the wash liquor. This changes the fatty acids contained in sebum into sodium soap, which is soluble in water. The transformation of sebum fatty acids into a solution through the action of alkaline agents is another detergency mechanism. It should be pointed out, however, that in hard water, sodium soap is converted into insoluble calcium (lime) soap, which can deposit on clothes. Also, the sebum triglycerides are not saponified, even at a pH of >11.

The Break-Up of Solid Polycrystalline Aggregates. By what mechanism is nonpolar fatty soil removed at a temperature lower than its melting point? In fact, it is removed by surfactants that penetrate tiny splits or cracks in the solids, breaking them up into fine particles that are subsequently dispersed into the detergent solution. Scott (25) proved this mechanism by showing that there is a high degree of retention of surfactants in solid tripalmitin. The break-up of solid aggregates can also be observed under the microscope. If we place a fragment of solid triglyceride onto an alkaline detergent solution, we observe that the solid is broken into a cloud of fine particles.

Wash Performance and Detergency Mechanisms

Washing textiles is a fairly complex process. As we have seen, many mechanisms can help with the removal of soil. Schematically, we can apply the different theories to different types of soil, as shown in Table 1.2.

In a laboratory, we can show any of the mechanisms; in the real world, however, it is not yet possible to prove that one mechanism is better than another and to quantify the difference. This is because other factors play a very important part in detergency, for example, agitation, or the structure of the fibers.

TABLE 1.2
Application of Theories to Different Types of Soil

Theory	Soil
"Rolling-up" theory	Fatty soil
Solubilization	Fatty soil
Thermodynamic theory	Greasy or particulate soil or a mixture of the two (spontaneous separation, Lanza process)
Electric and thermodynamic theories	Particulate soil
Mesophase formation	Polar fatty soil
Saponification	Fatty acids in soil
Break-up by retention of surfactants	Solid, nonpolar fatty soil

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CHAPTER 2

The Main Ingredients Used in Detergents and the Mechanisms by Which They Act

Before examining the main ingredients used in detergents and how they work, we will look at the primary factors that influence washing results. Of these, the main ones are the water, the types of soil, and the types of textiles.

The Influence of Different Factors on the Wash Process

Water

Detergent products, like washing machines, act on soil by using several properties of water, including the following: (i) it can more or less dissolve certain substances; (ii) it conducts heat; (iii) it is given energy by the motion of the machine drum; (iv) it can keep certain particles in suspension; (v) it wets textiles to a greater or lesser degree; (vi) it allows chemical reactions to take place; and (vii) it evaporates.

It is therefore a precious ally; unfortunately, however, it does not possess only positive qualities. Indeed, all natural waters contain mineral salts, including calcium and magnesium bicarbonates (soluble salts) that can become insoluble (carbonates) when exposed to higher temperatures. This is the "tartar" or "chalky limestone" so familiar to people living in certain areas, a substance which requires the formulator to include water-softening agents in the detergent compositions. Table 2.1 provides the various definitions used in France to describe water hardness.

In Europe, hardness is defined as French Degree Hardness (°FH) or German Degree Hardness (°DH). In the UK and the United States, other units are used.

TABLE 2.1
Definition of Water Hardness

Name	Abbreviation	Definition
Total hardness	TH	Calcium and magnesium salts
Temporary hardness	TAC	Calcium and magnesium bicarbonates and carbonates
Permanent hardness	TH–TAC	Neutral calcium and magnesium salts (or the overall content of calcium and magnesium sulfates and chlorides)
Alkalinity to phenolphthalein	TA	Alkalis alone
Alkalinity to Methyl Orange	TAC	Alkalis and carbonates, or carbonates and bicarbonates, or bicarbonates alone

These units convert as follows, given that the molecular weights of $CaCO_3$ and CaO are 100 and 56, respectively,

$$1° \text{ FH} = 10 \text{ mg } CaCO_3/L = 0.56° \text{ DH}$$
$$1° \text{ DH} = 10 \text{ mg CaO/L} = 0.78° \text{ FH}$$
$$\text{In UK (1 unit)} = 10 \text{ mg } CaCO_3/0.7 \text{ L} = 1.63° \text{ FH}$$

(In the U.S., hardness is expressed as ppm $CaCO_3$, i.e., 1° FH = 10 ppm $CaCO_3$)

The scientific measure is expressed as milliequivalents of calcium and magnesium per liter (meq/L); 1 meq/L = 5° FH. French degrees are also expressed in terms of concentration of free calcium, i.e., $1° \text{ FH} = 10^{-4} [Ca^{2+}]$.

Water hardness is of such importance to detergent manufacturers that in many cases, product dosage varies not only depending on the amount of soil on clothes, but also according to the hardness of the water used. This is particularly the case in France, where hardness varies widely from one region to another (e.g., 7–8° FH in Brittany and 55–60° FH in the North Pas de Calais area). By convention, the following three levels have been identified in France (these are the values that are to be found on detergent cartons): SOFT, <20° FH; HARD, from 20 to 35° FH; and VERY HARD, >35° FH.

Different Types of Soil

The types of soil encountered in the wash process can have many different origins, e.g., the human body, which is often in direct contact with clothes; the environment (the atmosphere which provides soot and dust); food, certainly the most frequent and the most varied source of soil and stains; or the workplace, in which the soil and stains found on a butcher's overalls, for example, are quite different from the soiled clothes of a mechanic.

Soil is generally classified into three main families. These include fatty soil, nonfatty soil, and particulate soil. They are made up of elements that are either soluble in water (e.g., salt or sugar) or insoluble in water (e.g., grease). This classification is more or less artificial because natural soil found on linen is usually a combination, for example, of greasy soil and particulate soil. These types of soil affix themselves to textiles in the following ways: physically (attractive forces), physicochemically (greasy secretions that attract dust), and chemically (colorants that penetrate deep into textiles).

Body Soil. This category includes traces of sebum (a deposit of fatty matter and skin, particularly on collars and cuffs), human waste (including perspiration), and blood.

Environmental Soil. This category includes mainly solid particles (earth, soot, or various kinds of dust), natural colorants (grass stains), or artificial ones (cosmetics, ink, or mineral oils).

Food Soil. This is the largest category. The quantity and type of stains are extensive; they include solids (e.g., chocolate or fruit) and liquids (e.g., wine, tea, or coffee). Food includes colorants of natural or artificial origin. Food soil includes these three basic food elements: (i) lipids (oil and grease, insoluble in water); (ii) carbohydrates, including sugars, which are soluble and therefore easy to remove; starches (e.g., pasta, flour, rice, or potatoes), which are sometimes invisible, but attract soil (starch is a real glue which attracts particulate soil); and cellulose (e.g., carrots or lettuce), which is easily removed despite being insoluble; (iii) proteins, including meat, eggs, milk, and cheese. Proteins coagulate in heat; large molecules have to be cut into smaller ones before they can be removed.

The Workplace. As mentioned above in our example of the butcher and the mechanic, a wide variety of soils can be found in the workplace. In the case of the butcher, the detergent will need all the strength of antiprotein agents, whereas for the mechanic, surfactants will do the work.

It will already be understood that in the battle against stains, the detergent is not the only participant. We will see later that other energies come into play (mechanical and thermal, in particular, contributed by the washing machine). But water remains essential as the vector of all other energies. For this reason we began this chapter with the subject of "water."

Different Textiles

Everyone is aware of the wide variety of textiles used today, particularly for clothing. Each requires specific treatment in the wash because it reacts differently to water, temperature, the machine, and the detergent. If we add the complication of color (of which there is a wide range dictated by fashion and the arrival of new finishes and fibers), the problem posed to the detergent formulator will be still more obvious! Textile fibers are classified into the three following groups, by origin: (i) *natural fibers*, including vegetable (cotton, linen) or animal (wool, silk); (ii) *artificial fibers*, which are derived from cellulose (viscose, acetate, rayon); and (iii) *synthetic fibers*, which are obtained from petroleum products (polyester, acrylic, polyamide). Some articles are made from a mixture of fibers (e.g., polyester/cotton), bringing the benefits of each. In this "jungle" of color varieties, textile fibers, and special treatments, the consumer fortunately is helped by the care label on clothes. When clothes are put into the machine, the label offers guidance concerning the temperature to use and precautions to take (e.g., do not iron, do not place in dryer, or do not use bleach). A series of pictograms exists to help the consumer (an idea first used by the French Committee for Labeling and the Maintenance of Textiles, COFREET). The different types of textiles are summarized in Table 2.2.

Textile Developments. Over the past 50 years, the market share of synthetic and artificial fibers has grown from 10 to >40%, and the trend is continuing; however, the future could surprise us by reversing this trend. The market, which was dominated

TABLE 2.2
Different Textile Types

Textile type	Characteristics	Recommended treatment
Natural vegetable fibers, e.g., cotton, linen	Resistant	Can take high temperatures, rough handling, and bleach (for whites only).
Natural animal fibers, e.g., wool, silk	More fragile. Lose 40% of their resistance when wet.	Require careful treatment. Should be washed and rinsed at 20–30°C maximum.
Synthetic fibers, e.g., nylon	Strong. Neither water nor soil can penetrate deeply, except for certain fats.	Do not like high temperatures. Can be difficult to wash.
Mixed fibers (synthetic and natural)	Worn more and more today, these modern textiles blend the comfort of natural fibers with the advantages of synthetics.	Wash temperature to be chosen on the basis of the most fragile fiber.
Artificial fibers e.g., viscose, acetate	Derived from natural vegetabe fibers.	More fragile than natural fibers; bleaching is discouraged.

in the 1950s by cotton, wool, and silk, began to diversify in the 1970s to include acrylic, viscose, and polyester; this trend continued into the 1990s and accelerated with the appearance of more comfortable and easy-care textiles such as microfibers, Lycra, Teflon-treated, easy-iron or no-iron, or antimicrobial fabrics. "Classical" detergents are not always suitable for these textiles as evidenced by yellowing of nylon some years ago.

In the 1970s, a study was conducted in conjunction with the French Textile Institute to localize and identify types of soil. Results showed that after a certain number of washes, fibrils formed in cotton, and particulate soil and fat became imprisoned in the interior of the cotton fiber (the lumen). Should the fatty soil not be washed out by the detergent, it would polymerize, giving a yellowish appearance; on the other hand, particulate soil caused greying, as we shall see below. In mixed cotton and polyester, fatty soil affixes itself to the polyester, giving a yellowing effect; it can even migrate to the cotton component, lodging itself in the lumen. Finally, wash must be sorted by color.

Main Ingredients and Their Mechanisms

Choice of Surfactants

We examined surfactants at length in Chapter 1. We will now look briefly at surfactants used in washing products. The choice of a surfactant for a laundering product depends on a number of factors, including the following: wash temperature, type of textile, foam level desired, builder used (phosphate or nonphosphate), the environment, the product form (liquid, conventional, or concentrated powder), and the method of manufacture [tower or nontower route (NTR)].

General Rule. Some general guidelines in choosing the surfactant are discussed here. We will often refer to "builders," which are discussed below; however, because we cannot discuss surfactants without referring to "builders," we offer some definitions at this stage. Originally, the term "builders" denoted additives that were combined with soap to improve wash performance. The term was subsequently used to describe water softeners, particularly phosphates and subsequently zeolites, silicates, or carbonates. When there are sufficient builders in a formulation, we say that the wash solution is "built"; when this is not the case, we say it is "underbuilt."

Surfactants are the most essential ingredient in a laundering product. As mentioned in Chapter 1, their function is to remove soil and to keep it in suspension in the wash solution, preventing redeposition on clothes—what we call detergency. Two important factors govern detergency, i.e., the solubility of the surfactants and their critical micelle concentration (CMC). To achieve a minimum level of detergency, surfactants must be soluble in the wash solution.

The Krafft point, or the temperature at which surfactants dissolve, increases for anionics with the length of the alkyl chain; for example, the Krafft point in the distilled water of a sodium lauryl alcohol sulfate is ~20°C, whereas that of C_{16}–C_{18} alcohol sulfate is ~50°C. But these values can change in the presence of other ingredients such as nonionics, builders, or other minerals. Addition of ethylene oxide to fatty alcohol sulfate lowers the Krafft point (1), so that lauryl ether sulfate (LES) has a Krafft point that is lower than its precursor C_{12}–C_{14} primary alcohol sulfate (PAS); this is why LES is used in low-temperature wash products (e.g., hand-washing products or dishwashing liquids). Linear alkylbenzenesulfonates (LAS) have a very low Krafft point; for example, C_{12} LAS has a Krafft point of <0°C in distilled water. For nonionics such as ethoxylated fatty alcohols, the temperature at which they become insoluble (known as the "cloud point") decreases as the length of the alkyl chain increases or the number of ethylene oxides decreases.

Surfactants must not dissolve too easily at the chosen wash temperature because there will be less adsorption to lower the interfacial tension of the fibers. To obtain good detergency with anionics, they must be neither too soluble nor too insoluble at the wash temperature. For nonionics, detergency for nonpolar soil has been found to be optimal at temperatures just above the cloud point, whereas for polar soil, the opposite is true (2,3). It is also generally accepted that nonionics are better than anionics at removing nonpolar soil, whereas the opposite is true for polar soil.

The choice of surfactant also depends on the quality and quantity of builders in the product. Among anionics, LAS is the most sensitive to the presence of Ca^{2+} and Mg^{2+} ions in water. If the quantity of builders is insufficient, calcium LAS precipitates, which reduces the concentration of surfactant and reduces detergency. Without precipitation, LAS detergency increases with concentration up to 0.6 g/L (4). PAS, LES, α-olefinsulfonate (AOS) and methyl ester sulfonates (MES) are less sensitive to Ca^{2+} and Mg^{2+} ions than LAS (5,6). This is also true for nonionics.

In a study comparing the efficacy of LAS with nonionics (4), it was shown that for a fatty alcohol ethoxylate, the concentration of nonionics required for optimal detergency is ~0.2 g/L, which is almost the same as the CMC of this particular nonionic.

Is it better to use one surfactant or a combination? In developing countries, in which washing is generally done by hand, LAS is used (although in some countries nonbiodegradable ABS is still being used) along with STP, carbonate, and silicate as builders. Since precipitation of LAS in underbuilt situations is reduced by the formation of mixed micelles with nonionic, addition of a small percentage of nonionics is recommended. But this addition of nonionics can reduce the foam properties of the product. In Europe, combinations of nonionics and anionics are generally used in proportions that vary from one-fourth to two-thirds. Most such products are nonfoaming. Soaps or silicones are used as antifoaming agents (see below). In the United States and Japan, the same combinations are used but without antifoam ingredients because the washing machines there are suds tolerant.

Different laboratory studies have shown the importance of the nonionic/anionic mixture in detergency on fatty soil. Quencer *et al.* (7) recently completed experiments on the removal of fatty soil (cetane) by a mixture of C_{16} alkyldiphenyl oxide disulfonate and (C_{12}–C_{13}) alcohol ethoxylate with 3 EO units. This study makes it possible to determine the optimum mixture of surfactants to obtain the best result on certain stains. The same type of study could be envisaged for other surfactants. Anionics with an alkyl chain from C_{12} to C_{15} are used in the industry. Nonionics often are fatty alcohol ethoxylates with alkyl chains from C_{12} to C_{18} and from 5 to 9 ethylene oxide units.

New Trends. Today, many manufacturers use more environmentally friendly surfactants that are biodegradable or "renewable." Examples include the following:

1. Vegetable oil (coconut)-based fatty alcohol sulfates (PAS).
2. Alkylpolyglucosides, which have many advantages (8). Combined with the right nonionics, they have a positive effect on removing oily stains. Their softening properties are better than those of nonionics. "Salting out" (the separation of phases in the presence of electrolytes) is weak, which is a definite advantage in formulating concentrated isotropic liquids; for structured liquids, this allows a better dispersion of liposomes (see also the discussion of structured liquids). The viscosity of the slurry can be reduced, giving a better yield when the powder is blown.
3. Fatty acid glucosamides (9).
4. Methyl ester sulfonates (10).
5. Ethoxylated fatty alcohols with a narrow distribution of ethylene oxide units: For a normal nonionic with an average of 7 ethylene oxide molecules, the number of EO units varies between 1 and 15. For the same nonionic with a narrow distribution, the number of ethylene oxide molecules varies between 3 and 12. This type of nonionic is more effective.

In powder production by atomization (spray drying), LAS is not problematic and is very stable. Powders with high levels of nonionics are more difficult to manufacture, i.e., the slurry (the paste to be blown) is more viscous and can produce blue smoke (and even catch fire) during blowing because ethoxylated fatty alcohols always contain volatile ingredients such as unethoxylated alcohol or low-EO ethoxylates. Under these circumstances, the amount of water in the slurry is increased to reduce both viscosity and the blowing temperature, resulting in a loss of tower productivity.

Blowing PAS-based powders presents problems intermediate between those of LAS and nonionics. Clearly, the choice of surfactants is less problematic when using the non-tower routes for concentrated powders. Concentrated products containing LAS, PAS, alkyl polyglucosides (APG®, in Europe), LES and AOS (United States and Japan) are available in the trade. MES may be used in the near future.

Levels of Surfactants to Use. It is difficult to give general rules on the level of surfactants to be used in a detergent. A number of factors need to be considered, including product density, types of builders used, and the nature of the surfactants. In developing countries, powders with density of 0.2 to 0.32 g/L generally contain between 16 and 22% LAS. In Europe, conventional powders with phosphate and a bulk density of ~0.7 contain surfactants at levels of 8–12%. In non-phosphate products, the levels are slightly higher to maintain the same wash performance. In concentrated powders, zeolite is generally used as a builder, resulting in higher density and lower recommended dosages. Surfactants represent between 16 and 22% of the formulations. In the United States and Japan, where concentrated powders predominate, the level of surfactants is between 20–25%. Table 2.3 compares the main differences in laundering conditions in Western Europe, the United States, and Japan. In Europe, water is generally harder, but the concentration of surfactants and builders as well as temperatures used are higher and wash cycles are also longer.

TABLE 2.3
Laundering Conditions in Europe, the United States, and Japan

	Europe	U.S.	Japan
Average water hardness (FH)	20	10	5
Average wash temperature	50°C	30°C	20°C
Volume of water	16 L	60 L	30 L
Average wash time	60 min	15 min	10 min
Average surfactant concentration	1.3 g/L	0.25 g/L	0.2 g/L
Average builder concentration	3.0 g/L	0.50 g/L	0.16 g/L

Water-Softening Agents

There are three widely used methods to prevent water hardness from interfering with washing performance, i.e., the *complexation* of ions Ca^{2+} and Mg^{2+}, the *ion exchange* of Ca^{2+} and Mg^{2+} with Na^{+} ions, and the *precipitation* of Ca^{2+} and Mg^{2+} ions.

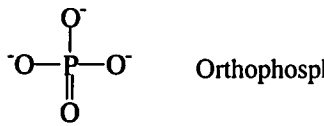
Complexing Agents

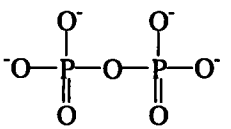
The best known complexing agent is tripolyphosphate.

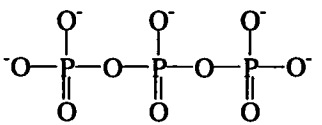
Phosphates. Since the Second World War, detergent formulations have included phosphates (mainly tripolyphosphate). Incorporation levels are generally between 28 and 40%, but can go up to 45 and even 60–65%. For cost reasons, and more importantly for environmental reasons, content is presently ~20%. There are many studies of this compound which we will not detail here. We will look simply at the chemistry of phosphates and the function of phosphates in detergent products

The chemistry of phosphates. Phosphates are complexing or chelating agents. A chelating agent is a chemical reagent that forms water-soluble complexes with metallic ions. Terms such as sequestration, *chelation*, and complexation are used to describe this reaction. Tripolyphosphate is called a builder like other water-softening agents.

Chemical structure of phosphates. The main phosphate formulas used in detergent powders are as follows:


Orthophosphate

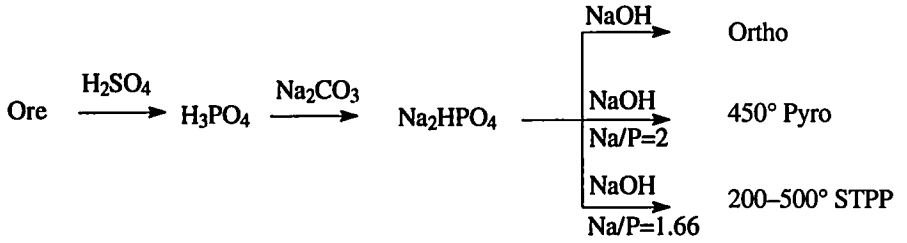

Diphosphate or pyrophosphate


Triphosphate "improperly called" tripolyphosphate

For simplification, these will be referred to as "ortho" (phosphate), "pyro" (phosphate), and TPP (tripolyphosphate) or STPP (sodium tripolyphosphate).

Phosphate manufacture. Before examining the different properties of phosphates, the following is an illustration of their manufacturing process. STPP is obtained by heating a solution of ortho containing 5 mol Na_2O and 3 mol P_2O_5. In general, slightly more Na_2O is used to prevent long chains from forming. At a drying

temperature between 350 and 400°C, a variety of STPP called Type II is produced. Between 450 and 615°C, another variant called Type I is obtained. The transformation between types is very slow and the transition temperature is ~415°C. At ambient temperature, both types can co-exist; most commercial STPP is a mixture of Type I and Type II. An illustration of the process is as follows:

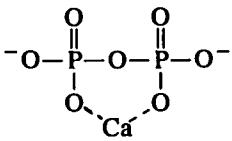


Physical properties of STPP. STPP is sold as a white powder of variable density and granularity. It also contains variable quantities of pyro and ortho. It can be anhydrous, partially hydrated (called prehydrated), or fully hydrated with six water molecules. Hydration is done in two stages as follows:

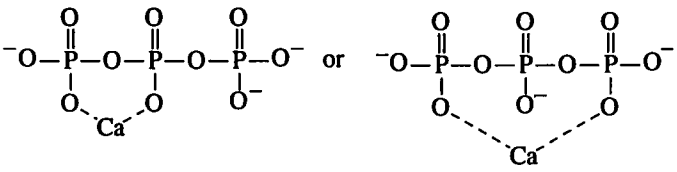
First phase (hydration)	$STPP_{solid} + 6\ H_2O$	→	STPP 6 H_2O in aqueous solution
Second phase (crystallization)	STPP 6 H_2O in supersaturated solution	→	STPP 6 H_2O solid crystals

From a purely chemical perspective, there is no difference between Type I and Type II STPP, anhydrous STPP, and hydrated. The only difference is the speed of hydration (Type I hydrates more quickly than Type II), the heat of hydration, and the crystalline structure. These physical characteristics are important for detergent powder slurry making. Analytical methods for categorizing STPP are as follows: (i) hydration: water loss in the *oven*; (ii) Type I, Type II: X-ray diffraction (structural difference) or measurement of the rate of temperature rise due to the difference in heats of hydration; (iii) STPP-pyro-ortho mixture: chromatography on paper or in a column using an autoanalyzer.

Complexation by phosphates. In complexation, the complexing agent reacts with metal ions in solution to form water soluble complex ions. The chemical structure of complexes with calcium takes a number of forms. With pyro, the structure is as follows:



With tripoly, the following two possibilities exist:



The complexation reactions are as follows:

$$Ca^{2+} + P_3O_{10}^{5-} \leftrightharpoons CaP_3O_{10}^{3-}$$

with the formation of a small amount of $Ca_2P_3O_{10}$ according to the following reaction:

$$Ca^{2+} + CaP_3O_{10}^{3-} \leftrightharpoons Ca_2P_3O_{10}$$

The reaction with Mg^{2+} is identical. The same is true of Na^+ as follows:

$$Na^+ + P_3O_{10}^{5-} \leftrightharpoons NaP_3O_{10}$$

There are also mixed ions CaNa or MgNa

$$Ca^{2+} + NaP_3O_{10}^{4-} \leftrightharpoons CaNaP_3O_{10}^{2-}$$

The curve in Figure 2.1 gives the concentration of free calcium as a function of the molar ratio STPP/Ca^{2+} starting with water at 40° FH.

Comment

We express (Ca^{2+}) where pCa = –log (Ca^{2+}).

At the equivalent point (where the molar concentrations of STPP and calcium are equal), the concentration of free calcium is low (~0.2° FH). Beyond the equivalent point, the concentration of free Ca^{2+} falls sharply as we add STPP to the solution; thereafter the reduction in free calcium becomes less and less evident as we continue to add STPP to the solution. Before the equivalent point, or when STPP/Ca^{2+} < 1:1, a precipitate forms as follows:

$$5Ca^{2+} + 2P_3O_{10}^{5-} \leftrightharpoons Ca_5(P_3O_{10})_2$$

This precipitate is greatest when STPP/Ca^{2+} = 2:5.

Stability of complexes. A complex is characterized by a stability constant, which is a quantitative measure of the affinity of a complexing agent for a given metal ion, i.e., the reaction between STPP and Ca as follows:

$$Ca^{2+} + P_3O_{10}^{5-} \leftrightharpoons CaP_3O_{10}^{3-}$$

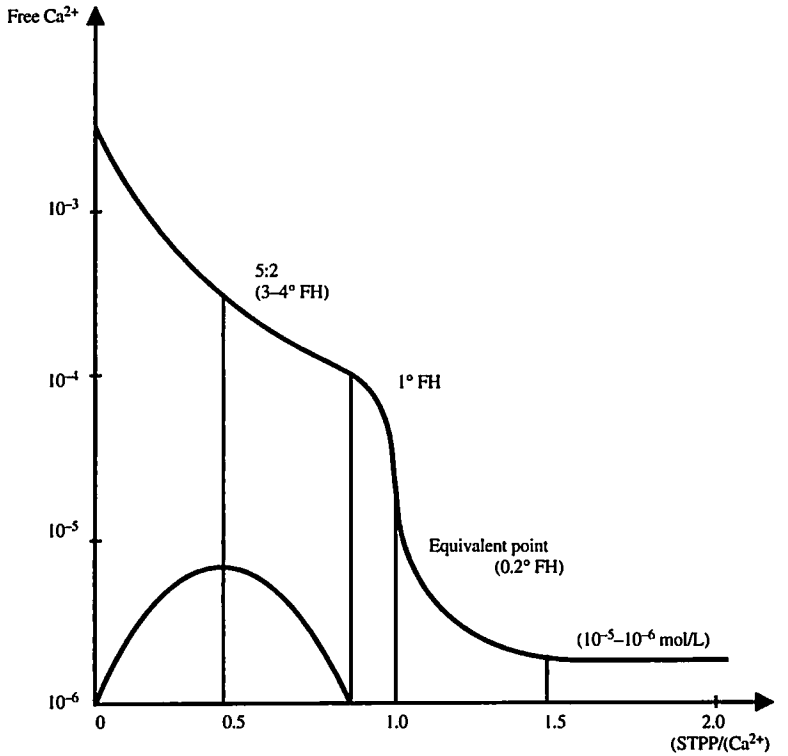


Fig. 2.1. Concentration of Ca^{2+} as a function of the ratio sodium tripolyphosphate (STPP)/Ca.

The stability constant of the complex is therefore: $k = (CaP_3O_{10}^{3-})/(Ca^{2+})\ (P_3O_{10}^{5-})$. It is apparent from this equation that if the value of the constant k is large, the ratio will be high, meaning that the complex is stable. The stability constant is usually expressed as log k or $pk = (-\log k)$. Factors influencing the stability of complexes include *pH* and *ionic strength.*

The stability constant of complexes is affected by variations in pH. At pH ≥9.5, excess STPP takes the form $P_3O_{10}^{5-}$ or $NaP_3O_{10}^{4-}$. As the pH decreases, a large part of the STPP is changed into $HP_3O_{10}^{4-}$ or $NaHP_3O_{10}^{3-}$. These ions predominate at pH <7–8. They complex Ca^{2+} and Mg^{2+} less strongly than $P_3O_{10}^{5-}$ or $NaP_3O_{10}^{4-}$. Thus, we find that the complexing constant decreases with pH.

Complexation is an ionic equilibrium. It is therefore normal that a high concentration of ions not involved in the reaction will have an effect on complexing efficacy. In general, high concentrations of anions and cations in the detergent solution (e.g., sulfate, silicate, K, or Na) tend to reduce the stability of phosphate complexes. It should be noted that in comparing stability constants, temperature and ionic strength must be taken into account. Finally, from the few available published

works, the following statements can be made: (i) for STPP, the Mg complex is more stable than the Ca complex. But for NTA and EDTA (see page 64), the opposite is true; (ii) relative to Ca, the stability of complexes in increasing order is EDTA > NTA > STPP > Pyro.

Precipitation reaction. In a detergent powder solution, there are numerous anions that can form insoluble salts (precipitates) with calcium in water. Complexants have the characteristic that they are likely to dissolve these precipitates and then to form soluble complexes. We are therefore in the presence of a competitive reaction between the complexing and the precipitating anions for calcium. In a detergent solution, the precipitating anions come from carbonate, alkylbenzenesulfonates, and soaps (laurate, oleate, and stearate), whereas the complexing anions come from STPP, pyro, and EDTA. The chemical reactions are as follows:

$$\text{Complexing agent} + \text{Ca} \rightleftharpoons \text{soluble complexes}$$

$$\text{Precipitating agent} + \text{Ca} \rightleftharpoons \text{insoluble precipitates}$$

In practical terms, to compare complexation and precipitation, we look at the concentration of free Ca^{2+} in each of the reactions, i.e., if the concentration of free Ca^{2+} is lower in the complexing reaction than in the precipitation reaction, the precipitate will dissolve and we will have a complexing reaction. In the opposite case, a precipitation reaction will occur and there will be no complexing. Finally, as we have mentioned previously, pyro is less complexing than STPP.

Hydrolysis of STPP and pyrophosphate. These phosphates hydrolyze in aqueous solution at concentrations close to those of the wash solution according to the following:

$$\text{pyro} + H_2O \rightarrow \text{ortho}$$

$$\text{STPP} + H_2O \rightarrow \text{ortho} + \text{pyro (equimolar mixture)}$$

In the first case, pyro hydrolyzes in turn, but more slowly (speed = one-third of the speed of STPP). Hydrolysis accelerates because the solution becomes is more acid and the temperature rises. The ionic environment also has a strong influence on the speed of hydrolysis, i.e., the increase in speed from the sodium medium to a medium with bi- or trivalent ions. We can say that cations (including H^+) accelerate hydrolysis, and that this increases when the ionic charge is high. The essential factor, however, remains temperature (a factor varying from 1 to 10 for the interval 0–100°C). In a detergent solution there is a mixture of STPP, pyro, and ortho. The last two do not come from a hydrolysis reaction during the wash, but from two other main sources. Pyro is formed during STPP manufacture (STPP received from suppliers contains 4–8% pyro), and there is also STPP breakdown during the manufacturing process (slurry making and spray drying).

The function of phosphates in detergent powders. The functions and properties that we will look at here *are mainly for products containing phosphates as the sole builder.*

Detergency involves a number of processes that are often more or less interdependent. These processes have the following components: wetting, adsorption of solids at the interface, emulsification, the removal of soil, and its dispersion in the wash solution. Detergency is therefore a very complex subject, and the exact and specific function of each ingredient in a detergent powder is often difficult to identify. It is nonetheless clear that complexants such as STPP have an essential function because washing efficacy is greatly reduced in their absence. We can conclude that STPP is important to detergency for a number of reasons including the following: (i) it forms soluble complexes with the alkaline earth ions present in hard water; (ii) it provides reserve alkalinity; and (iii) it has antiredeposition properties. Each of these is discussed below.

The formation of complexes. Calcium in water helps to fix mineral particles and organic soil such as free fatty acids with long carbon chains present in sebum. Most solid particles in suspension in a wash solution are negatively charged. The surface of textiles is also negatively charged (for example, carboxylic functions on oxidized cellulose). In this case, calcium serves as a bridge between particulate soil and the fiber surface. Sebum fatty acids form insoluble precipitates with calcium, which then deposit onto the fibers. The attachment of soil to fibers due to calcium is illustrated in Figure 2.2. Calcium is found in soil fixed to cotton or polyester fibers. The other negative effect of Ca^{2+} in the detergency process is that it forms precipitates with alkylbenzenesulfonate, greatly diminishing the concentration of this anionic surfactant. This is why complexants such as STPP are needed in washing powders to achieve good detergency.

Reserve alkalinity. The alkalinity of a complexant is its capacity to produce a high concentration of hydroxide ions (high pH) in detergent solutions. Its buffer function is its ability to maintain the pH over a wide range despite the addition of base or acid. The optimum pH level for good complexation and detergency is between 9 and 10.5. The pH of a detergent solution should therefore be maintained in this range in the presence of acids.

There are two main sources of acidity in detergent systems. The first one comes from acidic soil such as fatty acids, and the second, from the liberation of protons during the complexing process. Triphosphoric anions which are weakly acidic are

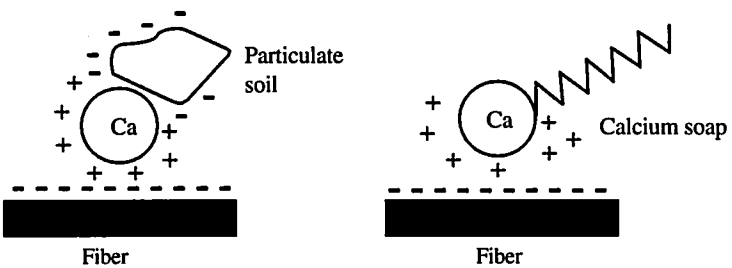


Fig. 2.2. Attachment of soil to fibers by Ca^{2+}.

strongly dissociated when a calcium complex is formed. Liberation of these protons together with fatty acids from oily soil will lower the pH of the detergent solution. STPP provides alkalinity to the detergent solution and maintains the pH in the target range (we should bear in mind that weak acid salts with a strong base give both alkalinity and buffering; the weaker the acid, the more alkaline will be the salt). Finally, it is worth noting that alkalinity and buffering can be obtained in detergents with other salts such as silicates, borates, and carbonates.

We will now deal with redeposition problems and mineral incrustation.

Antiredeposition role. Redeposition problems will be discussed below; for the moment, we will consider only the essential aspects of the problem. Electrolytes bring cations to the wash solution, which reduce the electrical double layer and cause a reduction in repulsive forces between particles and fibers. Electrolytes therefore favor redeposition. This effect increases as the concentration of electrolytes rises and the cations are di- or trivalent (Ca^{2+} or Al^{3+}). It explains why STPP, in complexing the troublesome cations, greatly reduces redeposition. An improvement in whiteness is indeed noted in laboratory trials in which the quantity of STPP exceeds the level corresponding to the equivalent point. However, if excessive STPP is used, the opposite effect will be obtained and redeposition will increase, which is comparable to the salt effect mentioned above.

A further mechanism linked to the antiredeposition function of STPP is the adsorption of $P_3O_{10}^{5-}$ anions on solid particles, which causes an increase in their charge (zeta potential). Charged solid particles repel each other. This produces stable dispersions, and particulate soil will not redeposit on fibers. A similar situation can occur with particles of fatty acid or oils. To achieve a given concentration of $P_3O_{10}^{5-}$ ions, we need a certain excess of STPP.

Mineral incrustation (ash). Calcium pyrophosphate $Ca_2P_2O_7$ is less soluble than calcium STPP $Ca_5(P_3O_{10})_2$. If we mix STPP and pyro in hard water, calcium pyrophosphate precipitates rather than calcium STPP. This happens even when pyro represents only 10% of total phosphates. Experiments have shown that mineral salts deposited on washed articles are made up mainly of calcium pyrophosphate. The deposited salts have a crystalline form that is even more insoluble than the amorphous form. To prevent these mineral deposits, the detergent powder should contain a sufficient quantity of STPP to dissolve the crystalline pyrophosphate salts deposited during previous washes. The quantity of STPP is all the greater if the powder contains a higher proportion of pyro (resulting from hydrolysis of the STPP *during* manufacturing). If the precipitate is made up of calcium pyrophosphate and calcium STPP, it is the latter that dissolves first at the next wash when the quantity of phosphate is sufficient to bring this about. In addition, when a solution contains an excess of STPP, its complexing action predominates; the contribution of pyro is negligible, given that the stability constant of its complex is 10 times smaller than that of STPP. When there is not enough STPP, even if the powder contains no pyro, there is a precipitate, i.e., $Ca_5(P_3O_{10})_2$. We saw above (Fig. 2.1) that this precipitate is greatest when $(STPP)/(Ca^{2+}) = 2:5$.

Higher temperatures encourage mineral incrustation on fibers by reducing the stability of pyro and STPP complexes, and by making the STPP Ca and pyro Ca salts less soluble. Experiments have shown that the percentage of ash increases with the wash temperature.

To summarize, to avoid mineral incrustation, we must reduce the amount of pyrophosphate in the powder because its calcium salts are highly insoluble. Sufficient STPP is required to avoid the $Ca_5(P_30_{10})_2$ precipitate and to dissolve salts deposited during previous washes.

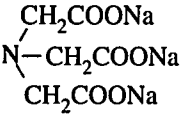
Redeposition and mineral incrustation. We have already seen that to avoid redeposition, the dispersion of soil must be stable. This will be achieved when the solution contains sufficient STPP for the concentration of free Ca^{2+} to be low and for that of the $P_3O_{10}^{5-}$ anion to be high. In this case, there will be neither redeposition nor mineral incrustation. In the opposite case, there will be precipitation of calcium (ash) and redeposition of soil (unstable dispersion because of free Ca^{2+}). We can therefore say that in most cases, heavy redeposition is accompanied by strong mineral incrustation (co-deposition).

Additional functions of STPP. Improvements in anionic and nonionic surfactant efficacy in the presence of sequestrants, particularly STPP, is due not only to the complexing reaction or to the dispersing action already discussed. Other factors must be considered, the most important of which are reductions in CMC, surface tension, and interfacial tension. Several writers have studied the influence of complexants on the CMC of surfactants. From their experience, it appears that STPP lowers CMC, which increases the solubilizing power of surfactants. It is therefore theoretically possible to reduce the dosage of surfactants in detergent formulations that contain high levels of STPP (for environmental reasons, this is not presently the case). It has also been shown that a solution containing both STPP and surfactants has a lower surface tension than a solution containing only surfactants. All of the above-mentioned secondary effects are certainly important in removing fatty soil by emulsification.

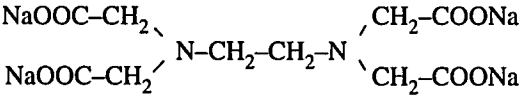
According to Hollingsworth (11), Ca^{2+} ions in the wash solution come not only from tap water but also from clothes. To decide how much STPP to use, it is therefore necessary to take into account the total amount of calcium in the water, i.e., Ca^{2+} in tap water + Ca^{2+} from clothes, known as "hardening up." Several studies have determined the concentration of free Ca^{2+} required to obtain good detergency. According to these studies, for the domestic stains already discussed, it would seem that to obtain good wash performance, sufficient STPP has to be used to obtain a concentration of Ca^{2+} of $\sim 10^{-5}$ mol/L. The quantity of STPP can be determined only after we know, from a washing habits survey, what is in the wash, the weight, the washing conditions (i.e., temperature, ionic strength, and pH), and the complexing constants of the different ingredients present in the wash solution (e.g., LAS, nonionics, carbonate, pyro, or ortho).

Other Complexing Agents. The other main complexing agents apart from STPP are the following (with their chemical formulas):

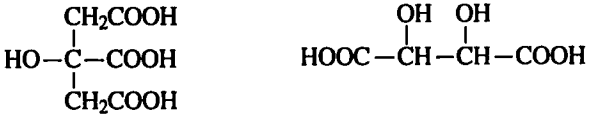
NTA (nitrilotriacetate)



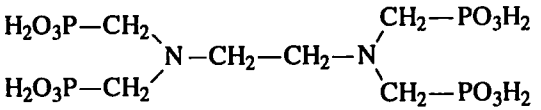
EDTA (ethylenediaminetetraacetate)



Citric acid and tartaric acid



EDTMP (ethylenediaminetetramethylene phosphonic acid; sold as Dequest ex Solutia, for example)



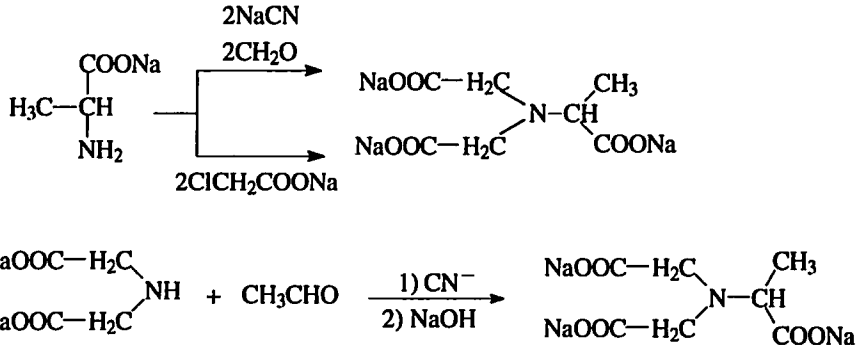
Aminocarboxylates (e.g., NTA or EDTA) are good complexing agents for almost all metal ions. They are easy to handle industrially, are chemically stable toward oxidation and reduction, and are insensitive to acids and bases. But some do not biodegrade readily (EDTA, for example). NTA degrades rapidly.

On the other hand, hydroxycarboxylates (citric acid, tartaric acid, gluconic acid) present no problems in biodegradability but their complexing qualities are less good.

Phosphonates are not very biodegradable, but their complexing quality is comparable to that of aminocarboxylates. They are used mainly (in small quantities) in certain laundry detergents, and also in household cleaners with bleach (at low concentrations to stabilize the bleaching system against heavy metal ions). They have the following functions: (i) inhibition of insoluble salts, i.e., anti-incrustation; (ii) stabilization of bleaching agents, in particular, peracids and the hydrogen peroxide activators, chlorinated products; (iii) deflocculation, i.e., the improvement of antiredeposition properties by keeping particulate soil in suspension; and (iv) removal of certain specific stains (which explains their use in some liquid detergent formulations). Their advantages in comparison with EDTA lie in the fact that they adsorb onto the sewage sludge and therefore do not convey heavy metals to the effluent.

The search for new complexing agents of this type is not easy. The following main issues are clear: Biodegradability is of the greatest importance, as are other aspects of safety to humans and other organisms (aquatic); efficacy (which should be at least equivalent to EDTA); and reasonable cost, as for all other raw materials. One product that seems to meet these conditions today is MGDA (methylglycinediacetic acid). Research done by BASF has shown an inverse correlation between the stability constant of the complexing agent molecule and its biodegradability, i.e., the stronger the constant, the poorer the biodegradability (12). In this respect, MGDA is intermediate between EDTA and NTA, as illustrated in Table 2.4.

The synthesis of this molecule can start either from alanine, using the Strecker reaction, by double addition of chloracetic acid (a), or by using a derivative of an iminodiacetic acid, adding acetaldehyde/cyanide also in a Strecker type reaction (b). After saponification, we obtain the sodium salt. Synthesis is therefore simple, using techniques, equipment, and raw materials that are also used to manufacture aminocarboxylates. The MGDA molecule is biodegradable, and its performance is good.



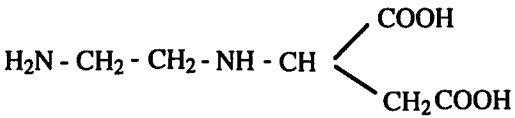
In liquid detergents, MGDA is as good as NTA in the removal of tea and blood stains. On the latter, it performs better than EDTA and EDTMP (which are not biodegradable).

TABLE 2.4
Stability Constants of Certain Complexing Agents[a]

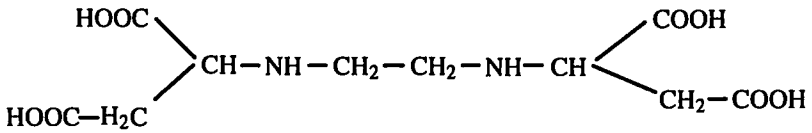
	STP	EDTA	MGDA	NTA	EDTMP
Ca^{2+}	3.5	10.6	7.0	6.5	9.3
Mg^{2+}	3.3	8.8	5.8	5.5	8.6

[a]Electrolyte concentration is 0.1 M at 25°C: log K.

A new type of chelation for transition metals has been presented by Dow Chemical as a *biodegradable molecule* (13), with very good complexing properties with Fe^{3+} and Ca^{2+} ions. This is ethylenediaminemonosuccinic acid (EDMS), with the following chemical structure:



In detergent formulations (whether for fabrics or dishes), this compound is as effective as Dequest or ethylenediaminedisuccinic acid (EDDS). The latter is also *biodegradable* but is more expensive. The chemical formula of EDDS is as follows:

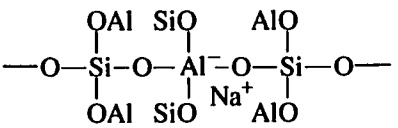


Ion Exchangers

Aluminosilicates (zeolites). Over the past few years, the use of ion exchangers in a number of detergent products (particularly those used for laundering) has increased considerably for environmental reasons. Today, Europe is divided between "STPP" countries (Spain and others), and "zeolite" nonphosphate countries (Holland, Germany, Italy). Sometimes the two builders coexist (France, UK). Most of the rest of the world (Latin America, the African continent, Eastern Europe, Central and South Asia, and Australia) are still "STPP." Parts of North America, Japan, and South Korea, on the other hand, are "nonphosphate." These new, insoluble raw materials, "zeolites," are in fact sodium aluminosilicates, the oldest of which is zeolite type 4A. Amorphous zeolite is produced by a reaction of sodium silicate with sodium aluminate. The change into crystalline zeolite comes from heat treatment. This produces a zeolite paste "slurry," which is changed to powder by spray-drying (14). Its ability to exchange Na^+ ions in the formulation depends on the size of the ions and their state of hydration, its concentration, the temperature, the pH, and the time. Calcium ions are thus exchanged very quickly and magnesium ions a little more slowly (there is also exchange with Pb, Cu, Ag, Cd, Zn, and Hg ions).

The zeolite formula is as follows:

$$Na_{12}(AlO_2)_{12}(SiO_2)_{12} \cdot 27\,H_2O$$



Na^+ ions are exchanged for Ca^{2+} ions. But more important than its chemical formulation as such, are the structure of the molecule's cavities and the form and size of the particles. The size of the cavities and the morphology of the crystals have an effect on the rate of exchange, i.e., smaller cavities will produce a slower rate of exchange (see Fig. 2.3).

In the trade, the average particle size of zeolite A is ~4 μm. Laundering performance of zeolite products is affected less by "underbuilt" conditions than phosphate-based formulations. But zeolite products are less effective at medium and high temperatures, short wash cycles, and when clothes are very dirty (15).

Recently, new types of zeolite have made their appearance. Particular mention should be made of the zeolite MAP (16) whose rate exchange is greater than that of zeolite 4A thanks to the flat shape of its crystals. The surface-to-volume ratio of MAP crystals is much higher than that of zeolite 4A. Zeolite MAP is sold by Crosfield under the brand name Doucil A 24. The differences in physical characteristics of these two zeolites are shown in Table 2.5.

The performance difference with respect to Ca^{2+} ions is ~10–15% in favor of zeolite MAP (17).

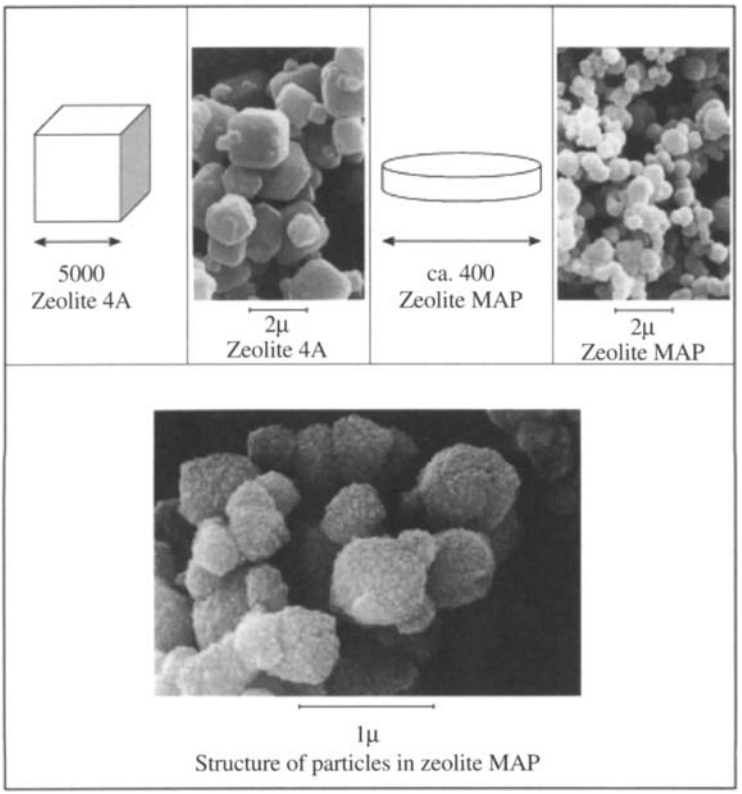


Fig. 2.3. Zeolite structure. Electron microscope pictures (Crosfield).

TABLE 2.5
Physical Characteristics of the Two Zeolites

	Zeolite 4A	Zeolite MAP
Crystalline structure	Single rigid crystals	Layered crystals
Granulometry	1–10 μm	0.7–2 μm
Size of pores	1 μm	0.3 μm

In addition, the map structure provides greater stabilization for the bleaching agents in powder formulations (18). Stability scores for percarbonate in a zeolite-based powder (storage at 37°C/70% relative humidity) are shown in Table 2.6. Finally, this new variety allows a greater quantity of liquid ingredients (surfactants) to be "absorbed" than does zeolite 4A, a fact that is not without significance in formulating increasingly concentrated products which place a premium on occupying the smallest volumes.

Other types of zeolite are mentioned in patents, such as X, Y, and HS. It would seem, however, that they are not yet being used in detergents currently on the market. Having said this, Degussa (19) recently developed zeolite X (under the brand name Wessalith XD) with good properties for superconcentrated powders, such as good dispersion in water, and a higher liquid absorption ratio (90 g of oil for 100 g of Wessalith XD, compared with only 35 g for zeolite 4A). The particles of these zeolites are spherical and show a greater rate of exchange. The pore dimensions of Wessalith XD are smaller (0.74 m), resulting in greater efficacy in exchanging Mg ions.

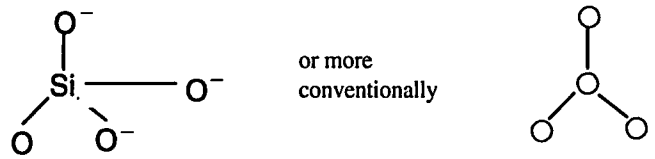
The main disadvantage of ion exchangers is that they can "treat" calcium ions in water, but (unlike sequestrants) cannot "get out" ions deposited on clothes, the soil, or on certain parts of the washing machine. This is why combinations ("cobuilders") are generally used, i.e., ion exchangers + STPP, carbonate, and silicates, which eliminate Mg^{2+} ions (which are barely exchanged by the Na^{+} zeolites). Moreover, because zeolites are insoluble, it is advisable to use dispersants such as polymers (which will be discussed below). It should be noted that zeolite and sodium silicate form an insoluble product. They can be mixed only in very small quantities in the slurry. Incorporation of higher levels of silicates in a conventional blown powder requires a special manufacturing process. Zeolite-based powders have a yellowish color, which is why it is advisable to use a small quantity of superbrightener such as Tinopal CBS or Blankophor BHC to provide better whiteness.

TABLE 2.6
Stability Scores for Percarbonate

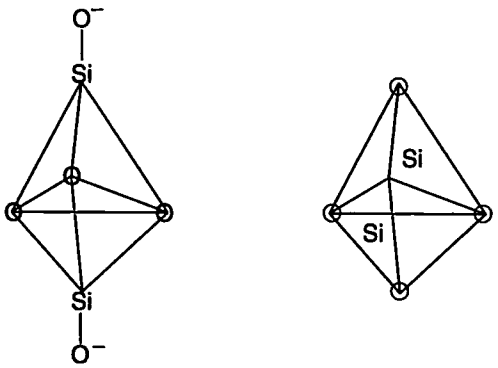
Amount of remaining percarbonate (%)	Zeolite 4A	Zeolite MAP
After 2 wk	15	85
After 4 wk	8	80
After 14 wk	0	50

Layered Silicates. The two main sodium silicates used in detergent products are sodium disilicate and sodium metasilicate (the latter is used only for machine dishwashing). Both are obtained by polymerization of orthosilicate.

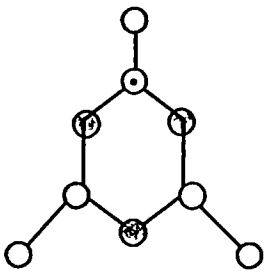
Orthosilicate. [Na_4SiO_4 (or $2Na_2O \cdot SiO_2$)]. Ratio $SiO_2/Na_2O = 1:2$. The structure is represented as a tetrahedron with Si in the center:



Disilicate. [$Na_2Si_2O_5$ (or $2SiO_2 \cdot Na_2O$)]. Ratio $SiO_2/Na_2O = 2$. It consists of two tetrahedra linked at their bases:



Metasilicate (or Monosilicate). If $n = 1 \rightarrow Na_2SiO_3$ (or $Na_2O \cdot SiO_2$). Ratio $SiO_2/Na_2O = 1$. If $n = 5$, we obtain the following structure:



Metasilicate, for example, is usually made by high temperature fusion, (~1300°C) of silica and carbonate Na (ratio of silicate to alkali = 1) as follows:

$$Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3$$
Quartz

Silicates as ion exchangers. Recently, in a number of countries, there has been a move in favor of a return to soluble builder systems. Zeolite, which is insoluble, accumulates in rivers and lakes and increases the amount of sludge to be dealt with during water treatment (20). There are a number of alternative systems, including cogranules of Na silicate + Na carbonate, amorphous Na hydrated silicates, and layered Na silicate. The cogranules of silicate and carbonate are made up 29% amorphous silicate/ 55% carbonate/16% water, which makes them efficient in eliminating calcium and magnesium and gives them high dispersing power and better environmental properties (no sludge in water treatment plants) (21).

The use of amorphous silicates in washing products has been the subject of publications and patents (22,23). These silicates are blown in towers and come in a granular form that can be post-dosed (high density products). Their detergent properties are good; they dissolve rapidly and have good buffering qualities. Their "ion exchange" properties are poor in soft or very soft water, but in hard water, they are very effective (precipitation of calcium silicate).

Despite constant improvement by silicate manufacturers of the water-softening properties of their products (with increased polymerization and molecular weight of the different silicates), most amorphous silicates are used because they provide a useful reserve of alkalinity in detergency and because they also have anticorrosive properties (water softening is left to STPP and zeolites).

There is a series of layered sodium silicates (polymerized crystalline substances) with interesting properties for use in detergents. Their manufacture and use in detergent products has been the subject of numerous patents (24–26). Amorphous disilicates (whose molecular structure consists of small chains or rings of silicate in disorder) are different from the δ-disilicates, which have an ordered inorganic polymeric structure. Their polymeric structure allows the δ-silicates to dissolve quickly in aqueous systems (especially when Ca^{2+} and Mg^{2+} are present).

During the washing process, sodium ions are rapidly replaced by calcium and magnesium ions, before the δ-disilicate can dissolve. As a result, it remains almost insoluble during the wash (at pH 10–11), in the form of exchanged silicate ions Na^+/ Ca^{2+}/Mg^{2+}. Silicate dissolves completely only at the end of the wash (rinsing) when the pH becomes neutral again. At this point, it becomes unstable, releasing its calcium and magnesium ions. The main strengths of layered silicates are as follows: (i) they provide good water softening; (ii) they have good exchange properties of Na^+ with Mg^{2+} and Ca^{2+}; (iii) they produce alkalinity and buffer; (iv) they absorb humidity and fix heavy metal ions (which stabilizes the bleaching systems); (v) they can adsorb surfactants; (vi) they help to keep soil in suspension in the wash solution; and (vi) they can be granulated and compacted. There is therefore a wide choice. The formulator has to choose the best "balance" between performance/ cost and ecology.

Precipitating Agents

Sodium carbonate is widely used in cleaning products, particularly in laundry detergents because it brings reserve alkalinity to the wash, it has good buffering properties, and it can also act as a water softener under difficult conditions (e.g., underdosage or very hard water) by precipitating the $CaCO_3$. Sodium carbonate is solely a "supplementary" raw material and cannot replace other water-softening agents.

Cobuilders

We have already mentioned in our discussions of zeolites, silicates, and sodium carbonate that in most cases, and for reasons of efficacy, the use of a single water-softening agent (except in the presence of high levels of STPP) will not give satisfactory results, which means, for example, in this case, elimination of hard water, reserve alkalinity, anticorrosion properties, cost, dispersing properties, antiredeposition, and anti-incrustation. "Coupling" of water-softening agents with polymers is very common today. We will deal with polymers in more detail later in this chapter.

Alkaline Agents

We have already discussed all alkaline agents and their functions in detergent formulas. To recap briefly, they are as follows: sodium tripolyphosphate (pH 9.5), which also gives good buffering, complexing, and antiredeposition; sodium perborate (pH 10.5), a bleaching agent generally associated with TAED (see below); sodium carbonate (pH >10), a water-softening adjunct and an inexpensive filler; silicates (pH 10 to >13), which have an anticorrosion function but which cannot be coupled with zeolites except at very low levels and never in the slurry (the paste to be spray dried in the tower) because they form insolubles; and sodium bicarbonate, which brings buffering when other raw materials are insufficient to fulfill this function.

To conclude this discussion, we will take a look at the research on builders and the patents registered during recent years. Research and innovation in polymers and the other builders represent a great part of the patents; zeolites appear only in connection with other types of builders. If for many years STPP was the "universal" water-softening agent, the market today is changing fast. Zeolite is gradually taking a significant market share; the development of carboxylates and biodegradable polymers is accelerating, and new silicates are coming on the scene. All of these ingredients will compete for manufacturers' and consumers' attention and will contribute to the sometimes conflicting priorities of ecology and cost/performance.

Bleaching Agents

A bleaching agent is a component that can remove the color from a substrate by means of a chemical reaction. The chemical reaction is an oxidation or a reduction that irreversibly degrades the color system. The process implies either the destruction or a change in the chromophoric groups that are responsible for absorption of light in the

visible (and hence confer color), and the decomposition of colored bodies into smaller and more soluble particles that will then be easier to remove. Bleaching agents are classified in three categories as follows: (i) reducing agents (e.g., sulfites or bisulfites); (ii) chlorine compounds; and (iii) compounds capable of delivering free oxygen.

Reducing agents can be efficient, but are greatly handicapped by their disagreeable smell, which is difficult to mask with perfume. They are not widely used in the detergent industry. Chlorinated products, particularly chlorine bleach, were the first bleaching agents to be used by consumers. The arrival of chlorinated agents for family use dates from the 1930s; they are still used in the United States for washing at low temperatures where perborate has practically no effect. In Europe, they are used in the rinse cycle in washing machines with a special bleach dispenser.

Chlorinated products have advantages, such as efficacy at low temperatures, at low concentrations, and at a low cost, but there are also significant problems associated with their use. They attack colors and optical brighteners (FWAs), are aggressive on certain natural fibers (wool, silk, and synthetics), and they yellow textile finishes. Consequently, their use is diminishing.

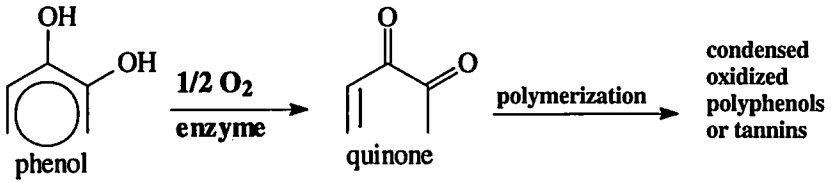
We will look only at the third category, under the following headings: the mechanism of bleaching, hydrogen peroxide precursors, hydrogen peroxide activators, peracids, bleaching catalysts, and photobleach.

The Mechanism of Bleaching

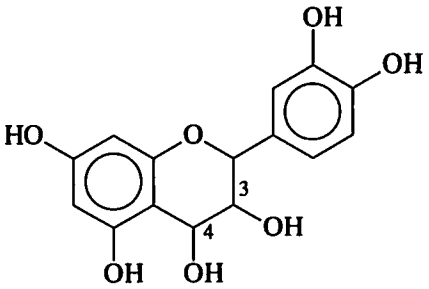
Before looking at the mechanism of bleaching, let us first look at the problems caused by stains.

The Nature of Stains. As mentioned above, there are four categories of soil to be found on clothes: oily soil (e.g., oil or grease), protein stains (e.g., blood or egg), nonfatty stains (e.g., fruit, tea, or coffee), and particulate soil. Fatty and particulate soil, and also protein stains are removed by the combination of surfactants with builders and enzymes, respectively. Nonfatty stains are removed by reducing or oxidizing agents; the most common of these in Europe is perborate.

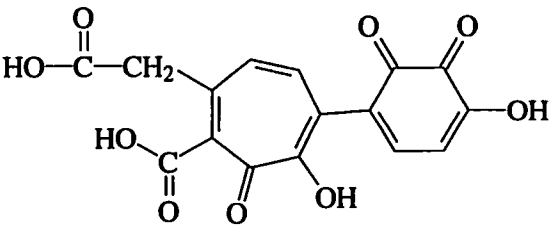
Let us consider nonfatty stains in more detail. According to several experiments, fruit stains can be classified as follows by their difficulty of removal: apple > plum > grape . . . orange > melon. The way in which these fruits stain cotton is similar to the fast "browning" of these fruits, observed in the fruit and juice industry. The industry classifies fruits, according to the speed with which they change color in the course of processing. It is interesting to observe that the "browning" classification below is very close to the classification by toughness of stain (27): apple > pear > plum > grapes . . . melon. Browning is explained by the presence of oxygen in the air; polyphenols in the fruit are oxidized and changed into quinones by enzymes called polyphenol oxidases. These quinones polymerize easily (nonenzymatic reaction) to form tannins and condensed polyphenol oxides, which explains the coloring of fruit stains and their browning caused by the presence of conjugated double bonds. The reaction is as follows:



Not all fruits contain tannins but they do all contain polyphenols (for example, flavane-3,4-diol), which tend to oxidize and then condense to give tannins. The structure of flavane-3,4-diol is as follows:



These polyphenols form bonds with polypeptides and proteins in natural fibers (natural wool), i.e., bonds between the OH of polyphenols and the carbonyl function of the CONH bonds of the peptides. The same kind of bond can establish itself with cellulose. These bonds are one of the reasons why fruit stains fix on natural fibers (e.g., cotton, wool, or silk). It is worth comparing these tannins with the pigment that colors tea; one of these structures is the following:



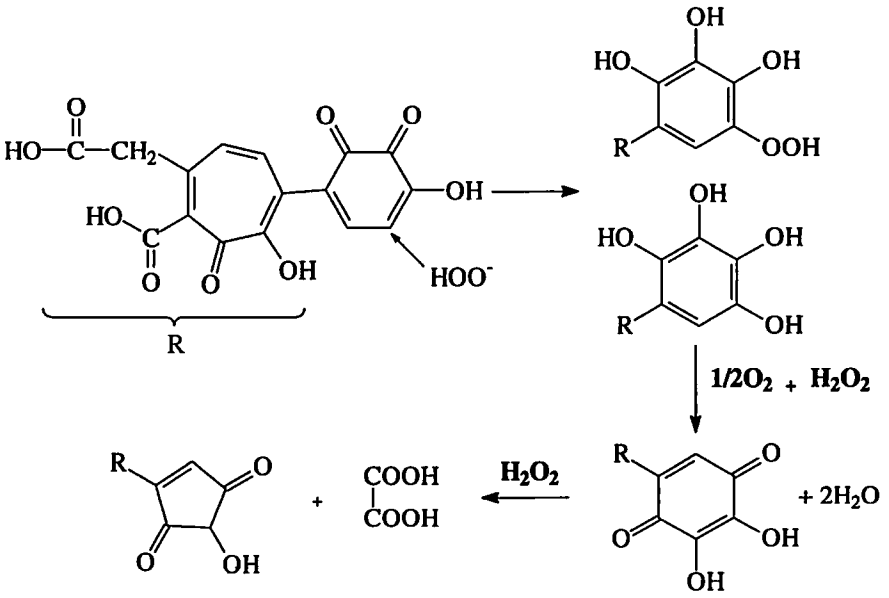
We can see in both cases the presence of conjugated double bonds and quinone functions. Experiments have shown that there is a correlation between tea stain (pigment) removal and wine stain removal (tannin) using perborate.

Bleaching Mechanism. Hydrogen peroxide is a weak acid that dissociates slightly in aqueous solution. Its pK_a is equal to 11.75. Nondissociated hydrogen peroxide is relatively stable; this is why all commercially available solutions have an acid pH. In an alkaline environment, hydrogen peroxide can behave in two ways as follows:

1. It can undergo an acid-base dissociation: $H_2O_2 \rightarrow HOO^- + H^+$
2. It can undergo dismutation: $2H_2O_2 \rightarrow 2H_2O + O_2$

The dissociation reaction produces the perhydroxyl anion HOO^-, which is a species known to cause bleaching (28). Each HOO^- gives an active oxygen. We can measure the percentage of active oxygen in a compound using the following formula: % active oxygen = (100 × the number of active oxygens × 16)/molar mass of the compound. Table 2.7 gives the percentage of active oxygen in a variety of hydrogen peroxide precursors.

Decolorization reaction. We showed above that the color of stains is due to the presence of conjugated double bonds in the tannin molecule of fruits and the pigment of tea. Bleaching removes the conjugated double bonds of colored substances fixed to the fibers (which may or may not be accompanied by removal of the stains). The removal of these conjugated double bonds is accomplished either by creating new bonds (as is the case for reduction) or by scission of the unsaturated bonds to create smaller molecules (as is the case in oxidation). We will look at oxidation later. The tea molecule can be broken up through a nucleophilic attack on the sites that carry a weak electric charge according to the following mechanism:



Several authors, Alfons Von Krause (29) among them, have examined the decolorization of carmine indigo and have proposed a radical solution. It would appear that the bond –O–O– of the perhydroxyl anion can be broken, freeing an oxygen atom, called *active oxygen.* This oxygen adds to a double bond to give an epoxide, which is subsequently hydrolyzed to form a diol. In this way, hydrogen peroxide

TABLE 2.7
Active Oxygen Levels of Some Hydrogen Peroxide Sources

Peroxides	Active oxygen levels (%)
H_2O_2 in 35% solution	16.5
Sodium perborate monohydrate	16.0
Sodium perborate tetrahydrate	10.5
Percarbonate	14.0

and other peroxide components (e.g., perborate, percarbonate, or the peracids) can destroy double bonds in the colored substances of tea and red wine—by oxidation.

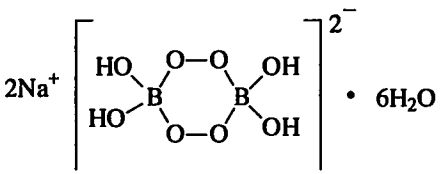
The dismutation reaction does not result in a bleaching action and may even reduce bleaching efficacy. The decomposition of hydrogen peroxide may be accelerated in the presence of heavy metals, such as iron, copper, or manganese. This explains why commercial hydrogen peroxide is stabilized by the use of additives such as magnesium silicate, while detergents contain a small quantity of complexing agents such as EDTA or EDTMP to avoid decomposition through catalytic reaction caused by trace heavy metals.

Hydrogen Peroxide Precursors

Perborate. As already mentioned, perborate has been used for a long time in Europe as a bleaching agent. Its use in detergent products has grown continuously, particularly with the arrival of washing machines that offer high-temperature cotton cycles up to 80–90°C. Before the arrival of activators such as TAED, perborate sometimes comprised up to one-third of European formulations. During the 1980s, its use spread to other countries and continents, notably the United States, South America, and Asia.

Chemical formulation. Before giving the chemical structure of perborate, let us look at the definition of per salts. At the present time, per salts are considered to be (i) components containing the –O–O– group: these are *true per salts (peroxidates)*; and (ii) components containing hydrogen peroxide from crystallization (H_2O_2): these are *false* or *pseudo per salts (hydroperoxidates)*. The structure of perborate has been the subject of many debates about whether it is a true or a pseudo per salt. The formula of perborate tetrahydrate would be as follows:

(a)



(b) $NaBO_2$, H_2O_2, $3H_2O$ in the case of a false per salt.

Hanson (30) has shown that perborate is a true per salt, with a type (a) formula. If $n = 4$, it is perborate tetrahydrate; if $n = 0$, it is perborate monohydrate.

Manufacture. Let us look at two industrial processes for manufacturing perborate tetrahydrate:

1. The chemical process involves the reaction of a sodium tetraborate solution with sodium hydroxide and hydrogen peroxide:

$$Na_2B_4O_7 + 2NaOH \rightarrow 4NaBO_2 + H_2O$$

$$NaBO_2 + H_2O_2 + 3H_2O \rightarrow NaBO_3 \cdot 4H_2O$$

Perborate is precipitated by cooling the solution to 10°C. The precipitate is then filtered, washed, and dried. The resulting product is 96.73% pure and contains 10.31% active oxygen.

2. The electrolytic process involves the electrolysis of a tetraborate solution and sodium carbonate:

$$Na_2B_4O_7 + 2Na_2CO_3 + 21H_2O \rightarrow 4(NaBO_3 \cdot 4H_2O) + 2NaHCO_3 + 4H_2$$

(Note: To obtain mono salts, tetrahydrate perborate is dehydrated.) Perborate comes in crystalline powder form (monoclinic crystal structure), which is dry and has good flow properties.

Study of aqueous solution perborate. From the literature available, it would appear that relatively little research has been done into aqueous solutions of perborate, particularly in the temperature ranges and at the pH that are of interest, *and that the distribution of the various chemical species is still quite unknown.* Lille University of Chemistry has gone further into the subject (28); below is a summary of their main findings.

In a perborate solution, the following chemical species are present: BO_2^-, H_3BO_3, H_2O_2, HOO^-, OH^-, H^+, $[B(OH)_3 \cdot HO_2]$. Concentrations vary with temperature and pH, but they can be calculated precisely using the mass conservation law and the constants K_1, K_2, K_3 for the different reactions. These constants have been determined experimentally by a potentiometric method at an ionic strength of 0.5 at temperatures between 25 and 70°C. The research has identified that the chemical species responsible for bleaching is the HOO^- ion. It has also shown that the concentration of this ion depends on temperature and pH, as shown in Figure 2.4. Using the curves, we can conclude that with a pH of 9–9.5 and at 40°C, the concentration of HOO^- is very low. This would explain why perborate has practically no effect in washes done at <60°C unless preceded by soaking in warm water for several hours (as is done for hand wash in a basin).

The bleaching function of the HOO^- ion. To confirm this theory, tests were conducted in a Terg-O-Tometer with a standard tea test cloth. The wash solutions contained increasing concentrations of HOO^- ions, determined by using the exact

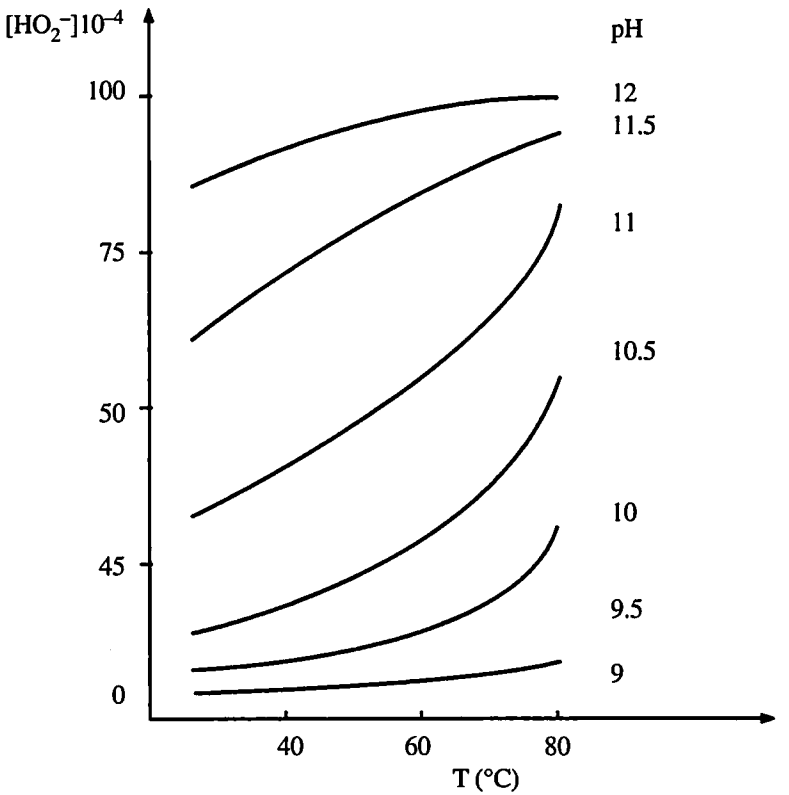


Fig. 2.4. Concentration of the HOO^- ion as a function of temperature and pH.

calculations above. The results (ΔR: $R_{final} - R_{initial}$) are shown in Figure 2.5. They show that bleaching of a tea test cloth is a linear function of the concentration of [HOO^-] ions. Oxidation causes the chains in the tannins or pigment molecules to break, which in turn reduces the amount of polymerization. Aldehyde or acid functions then form at the end of the chains.

The use of perborate tetrahydrate and perborate monohydrate. Perborate monohydrate offers a number of advantages over perborate tetrahydrate. These include the following: good solubility, more rapid formation of peracid in the presence of TAED; better stability, particularly in zeolite formulations and in hot and humid countries; better surfactant absorbing capacities, particularly of liquid nonionics; and the ability to generate more hydrogen peroxide for the same weight.

To obtain these benefits, the product is used in concentrated powders. Its disadvantages lie in its high cost and need for more delicate handling during powder manufacture (there exists a risk of autoxidation, so that it cannot be stocked in large silos). Because perborate tetrahydrate is less expensive, it is used in most powders in Europe. Its lower rate of dissolution can lead to what is known as "mechanical loss," in which

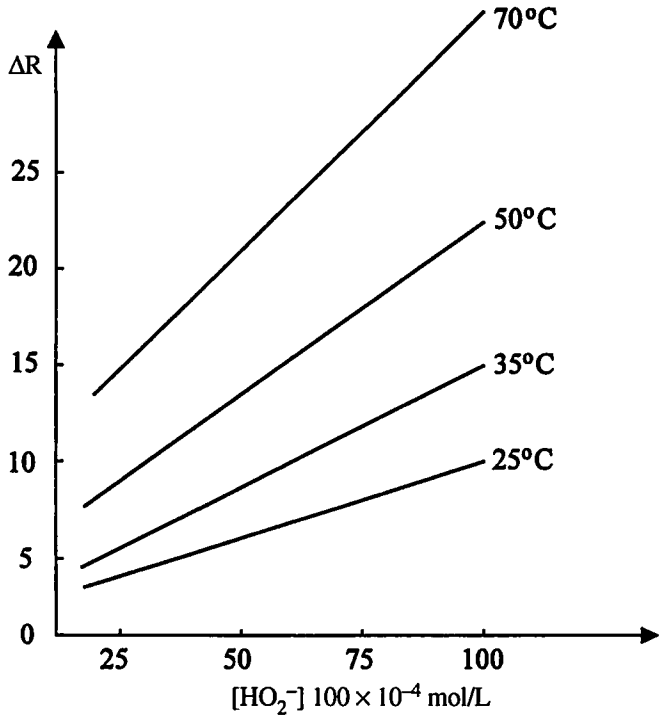


Fig. 2.5. Bleaching of tea test cloth as a function of the concentration of HOO^- at different temperatures.

a portion of the product gravitates to the bottom of the washing machine before being discharged at the end of the wash. For certain machines, this loss can be as high as 30–40% (see Chapter 11).

There is a further source of loss of hydrogen peroxide caused by catalase, which is an enzyme present on clothes. Catalase can originate from a number of sources, e.g., fruits or human skin (where it protects against attacks from free radicals). It is therefore to be found on dirty clothes. Catalase causes dismutation of hydrogen peroxide generated by the precursor system (e.g., perborate or percarbonate). This causes a loss of active oxygen for bleaching stains. The loss of hydrogen peroxide through catalase can be as high as 50–60%. Several inhibitors of catalase are known, including hydroxylamine NH_2OH, which is sometimes used in detergent powders.

Percarbonate. The formula for sodium carbonate peroxyhydrate is: $2Na_2CO_3 \cdot 3H_2O_2$. Unlike sodium perborate, this compound is not a *true peroxide* but a perhydrate, or an addition compound. Percarbonate is a very interesting replacement for perborate, with the following advantages: good dissolution properties; high levels of active oxygen; multifunctionality, i.e., a source of H_2O_2 and alkalinity; and risk free for the environment. It has good stability in phosphate-based detergent powders with

protective packaging, at 30°C and 80% relative humidity. It is unstable in conventional powders with zeolite. The reason for this lies in the presence of traces of transition metal and the level of free water in this type of formula. Today's concentrated powders, however, contain percarbonate because of their low water content. Different companies (e.g., Degussa, Kao, EKA Chemicals) have tried to solve the instability problem. The most promising solution seems to be to encapsulate percarbonate with organic, mineral, or polymer compounds.

Degussa (31) has developed Percarbonate Q30, which dissolves quickly and is very stable. It is comparable to perborate in the following ways: (i) in a concentrated powder without phosphate, Q30 is as stable as perborate monohydrate after 8 wk of storage at 30°C and 80% relative humidity (98% active oxygen remaining); (ii) in a dishwashing powder containing 50% prehydrated phosphate, and after 12 wk of storage at 35 and 80% relative humidity, 90% of the active oxygen is still present in perborate tetrahydrate, and 78% in Q30. The rate of dissolution of Q30 is intermediate between mono- and tetrahydrate.

Hydrogen Peroxide Precursors. A large number of perborate substitutes has been studied unsuccessfully over the years, including the following (32–34):

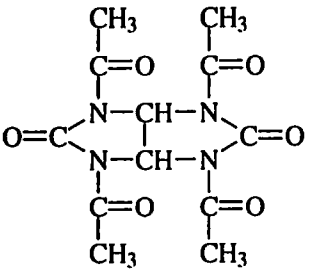
1. Polyvinylpyrrolidone/hydrogen peroxide complex
2. Urea/hydrogen peroxide complex (percarbamide)
3. Persulfates such as "Caroate," $2KHSO_5 - KHSO_4 - K_2SO_4$ (triple salt of potassium peroxomonosulfate)
4. Sodium persulfate, $4Na_2SO_4\,NaCl \cdot 2H_2O_2$

Unfortunately, all of these precursors show rather poor stability in detergent powders, and it is unlikely that we will see them used in the foreseeable future.

Hydrogen Peroxide Activators

Hydrophilic Activators. As we have seen, perborate is a good bleaching agent, but it is effective only above 60°C. The first oil crisis in the 1960s brought a drive to reduce energy consumption. Temperatures used in washing machines fell from boiling to 60°C and even 40°C. Effective bleaching agents had to be found for these lower temperatures. It was known that peracids containing –OOH groups gave much better bleaching than hydrogen peroxide; thus, researchers set about incorporating them into washing powders. Peracids can be dosed into detergents in two ways, either directly as free peracids, immediately available, or they can be formed "on site" by perhydrolysis, a reaction between an *activator* and a perhydroxyl anion from perborate or percarbonate. Peracids will be covered a little later; we will cover only hydrogen peroxide activators here. In Europe, four types of activators have been developed and produced industrially to make *peracetic acid*: These are TAGU, GPA, DAHT, and TAED.

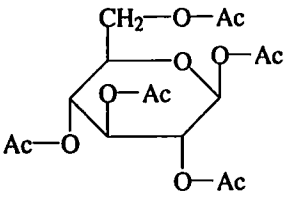
TAGU (tetraacetyl glycol urea) has the following chemical formula:



TAGU

This compound has the disadvantage of being expensive and only slightly biodegradable.

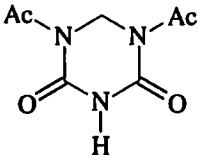
GPA (glucose pentaacetate) has the following chemical formula:



GPA

This compound is not very stable, and its manufacture is more complicated because of by-products (particularly acetic acid) that have to be eliminated.

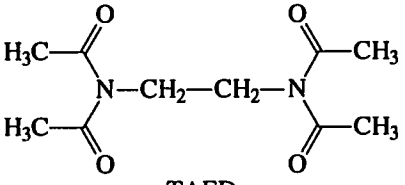
DADHT (diacetyldioxohydrotriazine) has the following chemical formula:



DADHT

This compound has the same disadvantages as GPA and is therefore not used in detergent powders.

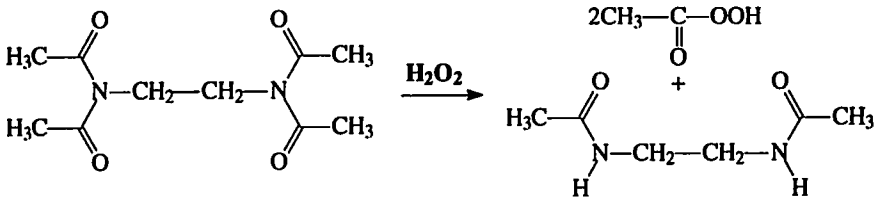
TAED (tetraacetylethylenediamine) has the following chemical formula:



TAED

This activator was first used by Lever in France in 1978; since then, it has become the best known and most widely used activator; it is present in >50% of detergents in Western Europe.

TAED gives peracetic acid according to the following reaction:



The perhydrolysis reaction should theoretically continue to give 4 mols of peracid/mol TAED; however, it stops at this stage because of the increase in pK_a of the *conjugated* acid of the leaving group, which changes from an amide (pK_a = 17) to an amine (pK_a = 35) (35).

[Note: At high pH (9.5–10), perhydrolysis is optimal.] On the other hand, for bleaching the pH should be lower. Such conditions can be achieved as a result of the formulation of the product and the wash conditions. At the start of the wash, the pH can be high (formation of peracid); then the pH drops because of the soil. Peracetic acid is soluble in water and is therefore present in the aqueous phase. Its bleaching action is due to random collisions with the surface of clothes. It is effective only above 40°C, as shown in Figure 2.6.

If the main effect of peracid is to whiten, it should be mentioned that it has secondary benefits that consumers may not necessarily notice, namely, its bactericidal properties. These have been studied by detergent manufacturers and also by TAED suppliers. Among the latter is the work done by Warwick International (36), which sells ready-to-use TAED granules. In Europe and the United States, as we

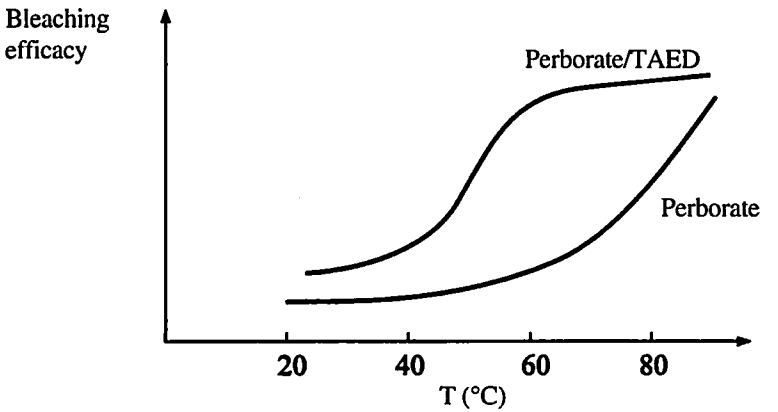
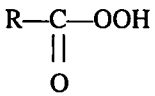


Fig. 2.6. Bleaching power of perborate and perborate/tetraacetylethylenediamine (TAED).

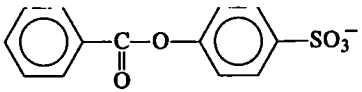
know, the clothes are washed at lower and lower temperatures to save energy, and in the rest of the world, cold-water washing is the norm. Under such conditions, bleach given off by powders containing only per salts has no effect on bacteria, and the consequences for hygiene are clear. These include the following: (i) microorganisms remain on the clothes, which are contagious to exposed populations such as children or old people, cause bad odors, and may cause mold when the climate is humid; and (ii) bacteria may be present in any water left inside the machine after washing, thereby contaminating clothes in the next wash and attacking parts of the machine, particularly if there is a lengthy period between washes. The antibacterial effect of peracid in low temperature washes has been demonstrated clearly.

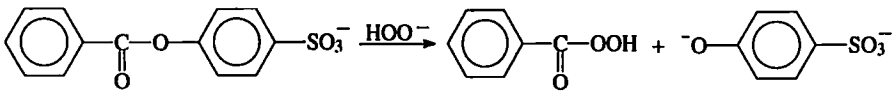
Hydrophobic Activators. The chemical formula of a hydrophobic peracid is as follows:



where R is an alkyl chain. Like surfactants, hydrophobic peracids have a hydrophylic and a hydrophobic part. Their ability to adsorb more easily at the textile interface or stain/detergent solution means they are more appropriate for low temperature washes. Some examples of activators that give hydrophobic peracids are as follows:

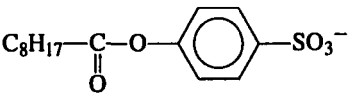
1. Benzoyloxybenzenesulfonate known as P15 (Monsanto), with the chemical formula:



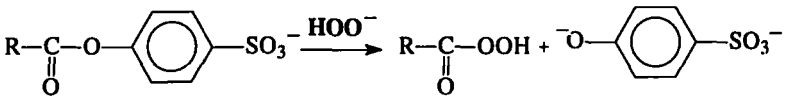


P15 perhydrolysis in solution generates perbenzoic acid, a more effective and more hydrophobic peracid than peracetic acid. Experiments have shown that on an equimolar basis, perbenzoic acid is much more efficient than peracetic acid for almost all stains and under different wash conditions. But to achieve the same concentration of peracid, it takes 2.63 times more P15 than TAED. However, because the speed of perhydrolysis of P15 is better than that of TAED, it can be used at a lower ratio of peroxide/P15. The optimal ratio depends on wash conditions and cost.

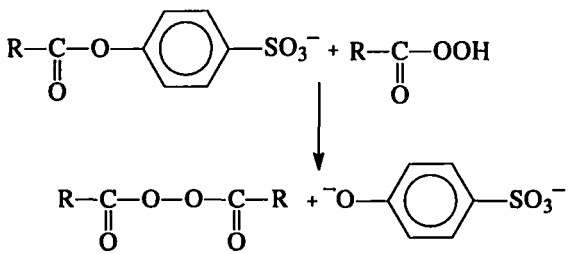
2. SNOBS (sodium nonanoyloxybenzenesulfonate), with the chemical formula:



The perhydrolysis reaction is as follows:

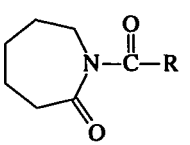


but there is a secondary reaction between the peracid anion and SNOBS:

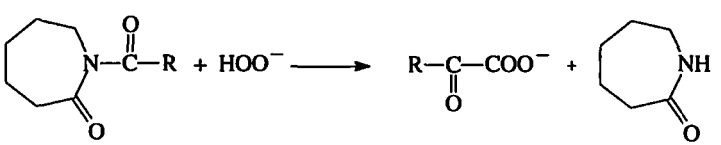


This reaction produces a diacyl peroxide, which is insoluble, disperses with difficulty, and forms a residue that settles on natural rubber parts of the washing machine, causing damage. This reaction can be minimized by using extra hydrogen peroxide or shorter alkyl chains. But this results in less efficient bleaching. The pK_a of the leaving group and the length of the hydrophobic chain can influence the efficacy of the perhydrolysis reaction. SNOBS is used particularly by Procter & Gamble in the United States and Japan, because detergent concentrations and wash temperatures are lower than in Europe.

3. *N*-Acyl caprolactam with the chemical formula:

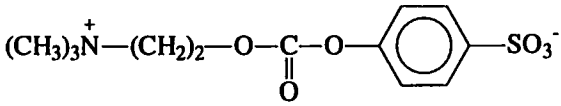


The perhydrolysis reaction is as follows:

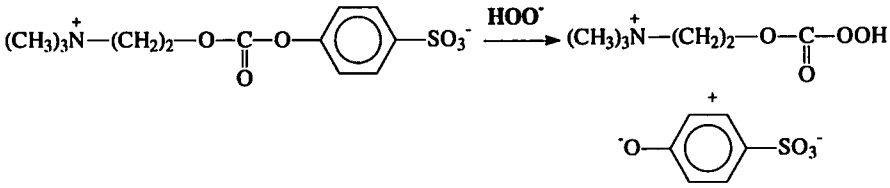


Compounds derived from lactams used as activators for hydrophobic peracids were developed by Procter & Gamble (37). They do not attack the rubber parts of machines because there is no production of diacyl peroxide.

Activators That Produce Cationic Peracids. There are precursors such as the following:



Perhydrolysis is achieved according to the following reaction:



Because of its cationic nature, the peracid formed is substantive to fabrics and therefore more efficient against stains. Reinhard (38) has shown that activators with nitrile groupings could be of potential interest. Among these compounds, the quaternary nitrile groupings could be of particular interest, providing good performance (cationic characteristic), low aggressivity toward textiles, and good biodegradability. Table 2.8 compares the costs of the different bleaching agents for the same stain removal performance at 40°C.

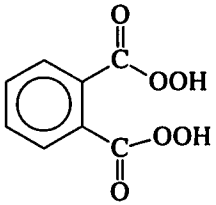
Free Peracids

The above hydrogen peroxide activators are used to generate percarboxylic acid for bleaching. Why do we not use preformed free peracids directly? These peracids do indeed exist, not only in theory but also on the market. Four examples are given.

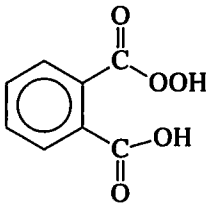
TABLE 2.8
Cost of the Different Bleaching Agents

	Cost
15% classical bleaching agents	100 (base)
6% nitriles	75
10% of components containing a catalyst (Salen)	85
PAP	125

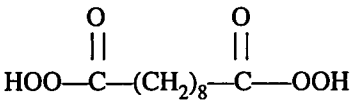
Diperoxyphthalic Acid. Its magnesium salt is known commercially as SUPROX (PPG Industries) and it has the following structure:



Monoperoxyphthalic Acid. Its magnesium salt is sold as H48 (Interox) and it has the following structure:



Diperoxydodecanedioic Acid (DPDA). Its structure is as follows:

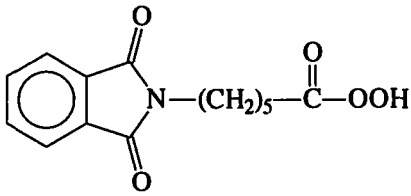


The main benefits of using peracids are the following: good efficacy at low wash temperatures (30°C), immediate bleaching as soon as peracids are added, and the absence of decomposition of blood in certain stains. It has been found that other bleaching systems such as perborate or perborate/activator decompose blood by generating residues that adhere to textiles and are difficult to remove with detergents. For example, when we do experiments with Empa 116 test cloth (containing blood), it becomes darker after washing. With preformed peracids, this does not happen. Peracids also have good antimicrobial properties, which give deodorant benefits at low wash temperatures.

Peracids also have significant disadvantages. These include instability in an alkaline environment (even when in granulated Mg salt form), difficulty in handling (risk of spontaneous combustion), deterioration of colored articles as a result of leaving white spots, and a poor cost/efficiency ratio. For these reasons, peracids have not been very successful to date, but interest levels remain high.

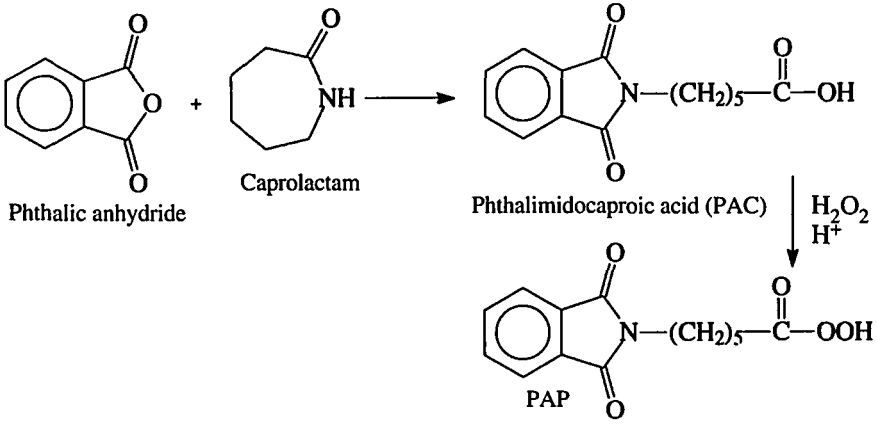
ε-N,N-Phthalimidoperoxycaproic Acid (PAP). For some years, research by manufacturers (Monsanto, Akzo, Hoechst, Procter & Gamble) has shown that the

presence of the amide structure in the peracid molecule can bring significant stabilization. The most promising product to date is phthalimidoperoxycaproic acid (PAP).



The synthesis gives good yields (95%). Numerous patents have been filed on the use of PAP in detergent formulations (39). The main advantages of this new peracid are the following (40): (i) it possesses good solubility; (ii) it is more effective than other peracids (e.g., H48 or DPDA); (iii) it is not aggressive to textiles and colored articles; (iv) it has excellent stability, i.e., a melting point >90°C; it is nonexplosive (ease of handling); and it suffers only a small loss of oxygen, even under severe storage conditions (loss of 10% of active oxygen after 4 wk of storage at 50°C; and (v) its biodegradability is comparable to that of linear alkylbenzenesulfonates.

The synthesis of this compound is quite simple:



Given its ease of manufacture, its price should become competitive with that of the perborate/TAED system.

Catalysts

Catalysts, like enzymes, which will be discussed later, are known to be very efficient systems. Adding relatively small quantities can significantly improve the

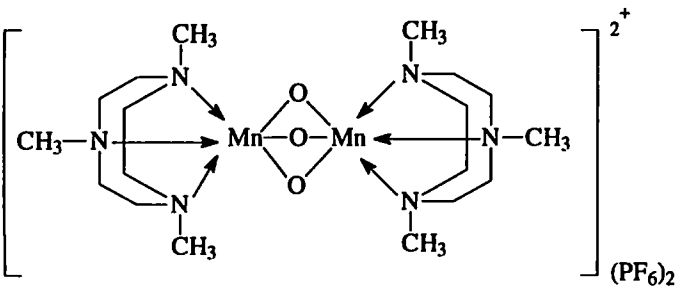
results of bleaching agents; this is not true for activators for which the industry norm is a ratio from 1:6 to 1:3 to bleaching agents. Catalysts cannot be used on their own. They have to be combined in systems containing a compound to generate active oxygen (perborate or perborate/TAED). The catalyst is composed of a complex between a metal ion and some relatively complicated ligands. The most common metals used are manganese and iron.

Mechanism of Catalyst Action on Stain Removal. The catalyst attacks stains selectively and weakens them before the bleaching system begins to work. The stain is "activated" and the catalyst becomes inactive, according to reaction, $Mn^{4+} + e^- \rightarrow Mn^{3+}$. The mechanism by which catalysts act on stains is as follows: The catalyst captures the electrons of the stain, which destabilize it and make it more sensitive to attack by the bleaching system. Once the stain has been "activated," it is easier to remove at ambient temperature. The bleaching system restores the electrons to the catalyst, which will then be regenerated. A catalyst is as active on hydrogen peroxide as on hydrogen peroxide precursors (perborate, percarbonate) or on the activator/hydrogen peroxide precursor (TAED/perborate) systems. It is very stable when it is in granulated form in detergent powders (41).

Catalysts also present a number of significant problems (42) including the following: (i) in the presence of Ca^{2+} or Mg^{2+} ions in the wash solution, the catalyst system can be deactivated; and (ii) metallic hydroxides can precipitate in the alkaline environment of the wash solution. These hydroxides can deposit on textiles and stain them. Reinhard (38) has studied 35 different complexes and has shown a correlation between bleaching efficacy and aggressivity on textiles. The best compromise would seem to be Salen (a manganese complex).

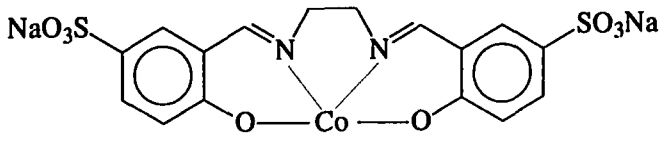
Examples of Catalysts. Catalyst patents and accompanying literature are numerous. However, their use is very limited because of the problems mentioned above; it should also be noted that certain components are not biodegradable and can be toxic to consumers and the aquatic environment. Two examples of complexes based on manganese and cobalt are as follows (43,44):

(a)



1,4,7-Triazacyclononane

(b)



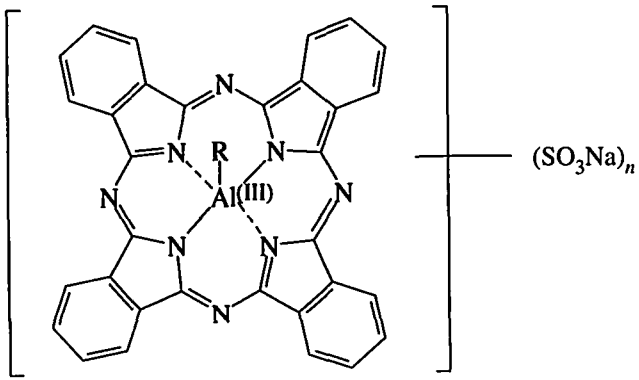
In combination with perborate or perborate/TAED, these catalysts can be very effective in machine dishwashing products (45).

Photobleach

As the name indicates, bleaching takes place with the help of sunlight photons, which decompose the water in damp laundry into "active oxygen" in the presence of phthalocyanine derivatives (called "photobleaches") according to the following mechanism:

$$PB + \overset{h\nu}{\rightarrow} PB^* \overset{H_2O}{\longrightarrow} PB + O_2^*$$

In this manner, activated oxygen oxidizes stains and microorganisms, yielding hygienically clean results. This mechanism implies that the laundry is exposed to sunlight either during soaking, during the wash, or during drying to receive the hv energy from the red part of the spectrum in sunlight. This system is widely used in countries in which laundry is dried out-of-doors in sunlight. It is used in both powder and liquid detergents. The chemical formula (ideal structure) of photobleach sold by Ciba Geigy under the trademark Tinolux BBS is as follows (46):



where $n = 3$–4 and R depends on pH.

In Procter & Gamble's patents (47), Zn replaces Al. The Zn phthalocyanine derivative should be sulfonated for adequate solubility, and it is preferable to use a tetrasulfonate to obtain optimal bleaching and to avoid coloration of washed articles. Unilever, in one of its patents, shows that certain electron donors such as

sodium sulfate, thiosulfate, cystine, and iron sulfate can significantly improve the efficacy of phthalocyanine derivatives (48).

Amounts of Bleaching Agents to Use

As we have seen, bleaching and stain removal are proportional to the effective concentration of active oxidizing agent (not taking into account mechanical loss or decomposition by catalase). For perborate on its own, commercial powders normally contain between 15 and 25% of perborate tetrahydrate. Zeolite-based products use perborate monohydrate at lower levels, given that the hydrogen peroxide content is higher. Powders with a perborate activator contain variable amounts of TAED (2–4%) and perborate tetrahydrate (8–15%). Perborate monohydrate is preferred in zeolite-based products, also at lower levels. Percarbonate can also be used in zeolite-based concentrated products. For catalysts, the concentration of Mn-based compounds in the wash solution can vary between 2.5×10^{-6} and 5.0×10^{-6} mol/L, depending on the type of complexant (49). For photobleaches, Ciba Geigy recommends the following: (i) from 0.01–0.03% for areas such as Southern Europe with intense sunlight; and (ii) from 0.03–0.06% for areas such as South America or Southeast Asia with a substantial amount of sunlight. To avoid staining or coloring of the wash, some manufacturers use a combination of bentonite (clay) granules and 1% Tinolux BBS. Such granules are sold by Süd Chemie AG under the brand name "Laundrosil."

Enzymes

Introduction

Sometimes known as diastases or ferments, enzymes are powerful organic biocatalysts produced by the cells of living organisms. They can be of animal (pancreatin) or of microbial (amylase, protease) origin. More than 70 years ago, enzymes were used by launderers to remove blood stains, but it was not until about 1965 that they became an important additive in household detergents. Two reasons explain why this process took so long: first, enzymes were expensive, coming from animal sources; and second, they were unstable when used in their original form. These difficulties were overcome, first at the request of the food industry, for which Novo Nordisk developed enzymes from bacterial sources under the name "Alcalase," then by detergent manufacturers who worked on *encapsulating* them to achieve good storage stability. Enzymes became progressively more widely used in household detergents and are now present in most of the world's brands. Over the last 10 years, enzymes have become one of the main ingredients in detergent formulations, for the following reasons:

1. Wash temperatures have fallen significantly over the past 20–25 years. Some stains that are easy to remove at 90°C become very problematic at 50 or 60°C.
2. With the development of concentrated powders and liquids, the efficacy of enzymes at very low incorporation levels has made them an ideal tool for the formulator.

3. Consumer expectations of wash results have changed. The main objective used to be to clean clothes, whereas today it is to care for clothes and to keep them "like new" for as long as possible—which explains the success of enzymes such as cellulase.
4. Enzymes biodegrade easily and meet environmental requirements, which have been key to their development.

Over the past 10 years, household detergents have moved from using only one enzyme (protease, i.e., the ancestor!) to two, three, and even four; their usage has widened to include machine dishwashing products, for example.

Classification of Enzymes

There are several ways in which enzymes are classified. Some enzymes have kept their original names, e.g., trypsin, pepsin, and papain. Most of the others have been named by adding the suffix "ase" to the name of the substrate they degrade. Thus proteases attack proteins, amylases attack starch, lipases attack grease or lipids, cellulase attacks cellulose, and so on. Whether the enzyme consists only of amino acids or not, we distinguish between proteinaceous and heteroproteinaceous enzymes in which the protein is associated with another group of a different nature (metal, sugars, lipids, or pigments). International nomenclature is based on the type of reaction catalyzed and distinguishes among the following: enzymes which act by scission (hydrolases, phosphorylases), transfer (oxidases, dehydrogenases, peroxidases, transaminases, transmethylases), isomerization, and polymerization.

Proteases belong to the hydrolases and are the most widely used. As their name indicates, they degrade proteins as illustrated in the following diagram:

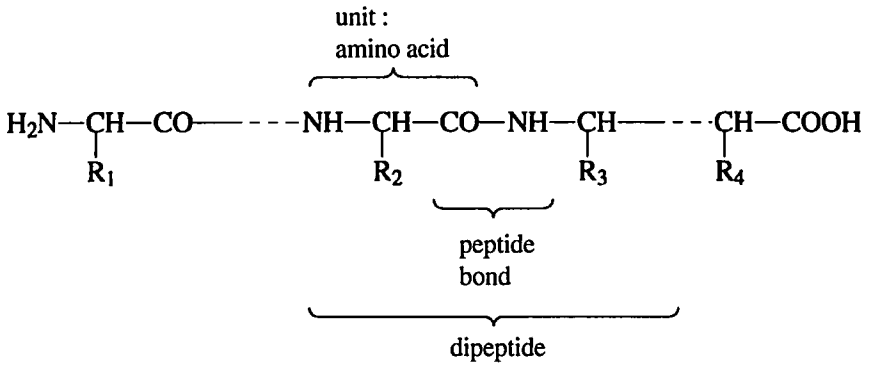
$$\text{Proteins} \xrightarrow{H_2O} \text{Polypeptides} \xrightarrow{H_2O} \text{Peptides} \xrightarrow{H_2O} \text{Amino acids}$$

According to how the proteases work, we find endopeptidases that attack internal peptide bonds in a specific manner (e.g., trypsin attacks the peptide bonds between basic amino acids) and the exopeptidases that work only on terminal peptide bonds.

The Structure of Enzymes

All enzymes include an essential proteinaceous fraction that gives them their specific properties. In addition, they can include a fraction, which can be a metallic ion (e.g., Fe, Mn, Mg, or Cu), or a more or less complex organic substance, or the two together, in which case these are called "heteroproteins." Most enzymes belong to this class. Enzymes with only amino acids (the basic unit of a protein) are called "homoproteins." Proteases belong to this class. The primary structure of homoproteins is defined by the nature, the number, and the sequence

in which the amino acids are linked in the protein chain. There are 22 types of associated amino acids:



In the interior of this molecule internal bonds are formed, giving it a particular spatial structure. The secondary structure of the molecule is *helicoidal* because of the presence of hydrogen bonds between the amino acid chains.

Covalent bonds of the disulfide type, which establish themselves between the sulfur amino acids (cysteine) of the same chain (intramolecular disulfide bridges) or between several polypeptide chains (intermolecular disulfide chains), give the molecule a rigid form. The active site on the enzyme (the combination of amino acids that cause the catalytic activity) and its fixing site (a succession of amino acids whose ionization allows the enzyme to combine with its substrate) are linked to this tertiary structure. In certain cases, the enzyme can have a quaternary structure in which two, three, or four molecules are associated. Water acts as intermolecular cement. The spatial configuration of the proteinaceous molecule plays a vital role in the specificity and the activity of the enzyme.

Mechanisms of Action of Enzymes

The Enzyme Reaction. All enzyme activity can be illustrated as follows:

$$E + S \overset{1}{\rightleftharpoons} ES \overset{2}{\rightleftharpoons} E + P$$

where E is the enzyme, S is the substrate, and P is the new substance obtained.

The reaction takes place in two parts: (i) the substrate, or the substance on which the enzyme is going to act, combines with the enzyme to form the ES complex; (ii) then the ES complex dissociates, regenerating the enzyme intact and the new substance. Figure 2.7 illustrates the enzymatic reaction.

Characteristics of Enzyme Reactions. Enzymes are biocatalysts that regulate biochemical reactions. They regenerate quickly and can therefore catalyze new

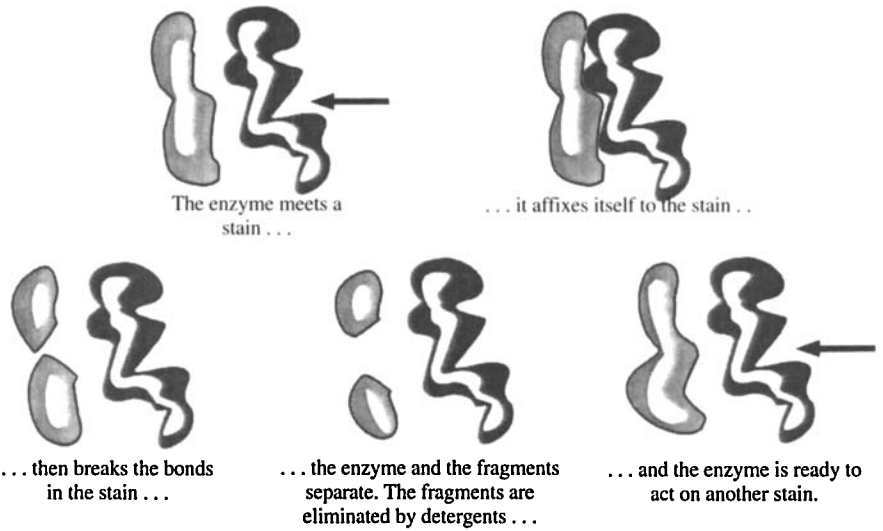


Fig. 2.7. How enzymes work.

reactions. Enzymes work at low levels (e.g., rennet congeals 70×10^6 times its weight of milk in 10 min at 40°C). The reaction is reversible, but the enzyme does not react in a reversible manner. The enzyme acts on a given substrate or on a group of substances with similar structures. This characteristic, called stereospecificity, is therefore more or less strict.

Enzyme Activity. To express enzyme activity, we refer either to the remaining substrate, or to the products formed by the reaction. The enzyme unit is defined under standard conditions of temperature, time, pH, and concentration of substrate. It is the quantity of enzyme that catalyzes the transformation of 1 μmol of its substrate at 30°C in 1 min.

1. For protease: Several units are used to measure enzyme activity of alkaline proteases used in detergents. The Anson unit (AU) is the quantity of enzyme that, under standard conditions, degrades sufficient denatured hemoglobin in 1 min to deliver a quantity of small peptides, unprecipitated by trichloracetic acid, giving the same color with a phenol reagent as 1 meq of tyrosine. The unit most frequently used is the glycine unit (GU); it is the quantity of enzyme that, under standard conditions, will degrade a sufficient quantity of casein for the result of the degradation to give, with the reagent, a color identical with that developed by 1 μg of glycine.
2. For lipase: Tri-, di-, and monoglycides are hydrolyzed (in decreasing order of activity). Triglycerides have been chosen arbitrarily to measure lipase activity. One unit will hydrolyze 1 meq of fatty acid triglyceride in 1 h at pH 7.7 and 37°C.

3. For α-amylase: One unit will liberate 1 mg maltose (starch) in 3 min at pH 6.9 and 20°C.
4. For cellulase: One unit will liberate 1 μmol of glucose (cellulose) in 1 h at 5 pH and 37°C (2 h incubation).

These are given as examples. Each manufacturer uses specific methods to define the unit of interest (the units are based on the catalytic effect of enzymes defined under optimal reaction conditions, pH, temperature, ionic strength, and substrate concentration). In reality, things are more complicated. For example, enzymes do not react with some pure and well-defined substrates, i.e., they catalyze the conversion of complex mixtures of ingredients whose molecular composition is rarely established. In addition, using a standard temperature (e.g., 25°C) can be quite misleading. In the following, we will show the influence of these various parameters.

Factors Influencing Enzyme Reactions. The enzymatic reaction depends both on the two elements of this reaction, the enzyme and the substrate, and on the physicochemical environment in which it takes place.

Effect of enzyme concentration. The rate of the reaction is proportional to the concentration of enzymes, provided the level of substrate is optimal. In cases in which the substrate content is high, saturation of the enzyme occurs, and the rate tends toward a maximum.

Affinity between the enzyme and its substrate. Under experimental conditions in which the substrate is excessive, V_m is defined as the speed of reaction that corresponds to the reaction rate at saturation. Then, when the rate of reaction is equal to one half of the maximum, we call the corresponding concentration substrate K_m, or the Michaelis constant, as illustrated in the curve in Figure 2.8. The opposite of this constant is the affinity constant, i.e., $1/K_m$. The affinity of the enzyme for its substrate increases as K_m decreases.

Factors affecting enzyme activity. Enzyme activity is affected by all physical, chemical, or biochemical changes. Such changes can be favorable (activators) or unfavorable (reversible or irreversible inhibitors). The presence of bivalent mineral ions (Mn, Zu, Ca) or of organic groups (thiols) is a favorable factor, whereas actions caused by strong acids or solvents inhibit the reaction irreversibly by denaturing the enzyme. Temperature and pH are factors that play a predominant role in the activation and inactivation of enzymes. Enzyme activity depends on the concentration of ions H^+ because the formation of the ES complex depends on ionization of the active center and the center of fixation of the enzyme. Depending on the enzyme, optimal pH is in a more or less wide range, at different levels, but generally close to neutral. Thus, in the case of detergents, research has been directed toward the development of enzymes that are stable and effective at high pH (9–12). Enzyme activity is closely linked to temperature, which has an energizing effect between 0 and 60°C (approximately). An increase in temperature helps activity and is reversible. Beyond 60°C, the protein structure in protease is changed (denatured); denatured protein has no activity and this inhibition is

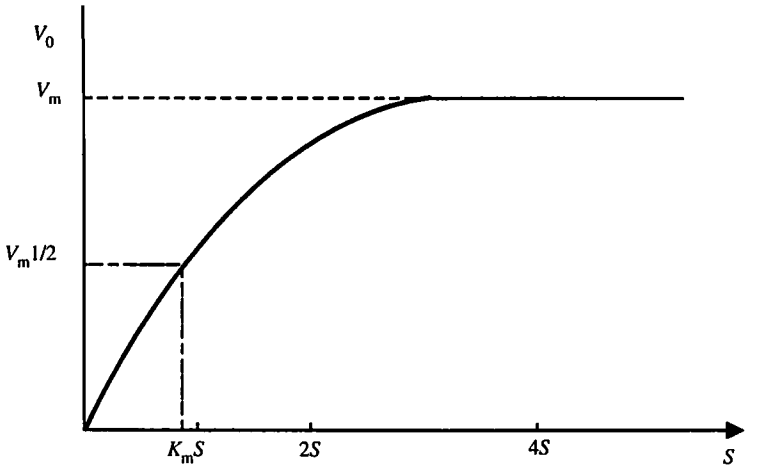


Fig. 2.8. Variation in the rate of reaction as a function of the concentration of substrate (*S*).

irreversible. Optimum temperature varies according to the enzyme. The curves in the next three figures show the variation in enzyme activity as a function of temperature and pH.

Figure 2.9 shows the variation in the enzyme activity of a protein as a function of pH at 37°C. We can observe that optimum pH is well above 10 at 37°C.

Figure 2.10 shows the variation in enzyme activity of a protease as a function of temperature at a pH of 8.5. We can see that the optimum temperature is ~60°C if the pH is 8.5 (for a given protease; for an alkaline protease, the pH can be 10).

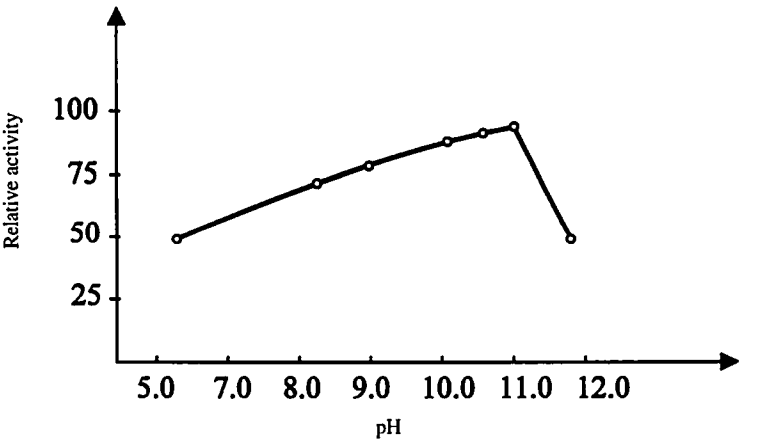


Fig. 2.9. Variation of enzyme activity as a function of pH.

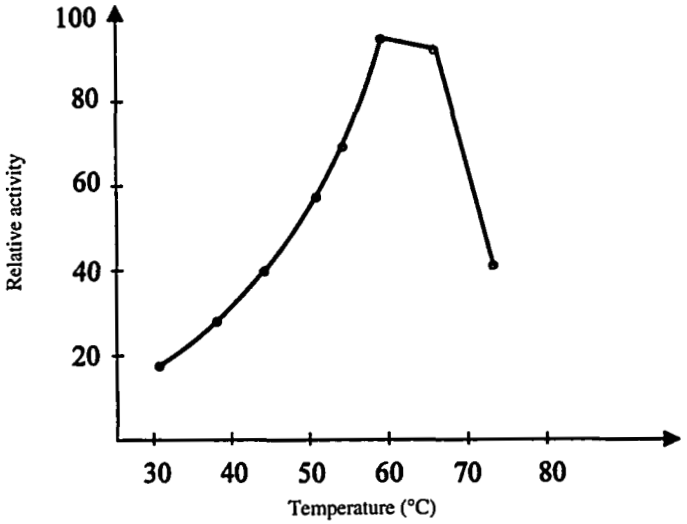


Fig. 2.10. Variation of enzyme activity as a function of temperature.

However, the activity curve = f (pH) is no longer the same when the temperature of the experiment is optimum. Figure 2.11 shows that at 60°C (optimum temperature), maximum activity does not occur at 10 < pH < 11 but at pH = 9.6. This is a consequence of the conflict between activity and destruction at high pH and temperature.

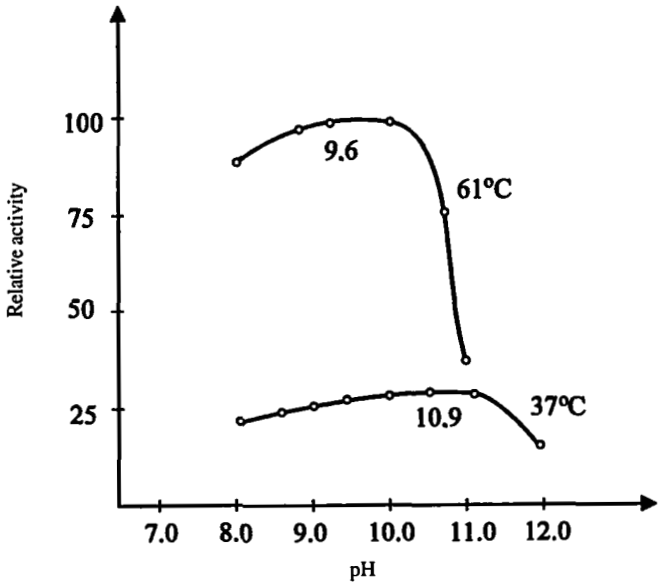


Fig. 2.11. Enzyme activity as a function of pH and temperature.

Loss of Enzyme Activity

We know that enzyme activity in a detergent powder decreases during storage and that the degree of loss will depend on the characteristics of the powder (e.g., granulometry, oxidants used, alkaline agents) and storage conditions (e.g., temperature, relative humidity, time). There are three types of reaction that lead to loss of activity, i.e., those that denature the enzyme by modifying its spatial structure breaking the intra- and intermolecular bonds, those that lead to autodigestion of the enzyme, with the enzyme itself becoming a substrate, and those that inactivate the enzyme. Several analytical techniques exist for evaluating the extent of activity loss. Experiments in which an enzyme, subtilisin, was exposed to the presence of different hydrated and nonhydrated salts led to the following conclusions: (i) enzyme activity is unaffected by contact with anhydrous salts; and (ii) enzymes are quickly denatured in the presence of hydrated salts ($Na_2SO_4 \cdot 10H_2O$, $Na_2CO_3 \cdot 10H_2O$, $NaBO_3 \cdot 4H_2O$); they then autodigest, leading to an extent of activity loss, which depends on the nature of the salt. We can conclude that deterioration is linked to the presence of water in contact with the enzyme. Deterioration is more or less rapid depending on the pH of the aqueous film formed around the enzyme (very fast deterioration with $Na_2CO_3 \cdot 10H_2O$ and $NaBO_3 \cdot 4H_2O$).

Encapsulation of Enzymes. Enzymes were originally sold in powder form containing 90–95% sodium sulfate and 5–10% pure enzymes. These enzymes cannot be used as such, because of dust problems and instability due to the presence of hydrated salts in the detergent. They must therefore be encapsulated. Originally, detergent manufacturers produced the enzyme granules themselves; today, however, manufacturers supply encapsulated enzymes (in the form of small "prills," for example). The main properties required of an enzyme granule are as follows:

1. Absence of dust, i.e., the granules should be quite hard in order not to cause dust during transport, unpacking, and manufacture.
2. Good solubility so that the enzyme is active from the start of the wash.
3. Good intrinsic stability, meaning that the granules should be stable throughout storage and before their incorporation into the detergent formula.
4. Good protection from other ingredients in the formula (e.g., water, oxidizing agents, or alkaline agents).
5. Absence of bacteria from the enzyme production process.
6. Good color (granules to be as white as possible).
7. Low odor that can be masked by perfume (powdered enzymes have a bad smell).
8. Constant quality standard in the granules from each production, given that the dosage level is very low (~1%).
9. Good flow properties to facilitate their incorporation into detergent powder.

Cold spray drying. A slurry is prepared containing a nonionic, anhydrous sulfate and enzymes; this slurry is then pulverized in *cold air* in a spray tower (50), yielding small white balls called "prills," whose formula is given in Table 2.9. These balls can be used directly in a detergent powder. However, to ease dosage and to ensure good homogeneity, the activity of the enzyme prills should not be too high, so that their incorporation level is not too low (0.3–1%).

Granulation using a "marumerizer." Novo Nordisk uses this process to produce enzyme marumes called "T granules" (51). A mixture such as that shown in Table 2.10 is prepared. The mixture is homogenized, then rolled to obtain a stick shape. Before they harden, the sticks are rotated in a marumerizer, which is shaped like a cooking pot, to obtain balls whose size depends on the incline of the marumerizer. These marumes can be used as such in detergent powder.

Encapsulation in noodle form using a granulator. This process (used by Lever in France in 1968) produces noodles made up of 80–82% nonionics (solid), 5–6% TiO_2, and 10–12% enzymes. It has been proven that enzyme noodles are more stable than granulated enzymes. In addition, they allow the incorporation of 1–2% of nonionics into the detergent formulation. Their main problem is homogeneity (coefficient of variation is higher for noodles).

Multilayered encapsulation. Genencor International has developed a granulation process called "Enzoguard" (52). The resulting granules have several protective layers, with the following advantages: (i) less dust, resulting in safer handling; (ii) better solubility, giving better performance; (iii) better storage stability; and (iv) better dispersion in powders because of a more even particulate granulometry, giving more even performance between one pack and another. The process is based on fluid-bed granulation technology. This technique allows several protective layers to be added to a preformed core. It should be noted that one of the layers is made up of the enzymes themselves.

Main Types of Enzymes: Function and Production

Proteases. As we have seen, proteases break up protein-based stains, such as blood, egg, milk, grass (chlorophyll), or keratin (on collars and cuffs). They are obtained from various organisms, e.g., *Bacillus licheniformis* or *B. lentus.* Their efficacy varies because three times more protease from *B. licheniformis* is required to obtain the same wash result as protease from *B. lentus.* The general hydrolysis by a protein (an endopeptide serine) is described in Figure 2.12 (53).

TABLE 2.9
Prill Formulation

	A	B
Ethoxylated tallow alcohol	54%	60%
Enzymes + sulfate	41%	40%
TiO_2	5%	—

TABLE 2.10
Preparation of Enzyme Marumes

NaCl	70–80%
Dextrin	2–4%
Ethanolamide (coconut)	3–4%
Polymers	1–2%
TiO_2	2–4%
Polyethylene glycol	2.5–4.5%
Enzymes	Balance

Lipases. Lipases work on greasy soil and stains; they catalyze the hydrolysis of insoluble triglycerides, such as salad oil or cosmetics. Their effect is more visible after more than one wash because lipases are more active during the drying process (the concentration of enzymes is increased by evaporation of water) than during the wash itself. The amount of residual greasy soil is therefore not reduced significantly during the first wash, but the triglycerides will have been partially hydrolyzed. Their complete removal is therefore easier at the following wash. The first lipases used in household detergents (at the end of the 1980s in Japan) were derived from *Humicola languinosa* (54,55). Others have since appeared (*Pseudomonas alcaligenes* and *Pseudomonas hendocina)* (56,57); knowledge of the three-dimensional structure of lipase has allowed manufacturers to improve its performance.

Using the example of Lipolase, we can see that the catalytic centers are analogous to those described above for protease serine (aspartic triad serine-histidine-acid). The catalytic center is found in a hydrophobic elongated "pocket"; differing from protease, it is completely "buried" behind a short helical segment. When a lipase molecule is activated at an oil/water interface, its form changes to make the active site accessible. The mechanism is shown in Figure 2.13 (53).

Amylases. α-Amylases (α-1,4-glucanohydrolases) break the α-1,4 bonds of starch polymers of high molecular weight, thereby reducing the viscosity of starch

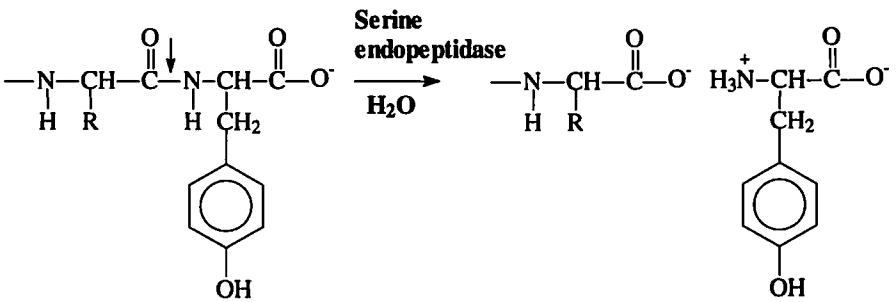


Fig. 2.12. Hydrolysis of peptide bonds.

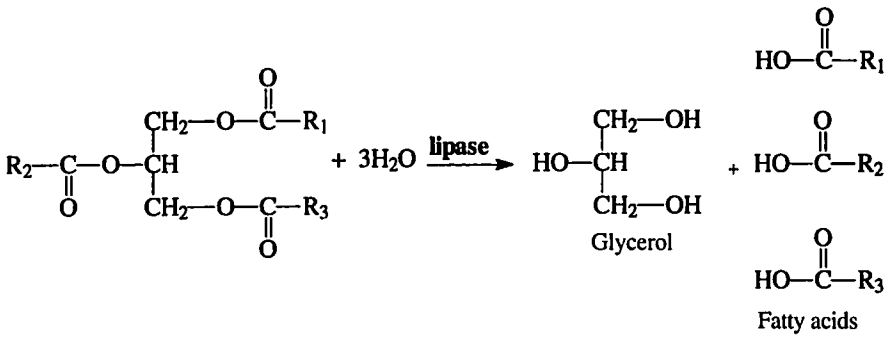


Fig. 2.13. Breakdown of triglycerides by lipase.

solutions. Adding α-amylases to a detergent helps break down starch molecules (e.g., pasta, potatoes, or combinations of starch and soil) into intermediate oligosaccharides or reducing sugars. These medium-molecular-weight composites are more easily removed by the mechanical action of the machine and the physicochemical action of detergents. The α-amylases most frequently used are of a bacterial type (Rapidase) or thermostable bacterial (Termamyl). Such α-amylases are dependent on the calcium content (hydrolysis of starch is helped by high levels of calcium). We can change this dependency on calcium by genetic engineering. The sources can be (58) bacterial α-amylase (*Bacillus subtilis, Bacillus amyloliquefaciens*) or thermostable α-amylase (*Bacillus licheniformis*).

Cellulase. Cellulases break down microfibrils that appear on cotton after repeated washing. This gives a softer wash and eliminates particulate soil caught in the fibers (thereby reducing greying). The removal of fibrils allows the surfactants and the lipase to act on greasy soil in the lumen. This gives better detergency. Cellulases help to restore original color. Because of its microbial origins (e.g., *Humicola, Trichoderma, Aspergillus,* or *Bacillus*), cellulase is not always effective at low temperatures and high pH. Cellulase is a complex enzyme that gradually breaks down the cellulose to glucose. The breakdown mechanism is illustrated in Figure 2.14.

Determination of Enzyme Level (Using the Example of Protease, the Most Common Enzyme)

The formulation is put together step by step, starting with laboratory testing of each prototype; once most of the formulation has been decided on, it should be tested under real conditions (washing machines) to fine-tune incorporation levels.

(Note: Consumer tests and panels can be used to confirm conclusions.) Enzyme efficiency is measured objectively using test cloths such as AS10 and EMPA 116 (see Chapter 1).

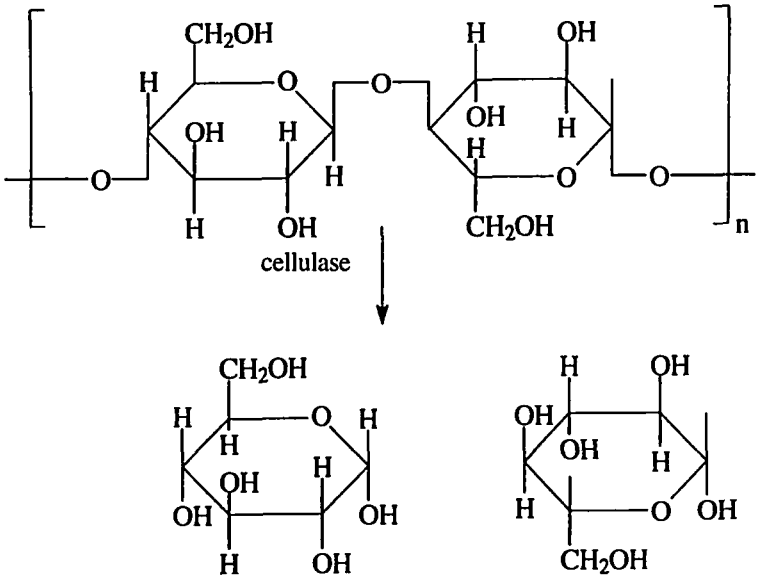


Fig. 2.14. Breakdown of cellulose by cellulase.

Laboratory Trials (Terg-O-Tometer). EMPA 116 cloth is not suitable for Terg-O-Tometer use with powders containing enzymes *and perborate.* It is suitable for nonperborate products. AS 10 cloth is recommended for measuring enzyme efficiency in powders with or without perborate, using Terg-O-Tometer tests.

Machine Trials. Tests using washing machines have led to the following conclusions:

1. EMPA 116 cloth: For an identical formulation, the higher the level of enzymes, the better the measure of enzyme efficacy.
2. AS 10 cloth: Higher levels of enzymes give better stain removal.
3. Real stains: Tests with varying levels of enzyme from 4 to 13 GU/ mg have shown that beyond 9 GU/mg, there is no gain in efficacy.
4. Real soil: Results are significantly better with a powder containing 9 GU/mg than with another powder containing only 2.5 and 1.5 GU/mg.

Choice of Enzymes. Table 2.11 gives an indication of the pH and temperature values to be used depending on the type of enzyme manufactured by Novo Nordisk. Similar recommendations are made by other enzyme suppliers, such as Genencor.

Trends

At the start of this chapter, we mentioned the substantial changes that enzymes have undergone over the years as a result of product development, changing wash-

TABLE 2.11
Values to Be Used for pH and Temperature Depending on Enzyme Type

Enzyme	pH	Temperature (°C)
Proteases		
Alcalase®	7–9.5	10–65
Savinase®	9–10.5	10–65
Everlase®[a]	9–10.5	10–65
Esperase®	10–11.5	40–75
Amylase		
Termamyl®	8–11.5	10–90
Ban®	7–9.5	10–40
Lipase		
Lipolase®	7–11	5–45
Cellulase		
Celluzyme®	7–9.5	20–70
Carezyme®	7–10.5	20–55

[a]Everlase® is an enzyme similar to Savinase®, but more stable in powders containing bleaching agents.

ing habits, and increasing environmental pressures. Today's biotechnology gives manufacturers the following possibilities:

1. To improve enzyme efficacy by modifying molecular characteristics, e.g., a selective change in the electric charge on the molecule should allow an increase in the affinity of the enzyme molecule with the detergent solution interface for a given soil to be treated; in the same way, it should be possible to change molecules to make enzymes more compatible with the environment in which they find themselves or in which we may wish to put them (in a detergent, particularly concentrated or liquid).
2. To provide enzyme activity at low wash temperatures.
3. To develop a lipase which works in the first wash.

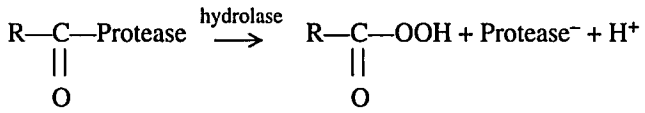
There are enzyme types that have not yet been used in detergent formulations and should reach the market in the years ahead, particularly for bleaching. These are discussed below.

Oxidases. These enzymes catalyze the oxidation of a substrate by molecular oxygen to produce hydrogen peroxide according to the following reaction:

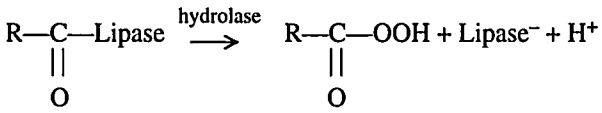
$$\text{Substrate} + O_2 \xrightarrow{\text{oxidase}} \text{Oxidized substrate} + H_2O_2$$

Examples of the substrates in question include alcohols (59,60), which are alcohol oxidases, and sugars (61), which are glucose oxidases. Alcohol oxidases seem more relevant for liquid detergents than for powders.

Hydrolases. These are enzymes that change hydrogen peroxide into peracids. The most attractive concept is one using hydrolase to change a known enzyme/alkyl complex into peracids, for example (62).



Hydrolase seems relevant for concentrated detergents because it removes the need for hydrogen peroxide precursors (8–15% less perborate monohydrate or percarbonate), allowing a further increase in the concentration of other ingredients. The major problem remains price, and also the need for perhydrolysis to become preferred to hydrolysis.



Peroxidases and Lactases. Peroxidases and lactases are enzymes that act, like oxidases, on hydrogen peroxide and molecular oxygen, respectively, but the substrates in this case are colorants (63).

Pectinases. Pectinases work on fruit stains (64), which, as we saw above, are among the most difficult to remove. Further progress remains to be made, notably in terms of efficacy and cost. Research will also be devoted to some enzymes (such as amylase but also protease) to be used for machine dishwashing as a result of the removal of metasilicate and bleach from current formulations. To conclude, one question that comes to mind is the following: When will a "100% enzyme" product make its first appearance?

Polymers and Antiredeposition Agents

We will now deal successively with redeposition theory, redeposition problems, and antiredeposition agents, principally polymers.

Redeposition Theory

Before going into the theory of redeposition, we should understand the nature of the soil that redeposits on the wash.

Characteristics of Redeposited Soil. As already stated on a number of occasions, there are three types of soil, i.e., a liquid compound that is mainly oil or

grease, a solid compound that is made up of small particles, and stains of various types. If we treat a cotton article on which soil has redeposited with a solvent to remove yellow organic matter, we will improve its whiteness only marginally. Alternatively, if we manage to eliminate particulate soil using an ordinary process such as soaking in hot water with a concentrated soap solution, we will restore the original whiteness. Thus we can see that yellowing is linked to oxidized fatty matter, whereas greying, or redeposition, is a problem caused by particulate soiling. We will now consider mainly the problem of particulate soils.

The Theory of Redeposition. Today, there is no available theory of redeposition, but it can be considered as an application of the general theory on the stability of colloids by Durjaguin-Landau-Vervey-Overbeek (D.L.V.O.) (65). Before summarizing this theory, and for a better understanding of redeposition, let us remind ourselves of some definitions. A textile and a particulate soil are represented by a flat surface and a sphere. In a wash solution, most textile surfaces and particles are negatively charged. Close to these surfaces, there are concentrations of ions with the opposite charge to ensure electric neutrality. As shown in Figure 2.15, the electrical double layer is defined by layers.

First, there is a compact layer of ions with opposite signs, called the *Stern layer.* Next, there is the Gouy diffuse double layer. This layer finishes at the point at which the concentration of ions inside the layer is the same as that in the solution. A layer of water molecules that is thicker than the Stern layer surrounds the charged surfaces by ion-dipole interaction. This water of hydration moves about with the particle itself. Each level shown in the figure has its own characteristics, i.e., there is a thermodynamic potential or Nernst potential on the surface of the substrate or particle, one potential on the surface of the Stern layer, and the zeta potential on the surface of the level that separates the water of hydration and the free water.

A wash solution containing particulate soil can be considered as a dispersion of solids in water or hydrosols. The solids are either hydrophilic or hydrophobic. Given the polar nature of hydrophilic particles, the free energy at the interface between solid and water is low; these particles disperse immediately in water, their

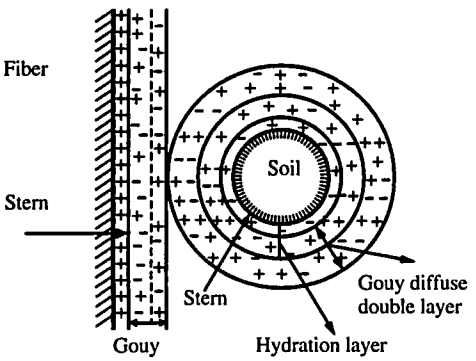


Fig. 2.15. The electrical double layer.

dispersion is stable, and there is no resulting redeposition. On the contrary, free energy at the interface between a hydrophobic solid and water is very high. Coagulation takes place, reducing free energy. The dispersion is unstable and redeposition occurs. Stillo and Kolat (66) mention three types of forces or potentials that govern the stability of a colloidal dispersion and show that deposition of soil is governed by three factors as follows:

1. An electric force that attracts or repels, which is due to the electrical double layer referred to above. This force is evaluated in terms of zeta potential, and is measured by the electrokinetic method.
2. Nonelectric, nonrepulsive forces.
3. Forces not influenced by the exterior environment such as the attractive Van der Waals forces, which result in two particles that are very close together becoming stuck together, and the repulsive Born forces, which prevent the interpenetration of two particles when they are in close contact. The curves in Figures 2.16–2.18 summarize the D.L.V.O. theory of the stability of colloidal dispersion.

Figure 2.16 shows the attractive and repulsive potentials taken individually as a function of the distances that separate two particles in the same charge (see section on detergency theory in this chapter). The two curves in Figures 2.17 and 2.18 show the potentials resulting from the superposition of the forces of particles in suspension.

Total potential energy V at a given distance (d) is composed of a term V_a (attraction) and V_r (repulsion) such that $V = V_a + V_r$. When the two particles approach each other, they repel each other as soon as their double layers start to overlap. The particles have to overcome this Coulombic barrier before they can get close enough to adhere by Van der Waals attractive forces. Thus, when this energy barrier (or the zeta potential) is high, the dispersion becomes very stable. Colloidal particles that have redeposited on the cloth are in a similar situation. The approxi-

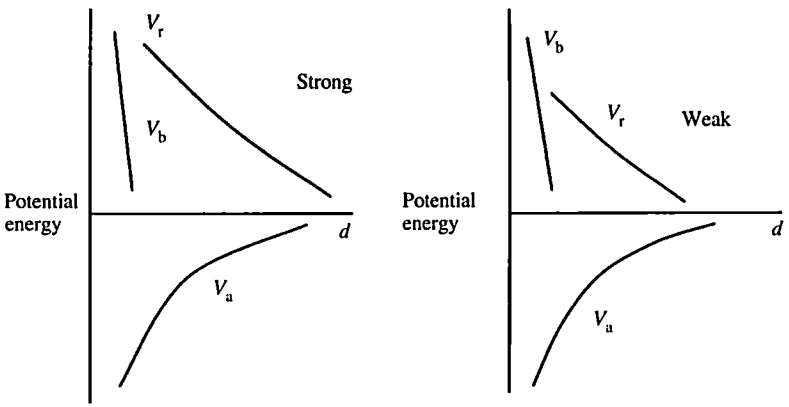


Fig. 2.16. Strong or weak repulsive forces; V_a = attractive energy; V_b = Born repulsive energy; V_r = repulsive energy.

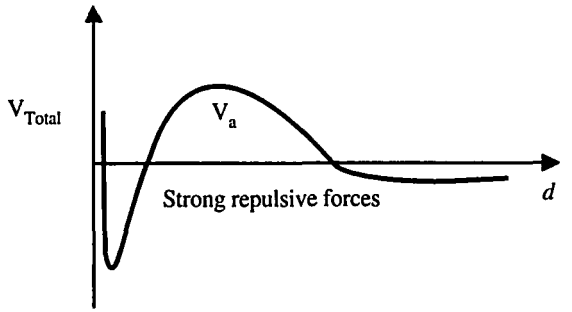


Fig. 2.17. Result with strong repulsive forces.

mate size of the energy barrier for a stable dispersion is 20–30 kT units (k = Boltzmann constant and T = absolute temperature).

It can be seen that there are two minima in the curve of energy potential. The first minimum is very low, and particles that are in this situation attach themselves strongly to each other; this destroys a dispersion and leads to coagulation. The second minimum is much less important. The corresponding energy is a few units of kT. Particles in this zone stick lightly to each other, a phenomenon which is known as flocculation. This phenomenon, which is less important for particles of small diameter, can be important in the retention of soil in the textile fibers. Finally, particles are retained not only by Van der Waals forces; they also can be trapped in microscopic cavities or crevices in fibers.

Redeposition Problems

As we have already pointed out, the use of synthetic detergents grew common after the Second World War. However, it was noticed that they caused far more greying than soap. Then came the introduction of synthetic textiles and automatic washing machines. We will now examine the influence of these factors on redeposition in domestic laundry.

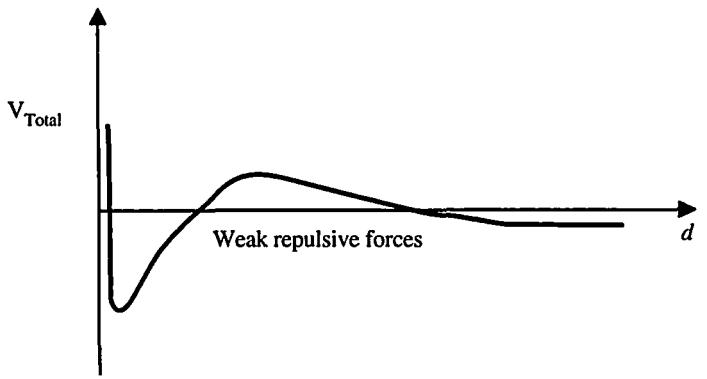


Fig. 2.18. Result with weak repulsive forces.

The Effect of Electrolytes. According to the above theory of the stability of colloidal dispersion, addition of electrolytes increases the redeposition of particulate soil on textiles. This is due to the compression of the electrical double layer that surrounds the surface of fibers and particles; this in turn reduces the zeta potential or the potential energy barrier. The effect of electrolytes on redeposition increases rapidly with the valence of their cations.

The Effects of Temperature. Temperature has the following four effects on redeposition: (i) it increases the kT kinetic energy of particles, and therefore redeposition; (ii) it reduces the viscosity of the solution, intensifies Brownian motion, consequently increasing redeposition; (iii) it softens some synthetic fibers and textile finishes, which can help adhesion and the accumulation of particulate soil; and (iv) it increases the solubility of surfactants, thereby reducing redeposition. For soaps and anionics, solubility increases sharply beyond the Krafft point; thus, their antiredeposition qualities improve with temperature. For nonionics, solubility also increases with temperatures up to the cloud point. There are then more surfactants in solution, and therefore more product adsorbed on the fibers and soil, and consequently less redeposition. For nonionics, the concentration is reduced above the cloud point (insolubilization), which can increase redeposition. Thus, for nonionics with a cloud point of 40°C, their antiredeposition properties increase between 20 and 40°C and then diminish between 40 and 80°C; for other nonionics with a cloud point >100°C, their antiredeposition properties increase steadily with temperatures up to 90°C (high temperature wash). It is likely that this latter effect of temperature on redeposition is more important than the three effects mentioned earlier.

Effect of Textile Type. Using the D.L.V.O. colloidal stability theory, we can conclude that redeposition becomes significant when the surfaces of fibers and particles are inert and nonpolar because there is no repulsive force. This is generally true for polyester, treated cotton, and hydrophobic carbon black. Many experiments have proven that hydrophobicity of fibers increases redeposition. This can also be explained when we think about free energy. The change in free energy that accompanies redeposition is explained by the following:

$$\Delta G = \gamma_{FP} - \gamma_{FW} - \gamma_{PW}$$

where γ_{FP}, γ_{FW}, and γ_{PW} represent interfacial energies between fiber and particle, fiber and water, and particle and water. We have already seen that the free energy of hydrophobic particles and fibers is great. Coagulation or flocculation causes a reduction in free energy; then $\Delta G < 0$ and there is redeposition:

$$\gamma_{FP} - \gamma_{FW} - \gamma_{PW} < 0 \quad \text{or}$$

$$\gamma_{FW} + \gamma_{PW} > \gamma_{FP}$$

In other words, redeposition is greater when the values of γ_{FW} and γ_{PW} are high (hydrophobic fibers and particles), and when γ_{FP} is low (γ_{FP} is low when the fibers and particles are hydrophobic). It should be noted that fatty matter can turn normally hydrophylic surfaces into hydrophobic surfaces.

Effect of the Degree of Soiling. Finally, let us look at the effect of the degree of soiling on redeposition. Several studies have shown that redeposition increases with the concentration of particulate soil in solution.

Antiredeposition Activity

We will examine the activity of surfactants, phosphates, and the other redeposition agents, notably polymers.

Surfactants. Surfactants adsorb onto fibers and particles.

Anionics. Anionics adsorb onto particles and fibers, increasing their charge or their zeta potential. The electrostatic barrier is strengthened. This results in greater stability of the dispersion, therefore less redeposition. Figure 2.19 shows the increase in height of the barrier with interfacial potential. For anionics to be effective, they must adsorb either onto the fiber, onto the particles, or ideally onto both.

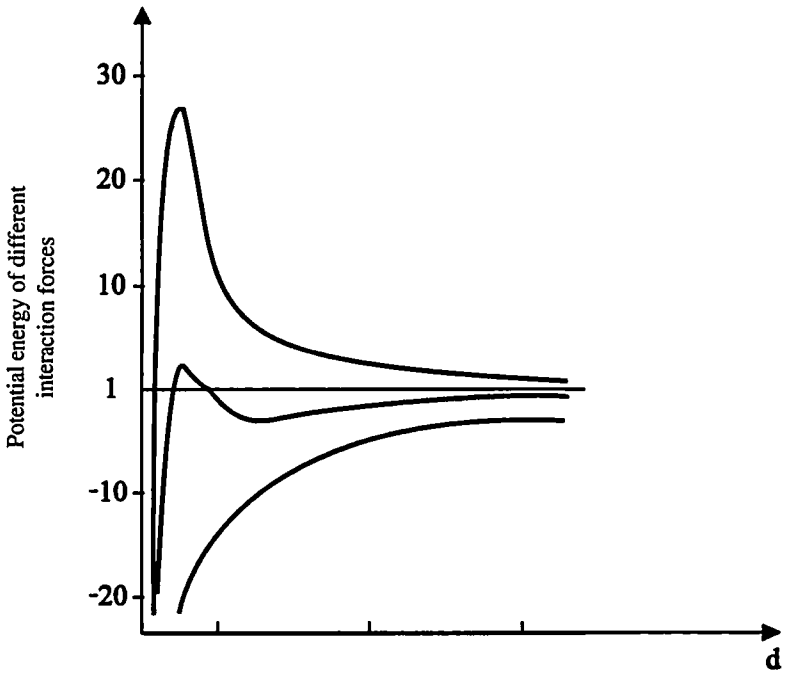


Fig. 2.19. Changes in the electrostatic barrier.

From a practical point of view, soaps generally have much better antiredeposition properties than synthetic anionics. The longer the hydrophobic chain in these molecules, the greater are their antiredeposition properties. This is true only for a given concentration of soil and surfactants. Finally, a high concentration of anionic surfactants can increase redeposition. This is similar to the case of addition of electrolytes.

Cationics. Cationics adsorb onto negatively charged surfaces by pointing their hydrophobic part toward the water, thus increasing the hydrophobic properties of the fiber or particle and resulting in increased redeposition. At a high concentration of cationic, there will be a second adsorption with the ionic part pointing toward the exterior. Negative surfaces become positive, with a consequent repulsive effect for hydrophobic particles. However, during rinsing, concentration diminishes, which causes desorption of the second layer. The surfaces become hydrophobic again and there is then strong redeposition. Thus, cationics are not suitable for use in washing clothes.

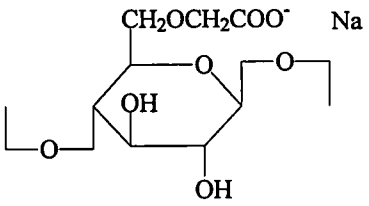
Nonionics. Nonionics adsorb onto fiber and particle surfaces by pointing their hydrophilic part toward the outside. The zeta potential is not changed by this adsorption because the molecules do not have ionized groups. In this case, the most important factors in dispersion are the outside barrier and the layer of water of hydration surrounding the adsorbed surfaces. The steric repulsive barrier, referred to by Stillo and Kolat (66), and the layer of water of hydration keep the particle from approaching the fiber, and redeposition is prevented.

Effect of polyphosphates. Polyphosphates complex divalent cations, notably Ca^{2+} and Mg^{2+}, whose negative contribution to redeposition has already been discussed. Beyond this main function, when polyphosphates adsorb on particles, the charge on the latter is increased considerably (67) and the repulsive forces between the particles are reinforced.

Polymers

Given the weakness of synthetic surfactants relative to soap with respect to redeposition, much research has been done to find solutions to this problem. Polymers are the primary focus.

Sodium Carboxymethylcellulose: SCMC. The main agent used for antiredeposition is sodium carboxymethylcellulose (SCMC), whose chemical *structure* is as follows:



SCMC improves antiredeposition properties in two ways, i.e., it changes the electrical charge of particles in suspension through adsorption at the interface of the solid and the liquid, and it changes the electrical and steric properties of the fiber surface by adsorption onto the textile. Because of the negative charges brought by the COO^- groups of SCMC, the zeta potential is increased, the potential barrier becomes stronger, and there is less redeposition. In addition, the presence of ionic groups increases the degree of hydration of cotton, which explains why there is also a repulsive force due to the steric barrier (nonelectrical force). Experiments by Irnell and Trost (68) have shown that a given quantity of SCMC applied directly to cotton cloth will be more efficient than the same quantity added to the wash solution. These experiments and others would seem to indicate that adsorption onto cotton is the main mechanism and that we can dismiss the effect of SCMC on the electrical properties of particles.

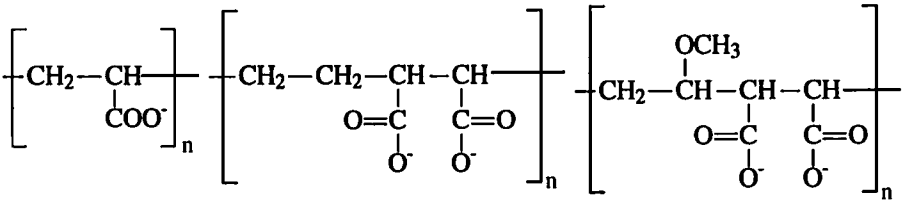
Experiments using radiolabeled ^{14}C SCMC have shown that this derivative *adsorbs only onto cotton, and not onto treated cotton, nylon, or polyester.* The adsorption is due to the fact that SCMC, having a similar molecular structure, deposits on the cotton surface and is held there by hydrogen bonds. In distilled water, adsorption is negligible. *The addition of salts increases adsorption considerably.* The amount of SCMC adsorbed depends on the concentration and the type of cations present in the solution, but it is independent of the type of anion. *Temperature has no effect* on the quantity of SCMC adsorbed at equilibrium. However, the rate of adsorption *is very fast* at the beginning, slowing toward the end. It is a linear function of $t^{1/2}$. SCMC desorbs slowly and weakly. The presence of *anionic and nonionic surfactants does not affect* the adsorption of SCMC on cotton. In alkaline solution, *pH does not affect* the quantity of SCMC adsorbed. In an acid environment, the maximum adsorption is at pH 4.

Experiments have also shown that the antiredeposition properties of SCMC decrease considerably when *the degree of substitution (DS) is >0.7.* In fact, it is probably truer to say that the efficacy of SCMC depends on *its molecular weight and its DS,* which govern its adsorption; it is clear, therefore, that if the DS increases, the molecular weight should be increased as a consequence (the degree of substitution is the *average number* of substitutions of hydroxyl groups by carboxylmethyl groups per monomeric anhydroglucose group of cellulose). Thus, it is important to note that SCMC is effective only on cotton articles. In the literature, other antiredeposition agents are cited, such as proteins rich in the amino acid proline, polyvinylpyrrolidone with a molecular weight of ~40,000. Other researchers have studied polymers such as polyvinyl acetates, polyvinyl alcohol, sodium alginate, and certain modified starches, but all have concluded that they are less effective than SCMC.

Other Polymers. Homopolymers and copolymers of acrylic acid and maleic acid, as well as their salts and derivatives, are well recognized as antiredeposition or complexing agents. One of the main copolymers is sold by BASF under the name Gantrez 119; it is a poly(vinyl methyl ether/maleic anhydride). According to the BASF literature, 1% of Gantrez can replace 8–10% of STPP. Experiments have shown that the use of 1–2% of Gantrez can indeed make possible a reduction in the

level of STPP in a formulation. However, during the 1980s, its use was not considered, in part because of cost problems and because, at the time, environmental pressures were not a factor. However, with the arrival of zeolite, "cobuilders" had to be found because zeolite on its own did not have all of the qualities of STPP.

At first, STPP was used in combination with a small percentage of polymers. There was then an increasing use of polymers (or their sodium salts); the two primary salts were the sodium salts of acrylic acid homopolymer (sodium polyacrylates) and the sodium salt of acrylic and maleic acid copolymer. The chemical structures of these polymers are as follows:



polyacrylic acid polyethylene maleic acid polyvinyl methyl ether maleic acid

Polyelectrolytes provide the twin functions of anti-incrustation and antiredeposition. *Anti-incrustation* is used in the two following cases: (i) in phosphate formulations, in the presence of an excess of calcium compared with complexing agents (e.g., underdosing on the part of the consumer or insufficient STPP in the formulation) or when there is much STPP breakdown into pyro and coprecipitation of insoluble phosphate salts with the soil; and (ii) in nonphosphate formulas with builders such as zeolite, carbonate, and silicate.

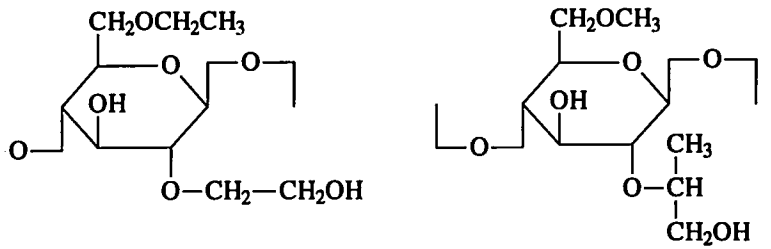
Antiredeposition. Dispersion and suspension of particulate soil in the washing solution averts greying of whites or the dulling of colored articles. Various studies have shown that the use of 1–2% of polyelectrolyte allows a reduction in STPP from 30 to 20% with a level of phosphate breakdown as high as 12–15%. In formulations without phosphates, incorporation of ~3% of polymers prevents incrustation and soil redeposition while increasing detergency.

The mechanism of polymer activity has not yet been clearly shown, but it is to be supposed that it involves the use of adsorption as follows: (i) on the precipitates, controlling their crystallization and inhibiting their growth so as to have an *optimal* size (neither too large nor too small) to avoid redeposition on cloth (as mentioned above); (ii) on particulate soils, increasing the negative charge in the washing solution, producing a stronger repulsive charge between particles, thereby avoiding flocculation followed by redeposition on the cloth.

Antiredeposition and soil release polymers. The development of synthetic fibers (particularly polyester) brought with it serious redeposition problems. As we saw above, the hydrophobic nature of polyester fiber raises the interfacial tension with water, i.e., γ_{FW} that is greater than cotton, resulting in greater redeposition.

The problem can be resolved by reducing the interfacial energy γ_{FW}. A number of products can have this effect of adsorption onto polyester.

Cellulose ethers. Examples of these are methylhydroxypropylcellulose and ethylhydroxyethyl cellulose (69,70). The adsorption of these compounds onto polyester has been studied by means of radioactive products. The presence of hydroxyl groups is responsible for this adsorption which reduces the interfacial

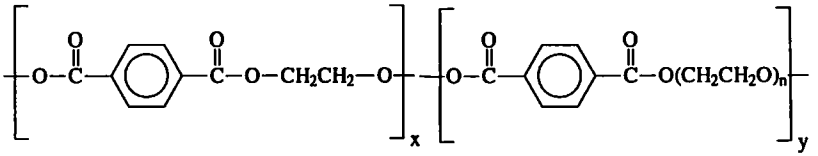


tension between polyester and water, γ_{FW}, and thus reduces redeposition. Let us remember the relationship in the case of redeposition with the change of free energy, i.e., $\gamma_{FW} + \gamma_{PW} > \gamma_{FP}$. We said that when γ_{FW} or γ_{PW} is large (which is the case for hydrophobic fibers or particles), redeposition will be increased, and in the opposite case (for example, when γ_{FW} is reduced by cellulose ether polymer), redeposition will be reduced. We can also explain antiredeposition by the stearic barrier that is caused by adsorption of molecules, thus preventing hydrophobic particles from approaching fibers. The mechanism of adsorption of cellulose ethers by polyester is not clear.

These polymers were used in the 1970s by Lever France in products for washing synthetics. The use of ether cellulose derivatives has other interesting benefits for polyester fibers including the following:

1. Easier removal of soil during subsequent washes (known as "soil-release"). Because of their adsorption onto fibers, these polymers protect fabrics against adhesion of soil. The soil/cellulose ether complex will be more easily removed at the next wash.
2. Greater wettability (lower γ_{FW} as shown above). In other words, we can say that polyester fiber, thanks to its cellulose ether derivatives, becomes polar (like cotton). This can be shown by placing a drop of water on polyester cloth washed with or without a cellulose ether derivative. In the first case, the droplet spreads rapidly on the textile, as on cotton.
3. An antistatic effect resulting from the polar characteristics conferred on the polyester by the derivative. Cellulose ether derivatives can be combined with homopolymers of acrylic acid or copolymers of maleic/acrylic acid to produce even better results. A powder containing this combination and without silicate is ideal for delicate washes because it has good physical properties and good washing performance (71).

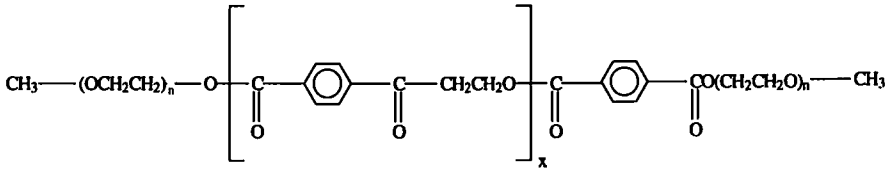
Other antiredeposition and soil release polymers. Other products can act like cellulose ether derivates on polyester, namely, polyethylene (PE) and polyoxyethylene terephthalate copolymers (POET) with the following chemical structure:



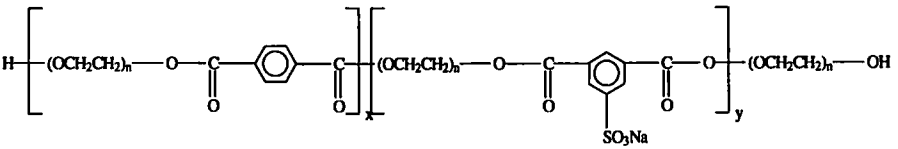
These derivatives are sold by ICI, for example, under the name Permalose T or Melease T (72). This molecule contains one part mimicking the structure of polyester and a hydrophylic part made up of ethylene oxide molecules. By adsorption onto polyester, this compound reduces the interfacial tension γ_{FW} (fiber-water) and gives the fiber the qualities mentioned above (antiredeposition, "soil release," wettability, and antistatic effect). It should be pointed out that Permalose will be effective only if the detergent contains a nonionic surfactant.

Other similar molecules have been patented by different companies. These include the following:

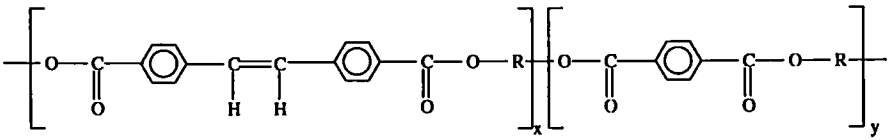
1. Tri-block nonionic oligomers with the following structure (73):



2. Terephthalate-based anionic polymers (74):



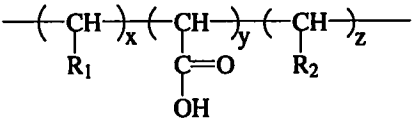
3. Terephthalate-based copolymers with an additional optical brightener structure:



where R is a mixture of CH_2-CH_2 and $CH_2CH_2(OCH_2CH_2)_n$.

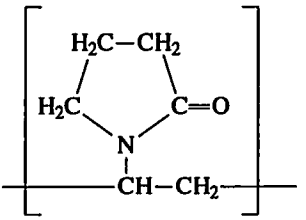
A new type of soil release polymer *for cotton* has been developed by National Starch (76). This is a copolymer made of anionic monomers and nonionics, with a

low molecular weight for greater solubility in water. It is a hydrophobically modified polyethylene glycol (HMPEG) with the following chemical composition:



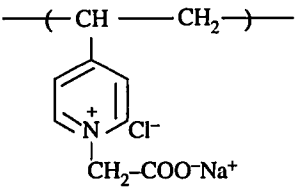
where R_1 and R_2 represent hydrophobic groups.

Dye transfer inhibitors. Among the many other polymers studied is polyvinylpyrrolidone (PVP). This polymer is used increasingly in products for washing coloreds (77). It has been shown that it helps to avoid dye transfer from colored articles to other articles (notably whites) in mixed wash loads. The chemical formula of this polymer is as follows:



where $n = 300–360$.

It should be noted that this polymer, which is widely used in products for color wash, is not efficacy in formulations containing only anionics as surfactants. A molecule has been developed and presented by ISP (International Specialty Products) (78) as a new material is more effective than PVP and is not deactivated by LAS. Its chemical structure is as follows:

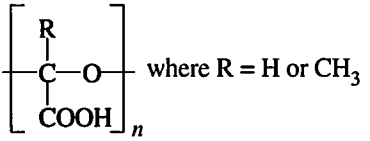


Poly(4-vinylpyridinium betaine)

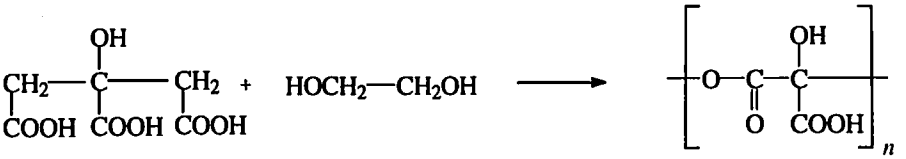
New Trends. A look at patents shows that there is much research in the area of biodegradable and renewable polymers to replace the acrylic homopolymers and acrylic/maleic copolymers, which are widely used today. Among the methods used to produce these new biodegradable molecules, some involve the introduction of "weak" bonds into the polymer chain, causing a break-up of the polymer into

biodegradable monomers. Some examples of these different areas of research are noted here.

Polyacetals and polyketals. Polyacetals and polyketals are obtained by polymerization of glyoxalic acid and the methyl ester of pyruvic acid (79–82) as follows:

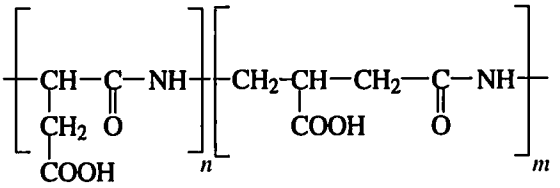


Polyesters. Polyesters are obtained by condensation of polycarboxylic acid monomers and diols such as ethylene glycol as follows:

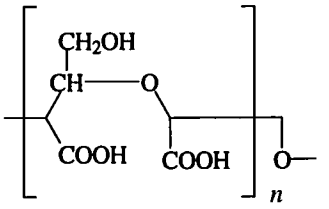


BASF has developed a similar product by condensation of tartaric acid with polyols (83).

Polyamides. Polyamides such as poly (aspartic acid) are being investigated (84, 85). L-Aspartic acid is obtained by an enzymatic reaction of ammonia with fumaric acid. Condensation at high temperature in the presence of an acid catalyst (to avoid producing a branched molecule) yields the following product:



Renewable polymers. In the case of renewable polymers, several methods are being developed, including oxidation of starch giving the following polymer (86):



None of these polymers is as yet sold commercially as a replacement for the polyacrylic acid homopolymers, and the acrylic acid/maleic acid copolymers. The challenge is to find the ideal molecule that meets the three key criteria of performance, cost, and biodegradability.

Amounts of Polymer to Use. For SCMC, given that the proportion of cotton articles in the wash is falling, incorporation should be from 0.5 to 1% of the formulation. For acrylic acid or acrylic/maleic acids, the following three possibilities exist: (i) If the powder contains enough STPP and if decomposition is low (10–12%), it is not essential to use polymers. However, if STPP decomposition is high, it is worth adding 0.3 to 0.5% of polymer to avoid redeposition and incrustation. (ii) If we want to reduce the amount of STPP for environmental reasons, and in the case of high STPP breakdown, we can add between 1 and 2% of polymers. (iii) For phosphate-free formulations containing ion exchangers or precipitating agents, the level of polymers can vary between 3 and 4% or even more for concentrated powders. For heavy metal chelating agents (e.g., phosphonates), incorporation is generally <1% to avoid decomposition of oxidants present in the detergent formulation.

Foam Boosters and Antifoam Agents

The Structure of Foam

Foam is an emulsion of two immiscible phases (e.g., water and air) that behave like an oil/water emulsion. Foam can be an advantage; for example, it is an indication of product efficacy (in hand washing or dishwashing), and can convey a certain "pleasant" feeling in soaps or shampoos. Foam can also be a problem, e.g., foam on rivers or overflowing in the washing machine or dishwasher. It is important to note, however, that the efficacy of a product is not directly related to the amount of foam. A nonfoaming product can be even more effective than a high-foaming product. Foam can be stable or unstable. Unstable foams last from a few seconds to several minutes. Stable foams have a longer life, up to several hours.

Foam is a very complex subject. The theories which have been proposed are sometimes in contradiction with experimental facts because the latter can be affected by unknown and uncontrollable phenomena, such as the presence of unidentified by-products. Despite this warning, we will try to summarize the theory of the formation and stability of foam because this will help us target our research toward foam boosters and antifoam agents.

Foam can never form in a *pure liquid* because this cannot give a certain elasticity to the membrane that surrounds a bubble of air, nor oppose the flow of liquid from this same membrane. Foam is produced by introducing air or other gases into a liquid phase with a certain elasticity. This can be done either by blowing or by mechanical action (agitation or rubbing during the wash). The air bubbles thus formed are encapsulated in a liquid film. These very thin films that separate the bubbles are like lamellar films of identical structure whose interfaces are very

close to each other. The stability or instability of foam is closely linked to the flow of liquid in the film that surrounds the gas. At first, when the lamellar films are relatively thick, *gravity* plays an important part in the flow of liquid between the foam bubbles. As the films become very thin, the effect of gravity is diminished, and interfacial interactions take on a more important role. This is what happens in a surfactant solution.

Indeed, when surfactant molecules are present in a liquid phase, adsorption at the interface between gas and liquid delays the loss of liquid from the lamellar film, and produces a mechanically stable system. This phenomenon is based on the following two theories: (i) the Gibbs effect according to which the surface tension of a surfactant solution decreases as the concentration of surfactant increases, up to the critical micelle concentration (CMC); and (ii) the Marangoni effect according to which the dynamic surface tension on a newly formed surface is always higher than the equilibrium value, which means that, during a very short period, the surfactant molecules must migrate toward the interface to lower surface tension.

These two effects are complementary and are termed the Gibbs-Marangoni effect (87). The Gibbs part refers to the effect of surfactant concentration and the Marangoni part refers to the speed with which the surfactants spread in the lamellar film. The Gibbs-Marangoni effect is the basis used for describing the effects of elasticity and the stability of the foam film, as the following example shows.

Consider two foam bubbles A and B as shown in Figure 2.20. When the lamellar film between the bubbles stretches by flowing (e.g., under the influence of gravity), a new zone is formed in which surfactant concentration is low; as a consequence, surface tension is higher (point a). This creates a surface tension gradient in the film, which in turn causes a migration of surfactant molecules from the area of low surface tension [i.e., where the concentration of surfactants is highest (point b)], toward the area in which surface tension is the highest (point a). These two effects prevent the

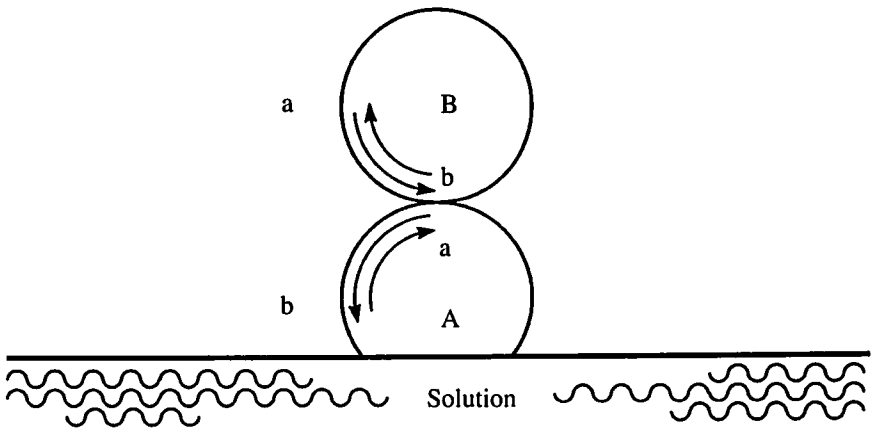


Fig. 2.20. The Gibbs-Marangoni effect.

film from becoming so thin that the bubble bursts. This is the foam mechanism explained by the Gibbs-Marangoni effect.

The Gibbs and Marangoni effect differs depending on the concentration of surfactants in the liquid phase. Thus, for the Marangoni effect, if the surfactant concentration is too low, surface tensions between the pure liquid and the solution will not be sufficiently different to allow the transfer of surfactant in the solution toward point (a). The foam is not stable. For the Gibbs effect, if the concentration of surfactant is low, the gradient in the surface tension of the film is inadequate to allow the migration of surfactant molecules toward zone (a), and the bubble bursts through lack of resistance. On the other hand, if the surfactant concentration is too high, the available quantity of surfactant will be such that a surface tension gradient can no longer form in the film.

The Gibbs-Marangoni effect is not the only theory to explain the formation and the stability of foam. Among other mechanisms we find the following:

1. Viscosity of the liquid phase. If this is high, it delays the flow of liquid from the films of adjacent bubbles, producing a "cushioning effect," which absorbs shocks.
2. Surface viscosity can also delay the flow of liquid between the film interfaces, thereby preventing the bubbles from bursting.
3. Electrostatic or steric repulsion between adjacent interfaces, due to adsorption of anionics and nonionics. This repulsion helps to stabilize the foam.

Foam Boosters

The formulator can change the foaming properties of a product depending on consumer needs. To do this, there are two options, i.e., the selection of foaming or nonfoaming surfactants and the use of additives that boost foam. A surfactant or a combination of surfactants can make up a foaming system. Also, an additive can produce a large quantity of foam with a low foaming surfactant, and *vice versa*, a high-foaming surfactant can be changed into a nonfoaming system with the use of suds depressants.

Choice of Surfactants. Generally the quantity of foam increases with surfactant concentration up to about the CMC. Thus, it is theoretically possible to predict the amount of foam of a surfactant on the basis of its CMC. However, this does not necessarily mean that the foam will be stable. All of the factors that can change the CMC can increase or decrease the foaming characteristics of a given class of surfactants. Such factors include temperature, the presence of an electrolyte, and the surfactant molecular structure.

The solubility of a surfactant is dependent on temperature. Thus, an anionic surfactant which is sparsely soluble at ambient temperature will not foam much at this temperature; it becomes more soluble and therefore foams more as the temperature increases. In contrast, for a nonionic, solubility (and therefore its foaming properties) declines with temperature above the cloud point. The presence of an electrolyte (inorganic salt), which lowers the CMC of a surfactant, can also change the foam profile of the surfactant.

Theoretically, the foam profile depends on the molecular structure of the surfactant. However, in reality this is more complex because there is no direct correlation between the foam profile of a molecule and the stability of its foam. Nevertheless there are some general rules.

1. A nonionic *foams less* than an ionic surfactant in aqueous solution. Indeed, by its nature, the nonionic has a larger surface per molecule; it is therefore more difficult for adsorbed molecules to exercise sufficient lateral interaction to produce large interfacial elasticity. On the other hand, anionics create an electrical double layer through adsorption at the interfaces; this causes adjacent bubbles in the foam film to repel each other, and increases foam stability.
2. For the same class of surfactants, the lower the CMC, the greater are the foaming characteristics. Thus, the solubility of an alkyl sulfate is reduced (and therefore its CMC) as the length of the carbon chain increases and its foaming capacity increases. However, the reverse is true for this class of surfactants in the case of branched carbon chains or when we displace the hydrophilic group toward the interior of the chain; we increase the CMC, and lower the foam profile.
3. The anionic counterion can also affect the foam profile. It can be completely detached from or closely linked to a negatively charged moiety. This results in an important change in the degree of solvation and also the number of associated solvent molecules (as we saw above). According to Kondo *et al.* (88), foam stability of dodecyl sulfate decreases in the following order depending on the counterions: given that the ammonium is completely dissociated, whereas the tetrabutylammonium is strongly bonded.

$$NH_4^+ > (CH_3)_4N^+ > (C_2H_5)_4N^+ > (C_4H_9)_4N^+$$

Use of Additives. The use of an additive can affect foam stability by changing any one of the factors discussed in the previous paragraphs, such as the Gibbs-Marangoni effect, the viscosity of the liquid phase and the lamellar film interfacial layer, or electrostatic or steric repulsion. Thus, a low-foaming surfactant can become high-foaming in the presence of another surfactant molecule that has negligible or no detergency efficacy at all. Numerous additives can change the micellization properties of a surfactant, and thus change its foam profile and foam stability. We have already referred to the presence of inorganic electrolytes. Here are a few other examples, mainly of polar organics.

According to Schick and Fowkes (89, 90), addition of certain polar organics can lower the CMC of surfactants. In their work, they found that the use of a compound with a linear carbon chain of the same length as that of the surfactant was the most effective means of stabilizing a surfactant foam. The following foam boosters are listed in order of increasing efficacy: glycerol ether < sulfonyl ethers < amides < N-substituted amides. In practice, mono- or diethanolamide is used as a foam booster in high-suds powders, dishwashing liquids, and shampoos.

Antifoam Agents

Antifoam agents reduce or eliminate foam in a product. They either prevent foam from forming or they accelerate its destruction. In the former case, it is inorganic ions such as calcium that affect the electrostatic stability or reduce the anionic concentration (by precipitation). In the latter case, inorganic or organic compounds replace surfactant molecules in the bubble film and reduce foam stability. We will examine some examples and mechanisms of antifoam agents (91).

First, the addition of nonionics to anionics considerably reduces foam. However, this system (called binary) still has too much foam to be usable in European drum machines. To produce a nonfoaming formula, we add a small percentage of soap. In the presence of calcium in the wash solution, the soap forms insoluble calcium soaps, which are more or less hydrophobic. These particles lodge themselves in the foam film, which thus becomes heterogeneous. The part of the film that is in contact with a hydrophobic particle becomes thinner and thinner, and eventually a hole is formed and the bubble bursts (see Fig. 2.21).

The anionic/nonionic/soap ternary system has been used by most detergent manufacturers for a long time in nonfoaming products for use in European drum machines. The most effective soaps have long saturated carbon chains. Their effectiveness by oil type, in order of decreasing effectiveness, is as follows: whale > rapeseed > stearate > tallow > coconut. Some formulations still contain soap, but with some negative consequences, i.e., they are inefficient in soft water (no formation of calcium soap) and they produce caking (gelling) in the machine powder dispenser, particularly in cold water or when water pressure is low.

The literature mentions hydrophobic colloidal particles such as clay and hydrophobized silica that can be used as suds depressants. Some manufacturers have produced antifoams based on hydrophobic particles to replace soaps. Among these are hydrophobized silica (Sipernat, Degussa). Experiments have shown that these products are not effective enough and cannot be used directly in the detergent manufacturing process. The ternary system has slowly been replaced by a mixture of binary anionic/nonionic, with antifoam agents included. Work has been done on the following systems: (i) stearyl phosphate (Hostaphat MDST, Hoechst [now Clariant], which

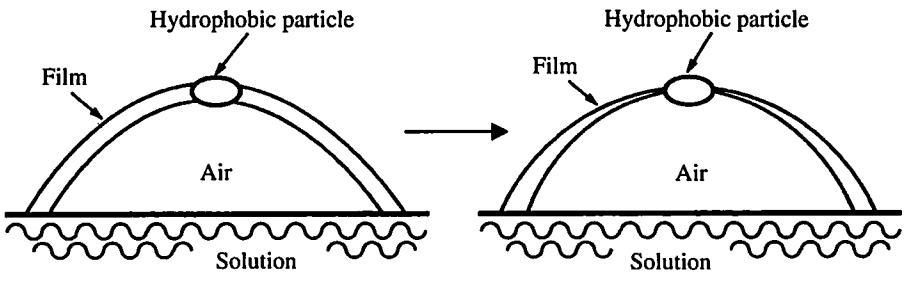


Fig. 2.21. A hydrophobic particle breaks a foam bubble.

is a mixture of mono- and distearyl phosphate); (ii) oils and waxes; and (iii) silicones. These organic compounds use a "spreading" mechanism, i.e., their molecules migrate toward the film surface where they replace the surfactant molecules. This reduces interfacial viscosity, reduces film elasticity, increases liquid flow, and lowers the Gibbs-Marangoni effect.

Thus, a surface with foam is replaced by a surface with less foam. This can happen only with compounds with low surface tension that can spread over the surfaces of the foaming solution (Fig. 2.22). This property is expressed as a "spreading" coefficient, S, in the following formula:

$$S = \gamma_F - (\gamma_A + \gamma_{FA})$$

where γ_F is the surface tension of the foaming solution, γ_A is the surface tension of the antifoam agent, and γ_{FA} is the interfacial tension of the foaming solution/antifoam. To be efficient, an antifoam should have a positive S coefficient to be able to spread over the foaming solution.

Silicones generally have low surface tension (~18–26 mN/m). Let us consider a silicone in a solution of Na alkylbenzenesulfonate. Let the surface and interfacial tensions be as follows: $\gamma_F = 35$ mN/m, $\gamma_A = 21$ mN/m, and $\gamma_{FA} = 6$ mN/m. We can now calculate spreading coefficient S as follows:

$$S = \gamma_F - (\gamma_A + \gamma_{FA}) = 35 - 21 - 6 = 8$$

This value is positive, which is why silicone is an effective antifoam for an Na alkylbenzenesulfonate solution. But silicone can be a poor antifoam in the case of a surfactant with lower surface tension where the S coefficient becomes negative. Results from a number of tests show that the effectiveness of stearyl phosphate is limited to formulations containing only, or at least a high proportion of, nonionics. It works less well for products with a high level of anionics (e.g., LAS/nonionic = 8/4).

It has been found that the combination of oil with a hydrophobic particle has better antifoam properties than oil on its own. The following systems have been developed: oil + paraffin + hydrophobized silica and silicone + hydrophobized silica.

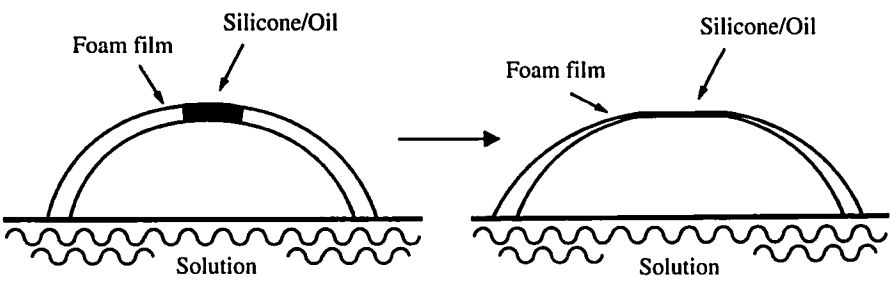
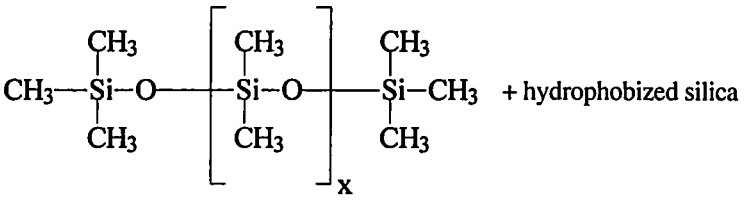


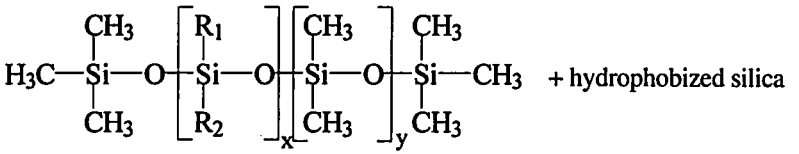
Fig. 2.22. Foam is broken up by a low surface tension fluid.

A mixture of oil, paraffins (with different melting points), and hydrophobized silica can control foam for the entire machine wash cycle, as shown in Figure 2.23 (92).

Between 15 and 40°C, the oil is the active agent; between 40 and 60°C, it is the paraffin, with a melting point of ~40°C, that takes over from the oil (which has become ineffective because it has emulsified in the detergent solution); between 60 and 90°C, it is the paraffin, with a melting point of 60°C, that replaces the previous paraffin. If oil alone is used with silica, foam curve 1 is obtained. With the mixture of oil + 40°C paraffin + silica, curve 2 is obtained. With a mixture of oil + 2 paraffins + silica, curve 3 is obtained. Studies have also been done on a mixture of hydrophobized silica, silicones, or modified silicones. Some examples are shown in the following:



Dimethyl siloxane



Modified silicone

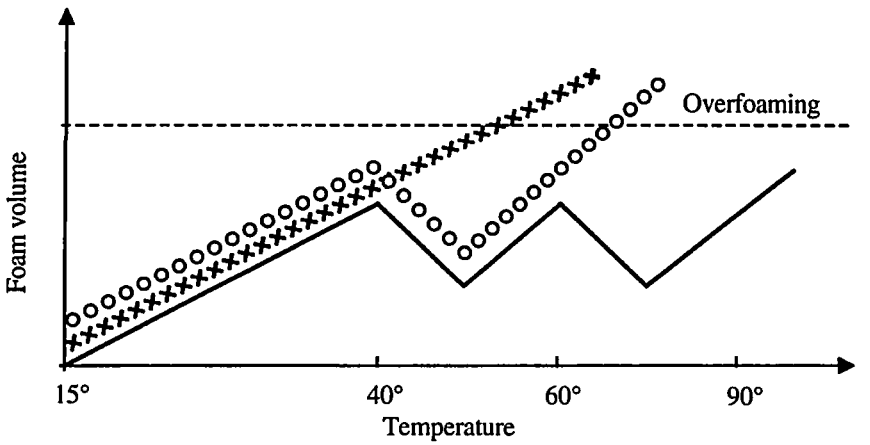


Fig. 2.23. Foam level in a washing machine with or without antifoam. ×, vil + silica; O, vil + 40°C paraffin + silica; —, vil + two paraffins + silica.

where R and R_1 represent identical or different alkyl or aryl groups. Results achieved with these "compounds" are satisfactory. Compared to soaps, they present a number of advantages including flexibility in formulation, efficacy regardless of the water hardness and wash temperature, improved behavior of the powder formulation in the machine distributor (good dispensing properties), and competitive costs (reduced risk of out-of-stock or price fluctuations).

The compounds for these studies are manufactured either "in-house" or are sold ready to use, such as Q2-3008 (Dow Corning) or Rhodorsil (Rhône Poulenc [now Rhodia]). The results in both cases are the same, if the "compounds" are well encapsulated (93–97). The compounds lose their activity if they are introduced directly into the slurry or into powders containing a high percentage of alkylbenzenesulfonate. This is probably due to the adsorption of alkylbenzenesulfonate (because of its negative charge) onto the particles of hydrophobized silica. This adsorption can have two effects, i.e., the silica loses its hydrophobic properties, making the compound ineffective, or the surface tension of the new silicone-silica-LAS compound approaches that of LAS. Consequently, the spreading coefficient *S* decreases and can even become negative. It has also been noticed that detergents containing pure nonionics do not deactivate silicone-silica compounds. This is probably due to the fact that nonionics are not adsorbed onto the hydrophobic silica particles because they do not carry a charge.

Fluorescent Whitening Agents (FWAs)/Optical Brighteners

The search for "whiteness," which is synonymous with hygienic cleanliness, dates far back in history and represents important priorities for mankind. A step forward in the search for whiteness was achieved when launderers observed that after blue colorant was used on yellowed articles they appeared whiter, but duller. This gave birth to the use of "Reckitt-type" blueing agents in the wash. Current usage refers to optical brighteners as fluorescent whitening agents (FWAs). We will use this term in the following discussion. The way was opened for FWAs when the physician G. Stokes discovered fluorescence in 1852 using Spath fluor spar (fluorite) and uranium glass to transform invisible ultraviolet (UV) light into visible light. The first step was completed in 1929 with the Krais experiment. Krais impregnated a piece of linen with an extract of horse chestnut and managed to whiten the cloth. The principal active constituent is esculin, a derivative of 6,7-dihydroxycoumarine. The first patent covering the use of these derivatives was taken out by Ultrazell in 1935, six years after Krais's discovery. This patent used a fluorescent compound found in starch to whiten textiles, replacing chemical agents and blueing. Other patents describe the use of these derivatives to whiten powders and soaps (Unilever 1943) or to whiten textiles (I.G. Farben Industrie 1940). However, these compounds were not light-stable and thus did not become widely used. The decisive step in the use of FWAs was taken in 1941 with the introduction of synthetic derivatives of stilbene, under the name Blankophor B. I.G. Farben Industrie patented their use as optical brightening agents in detergents, soaps, photographic

papers, and other products. From then on, intensive industrial development has led to >1000 FWAs sold on the market today. Given the wide range of available FWAs, extensive research has been conducted to rationalize and optimize their use in detergent powders. Before looking at the practical aspects of the problem, we will look briefly at the mechanism and the chemistry of FWAs.

Mechanism of Action of FWAs

Physical Notion of Absorption of Light. The main action of colorants is explained by the absorption of a part of the incident radiation. In other words, matter without color is matter with a strong reflectance of light. If a colorant is fixed to the matter, it absorbs part of the radiation of a certain wavelength; the quantity of light reflected is less. A simple example is the color red. The colorant in question absorbs part of the blue, green, and yellow light; only the red light, which is not absorbed, is reflected by the object, which takes on a red hue.

Let us now look at the process of absorption. A photon of incident radiation is absorbed by a molecule of matter and transfers its energy to the molecule. This energy raises the level of an electron in the molecule from its ground state S0 to an excited state S1. Only electrons with energy equal to the difference S1 – S0 enter into excitation to S1. As the excited molecule returns to its ground state, it loses energy. A number of cases can arise. Figure 2.24 illustrates the different phenomena that can occur during the change from state S1 to state S0. The electron can return directly to state S0 or change to a metastable state of energy T1 called the triplet state.

The life of an electron in state T1 is quite long. Collisions between the excited molecule and its neighbors are possible. This causes energy loss in the form of thermal radiation, and there is no emission of light by the excited molecule. An electron in state T1 can return to state S0, and this causes emission of energy in the form of radiation of light, which is *phosphorescence.* When the electron returns directly

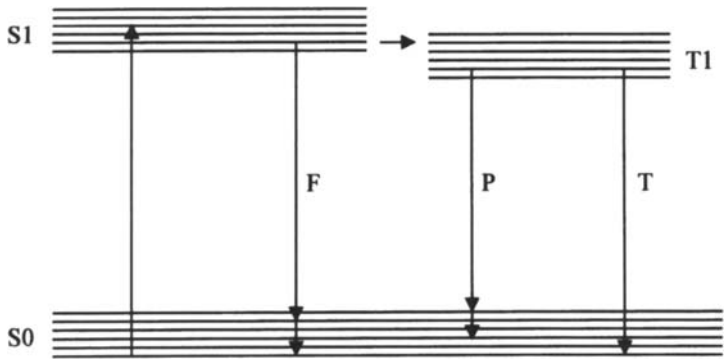


Fig. 2.24. Phosphorescence and fluorescence.

from state S1 to state S0 without transiting *via* state T1, there is also an emission of energy in the form of radiation of light, which is called *fluorescence.*

From a practical point of view, the difference between phosphorescence and fluorescence lies in the time lapse between the suppression of the source of exciting light and the reemission of light by the excited molecule. This lapse is longer for phosphorescence because of the long lifetime of the intermediate excited state T1. For a molecule to absorb light radiation, it must have free electrons, double bonds (π bonds), particularly when these are conjugated. This is the case for aromatic systems, heteroaromatics or –CH=CH–; –CH=N– groupings.

How FWAs Work. FWA molecules are rich in –CH=CH– or –CH=N– groupings that are generally combined with aromatic or heteroaromatic rings. These molecules have an excited energy state S1 that corresponds to the absorption of radiation of wavelengths in the UV region, and to emit visible radiation of wavelengths situated in the blue part of the spectrum when the molecule changes from excited state S1 to ground state S0.

Let us now look at how an FWA contributes to the process of bleaching cloth. White cloth has a reflectance profile similar to that shown in curve 1 in Figure 2.25. If this cloth contains impurities (through degradation or soil), its reflectance curve becomes curve 2 with the absorption in the blue region. This absorption results in an excess of yellow light in the reflected light, which gives a yellow appearance to the cloth. The yellow tinge of the cloth can be removed partially by a blue colorant that absorbs the excess yellow light so that the object appears white; however, this correction is obtained at the cost of a reduction in the amount of light reflected, which in turn causes the cloth to appear less bright. Its reflectance is represented in curve 3.

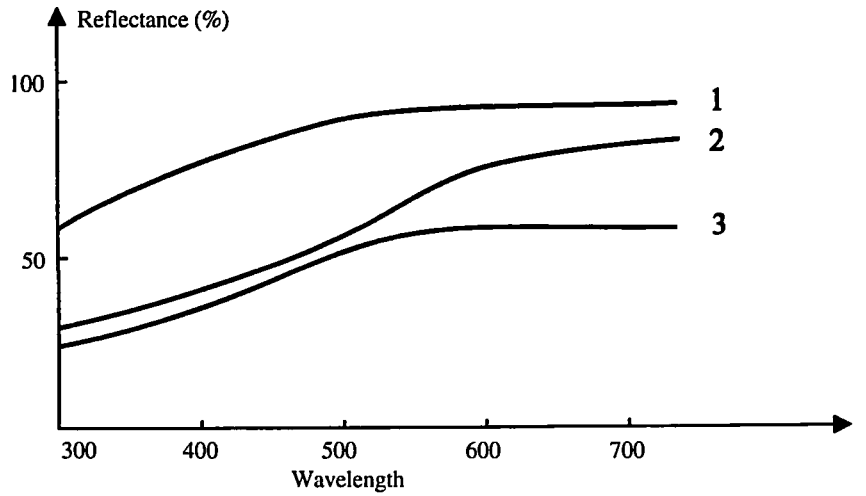


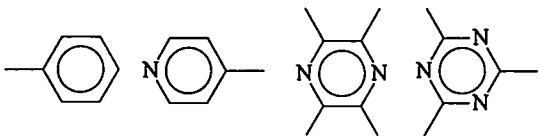
Fig. 2.25. Reflectance curves of a white cloth.

FWAs do not suffer from this disadvantage. As mentioned above, FWAs are substances that absorb UV radiation in daylight and reemit absorbed energy in the form of visible light in the blue part of the visible spectrum. Following this conversion of light, the object reflects more visible light than was originally emitted; the object appears not only whiter but also brighter and more luminous. The curves in Figure 2.26 are reflectance curves for a cloth without FWAs (curve 1), a cloth with FWAs (curve 2), and a curve of fluorescence of an FWA itself (curve 3).

Chemistry of the Best Known FWAs

Nature is very rich in fluorescent compounds; large amounts of such compounds are found in plants, animals, and humans in which they assume functions essential to life. Examples include tyrosine amino acids, tryptophan, and some vitamins. However, it has not proved possible to identify natural substances that satisfy all of the requirements for an FWA (e.g., available quantity, cost, stability, or precise color). Therefore, chemists have had to develop this new class of products.

Chemical Structure of FWAs. The chemical structure of FWAs is varied (as already stated, there are >1000 commercial varieties). The most appropriate systems are built from aromatic or heteroaromatic moieties linked either directly or by intermediate ethylene bridges. For example, the following are some of the most important structures:



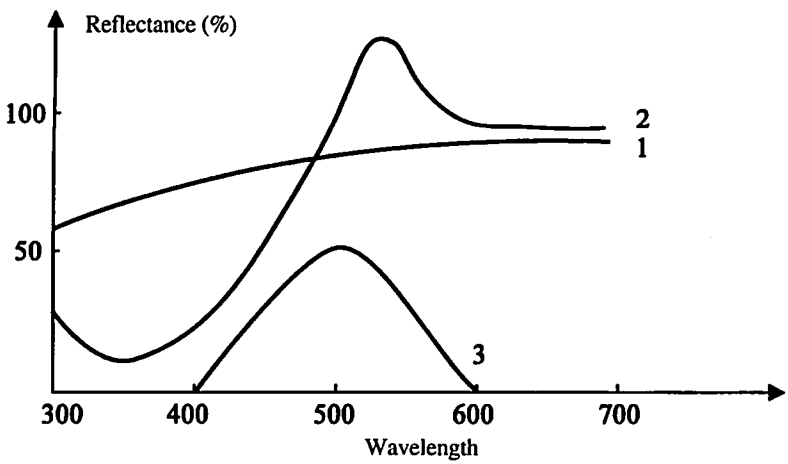
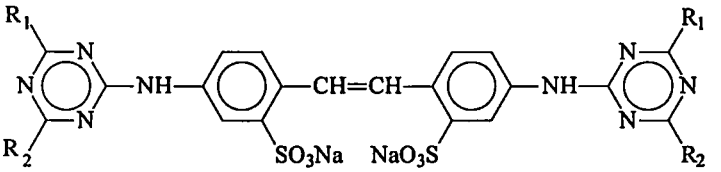


Fig. 2.26. Reflectance curves with and without FWAs.

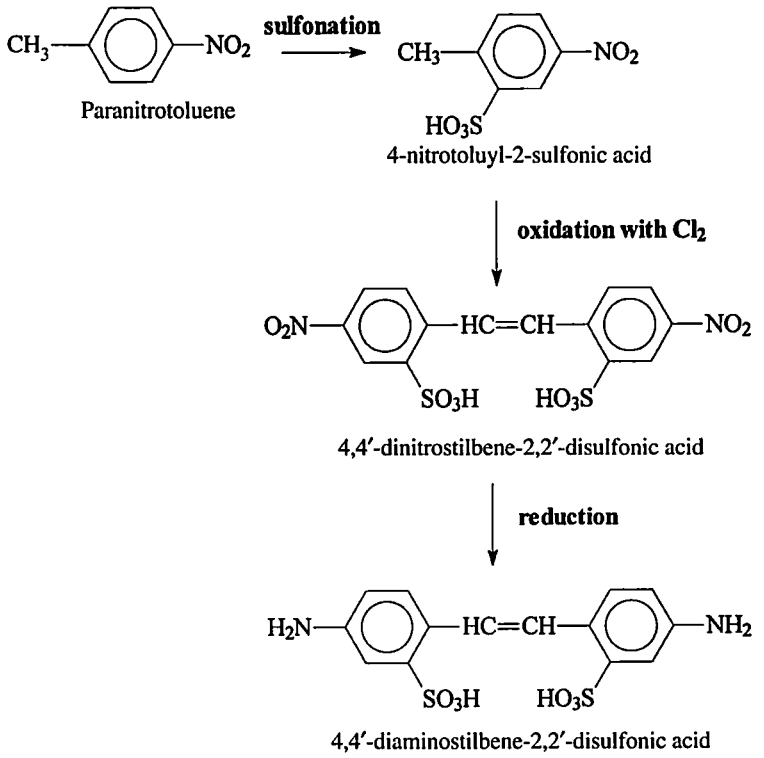
The most widely used FWAs in detergent powders are derivatives of 4,4′-diaminostilbene-2,2′-disulfonic acid with the following structure:



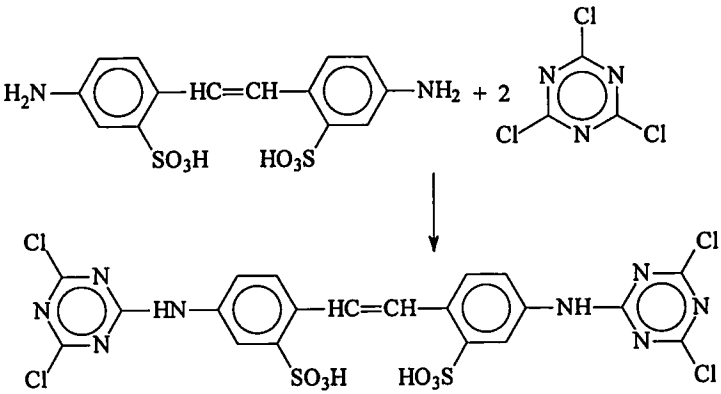
The R_1 and R_2 groupings vary greatly. They give specific properties to the FWA, such as solubility or substantivity.

Dimorpholino-Type FWAs. Synthesis. It is not possible to discuss the synthesis of all, or even the main, FWAs here. We will take just one example, i.e., the preparation of the dimorpholino-type FWA, which is widely used in liquid and powder detergents.

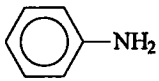
1st stage: Preparation of diaminostilbenedisulfonic acid



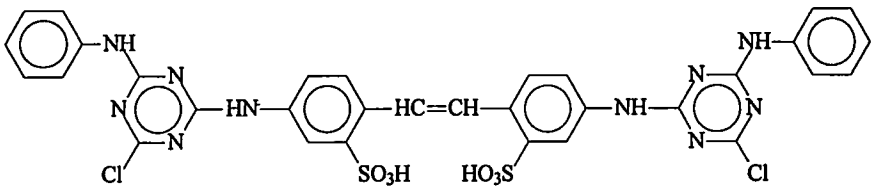
2nd stage: Addition reaction



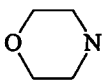
3rd stage: Substitution reaction. The Cl atoms are substituted by the following:
Two aniline groups:



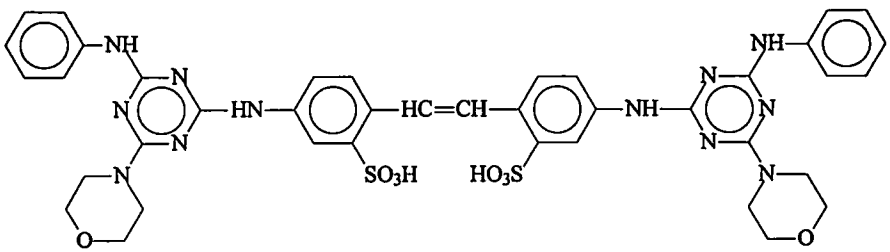
which yields the first substitution:



Two morpholine groups:

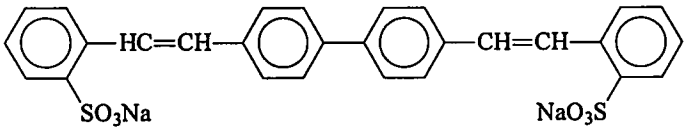


and then the second substitution:

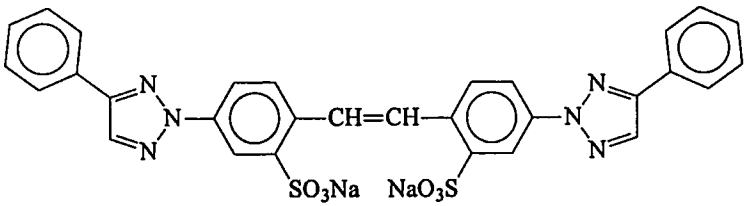


Neutralization gives disodium 4,4′-*bis* (4-anilino-6-morpholino-5-triazin-2-ylamino)-stilbene-2,2′-disulfonate. These types of FWAs are sold under various trade names, including Tinopal DMS (Ciba-Geigy), Blankophor MBBH (Bayer), and Optiblanc 2M (Sigma).

Superbrighteners. Apart from dimorpholinos, "superbrighteners" with the following characteristics are used: (i) better solubility in cold water; (ii) good stability toward oxidizing agents (even bleach); (iii) good light stability; and (iv) whiter powder. The chemical structures of these FWAs are as follows:



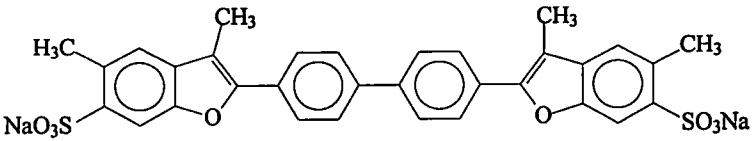
disodium 4,4′-*bis* (2-sulfostyryl) biphenyl (e.g., Tinopal CBS-X, Ciba-Geigy)



disodium 4,4′-*bis* (4 phenyl-1,2,3-triazol-2-yl)-stilbene-2,2′ disulfonate (Blankophor BHC, Bayer)

These superbrighteners tend to be used in countries with plenty of sunlight.

With the development of compact powders, it has become necessary to develop still more stable FWAs because of the presence of stronger oxidizing agents (peracids) and the closer contact between powder particles. The following is an example developed by Ciba-Geigy:



Sodium dibenzobiphenyldisulfonate (DBFBF FWA, Ciba-Geigy)

The Use of FWAs in Cotton Wash

Loss of whiteness in new cloth is the result of a change in its surface condition. There are many reasons for this change, including fiber deterioration, organic, or inorganic

soil. This loss of whiteness can be compensated for in different chemical and optical ways, e.g., use of detergents, oxidants or reducing agents, blue colorant (blueing), or FWAs. Some general principles regarding the use of FWAs in washing cotton articles are presented here.

Comments

FWAs today are truly effective only on cottons. FWAs for white nylon exist, but this type of textile has practically disappeared. Nor are there FWAs for polyester.

Factors That Influence the Whiteness of Brightened Cloth: Whiteness and Fluorescence. Fluorescence is the difference between the reflectance of a brightened cloth and one that is unbrightened. In practice, this fluorescence is measured as the difference in the reflectance of the cloth with and without UV light, at the wavelength corresponding to the maximum reemission of the visible light. This gives the following relationship:

$$F = R\ 460 - R * 460$$

where F is fluorescence, where R is the total reflectance at the wavelength of 460, and $R * 460$ is the reflectance without UV (i.e., with a UV filter) at the same wavelength. For a given cloth, the visual whiteness is proportional to the intensity of fluorescence as shown in Figure 2.27. This relationship is not valid for very high concentrations of FWAs on cotton (Fig. 2.28).

Factors That Influence the Concentration of FWAs on Cotton. As shown in Figure 2.28, up to a certain limit, the degree of whiteness is dependent on the concentration of FWAs adsorbed on cloth. This concentration itself is dependent on a number of factors that we will examine in the following chapters.

The solubility of FWAs. In general, the higher the concentration of FWAs in the solution, the higher is the quantity that will be adsorbed on cotton in the wash. In most cases, almost all of the FWAs in solution will be adsorbed on cotton, and it is therefore essential that they be soluble and dispersed in the solution. FWA mole-

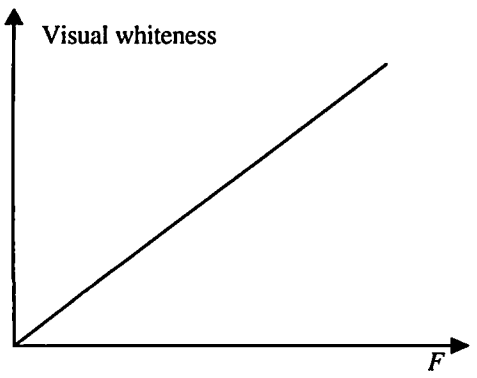


Fig. 2.27. Visual whiteness as a function of fluorescence.

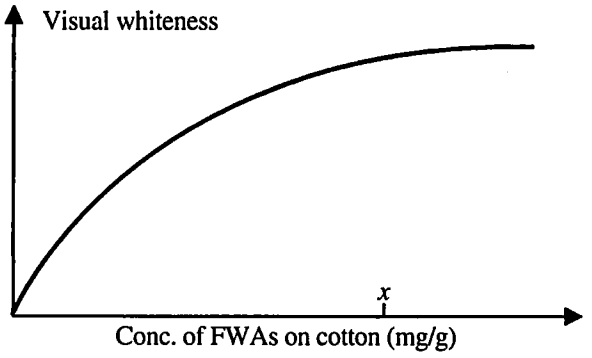


Fig. 2.28. Visual whiteness as a function of the concentration of FWAs.

cules tend to *associate* in the solution, and this phenomenon increases with concentration. Individual molecules adsorb more rapidly on cotton than associated molecules; thus it is important to keep the molecules apart in the solution.

In general, an amorphous structure is more soluble than a crystalline structure, i.e., large crystals are less soluble than small ones. A change in crystallinity takes place when an FWA is subjected to high temperatures (100°C); the crystals become colorless and only slightly soluble.

Consider the case of dimorpholino types. In Figure 2.29, we can see the rate of dissolution of the different grades (microfine, pure, regular) of this FWA at 25°C. The observed differences are due only to the shape and size of the crystals.

Alkaline pH. An alkaline pH favors dissolution of FWAs because they are completely ionized. To summarize, for a given FWA to dissolve completely in cold water, it must be very finely divided, not very concentrated, and the pH of the environment must be alkaline. In practical terms, the brightening power of any two detergent powders can be compared only in washes at low or medium temperatures. At the boil, the solubility of FWAs is excellent. The FWAs adsorbed on articles during previous washes go into the solution, and an equilibrium concentration is established among all of the articles in the wash.

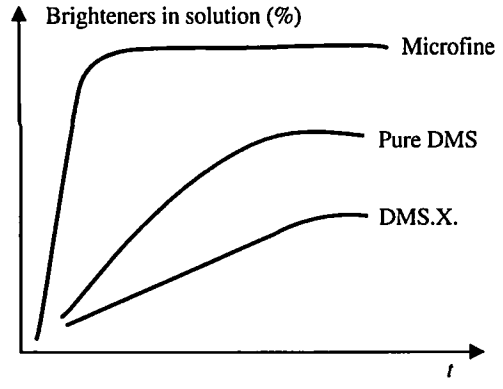


Fig. 2.29. Speed of dissolution of FWAs as a function of their granulometry.

FWA Loss. The causes of loss of FWAs include soil, light, nonionic detergents, and chemical bleaching agents. We will examine each of these factors in turn.

Soil. Soil that is present on the surface of fibers (either because it has not been removed or because it has redeposited) can limit the adsorption of FWAs on cotton and thus reduces the quantity of FWAs present there. In addition, this same soil can absorb part of the fluorescence from FWAs, thus reducing their efficacy.

Light. FWAs with an ethylene bridge –CH=CH– can exist as *cis* and *trans* isomers. It has been found that only the *trans* form absorbs UV light in the range 340–400 mm; it is therefore fluorescent. The *cis* form is inactive. Light changes the *trans* form into the *cis* form. This change occurs rapidly when the FWA is in solution. It is slower and more difficult when the FWA has already been adsorbed by the substrate (the fibers). Thus, light can destroy an FWA solution in a few seconds, but once the FWA has been adsorbed on the fiber, it remains active even when exposed to light for long periods. Light stability therefore depends on the ease or difficulty with which an FWA changes from the *cis* to the *trans* form. An FWA is light-stable when its chemical structure is rigid and it opposes all rotational changes. Decomposition products can have a yellowish color. When cotton carries a high concentration of FWAs and is exposed to daylight, it will yellow with time. However, the decomposition products and the associated yellowing can be removed by *an effective wash.*

Nonionics. Anionics and soaps have relatively little effect on the adsorption of FWAs by fibers. Nonionics, on the other hand, have a very negative effect on adsorption. It is believed that, in general, anionic FWAs form aggregates with nonionics, which causes a reduction in the quantity of FWAs adsorbed.

Oxidants. Most brighteners are attacked by bleach when they are in solution. They are more stable once they are adsorbed onto the fibers. Thus, FWA decomposition by bleach takes place in the wash solution before they are adsorbed onto cotton. This decomposition is dependent on a number of factors, including the following: (i) the structure of the FWAs since some are more chlorine-stable than others (e.g., Tinopal CBS, Blankophor BHC); (ii) concentration of chlorine because the loss of FWAs is a linear function of the concentration of active chlorine in the solution; and (iii) the detergent system because nonionics protect FWAs from chlorine by surrounding them with their micelles. Cotton FWAs are generally stable in the presence of peracetic acid formed by the reaction of TAED with perborate. However, these FWAs often contain impurities that react with peracids to give a disagreeable odor and a pinkish color to the detergent. To avoid this, only pure FWAs should be used.

Amount of FWAs to Use in Detergent Powders. Before considering this question, there are two clarifications that will help define the problem: FWAs are not 100% active—they also contain inorganic sulfate salts. The activity of an FWA is defined by the value E_1^1, which is the extinction coefficient of a 1% FWA solution in a 1-cm thick cell. For a given type of FWA, the higher the E_1^1 value, the

higher is its concentration. The percentage of FWA will always be expressed with a given E_1^1 value. All cotton articles are optically pre-brightened during manufacture of the cloth. The brightening function in the wash is intended to replace the loss of FWAs when clothes are worn, or to give extra whiteness when the original brightening of the textile is inadequate.

Practical experiments can be carried out to optimize the amount of FWAs to be incorporated into a powder. An example of results is given in Figure 2.30. This is the response curve (preference) of consumers to different levels of concentration of FWAs adsorbed on cotton (expressed in milligrams of FWAs per gram of cotton). To reach maximum whiteness requires a concentration of z mg/g. Beyond this value, there is a risk of rejection by consumers. On the basis of these results, we can decide how much FWA to use. For example, to maintain whiteness, it is enough to use y mg of FWAs/g of cotton for FWAs with a given E_1^1. The x value corresponds to the economical level, i.e., the minimum level required to avoid yellowing.

The Effect of FWAs on Colored Articles

A cloth has a given color because all of the other colors of the spectrum have been absorbed. For example, for a blue cloth, the wavelengths corresponding to red, yellow, and green have been strongly absorbed, compared with blue or violet. Figure 2.31 gives the reflectance spectrum of a blue cloth that has been washed with a product containing an FWA. The difference is very clear in the UV area.

When a dark cloth is treated with FWAs, the amount of available UV light is very small (because of its absorption by the dark blue colorant); therefore, the FWA cannot absorb UV light and cannot reemit visible light, i.e., there is no fluorescence as shown in curve B in Figure 2.31. FWAs are ineffective on dark-colored articles. Light blue cloth absorbs much less UV, which allows the FWAs to act fully (curve A). For other colors, the phenomenon is identical and depends principally on the absorption of UV

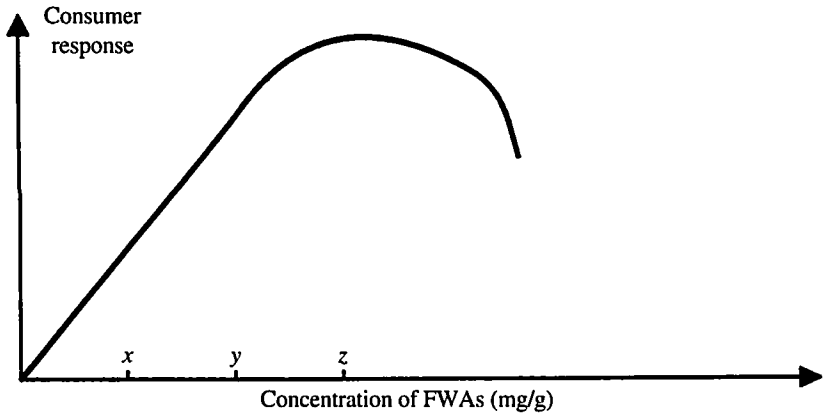


Fig. 2.30. Practical appraisal of whiteness as a function of the concentration of FWAs.

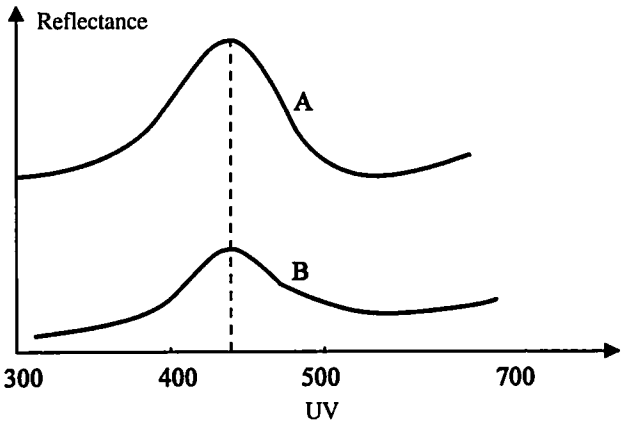


Fig. 2.31. Reflectance spectrum of a blue cloth.

light by the colorant. Thus, for pastel colors, FWAs change the appearance of the reflectance curve, which becomes more luminous and can result in a slightly different color; this can be a negative point for the consumer.

Article Yellowing (Caused by FWAs on White Cotton)

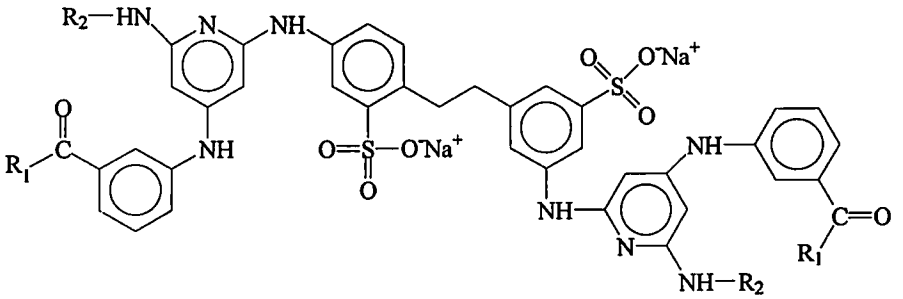
When brightened white cotton articles are exposed to light, they can become yellow. This is due to photodecomposition of FWAs such as the stilbene type. The mechanism of decomposition as well as the chemical structure of the consequences has been studied by Ciba (98). The decomposition products (photoisomers) are colorants that can be adsorbed onto cotton to give a yellowish color. It has been shown that super FWAs such as Tinopal CBS (distyrylbiphenyl) are much more light-stable and are recommended for use in countries in which there is a lot of sunlight.

The Influence of FWAs on Detergent Powder Color

FWAs can whiten the detergent powder when they are completely dispersed. However, they can sometimes color the powder yellow or pink, for example. There are various reasons for this discoloration. First, there may be impurities in the FWAs, which can cause discoloration. It may also result from the presence of certain crystalline forms in the FWAs, e.g., the hydrated sodium salts of the dimorpholino-type FWAs finely dispersed in the detergent powder will give a yellowish color. Finally, coloring can be explained by a chemical reaction between the FWA and/or its impurities with the different powder components such as perborate, STPP, or perfume. It is difficult to anticipate all possible causes for discoloration of a powder, and it is therefore recommended that storage tests for new FWAs be done in the presence of all of the ingredients in the blown powder, to determine whether discoloration is likely to develop.

Protection Against the Sun

We know that prolonged exposure to sunlight, or rather to UV radiation, can cause burning of skin and even skin cancer. We can therefore ask ourselves whether clothes alone are an adequate protection against the sun's rays in certain countries. Ciba (99) has developed a molecule that has great affinity for cotton and also provides a sunscreen. Its chemical formulation is as follows:



This molecule is colorless but behaves as a textile colorant for cotton. It can therefore be used in laundry products. We should remember that protection against UV light is expressed in SPF (Skin Protection Factor). Thus a SPF of 20 means that only one twentieth of the biologically active UV light passes the screen. The SPF value is dependent on a number of factors, as follows:

1. The type of textile: Cotton absorbs more UV light than wool or polyester.
2. Tension: A fabric with elastic properties worn close to the skin can reduce the SPF value.
3. Dampness: A damp fabric also reduces the SPF value.
4. Thickness: Little UV light will pass through very thick textiles.
5. Color: Most colored textiles absorb UV light. Pastel colors absorb less than dark colors.

To give examples, a T-shirt will allow as much UV radiation to penetrate as sunscreen with an SPF of 7; in both cases, 85% of the rays are screened, but 15% get through. Clothes containing UV screens have been popular for some time in Australia and New Zealand, and they are beginning to appear in Europe.

Fillers

All of the ingredients in a detergent are not active. In so-called conventional powders, some ingredients do not play a part in wash performance. However, some of these components are necessary for the manufacturing process, such as water (in sufficient quantity to hydrate the salts, particularly in phosphate formulas), and toluenesulfonate (to reduce slurry viscosity), for example. In general, powders contain a certain quantity

of fillers. The most frequently used of these is sodium sulfate, which is cheap because in general it is a by-product of chemical manufacture. In a small number of countries calcite is used. For concentrated powders, fillers are removed as much as possible, i.e., they contain minimal quantities of water (both in the powder and the ingredients, e.g., perborate monohydrate in place of perborate tetrahydrate) and minimal quantities of sodium sulfate (by-product of LAS or PAS).

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CHAPTER 3

Detergent Powders, Bars, Pastes, and Tablets

Powder Detergents

See Chapter 2 for details on the raw materials referred to in this section.

Conventional Powders

"Classical," "traditional," or "conventional" powders continue to represent >60% of world production, but usage varies greatly by country. The main characteristic of conventional powders is their high level of secondary ingredients; these help in the manufacturing process or act as fillers and have little effect on product performance. Powder densities vary from 200 g/L (e.g., in some developing countries) to 700 g/L (e.g., in France). There are two main product types, i.e., foaming and nonfoaming.

Traditional Foaming Formulations. This type of product is used for hand and machine washing; for hand washing, foam is important in this application because it is a sign of efficacy for the user. When no foam is visible, the solution is no longer active (too much soil or calcium) and it has to be changed. Foaming formulations are also used in suds-tolerant washing machines (e.g., in North America or Southeast Asia).

The surfactants used are predominantly anionics such as alkylbenzenesulfonate (ABS), particularly in developing countries, and the more ecological linear alkylbenzenesulfonate (LAS) in other countries. There are also local variants, such as primary alcohol sulfate (PAS) in the Philippines, where it represents a substitute for imported raw materials. Nonionics are sometimes added in a complementary role but at levels one-fifth/one-fourth of those of anionics.

Builder and cobuilder levels depend on a number of factors, particularly water hardness and types of soil (e.g., pH or antiredeposition), and also cost. In general, sodium tripolyphosphate (STPP), Na silicate, or Na carbonate are used. Secondary ingredients (e.g., Na sulfate or calcite) complete the formulation and help to reach the required product density at the lowest cost. Other ingredients, including fluorescent whitening agents (FWAs), enzymes, or "photobleach," bring benefits other than detergency (for example, "brightness" of the wash or specific stain removal). Table 3.1 presents an example of a formulation for washing by hand. Such powders do not include bleaching systems such as perborate or perborate/tetraacetylethylenediamine (TAED). However, they can include photobleach.

Table 3.2 presents an examples of formulations for use in machines. These formulations differ slightly depending on the presence (P) or absence (zero-P) of phosphates and the use of bleaching agents (+/– activators), such as perborate, perborate/sodium nonanoyloxybenzenesulfonates (SNOBS), or perborate/TAED.

TABLE 3.1
Example of a Formulation for Washing by Hand[a]

Ingredient	(%)
Anionics: ABS or LAS	15–30
Nonionics	0–3
STPP	3–20
Na silicate	5–10
Na carbonate	5–10
Na sulfate	20–50
Ca carbonate	0–15
Bentonite clay/calcite	0–15
Enzymes, FWAs, SCMC, perfume	+
Water	Balance

[a]Abbreviations: ABS, alkylbenzenesulfonate; LAS, linear alkylbenzenesulfonate; STPP, sodium tripolyphosphate; FWAs, fluorescent whitening agents; SCMC, sodium carboxymethylcellulose.

Traditional Nonfoaming Formulations. Nonfoaming detergents are formulated for use in European-type washing machines and include the ingredients shown in Table 3.3. Products are differentiated by the levels of ingredients, which differ in the use of premium or cheaper products, and in the presence of antifoam agents. For example, in premium products we may find "cocktails" of enzymes (protease + amylase + lipase + cellulase) and bleaching agents with or without activators (perborate or percarbonate + TAED), whereas cheaper products do not contain an activator and generally contain only one enzyme (protease).

TABLE 3.2
Example of Formulations for Use in the Machine[a]

Ingredient	Phosphate formula (%)	Zero-phosphate formula (%)
Anionics	10–20	10–20
Nonionics	0–5	0–5
Soap	0–1.5	0–2
STPP	15–30	—
Zeolites[b]	—	15–35
Na silicate	5–15	2–5
Na carbonate	5–15	5–20
Na sulfate	5–15	5–30
Na perborate (mono- or tetrahydrate)	0–15	0–15
TAED or SNOBS	0–4	0–4
Polymers	0–2	0–5
Enzymes, FWAs	+	+
Perfume	+	+
Water	Balance	Balance

[a]Abbreviations: STPP, sodium tripolyphosphate; TAED, tetraacetylethylenediamine; SNOBS, sodium nonanoyloxybenzenesulfonates; FWAs, fluorescent whitening agents.
[b]In Canada, NTA replaces zeolite.

TABLE 3.3
Examples of Phosphate-Based Formulations[a]

Ingredient	Premium (%)	Cheap (%)
LAS	5–10	5–7
PAS	0–5	0–2
Nonionics (AE 5–9 EO)	3–7	2–5
Soap	0–3	0–2
STPP	20–25	15–25
Na silicate	4–8	4–8
Na carbonate	5–10	5–10
Na sulfate	15–25	15–35
SCMC	+	+
Polymer	0–2	—
Complexant (phosphonate)	–/+	
Enzymes		
Protease	+	+
Amylase	–/+	—
Lipase	–/+	—
Cellulase	–/+	—
Antifoam	–/+	–/+
Perborate ($4H_2O$)	15–25	10–20
TAED	2–5	0–2
FWAs	++	+
Perfume	++	+

[a]Abbreviations: LAS, linear alkylbenzenesulfonate; PAS, primary alcohol sulfate; AE, alcohol ethoxylates; EO, ethylene oxide; STPP, sodium tripolyphosphate; SCMC, sodium carboxymethylcellulose; TAED, tetraacetylethylenediamine; FWAs, fluorescent whitening agents.

Formulations without phosphate. In zero-phosphate formulations, the percentage of zeolites varies from 20 to 30%, the polymer content is raised (up to >5% in a premium formulation), and the levels of silicate and phosphate are lower. To compare formulations (foaming/nonfoaming) among Europe, the United States, and Japan, the main ingredients are as listed in Table 3.4. The main differences in these formulations lie in the high levels of anionics and the absence of bleaching and antifoam agents in the United States and Japan.

Detergents with Softeners

A little later in this book, we will look at how formulators have tried to resolve the problem of harshness in clothes which develops over time after many washes (see also Chapter 5, Fabric Softeners). Certain manufacturers have tried to find the "universal" product that will both clean and bring softness to the wash. The first attempts to combine detergents and softeners ("Softergents," soft- from softener and -ergents from detergents) were made with the main wash detergents in the United States. One method was to include cationics (+) in the detergent formulation, which

TABLE 3.4
Comparison of Traditional Powders in Europe, the United States, and Japan[a]

Raw materials	Europe (%)	U.S. (%)	Japan (%)
Surfactants			
Anionic	5–15	8–22	15–25
Nonionic	3–7	0–6	0–4
Builders and others	30–45	30–50	25–40
Perborate	15–25	—	—
TAED (Europe)	2–5	—	—
SNOBS (U.S., Japan)	—	0–4	0–4
Secondary agents	15–25	15–30	25–40

[a]Abbreviations: TAED, tetraacetylethylenediamine; SNOBS, sodium nonanoyloxybenzenesulfonates.

normally cannot be achieved without an interaction with the anionics (–). This produces the following results: an increase in soil redeposition, a general reduction in detergency, and neutralization of the softening effect of the (quaternary) cation.

The use of amines limits this interaction between anionic and cationic. This was studied by Procter & Gamble and is the subject of a number of patents (1–3). These inventions are based on the high pH of the wash solution, which helps the inhibiting action of amines whose melting point is 32–93°C and whose solubility in water is <50 ppm at 25°C. The inclusion of cationic and amine is achieved with the help of granules made of the same two ingredients mixed under heat with Smectite-type clay. Once cooled, the mixture is ground and sieved to obtain granules between 50 and 100 μm in size to avoid segregation in the washing powder. Clay has two functions, namely, to soften water and to give a certain softness to the fabric. The ratio between quaternary ammonium chloride and *n*-methyltallowamine varies between 3:2 and 2:3.

Colgate uses Bentonite granules (4–6) in their powders with incorporated softener. These clays are dosed to ~10% of the detergent powder, in the form of granules of between 170 and 420 μm, which are made by agglomeration. A patent from Unilever shows that good quality natural clay of a certain granulometry can be used instead of the above-mentioned agglomerates and at lower cost (7,8). In Germany, products made of granules are available; they are sold in plastic bottles under the brand names Pur and Fresh Start. These products contain only nonionics as surfactants. In principle, the above-mentioned problems of incompatibility would not arise if a cationic were included in these formulations (9).

Tertiary amine can also be used as a softener in a powder detergent. In principle, the use of this compound helps prevent the anionic/cationic interaction. The amine can be of the *n*-methylditallowamine type, for example, with an isoelectric point at ~8.8 (10). In the wash solution, the pH is higher (9.5–10.5) and the amine is neutral or has a negative charge. There will therefore be no reaction with the anionic, which is insoluble and is simply dispersed. But during the first rinse, the pH drops suddenly and the amine becomes a cationic, which can redeposit on the cloth in the form of finely divided particles.

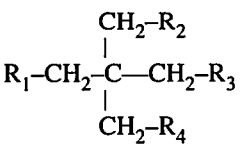
TABLE 3.5
An Example of a New Biodegradable Formulation That Provides Softening[a]

Ingredient	(%)
LAS	2.00
Nonionics	3.90
Stearyl hydroxyethyl imidazoline	1.00
Na silicate	4.00
STPP	23.00
Anhydrous sodium carbonate	5.00
Dequest	0.38
FWA	0.21
Silicone	0.18
Soda	1.00
Perborate tetrahydrate	12.00
Protease	0.30
Montmorillonite clay	16.00
Methyl siliconate K	0.50
Hydroxylamine sulfate	0.30
EDTA	0.89
Na aluminosilicate	0.25
Pentaerythritol distearate	6.00
Anhydrous sodium sulfate	13.59
Perfume	9.00
Water	Balance

[a]Abbreviations: LAS, linear alkylbenzenesulfonate; STPP, sodium tripolyphosphate.

Amines can be incorporated into powders in granular form. Granules are made by pulverizing the softening agent on perborate monohydrate (11) or on spray-dried zeolite (12), which absorbs liquid compounds very well. The combination of amine and cellulase gives an even better softening effect on textiles (13). In a more recent patent, Colgate Palmolive describes new biodegradable compounds that can be included in detergent powders to provide softening benefits (14). These are fatty acid mono- or dipentaerythritol esters, or fatty acid pentaerythritol esters. An example is given in Table 3.5.

The chemical formula of monopentaerythritol monostearate is as follows:



where $R_1 = CH_3–(CH_2)_{10}–COO–$ and $R_2 = R_3 = R_4 = OH$.

Although the idea of a two-in-one detergent/fabric softener is very attractive, the actual performance of a Softergent is still far from competitive with the separate use

of a detergent and a softener added to the final rinse in the washing machine. It is possible, however, that with the development of tumble dryers, there may be a new technological battle, to the great delight of the formulators!

Powders for Delicate Wash and Colors

Most developed countries have tried to adapt their products to consumer needs. In general, a conventional powder is for "all washes," meaning that it can wash very dirty clothes at high temperature and with strong mechanical action, and also delicate and colored articles, which require much more care and attention, with gentle agitation and low temperature. Unfortunately, the formulator knows that there are certain ingredients in this type of product that can be aggressive on more sensitive clothes. This is why specific formulations were developed for delicate wash (even though the consumer is generally happier using only one product).

Technical Elements

The different technical elements to be kept in mind in formulating a product for delicate wash are discussed here.

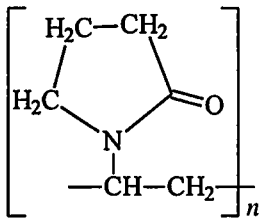
pH. If colors are not sufficiently fixed to cloth, a high pH could liberate them in the wash under certain conditions (high alkalinity favors hydrolysis of the bonds between colorant and fiber). A pH of 9.5 is achievable with the addition of acid LAS to the slurry or, more easily, by postdosing bicarbonate and/or citric acid.

Removal of Fluorescent Whitening Agents (FWAs). When FWAs are adsorbed on cotton, they absorb invisible ultraviolet (UV) light which they re-emit in the form of visible blue light. This blue light can have a noticeable effect on colors (particularly pastels) after a certain number of washes.

Removal of Bleaching Agents. Oxidizing agents act directly on most colorants with the result that colors fade with time, or white spots can appear if, for instance, the powder dissolves poorly.

Antiredeposition Polymers and "Soil Release." In general, antiredeposition polymers are important both for their cleaning effect and for their effect in reducing loss of color. They generally are acrylic acid homopolymers or acrylic maleic acid copolymers. Polymers are also used to help soil release. By adsorbing on polyester (and cotton polyester) they change the surface of these fabrics, making them less hydrophobic. The removal of certain oily soils is made easier (e.g., lipstick, make-up, edible oils, or sunscreens). These polymers, as stated above, are generally cellulose ethers or terephthalate-based derivatives.

Dye Transfer Inhibitors. The best known is polyvinylpyrrolidone (PVP); it is soluble in water and effective in preventing dye transfer from one article to another (or from one part of an article to another, if the color is different) (15). It works by complexing dyes dissolved in the washing solution and preventing them from adsorbing on the cloth, as illustrated in Figure 3.1 (without PVP) and Figure 3.2 (with PVP, thus inhibition of dye transfer). PVP works better in nonionic formulations, and on anionic, acid, or direct dyes. The structure of PVP has the following basic pattern (repeated 360 times):



Polyvinylpyrrolidone

Enzyme System. For fine and color wash formulations, it is preferable to use a "cocktail" of protease, lipase, and amylase, which covers a large range of soil, given that the detergency will be reduced by the lower pH. Extra benefits of cellulase are that it will bring some softening and will help maintain color by preventing greying caused by redeposition of particulate soil in the cotton fibrils.

Other Ingredients. In areas in which water is heavily chlorinated, aluminum sulfate can be added to inhibit chlorine from attacking colors.

Tables 3.6 and 3.7 present examples of a conventional delicate wash powder formulation, with and without phosphate. Table 3.8 gives examples of concentrated powders positioned for use on colored articles.

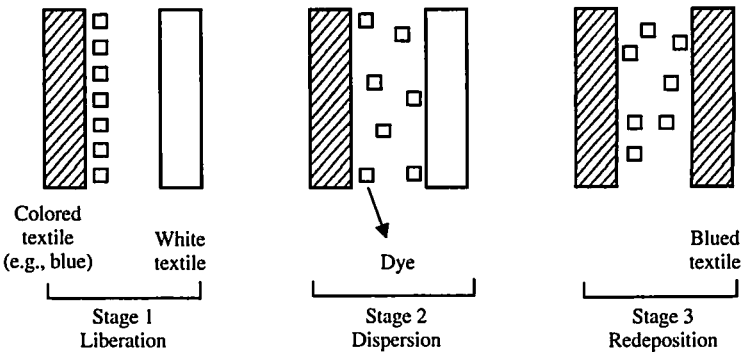


Fig. 3.1. Dye transfer during the washing process.

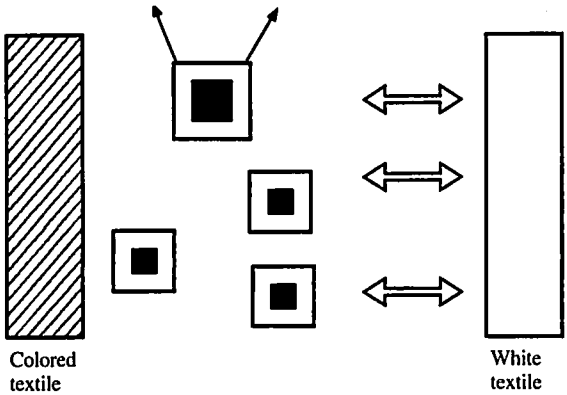


Fig. 3.2. Dye transfer inhibition by polyvinylpyrrolidone (PVP).

Concentrated Powders

For many years, traditional powders were the only ones on the market. Their density increased slowly but steadily (in France, for example, they moved from 400–450 g/L to 500–550 g/L in the space of 15 years) to reach 650–700 g/L in the 1990s. However, these cannot really be described as concentrated powders. Concentrated products were already on the market in Japan and also in Europe where they were sold door-to-door.

TABLE 3.6
Phosphate Formulation for a Conventional Powder for Delicate Wash[a]

Ingredient	(%)	
LAS	6–14	
Soap	0–4	
Nonionics (C_{13}–C_{15} 7 EO)	3–6	
STPP	25–30	
Na sulfate	35–40	
Acrylic/maleic copolymer	0–2	
Na silicate	4–8	
SCMC	0–0.05	
PVP	0–0.5	
Enzymes		
Protease	+	Depending on
Amylase	–/+	formulation
Lipase	–/+	cost
Cellulase	+	
Citric acid/bicarbonate	–/+	
Antifoam	–/+	
Perfume	+	
Water	Balance	

[a]Abbreviations: LAS, linear alkylbenzenesulfonate; EO, ethylene oxide; STPP, sodium tripolyphosphate; SCMC, sodium carboxymethylcellulose; PVP, polyvinylpyrrolidone.

TABLE 3.7
Nonphosphate Formulation for a Conventional Powder for Delicate Wash[a]

Ingredient	(%)
Na ABS	8–20
Soap	0–3
Nonionics (C_{13}–C_{15} 7 EO)	4–8
Zeolite	25–40
Na carbonate	7–15
Na silicate	0.5–3
Na sulfate	10–30
PVP	0–0.5
SCMC	0–0.5
Acrylic/maleic copolymer	4–5
Citric acid/Na bicarbonate	–/+
Enzymes	
Protease	+
Amylase	–/+
Lipase	–/+
Cellulase	+
Antifoam	–/+
Perfume	+
Water	Balance

[a]Abbreviations: ABS, alkylbenzenesulfonate; PVP, polyvinylpyrrolidone; SCMC, sodium carboxymethylcellulose.

Quality was well below consumer expectations, with poor physical properties, caking, and poor performance. The dry mix manufacturing process could not match the quality of conventional powders. A big step forward was made by Kao of Japan when they launched a truly concentrated powder called Attack in 1987.

Advantages

For the Consumer. Concentrated powders are easy to transport, store, and use. As a result of a new manufacturing process, they comprise a revolutionary new wash technology with all the advantages of blown powders and without the disadvantages of the dry-mixed powders.

For the Trade. Concentrated powders require less space to stock and display, and they offer good margins.

For the Manufacturer. The advantages to the manufacturer include the following: being first in the market with a truly innovative product; having good margins related to less packaging, lower distribution and formulation costs (no sulfate); and offering a positive step forward for the environment. All major manufacturers followed Kao and launched concentrated powders, which have grown continuously since 1987–1988 to reach 13% of world markets in 1991 and 22% in 1996. In Japan, concentrates now have 85% of the market. In Europe, their development has

TABLE 3.8
Example of a Concentrated Powder Formulation for Colored Articles[a]

Ingredient	(%)
LAS	10–15
Nonionics (C_{13}–C_{15} 7 EO)	5–15
Soap	0–3
Zeolite	30–40
Copolymer	4–6
Na citrate	15–20
Na carbonate	4–15
Na silicate	1–3
Na sulfate	1–5
SCMC	0.5–1
EDTMP	0–2.5
PVP	1–2
Enzymes	
Protease	+
Amylase	+
Lipase	+
Cellulase	+
Antifoam	+
Perfume	+
Water	Balance

[a]Abbreviations: LAS, linear alkylbenzene sulfonate; EO, ethylene oxide; SCMC, sodium carboxymethylcellulose; EDTMP, ethylenediamine tetramethylene phosphonate-Na salt; PVP, polyvinylpyrrolidone.

been slower, and there are differences among countries. The Scandinavian countries and environmentally sensitive countries, such as the Netherlands and particularly Germany, use much greater quantities than do Southern European countries such as Spain and Portugal. In France in 1996, five times more conventional powder than concentrated was used (64% share versus 13.2%).

Formulation Principles

To formulate a concentrated product, the formulator must perform the following tasks: (i) remove all ingredients that do not contribute to performance, such as fillers; (ii) minimize the amount of water in the product, e.g., perborate monohydrate is preferred to tetrahydrate; (iii) use the densest raw materials available whose granulometry will fill all "empty" areas and the interior of empty particles.

Figure 3.3 shows that there is unused space inside and between the particles of a conventional powder. Figure 3.4 shows the ideal characteristics of a concentrated powder. The spaces are filled more completely, both inside the particles (by nonionic liquids) and between them, because the particles are smaller and more evenly shaped.

Some raw materials lend themselves better to densification. For example, zeolite is easier to use than STPP, because it absorbs larger amounts of surfactants

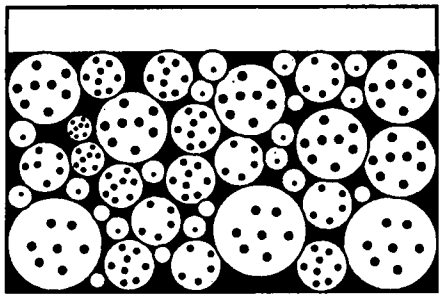


Fig. 3.3. A conventional powder.

(e.g., liquid nonionics). The ideal is to find "multifunctional" raw materials. For example, use of Na percarbonate instead of perborate reduces the need for added Na carbonate. At equal weight, percarbonate gives a better yield in active oxygen than perborate. Enzymes play a very interesting part for the formulator because they give high performance at low levels.

The following two essential factors must be considered in the production of a concentrated powder: (i) the increase in active ingredients and the elimination or reduction in filler (sulfate) and water; and (ii) the increase in density. The main problem is the increase in surfactant levels.

Consider the following example of a concentrate with phosphate (16). The surfactants in the wash solution should be at the same concentration as that in a conventional powder. In France, we have the following example:

$$V\,(\text{dosage}) \times d \times Y\%\ \text{surfactants} = 290\ \text{mL} \times 0.55 \times 10\% = 16\ \text{g of surfactants}$$

where V is the average volume used by consumers (290 mL), d is the average density (0.55), and $Y\%$ is the average surfactant level of a conventional powder (10%). For a powder twice as concentrated in terms of volume, the requirement is as follows:

$$145 \times X \times Y = 16\ \text{g}$$

where X is the density and Y is the % surfactants. Experience shows that the maximum density of a blown powder is about 0.65. Thus, the percentage of surfactants is as follows:

$$Y = 16\ \text{g}/145 \times 0.65 = 17\%$$

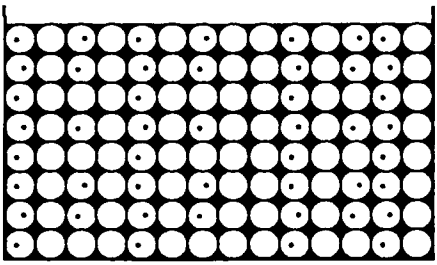


Fig. 3.4. A concentrated powder.

In reality, it is not easy to produce a blown powder with 17% surfactants without using special processes.

One of the processes involves spraying part of the nonionic liquid on the base powder and another part onto the spray-dried zeolite particles, which have high absorbency (>28%). For the builder, we saw in Chapter 2 that we can replace 30% STPP with 22% STPP + 2% polymers. In addition, by using more efficient surfactants, a higher level of enzymes, and a more effective bleaching system, we can further reduce recommended dosage. In this way, the powder concentration can be doubled in volume while maintaining good physical properties, such as powder flow and dispensing, so that machine powder dispensers can be used for both the main wash and the prewash.

The level of surfactants in concentrated products without phosphate is less problematic because zeolite can absorb them more easily, particularly liquid nonionics. Using different manufacturing processes, such as spray drying + granulation, or NTR (nontower route), which we will look at in Chapter 12, still higher densities can be obtained. Tables 3.9 and 3.10 give examples of formulations of concentrated powders with and without phosphates, respectively.

Unilever sells powders that are even more concentrated, up to 900 g/L, containing high levels of natural PAS, whereas Procter & Gamble has recently launched a concentrate containing n-methyl glucoside and layered silicate. Table 3.11

TABLE 3.9
Formulation of a Concentrated Powder with Phosphates[a]

Ingredient	(%)
LAS Na	12–15
Nonionics	4–8
Soap	0–2
STPP	20–25
Zeolite	0–5
Na carbonate	2–20
Na silicate	3–7
Na sulfate (impurities)	0–2
Polymer	0–2
Perborate monohydrate	10–15
TAED	4–8
FWA	0.15–0.30
SCMC	0.5–1.5
Enzymes	
Protease	8–12 GU/mg
Lipase	++
Antifoam	–/+
Perfume	++
Water	Balance
Density (g/L)	~650–750

[a]Abbreviations: LAS, linear alkylbenzenesulfonate; STPP, sodium tripolyphosphate; TAED, tetraacetylethylenediamine; SCMC, sodium carboxymethylcellulose; GU, glycine unit.

TABLE 3.10
Formulation of a Concentrated Powder Without Phosphates[a]

Ingredient	Type A (Zeolite) (%)	Type B (Zeolite/Citrate) (%)
Na PAS	—	2–5
Na LAS	7–15	10–20
Nonionic (7 EO)	5–12	5–12
Soap	1–3	0–1
Zeolite	25–30	15–20
Polymer	3–5	4–6
Na carbonate	10–15	12–16
Na silicate	0.5–1	4–8
Na citrate	—	8–12
Perborate monohydrate/percarbonate	12–18	12–18
TAED	5–8	5–8
EDTMP	0.3–0.6	0.3–0.6
Dimorpholino-type FWAs	0.1–0.25	0.1–0.25
Superbrighteners (FWAs)	0–0.02	0–0.2
SCMC	0.4–1	0.4–1
Antifoam	–/+	–/+
Enzymes		
Protease	8–12 GU/mg	8–12 GU/mg
Lipase	++	++
Perfume	++	++
Water	Balance	Balance
Density (g/L)	~600	~720

[a]Abbreviations: PAS, primary alcohol sulfate; LAS, linear alkylbenzenesulfonate; EO, ethylene oxide; TAED, tetraacetylethylenediamine; EDTMP, ethylenediamine tetramethylene phosphonate-Na salt; SCMC, sodium carboxymethylcellulose; GU, glycine unit.

shows a comparison among concentrated powders in Europe, the United States, and Japan.

As for conventional powders, the main differences lie in the levels of anionic surfactants (foam) and bleaching agents (lower wash temperatures).

Comments

Some concentrated and superconcentrated products do not flow well in the machine powder dispenser, in which case they can be dosed using distributors (such as a ball), which is placed inside the machine together with the laundry.

Bars and Pastes

General Points

In 1996, bars and pastes amounted to ~1.7×10^6 T worldwide. Their use is found predominantly in developing countries and for hand washing. Laundry habits vary

TABLE 3.11
Comparison Among Concentrated Powders in Europe, the United States, and Japan[a]

Ingredient	Europe (%)	U.S. (%)	Japan (%)
Surfactants			
Anionics	5–15	15–25	30–35
Nonionics	5–12	5–12	2–6
Builders	20–40	20–40	15–40
Polymers	3–5	0–4	0–4
Perborates	16–25	0–5	0–15
Activators			
TAED	4–7	—	—
SNOBS	—	0–4	0–4
Other	0–5	0–5	0–5

[a]Abbreviations: TAED, tetraacetylethylenediamine; SNOBS, sodium nonanoyloxybenzenesulfonates.

little from one country to another. Clothes are first sorted, with whites and less dirty clothes washed first. Washing is done in one or several basins, close to a source of water, for example a river in Jamaica or a well in the Philippines. The water is therefore cold. Dirty clothes are treated, for instance, by using soap on dirt and stains, and then other articles are washed one by one. Presoaking is often used and may last from a few minutes to a whole night. After treatment, the laundry is rinsed thoroughly and hung in the sun to dry.

In some countries in which machines have made their appearance, it is common for people to continue to hand wash as a sign of care for clothes. The machine is used more as an occasional aid than as the main contributor to the laundering process. Thus in Mexico, for example, more than half of all wash loads is done both by hand and in the machine! As we have already said, the formulator should know the habits in each country because local habits can be important. For example, in the Ivory Coast, the same paste-based washing solution is used for clothes and dishes.

Formulations and Technologies

Where water is very soft or the washing solution is to be reused, a lot of builder is not required; however, the initial pH should be high to minimize reduction in the pH of the wash bath, which would lead to inactivation of STPP and precipitation of the anionics. Silicate helps to keep the pH at the right level and gives structure to the product. There are two types of bars, i.e., hard soaps and "syndets" or synthetic detergents. Table 3.12 compares the two types.

Syndets in bar or paste form are made from the same raw materials, including surfactants, to remove soil and generate a lot of foam. ABS is still the most widely used today, but government and environmental pressures are driving the increased usage of linear LAS. LAS requires extra additives such as zeolites, phosphates, and magnesium sulfate, which help syndets to harden quickly. Some countries produce

TABLE 3.12
Comparison Between Hard Soap and "Syndets"

	Characteristics	Raw materials	Advantages	Disadvantages
Hard soaps	Contain a lot of water	Soap Some additives (silicate, clay to reduce cost)	Good performance Softness Low price	Performance and foam level dependent on water hardness
Syndets in bar		Surfactants Builders Additives and secondary ingredients to reduce cost	Better performance Less sensitive to water hardness	More costly than hard soap

their own surfactants from locally available raw materials. For example, in the Philippines, coconut oil is used to make PAS, and formulations have to be adapted to obtain the required foaming properties, performance, and hardness of product.

The raw materials also include a builder system to avoid the negative effect of calcium and magnesium ions on performance. Builders also give better consistency and antiredeposition properties to the product. Phosphates are generally used, often in combination with the less expensive sodium carbonate. In addition to phosphates, antiredeposition is improved by the presence of specific agents such as sodium carboxymethylcellulose (SCMC). Most syndets, whether bar or paste, contain FWAs. These have to be specially selected to take into account that laundry is dried in the sun, i.e., they should be UV-resistant.

Photobleach such as phthalocyaninesulfonate is sometimes included. It absorbs energy (in the red) that is subsequently transmitted to oxygen molecules in water to produce active singlet oxygen, which acts on stains such as coffee, tea, and fruits.

Bentonite clay can be added to give softness to the wash, and antibacterial agents such as pine oil are sometimes included. Perfume may be used to cover base odor and to attract consumers. Other possible materials include a TAED/perborate bleaching system (in the Philippines, for example) or enzymes (protease).

Secondary ingredients are present in all formulations because they help to bind the raw materials together, help in the manufacturing process, and are relatively cheap. They include calcium carbonate, clays, starch, or talc. Examples of formulations of bars/pastes for laundering and pastes for dishwashing are given in Tables 3.13 and 3.14, respectively.

Premeasured Detergents

An important operation in the wash process is to dose the right amount of product. Manufacturers recommend dosages based on water hardness and degree of soiling of the wash load, but generally it is the consumer who decides how much to dose on the basis of experience. This is one of the reasons why concentrates have difficulty

TABLE 3.13
Formulation of Bars/Pastes for Laundering[a]

Ingredient	(%)	
ABS/LAS	15–30	
STPP	2–10	
Na carbonate	5–10	
Alumino silicate	0–5	
Na silicate	2–5	
Calcite	0–20	
Urea	0–2	(foam activator)
Glycerol	0–2	(humidifier)
FWA	+	
Perfume	+	
SCMC	+	
Al sulfate	0–5	
Kaolin	0–15	
Na sulfate	5–20	
Perborate/TAED (in bars)	–/+	
Enzymes (in bars)	–/+	
Water	Balance	

[a]Abbreviations: ABS, alkylbenzenesulfonate; LAS, linear alkylbenzenesulfonate; STPP, sodium tripolyphosphate; FWA, fluorescent whitening agent; SCMC, sodium carboxymethylcellulose; TAED, tetraacetylethylenediamine.

breaking into the market. In the French market, for example, it would appear that consumers have not yet found the right mix of dosage, wash performance, and cost per wash. To help solve this problem, a number of manufacturers hit on the idea some years ago of premeasured sachets to be added directly to the machine. But with detergents, as with many other product categories, it is not always best to be first with innovation, and the sachet idea has proved to be a slow burner.

Today, as washing habits have become more practical and the pressure of ecology on daily life is increasing, new forms of premeasured products are appearing on the

TABLE 3.14
Formulation of Pastes for Dishwashing[a,b]

Ingredient	(%)
ABS/LAS	16–28
Na carbonate	5–10
Al sulfate	0–5
Na silicate	2–5
Na sulfate	15–25
Perfume	+
Preservatives	+
Colorants	+
Water	Balance

[a]This type of product is very common in Turkey and Colombia.
[b]Abbreviations: ABS, alkylbenzenesulfonate; LAS, linear alkylbenzenesulfonate.

TABLE 3.15
Example of a Trade Formulation of a Laundry Tablet[a]

Ingredient	(%)
Anionics	10–14
Nonionics	4–8
STPP	40–60
Perborate/percarbonate	10–18
TAED	2–5
Carbonate	2–10
SCMC	0.5–1.5
Polymers	0–2
Protease	8–12 GU/mg
Dequest	–/+
FWA	0.2–0.35

[a]Abbreviations: STPP, sodium tripolyphosphate; TAED, tetraacetylethylenediamine; SCMC, sodium carboxymethylcellulose; GU, glycine unit; FWA, fluorescent whitening agent.

market. Most significantly, and at this very moment, it would appear that detergent tablets have a good future. Indeed, if we look at the tremendous progress of tablets for dishwashing, we can surmise that the laundry detergent market may be about to change very quickly.

Detergent Tablets

These are generally manufactured using conventionally blown powders. The main difficulty is to produce a tablet that is strong enough to withstand packing, storage, and transport, while still dissolving easily on contact with water. The earliest patents date

TABLE 3.16
Formulations of Polymers That Improve Tablet Performance

Ingredient	A (Experimental product) (%)	B (Competitor) (%)	C (Competitor) (%)
Anionics	5–15	—	5–15
Noninonics	5–15	25	5–15
Soap	<5	—	<5
Zeolite	>30	>30	15–30
Polymers	<5	<5	<5
Phosphonate	<5	<5	<5
FWAs	5–15	5–15	5–15
Enzymes	+	+	+
Density	885	760	685
Quantity of product dissolved after 10 min	68	25	35

Abbreviations: FWAs, fluorescent whitening agents.

from the 1960s (Colgate). Then Lion in Japan took out other patents covering the use of high-density formulations that could be used in tablet form in cold water (10°C). More recently, we have seen the arrival—first in Spain and then in France and Britain—of premeasured tablets for laundering, and numerous patents have been filed by the major manufacturers. These tablets are quite similar to concentrated powders with phosphates. The main demand on technology is to choose raw materials and special ingredients that will allow the tablet to dissolve easily on contact with water. Table 3.15 gives an example of formulations available in the trade.

Improved Tablet Dissolution. Specific polymers have been developed by the Norsohaas Company (17) to improve tablet performance in terms of both hardness and solubility. The formulations given in Table 3.16 have been tested.

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CHAPTER 4

Liquid Detergents

In the world of household detergents, consumers look for effective and up-to-date products. For this reason, dishwashing powders such as Lever's Rena in France were replaced many years ago by dishwashing liquids, which dissolve more easily in water and are easier to dose. Similarly, scouring powders such as Vim have been replaced by creams such as Cif, Ajax, and Mr. Clean, which are easier to use (on a sponge, for example) and can reach difficult places. This trend is also true for laundry detergents.

As is often the case, the trend started in the United States with Wisk, which attained a large market share in the 1970s. Some years later, the idea crossed the Atlantic and in the mid-1980s, all manufacturers introduced liquid laundry detergents into the market. Considering the example of Wisk, transfer of the formulation to the European continent was not easy. Consumers accepted the concept very well, but the American product did not suit European consumers. Here again, we see the vital importance of laundry habits. The American product was therefore completely reformulated (1); even then, consumers were not satisfied with its performance. Apart from their original form and appearance, liquid detergents have been successful because of their ease of use, allowing the consumer to dose exactly the quantity required. In addition, as we saw earlier in discussing laundry habits, stains are one of the consumer's biggest problems; a liquid can be used to treat a precise area, whereas a powder must first be made into a paste. A liquid will go into solution, allowing the ingredients to become active instantly, from the beginning of the cycle. Finally, a 1.5- or even 3-L bottle of liquid is easier to carry and store than a 5- or 8-kg box of powder.

Formulation Principles

Ideally, a liquid should include all of the ingredients of a conventional powder to give equivalent performance. Unfortunately, the reality is more difficult, and the formulator has to overcome two main problems: the need to soften water to achieve good detergency and dissolve more easily in water and the instability of bleaching agents in aqueous formulations.

Water Softening

We have already discussed the negative effects of calcium on washing performance and the need for builders in Chapter 2. The formulator has the following three options: (i) soluble builders of the citrate type, which are not very useful because of the "salting out" phenomenon, or separation of the organic phase caused by the presence of electrolytes; (ii) soap, which requires large quantities of surfactants to disperse and solubilize the calcium soaps that form in hard water (this

is the basis of *isotropic liquid* formulations); and (iii) conventional builders, such as sodium tripolyphosphate (STPP) and zeolites. The only problem with the latter is that they are solids, which would have to be put into suspension in water. This is the basic principle of *structured liquids.*

Both the appearance and the performance of these two types of liquid are quite different, which gives the consumer a wide choice based on different marketing concepts. Isotropic liquids are generally colored, only slightly viscous, and rich in surfactants; they are therefore very efficient in removing oily soil, whereas structured liquids are more viscous and are generally comparable to powders in their detergent efficacy.

Isotropic Liquids

Traditional Liquid Detergents

At the heart of the formulation lies the choice of surfactants, i.e., soap and fatty acids, in particular, but also the other nonionic and anionic surfactants, and the hydrotopes that give stability to the formula.

Choice of Surfactants. The choice will depend on the answers to many questions such as the following: What is the water hardness? What types of stains are the most critical? What are the most extreme conditions of storage likely to be encountered? What is the important common wash temperature? What is the target cost?

For example, a mixture of 18–20% nonionics (7-EO ethoxylates) with 6–8% linear alkylbenzenesulfonate (LAS) will give both excellent results on oily stains and good stability in the cold. Soap, a eutectic 40/60 mixture of oleic acid and lauric acid is possible; the oleate will react with calcium, whereas the laurate (the main ingredient of soap) will help solubilize the oleate. The formulator will use a basic formulation and then test different combinations ("mapping" exercise) using a classical ternary diagram (e.g., total surfactants 40%; see Fig. 4.1).

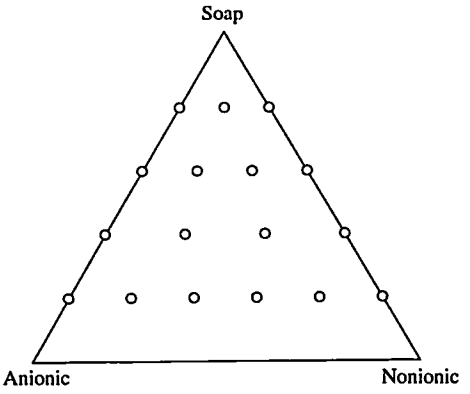

Fig. 4.1. Ternary diagram for an isotropic liquid detergent.

For each of the points tested, we must evaluate efficacy in the laboratory on test cloths and stains, cost and stability, and then choose the best compromise. The same exercise is repeated with different levels of surfactants, e.g., 30 or 35%.

Choice of Hydrotopes. Once the level of surfactants is known, we need to find the hydrotope(s) that will ensure stability under all storage conditions; the quantity to use is adjusted during storage trial observations. Ingredients used either singly or in combination include propylene glycol, ethanol, and triethanolamine.

Enzymes. The choice is the same as for powders; for example, proteolytic enzymes can be used against protein stains and amylolytic enzymes against starch-based stains, such as banana or cocoa. The enzyme will be stabilized by, for example, the joint action of boric salts with a di- or triol(glycerol) and an alkanolamine such as triethanolamine.

Ethylenediaminetetramethylene phosphonate-Na salt (EDTMP). This type of ingredient can be used to increase product efficacy on stains such as tea, coffee, wine, or fruit and to compensate for the absence of classical bleaching agents because it is impossible to incorporate the tetraacetylethylenediamine (TAED)/ perborate system into a formulation containing water.

Fluorescent Whitening Agents (FWAs). Experience will help the formulator to choose the right FWAs for the wash temperature. For example, a mixture of CBS and DMS-X (Ciba) will give good brightening over a wide temperature range.

Antifoam/Suds Depressants. In soap-based isotropic formulations, only a small quantity of antifoam is required because the precipitation of calcium oleate into the wash solution already reduces foam considerably. Silicone-based antifoams such as DB 100 (Dow Corning) used at ~0.05% will help suppress foam in soft water, and also prevent excessive aeration of the product during manufacturing.

Other Ingredients. These include opacifiers, used purely for marketing reasons to give an opaque appearance to the product, and perfumes and colorants. The latter are not chosen by the formulator, whose responsibility will be limited to testing stability in the product. Table 4.1 presents formulations for single-phase, low-viscosity Newtonian liquids (100–250 mPa · s at 21 sec^{-1}) with a density close to 1 kg/L. Other formulations are presented in Table 4.2.

Isotropic Liquids for Delicate Wash

Within the category of isotropic liquids, those used for delicate wash are an interesting group to examine in that they seem to be developing more quickly than main wash liquids. Today, we know several things about these liquids. Delicate wash liquids can be divided into three segments, i.e., "classical" liquids, concentrated liquids for direct application, and liquids that are mild to the skin.

TABLE 4.1
Formulations for Single-Phase, Low-Viscosity, Newtonian Liquids[a,b]

Ingredient	A (%)	B (%)
Triethanolamine LAS	15	30
Ethoxylated fatty alcohol (7 EO)	30	15
Stearic acid	15	15
Citric acid	0.2	0.2
Diethylenetriamine pentamethylene phosphonic acid	0.3	0.3
Protease	0.05	0.05
FWA	0.25	0.25
Silicone emulsion (e.g., DB 100, Dow Corning)	0.2	0.2
Ethanol	10	10
1,2-Propanediol	5	5
Triethanolamine	to adjust the pH to 7	
Water	Balance	Balance

[a]Abbreviations: LAS, linear alkylbenzenesulfonate: EO, ethylene oxide; FWA, fluorescent whitening agent.
[b]*Source:* Reference 2.

Classical Liquids. In Western Europe, these do not form a homogeneous group because they can be subdivided into three types based mainly on the surfactant levels they contain, as shown in Table 4.3. In 1984, most of these products were based on linear alkylbenzenesulfonate (LAS) and fatty alcohol ether sulfate. Ten years later, in certain countries such as Germany and Scandinavia, LAS is far from being the leading surfactant on the market, having been dropped, along with paraffinsulfonates, from many products.

Concentrates for Direct Application. These can be compared with classical liquids, but they are intended to be used by the consumer at one-half or one-third of normal dosage levels. They are usually found in the countries in Groups 1 and 2 in Table 4.3. In Germany, concentrated liquids attained almost 30% of the liquid detergent market within a year of their launch, and today, most major manufacturers have concentrated liquids in the Western European markets.

TABLE 4.2
Other Possible Formulations of Newtonian Liquids[a,b]

Ingredient	(%)	(%)
Potassium soap	22	35
Ethoxylated fatty alcohol (C_{14}–C_{18}, 5–10 EO)	5	9
Na LAS (C_{10}–C_{14})	4	10
Potassium	0.1	5
Triethanolamine	2	5
Alcohol (C_1–C_3)	8	10
Water, perfume, FWAs	Balance	Balance

[a]See Table 4.1 for abbreviations.
[b]*Source:* Reference 3.

TABLE 4.3
Distribution of Isotropic Liquids

Group	Country	Surfactant (%)
1	Portugal, Spain	10–15
2	Benelux countries, Germany, Italy, Switzerland	18–27
3	France, Great Britain	35–40

Liquid Detergents with Skin Care Properties. Care for the consumer led to the arrival in 1992 of products for sensitive hands. Once again, Germany took the lead. The products look very different from classical liquids because they are transparent like water and are sold in completely transparent polyethylene terephthalate (PET) bottles.

Changes in Formulation of Delicate Wash Liquid Detergents. Anionics. In Western European countries, and particularly those in which environmental factors are important, LAS has been gradually replaced by paraffinsulfonate, fatty alcohol sulfate, or fatty alcohol ether sulfate. This move is also justified technically because the replacement ingredients are effective on many kinds of domestic soil. In the United States, LAS is still very common; some manufacturers traditionally use fatty alcohol sulfate or ether sulfate. In Japan, LAS has lost its leading position to ether sulfate and α-olefinsulfonates.

Nonionics. Detergents containing high levels of ethoxylated fatty alcohols are very common in the market; they are associated with environmental and skin care considerations. The use of amine oxides in Europe and the United States is declining. Three new surfactants have made their appearance, i.e., alkyl polyglycosides, N-alkyl glucosamides, and methyl ester sulfonates (MES).

As we have seen, isotropic liquids are very attractive today because of their modernity and practicality. Nevertheless, in Europe they have the disadvantage of a low viscosity, which makes it impossible to dispense them in the powder distributor of drum washing machines, where they partly disappear into dead spaces of the machine, after which they are no longer available for the wash. This is known as "mechanical loss," which will be described later. To solve this problem, manufacturers, starting with Procter & Gamble and the "Vizirette," introduced the "dosing ball," which allows the metering of a precise quantity of liquid needed for optimal performance, because the ball is placed in the interior of the wash load.

Structured Liquids

The technology used for structured liquids is much more complex than that for isotropic liquids in which the ingredients are simply mixed. Stability and viscosity are the two essential elements in the *composition* and *manufacturing process* of a

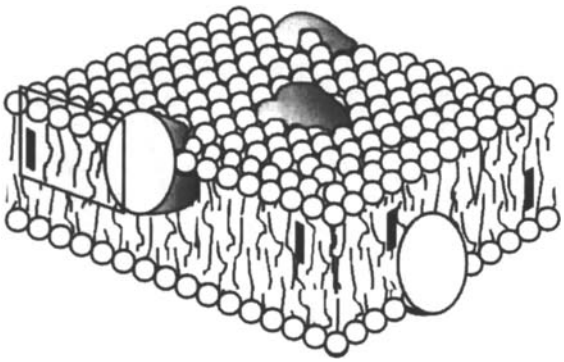

Fig. 4.2. Cellular membrane.

structured liquid. The "challenge" is straightforward, namely, how to include solid particles of STPP and zeolite in a liquid that remains stable.

Formulation Principles

The principle is based on the lamellar model, and on both amphiphile molecules, which form cellular membranes containing protein particles (Fig. 4.2) and multi- and single-lamellar vesicles (liposomes) (Figs. 4.3 and 4.4).

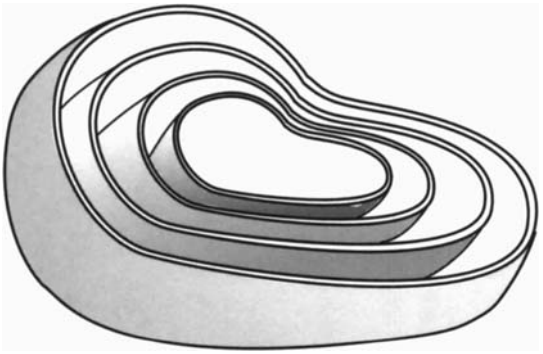

Fig. 4.3. Multilamellar vesicles.

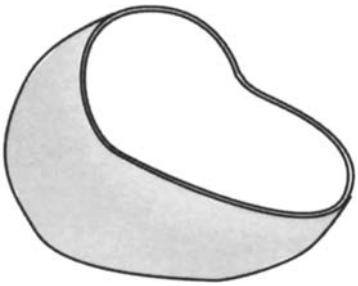

Fig. 4.4. Unilamellar vesicle.

The idea is based on nature's concept of making a structured liquid, i.e., a base is made by dispersing vesicles in an aqueous phase into which solid particles are introduced and maintained in suspension. Different patents, particularly those by Unilever (4,5), lay out the formulation principle behind structured liquids, which we will explain below.

At low concentrations, surfactants exist as molecules or micelles. An increase in the concentration of surfactants and/or the addition of electrolytes brings about the structured system. Agglomeration yields lamellar or crystalline phases, or lamellar vesicles (onion) (Fig. 4.5).

The lamellar phases can be obtained with anionics alone or a combination of anionics and nonionics. The vesicles are called "spherulites," which have a configuration of double concentric layers of surfactant molecules, separated by layers of water or electrolyte solutions (Fig. 4.6).

The vesicles are dispersed somewhat closely to each other in a liquid phase to make up the stable structured base in which solid particles can be held in suspension (Fig. 4.7). The presence of vesicles and their structure can be examined by using a number of techniques, including rheology measures, neutron or X-ray diffraction, and the electron microscope (6). The photograph in Figure 4.8 shows the lamellae of a vesicle, whereas that in Figure 4.9 shows dispersion of lamellar vesicles.

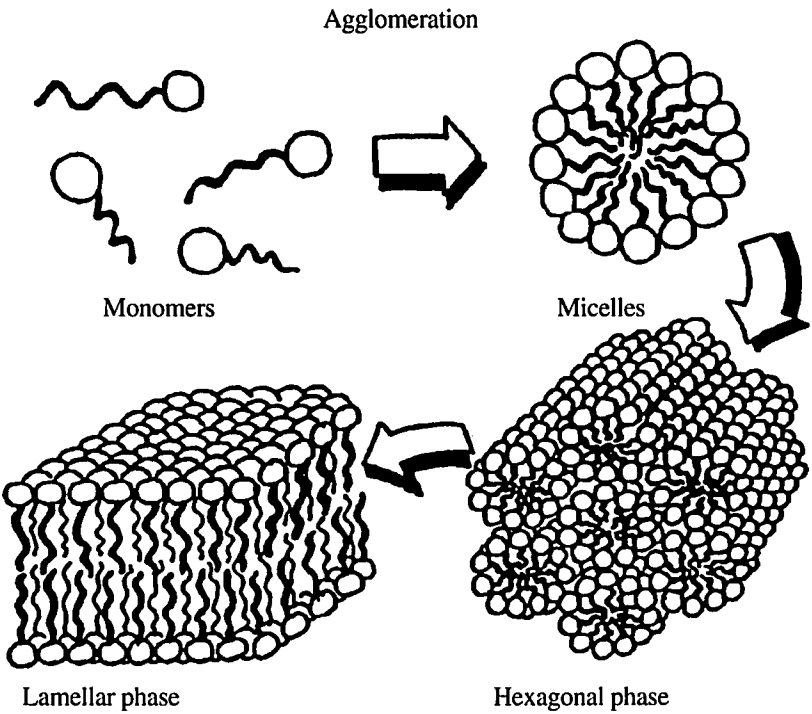

Fig. 4.5. A liquid crystal.

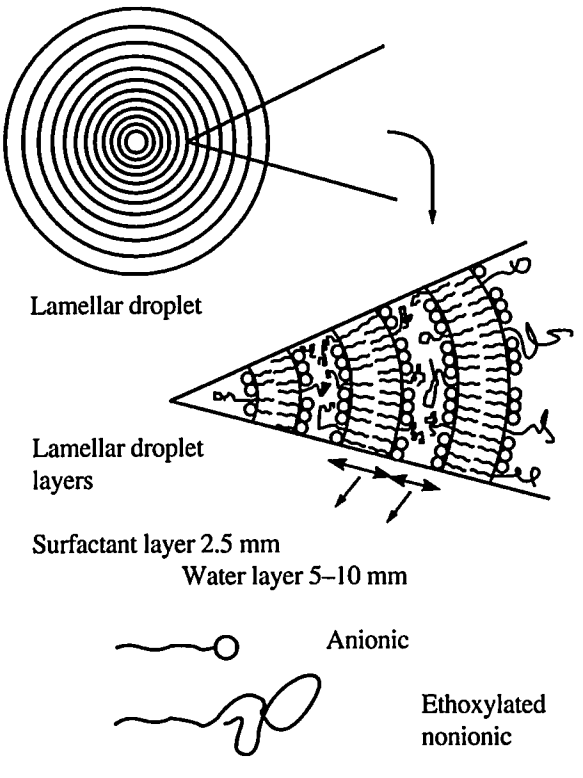

Fig. 4.6. Schematic representation of a lamellar (onion) vesicle.

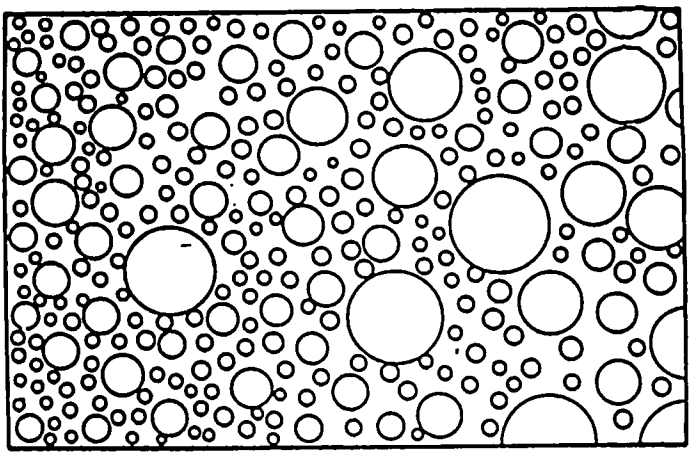

Fig. 4.7. Schematic representation of a lamellar dispersion.

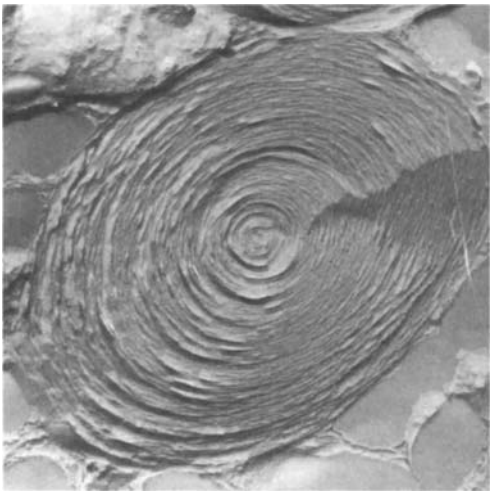

Fig. 4.8. Lamellar layers of a vesicle (electron microscope photograph).

An electrolyte such as STPP can be dissolved in the aqueous phase or can exist as solid particles beyond its saturation point. These particles, like other solids such as zeolite or calcite, can be suspended in the structured base. But two major problems exist in the formulation of structured liquids, namely, stability and viscosity. In general, the higher the volume fraction of the dispersed phase (vesicles),

Fig. 4.9. Dispersion of lamellar vesicles (electron microscope photograph).

the better is the stability. However, the high volume fraction of the dispersed phase can cause a large increase in the viscosity of the formulation, which creates problems for liquid flow. A compromise must therefore be found. When the volume fraction of the dispersed phase is ~0.6, the vesicles are barely touching each other, which gives both satisfactory stability and reasonable viscosity (~1 Pa · s at 21 s^{-1}). The curve in Figure 4.10 shows the viscosity as a function of the volume fraction Φ of the lamellar phase using the base formulation given in Table 4.4.

A further difficulty in formulating a structured liquid lies in the flocculation of vesicles (Fig. 4.10). This can cause either an increase in viscosity, due to the more rigid structure of the base, or product instability. One way to avoid flocculation is to further increase the number of vesicles, but this in itself leads to an increase in viscosity. The authors of the patents (4,5) found that the use of a small quantity (0.01–1%) of so-called "deflocculating polymers" overcame instability and viscosity problems while increasing the amount of surfactant in the product. The theory of how these polymers work is also given by the authors (4,5). The hydrophobic part of the polymer is incorporated inside the external layer of the vesicle, while the hydrophylic part is outside this layer. This produces repulsive forces, on the one hand between the surfactant molecules of the layer and, on the other hand, between adjacent vesicles. This leads either to an increase in base stability, or to a drop in viscosity, due to the deflocculation effect of the polymers. The consequences are as follows: (i) lower viscosity at an identical level of surfactants (easier pouring); (ii) equal viscosity but at

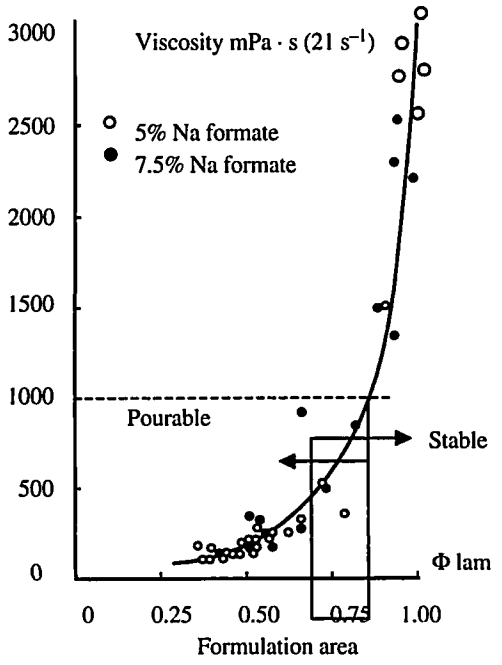

Fig. 4.10. Viscosity as a function of the lamellar phase.

TABLE 4.4
Base Formulation of Structured Liquids

Ingredient	(%)
Surfactants	20
Na formate	5.0–7.5
Na citrate · $2H_2O$	10
Borax	3.5
Tinopal CBSX	0.1
Perfume	0.15
Water	Balance

higher surfactant levels, allowing extra concentration (Fig. 4.11); (iii) the option to include other ingredients that tend to increase viscosity, e.g., zeolites.

In certain cases, deflocculation polymers can be located in the external layer but also inside the vesicle. Under such conditions, there is again less flocculation but two opposite effects are produced:

1. Attractive forces between the vesicles are reduced, resulting in a greater distance between them and a reduction in viscosity.
2. The attractive forces between the lamellae of the vesicle are also reduced; this causes an increase in space in the aqueous interlayers, the liposome becomes larger, and viscosity increases.

Under these conditions there will either be an increase in viscosity or the opposite will occur. The deflocculation polymers mentioned in the patents are, for example, those obtained from condensation of monomers of the unsaturated C_{1-6} fatty acid type, ethers, or alcohols. It can be seen from Figure 4.12 that the area which gives both a stable liquid and one that is easy to pour is very small. The formulator is maneuvering within a very small region. The formulator must study

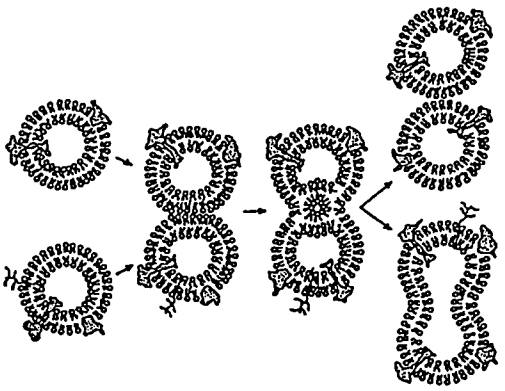

Fig. 4.11. Flocculation of vesicles.

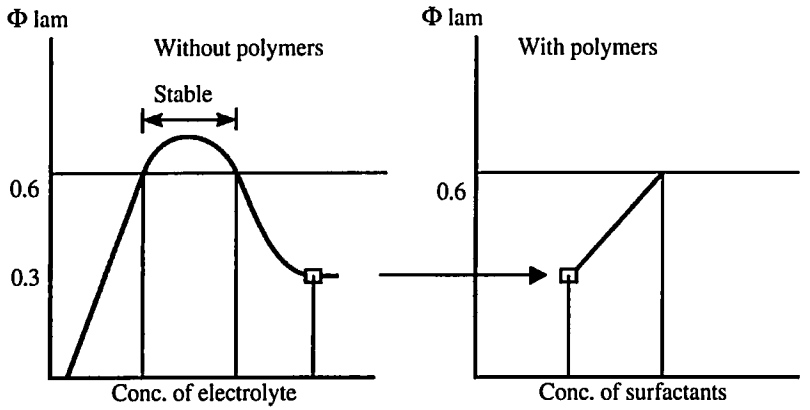

Fig. 4.12. Increase in concentration of surfactants at constant viscosity.

each type of surfactant used in order to achieve the most stable base and also the best-performing product.

Anionics. A compromise has to be made between long- and shorter-chain LAS. For example, an LAS with a distribution of carbon chains between 10 and 14 (with a molecular weight of ~320) is a good choice, giving good detergency and a more rigid lamellar structure.

Soap. Soap obtained by potassium neutralization of distilled peanut fatty acid will give better stability than tallow soap or stearates; the latter yield very viscous liquids. The potassium soap also provides better detergency because it is richer in oleates.

Nonionics. The choice here is wider because all nonionics behave in the same way if the solution is saturated in (insoluble) electrolytes. For example, linear C_{13}–C_{15} fatty alcohol-7-EO can be used.

Balance Among LAS/Soap/Nonionics. It is the proportion among the three active ingredients that dictates the *viscosity* and *stability* of the product as well as its detergency and foam performance. Different ratios can be tested in the laboratory using a ternary diagram, each successive trial adding to a "map" of the different structuring zones. An example is given in Figure 4.13. This type of diagram is generally drawn up using only part of the formulation, e.g., without particles in suspension or minor ingredients such as enzymes or antiredeposition agents. If this part is stable, the final product will generally be stable, and time will have been gained.

Electrolytes. There are two main classifications of electrolytes, i.e., "strong" (e.g., sodium chloride or sodium sulfate) and "less strong" (e.g., STPP or sodium citrate). The separating capacity of the actives in the electrolyte solution, and its micellar structuring power, will depend on this relativity. Experiments have shown that better

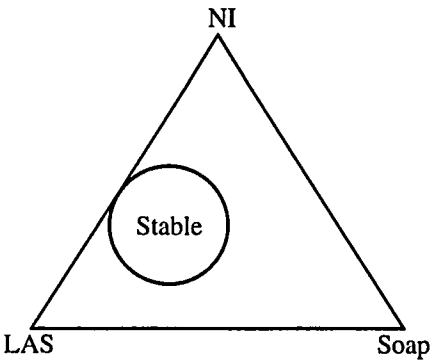

Fig. 4.13. An example of a ternary diagram. Abbreviations: NI, nonionics; LAS, linear alkylbenzenesulfonate.

stability can be obtained with weaker electrolytes such as phosphates, rather than with sodium carbonate, for example, which is a step in the right direction for liquid detergents. The goal is incorporate a high level of STPP while keeping an acceptable level of viscosity, e.g., 500–1000 mPa · s at 21 s^{-1}. In this case, it is essential that the solution be saturated in STPP. Because the limit of solubility of STPP (anhydrous to start with) is ~10%, the balance is present in the form of hexahydrated particles, which are in suspension in the structured liquid.

> **Comment**
> The presence of perfume is recommended because it improves the stability of a structured liquid and therefore increases the stability zone in the ternary diagram for a given active system.

Stabilization of Enzymes. Enzymes, as usual, cause problems for formulators. For enzymes to be stable, they require a neutral environment, whereas the product requires a high pH to be efficient in terms of detergency. The solution (7) is to "make" a complex from sodium pentaborate or sodium borate and glycerol, which liberates H^+ ions and allows the pH to drop to ~7, thereby ensuring enzyme stability. In the presence of water in the washing solution, the reaction is reversed and the pH increases to ~9, giving good washing efficiency. In the product, complex formation and liberation of H^+ ions is as follows:

$$\text{Pentaborate (or borate)} + \text{glycerol} \rightarrow \text{complex} + H^+$$
$$\text{pH to } \sim 7 \Rightarrow \text{good enzyme stability}$$

In the washing solution in which the product is diluted, the complex dissociates with capture of H^+ ions as follows:

$$\text{Complex} + H^+ \rightarrow \text{pentaborate (or borate)} + \text{glycerol}$$
$$\text{pH} \sim 9 \Rightarrow \text{good detergency}$$

Two similar formulations for a hand washing liquid are given in Table 4.5. Formulations for a liquid detergent for machine use are given in Tables 4.6 and 4.7. An example of a formulation without phosphate is given in Table 4.8.

TABLE 4.5
Two Similar Formulations for a Hand Washing Liquid[a,b]

Ingredient	1 (%)	2 (%)
Alkylbenzenesulfonate	6.5	8.5
Potassium soap	1.5	2.2
Nonionics	2.5	3.5
SCMC	0.05	0.05
Sodium tripolyphosphate	30	27
Sodium silicate	2	2
FWA	0.1	0.1
Perfume	0.4	0.4

[a]Abbreviation: SCMC, sodium carboxymethylcellulose; FWA, fluorescent whitening agent.
[b]*Source:* Reference 8.

Concentrated Liquids

As part of the trend toward higher concentration for reasons of practicality and ecology (fewer chemicals and less packaging discharged and less energy used), isotropic liquids, as well as structured liquids, have seen more compact spin-offs appear in recent years; these reduce the dosage by one-half. It is not possible to make a more concentrated isotropic liquid simply by increasing the quantities of builder and actives (which would give a thick/pasty product, or which would require large quantities of hydrotopes). A good formula can be obtained by doing the following: (i) using deflocculation polymers; (ii) choosing the right surfactants [secondary alkanesulfonates (SAS), nonionics, amphoterics]; (iii) reducing significantly the amount of soap, thus

TABLE 4.6
Formulation of a Liquid Detergent for Machine Use[a,b]

Ingredient	(%)
Alkylbenzenesulfonate	6
Soap	2.4
Nonionics	3.5
Toluenesulfonate	1
SCMC	0.1
Sodium tripolyphosphate	25
FWAs	0.1
Enzymes (protease)	9 GU/mg
Pentaborate	2
Glycerol	5
Perfume	0.5
Water	Balance
Density	1.3–1.4 kg/L
Viscosity	250–400 mPa · s (21 s^{-1})

[a]Abbreviations: SCMC, sodium carboxymethylcellulose; GU, glycine unit; FWAs, fluorescent whitening agents.
[b]*Source:* Reference 7.

TABLE 4.7
Other Formulations for a Liquid Detergent for Machine Use[a,b]

Ingredient	A (%)	B (%)	C (%)
LAS	6	6	6
Potassium oleate	1.5	1.5	1.5
Nonionics	2.5	2.5	2.5
Diethanolamide (coconut)	1	1	—
SCMC	0.1	0.1	0.1
STPP	26	26	26
Sodium tetraborate	4.6	—	—
Sodium metaborate	—	5	—
Borax	—	—	2
Glycerol	3	—	5
Silicone	0.2	0.2	0.2
FWAs	0.1	0.1	0.1
Enzymes (GU/mg)	8	8	8
Water, perfume	Balance	Balance	Balance

[a]Abbreviations: LAS, linear alkylbenzenesulfonate; SCMC, sodium carboxymethylcellulose; STPP, sodium tripolyphosphate; FWAs, fluorescent whitening agents; GU, glycine unit.
[b]*Source:* Reference 7.

requiring less hydrotope while permitting higher concentration; and (iv) changing builders (soap/soluble builders) system. The choice of ingredients must meet the following three requirements: (i) good efficacy (particularly in an underbuilt environment); (ii) "self-hydrotroping" behavior, which allows a considerable reduction in

TABLE 4.8
Formulation of a Structured Liquid Without Phosphate[a,b]

Ingredient	(%)
LAS	7.7
LES	2.4
Nonionics	2.4
Zeolite	20
Polymers	3.5
Citric acid	1.5
Glycerol	8
Borax	5.7
$CaCl_2$	0.3
Enzymes	0.5
FWAs	0.05
Silicone	0.35
Perfume	0.2
NaOH	to adjust pH to 8.5

[a]Abbreviations: LAS, linear alkylbenzenesulfonate; LES, lauryl ether sulfate.
[b]*Source:* Reference 4.

TABLE 4.9
Concentrated Liquids with Deflocculating Polymers: Example 1[a,b]

Ingredient	(%)
LAS	12.3
Nonionics	15.4
Na oleate	7.5
Na laurate	5.1
K_2SO_4	6.0
Glycerol	5.0
Borax	3.5
Dequest	0.4
Silicone	0.1
Savinase	0.3
Amylase	0.1
Tinopal	0.1
Perfume	0.3
Deflocculating polymers	2.0
Water	Balance

[a]Abbreviation: LAS, linear alkylbenzenesulfonate.
[b]*Source:* Reference 5.

the quantity of hydrotropes to be added; and (iii) environmental acceptability. To illustrate these points, Tables 4.9–4.11 present some examples of concentrated liquids with deflocculating polymers.

TABLE 4.10
Concentrated Liquids with Deflocculating Polymers: Example 2 (with Phosphate)[a,b]

Ingredient	(%)
LAS	20.6
Nonionics	4.4
Glycerol	5.0
Borax	3.5
STPP	22.0
Silicone	0.25
Gasil (silica)	2.0
SCMC	0.3
Tinopal	0.1
Blancophor	0/0.2
Dequest	0.4
Perfume	0.3
Alcalase	0.5
Deflocculating polymers	1
Water	Balance

[a]Abbreviations: LAS, linear alkylbenzenesulfonate; STPP, sodium tripolyphosphate; SCMC, sodium carboxymethylcellulose.
[b]*Source:* Reference 5.

TABLE 4.11
Concentrated Liquids with Deflocculating Polymers: Example 3 (Without Phosphate)[a,b]

Ingredient	(%)
LAS	9.2
Nonionics	17.3
Na oleate	5.6
Na laurate	3.8
Citrate Na $2H_2O$	10.0
Glycerol	5.0
Borax	3.5
Dequest	0.4
Silicone	0.1
Savinase	0.3
Amylase	0.1
Tinopal	0.1
Perfume	0.3
Deflocculating polymers a	2.0
Deflocculating polymers b	1.0
Water	Balance

[a]Abbreviation: LAS, linear alkylbenzenesulfonate.
[b]*Source:* Reference 5.

Nonaqueous Liquids

The major problem with liquid detergents is the lack of bleaching agents; this means that results are not as good as with powders, particularly on stains such as wine, tea, or coffee. To solve this problem, sachets have been put on the market containing TAED and perborate to be added to the wash load in addition to liquid detergent. The sachets may be made of soluble polyvinyl acetate (PVA), which dissolves during the wash process, or of nonwoven cloth, which is recovered at the end of the wash (10). The results are often better than with powders because there is less mechanical loss of perborate, less decomposition by catalase, better peracid formation, and less aggressive reaction between peracids and enzymes, for example. This concept has not been successful with consumers, however, because of the added step in the laundering operation.

Manufacturers such as Colgate and Unilever have tried to develop a *complete liquid* with all of the ingredients of a powder and, in particular, bleaching agents, which the presence of water in the formulation will not allow. The idea, therefore, is to remove the water completely from the formula to be able to include perborate and TAED. This poses enormous problems of stability, choice of ingredients, and manufacturing process. As of today, such products have achieved only minor market shares in one or two countries in Europe. Table 4.12 presents some examples of the formulations disclosed in the patents.

TABLE 4.12
Examples of Formulations of a Complete Liquid[a,b]

Ingredient	A (%)	B (%)
Nonionics	27.5	30.0
Glyceryl triacetate	12.5	13.0
Acid LAS	4.0	4.0
Soap	2.0	—
Silica (aerosol)	0.3	0.3
Na carbonate	27.5	18.0
Na bicarbonate	—	12.4
Na disilicate	3.5	—
Perborate monohydrate	11.0	10.5
TAED	4.0	3.0
Copolymers (CP5 type)	4.0	4.0
Minor ingredients	Balance	Balance

[a]Abbreviations: LAS, linear alkylbenzenesulfonate; TAED, tetraacetylethylenediamine.
[b]*Source:* Reference 11.

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CHAPTER 5

Fabric Softeners

The Theory of Harshness

Previous chapters have outlined the technology required to manufacture and continuously improve laundry products. Although the main objective is to wash clothes and remove soil, it is also necessary to keep clothes pleasant to wear over a long period of time. A major problem is that harshness builds up wash after wash—what could be worse than a bath towel that feels as stiff as a board instead of being as soft as a feather? In the 1970s, Unilever conducted studies on harshness with the French Textile Institute. Observations by an electron microscope showed minute threads, or fibrils, on cotton fibers as illustrated in Figure 5.1.

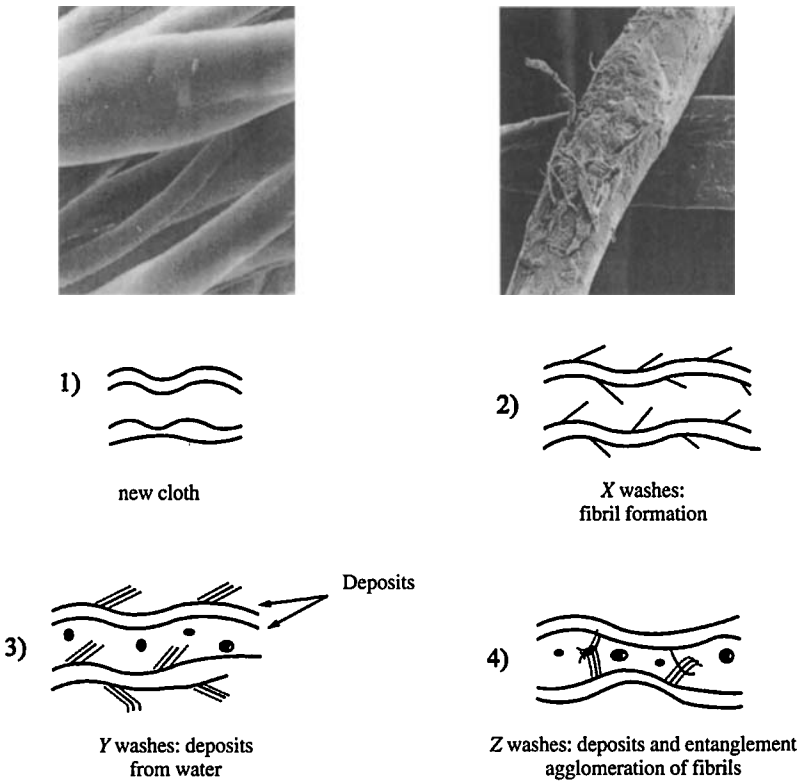


Fig. 5.1. Formation of cotton fibrils after *X* washes. *Source:* Novo Nordisk.

Fibrils are caused by the progressive deterioration of textile fibers over a number of washes. They cause four major problems:

1. Fibrils cause harshness.
2. Fibrils are a favored spot for hard water salts (precipitates) and particulate soil to deposit, causing greying.
3. Fibrils tend to reduce detergent penetration and the enzyme activity of lipases, thus reducing wash performance.
4. For colored cloth, the greying caused by fibrils changes the dispersion of surface light, and articles appear dull.

According to this analysis, if textiles were always dried in a static position, the result would be entangled fibrils. The salts mentioned above originate mainly from water (e.g., calcium or magnesium), as well as from the decomposition of some detergent ingredients, such as boron salts. To confirm the hypothesis that fibrils are the cause of harshness, experiments were conducted using cellulase. It was shown that when fibrils are prevented from forming, the textile remains softer.

> **Comments**
> In the 1970s, cellulase could be used only at a very low pH (4–4.5), which is incompatible with the higher pH of wash solutions. An acidic liquid detergent containing cellulase was used for the prewash cycle and a normal washing powder for the main wash. In this series of experiments, fibrils were eliminated, and cotton articles became softer. These days, thanks to biotechnology, cellulases are effective at alkaline wash pH. These cellulases are marketed by different companies, such as Novo Nordisk and Genencor International.

Factors influencing harshness are listed in Table 5.1. The most important factor is the drum washing machine because of the effect of its relatively violent mechanical action on clothes. Finally, it should be noted that the softness of the wash also depends on the ratio of the quantity of clothes to the volume of the drum. Filling a machine completely will not result in optimal softness.

Solving the Problem

Mechanism

Given these facts, products were developed to limit the development of harshness; they were originally called textile "softening" agents. Before the arrival of synthetic

TABLE 5.1
Factors Influencing Harshness

Machine	Hard water	Detergent	Static electricity	Drying with light movement (wind)	Tumble dryer
++++	+++	+	+++	++	(+)

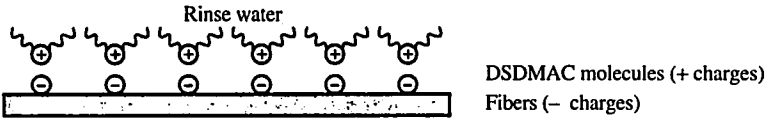


Fig. 5.2. Adsorption of cationics on textiles.

detergents, softeners were not needed because washing products were soap-based at the time; as we have already seen, the salts present in hard water react with soap to form calcium soaps, whose "lubricating" effect cancels out textile harshness. Textile softening agents were developed with this same idea in mind, i.e., to lubricate the fibers. The first products of this type appeared in the United States in 1953. The principal ingredient in these formulations was known as "DSDMAC" (pronounced "desdimac"): distearyldimethylammonium chloride.

Because it is not possible to mix this kind of positively charged molecule with negatively charged anionics, addition of cationics to a detergent formulation proved very difficult (see Chapter 3). A new kind of product was therefore created, and washing machines were modified to permit the introduction of softening agents at the end of the rinse cycle in order to optimize their efficacy. By this stage, most of the detergent has been washed out and if bleach has been used in the first rinse, it will have disappeared completely. The mechanisms involved are described here. In the wash solution, fibers are negatively charged and thus have a natural tendency to attract DSDMAC molecules (Fig. 5.2).

The hydrophobic part of the DSDMAC molecule is comprised of stearyl groups (or hydrogenated tallow), which are the source of lubrication, exactly as are the fatty acid chains in soap. The advantages of these new ingredients are: (i) their antiharshness effect, which is felt immediately; (ii) their lubrication, which makes ironing easier; (iii) their antistatic benefits (a real problem with some synthetic fibers such as polyamide); and (iv) their formulation helps solubilize perfume, which will deposit on fibers at the ideal moment, i.e., the end of the wash. For this reason, textile softening agents became known as conditioners.

Choice of Raw Materials. Ideal raw materials should soften the wash without changing its water absorption capacity and without short-term negative effects, such as a fatty feel or accumulation, or longer-term effects, such as skin irritation or a detrimental effect on the environment. The main parameters to guide the formulator are discussed below.

Build-up. Egan's (1) studies of different raw materials showed that, in general, the best softening agents were those that had the poorest textile rewetting properties. This is perfectly understandable once we know that the softening effect is obtained because of long hydrophobic alkyl chains. The more the surface of the textile is covered with these chains, the harder it is for water to penetrate the textile. In Hughes's (2) studies of softener adsorption on cotton, he showed that DSDMAC accumulates on textiles, as shown in the curve in Figure 5.3. This phenomenon is increased by the

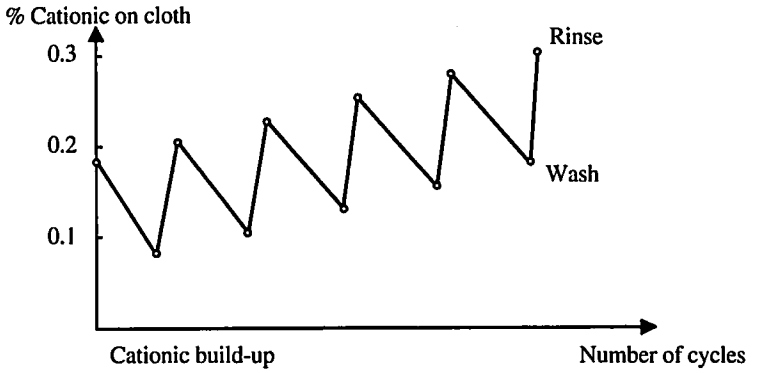


Fig. 5.3. Cationic build-up.

"carry-over" of detergent ingredients (e.g., polyphosphate or anionics) onto cloth, which increase the negative charge on cotton by attracting the positive charges of DSDMAC even more strongly (3).

Deposits on cloth. The adsorption isotherms of DSDMAC show that it is strongly adsorbed on fibers, without going beyond a monolayer (and probably less). Laboratory experience (to reveal the presence of cationics on textiles by *colored disclosing materials*) has shown that because of its insolubility in water, DSDMAC does not spread uniformly over the laundry articles. There is more of an aggregation than an even deposit.

Types of raw materials. Different factors must be taken into account, including the following:

(i) performance (softness + antistatic added + benefits such as ease of ironing);
(ii) concentration (in addition to conventional products, 3× and 5× concentrates have appeared, as well as dilutable products);
(iii) direct effects on individuals, such as allergies and irritation, giving rise to hypoallergenic products (present in many other detergent product groups); and
(iv) the environment, i.e., biodegradability and ecotoxicology.

Table 5.2 shows the differences between one compound and another (Egan) in terms of softness on terry cotton judged by feel (max = 5) and antistatic (max = 4).

TABLE 5.2
Differences Among Compounds in Softness and Antistatic Scores

Compound	Softness score (max = 5)	Relative antistatic score (max = 4)
Distearyldimethylammonium chloride	5	3
Distearyldimethylammonium methosulfate	4.5	2
Dialkyl amidoimidazoline methosulfate (tallow)	4	1
Quaternary amidoamine methosulfate	2.5–3	4

Table 5.2 illustrates the difficulty of obtaining good softness (→ cotton) and good antistatic (→ synthetics) at the same time. For this reason, various combinations of compounds are used. From the mid-1970s to the mid-1980s, most formulations were based on DSDMAC or DHTDMAC di(hydrogenated tallow)dimethylammonium chloride), while a number of others used quaternary imidazolines or quaternary amidoamines. Actives were incorporated at ~5% (4–6). The introduction of concentrates in 1979 in Germany, followed by other European countries and the United States, brought a new trend in the use of binary active systems such as fatty acids or fatty acid esters combined with DSDMAC to obtain a better performance/cost ratio.

Nonionics associated with DSDMAC were used as emulsifiers and, in certain cases, claimed softening benefits. Examples include the combination of DSDMAC with alcohol ethoxylate (C_{14}–C_{15} alcohol-7 EO) or glycerol stearate (mixed mono-/di-/triester). In this case, there is competition in the adsorption of cationics and nonionics (fewer cationics adsorbed). On the other hand, the hydrophobic problem (loss of water absorptivity) linked to an excess of cationics is solved by the presence of nonionics. More recently, environmental pressures have gradually pushed manufacturers into replacing DSDMAC. Over the last few years, DSDMAC volumes have dropped by 70% in Europe and 20% in the United States. In Europe, the substitutes are quaternary esters, which biodegrade more quickly and are less toxic to aquatic life. In the United States, the replacements include imidazolines and quaternary amidoamines.

Since 1990, new molecules have begun to be used in softeners. Their chemical structures are all similar to that of DHTDMAC in that they combine two C_{16}–C_{18} alkyl chains, which give softness, and a cationic nitrogen function, which adds substantivity to textiles. In addition, all of these new raw materials have at least one ester group between the cationic nitrogen and the alkyl chains, which is why they are called amine esters and quaternary esters. The ester groups are quickly hydrolyzed and degraded by microorganisms in sewage treatment plants (→ degradation to C_{16}–C_{18} fatty acids and smaller cationic metabolites). The fatty acids are then metabolized into CO_2. The latest generations of softeners contain a large number of compounds, including the following: (i) ester quats of triethanolamine fatty acids (4); esters of mono- or dipentaerythritol fatty acids (5); (iii) diester quats such as *N,N,N*-triethanolamine dialkyl ester quaternary ammonium (6); and (iv) substituted imidazoline esters, the esters of quaternary ammonium salts (7). The degradation principle of these new molecules is based on hydrolysis of the ester group, as shown in Figure 5.4.

In addition to their environmental benefits, these new surfactants must have properties equal to those of as DSDMAC, be reasonably priced to avoid higher

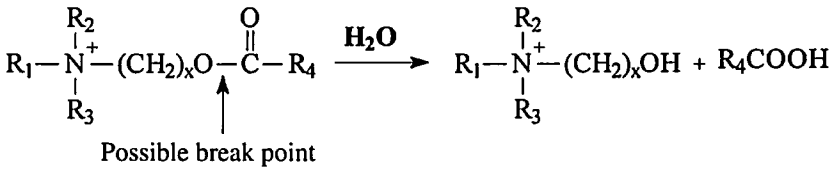


Fig. 5.4. Degradation principle for the ester quat molecule.

costs, be capable of concentration levels of up to 20 or even 30% yet maintaining low viscosity, and be chemically stable both in the product and over a long storage life. The compounds may not meet all of these conditions completely, but their general performance today is already very good.

Examples of Fabric Softener Formulations

Until the 1980s, there was only one "traditional" single-concentrate kind of softener on the market. Then the 3× and 5× concentrates arrived. In the United States, products contained 3–4% actives (imidazoline or aminoamide), compared with 5–7% DSDMAC in Europe. Innovation in this product category in the United States was delayed by the spread of tumble dryers and the accompanying expansion of dryer-added softening products; since 1980, however, technical progress with concentrates has given new life to the segment. In 1981, Lesieur Cotelle introduced a product in a 250-mL sachet (in France) under the Minidou brand name, to be diluted before use. The consumer mixed the contents with 750 mL of water to obtain 1 L of traditional softener; this gave birth to the 4× concentrates. These formulations were based on quaternary diesters. Their launch had a large effect in France, but it took several years for the concept to be adopted elsewhere.

In Europe, the first major change occurred in Germany with the introduction of 3× concentrates by Procter & Gamble, followed by the other major manufacturers. These conditioners were packaged in the same 1-L bottles as conventional products with a 5% active level. The advertising appeal was in the practical aspect of having a more convenient product to carry home, with 1 L giving the same results as given earlier by 3 L. The main raw material was DSDMAC, along with auxiliary conditioners and emulsifiers such as fatty acids, ethoxylated nonionics, and others such as glycerol monostearate to assist in manufacturing and to reduce costs. In France, apart from copies of Minidou (which had gained a 22% market share by 1986–1987), the market remained quiet until the arrival of Procter & Gamble's Lenor 3× concentrate. At the end of 1987, Procter & Gamble introduced a new 1-L concentrate that could be diluted into 4 L of conventional product. Numerous variants with the same formula but different fragrances appeared subsequently.

Traditional Softeners. In dilute formulations, the level of actives is usually ca. 7%, either with a single active or "mixed actives." Table 5.3 gives two examples of single-active formulations.

Comments

Two ingredients used in these products will be discussed in Chapters 6–10, i.e., antioxidants and preservatives. In general, antioxidants are the heavy metal complexing agents discussed in Chapter 2. In certain cases, butylated hydroxytoluene (BHT) is used (see Chapter 9 for a discussion of shampoo formulations). Formulations generally use formaldehyde and Bronopol as preservatives to prevent the development of certain organisms (see Chapter 9, shampoo formulations).

TABLE 5.3
Formulations of Dilute Traditional Softeners (Single Active)[a]

Formula A	
Ingredient	(%)
DSDMAC (75% active)	6–9
Perfume	0.2–0.5
Colorant	0.001
Water	Balance
Formula B	
Quaternary dialkylimidazolines (75% active)	6–9
Perfume	0.2–0.5
Colorant	0.001
Preservative	+

[a]Abbreviation: DSDMAC, distearyldimethylammonium chloride.

Table 5.4 presents possible formulations with mixed actives.

Formulations with 8–10% actives. At higher active levels, viscosity increases sharply; this can be adjusted by addition of a small amount of polyethylene glycol. A small amount of hard water or sodium chloride will have the same effect. James and Ogden explain variations in viscosity as follows (8): When DSDMAC dispersions are prepared at temperatures above the melting point (~40°C), electrolyte levels in the vesicles and in water are in equilibrium. By dropping the temperature and adding electrolytes to the dispersing environment, the bilayers of DSDMAC behave like semipervious membranes; a difference in osmotic pressure is produced, i.e., water leaves the dispersed particles (vesicles) and dilutes the dispersing environment, which balances the osmotic pressure. This phenomenon shrinks the dispersed particles and increases the distances between them, and reduces their interaction (Fig. 5.5). The outcome is a

TABLE 5.4
Formulations of Dilute Traditional Softeners (Mixed Actives)[a,b]

Ingredient	A (%)	B (%)	C (%)	D (%)
DSDMAC	2–3.5	3–4	4–6	4–6.5
Imidazoline	4–5.5	0.5–30	—	—
Diethanolamide	—	—	0.5–1	—
Stearic acid	—	0.3–0.8	—	1–2
Silicone	0.1–0.3	0.1–0.3	0.02–0.05	—
Glycerol ester	—	0.5–1.5	—	—
Polyethylene glycol	1–2	—	—	—
Perfume, color, water	Balance	Balance	Balance	Balance

[a]Raw materials considered as 100%.
[b]Abbreviation: DSDMAC, distearyldimethylammonium chloride.

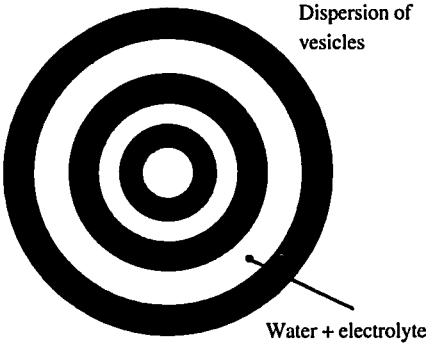


Fig. 5.5. Diagram of distearyldimethylammonium chloride (DSDMAC) bilayers and a multilamellar vesicle (each line represents a bilayer membrane).

reduction in viscosity. If excessive amounts of electrolytes are added, the particle density becomes so high that they deposit and phase separation occurs.

If (quaternary dialkyl) imidazolines are used in place of DSDMAC, manufacture is very simple. For example, in a formulation containing 5% actives, the colorant is mixed first in water, followed by the actives. Finally, perfume and preservatives are added (at ~30°C). Higher viscosities can be obtained by using demineralized water, dropping the mixing temperature, or increasing the active concentration. Some amidoamines can be worked in cold water, which further simplifies the manufacturing process.

Concentrated Rinse-Conditioners. At the beginning of the 1980s, Germans used more fabric conditioners than any other group on Earth: 6 L/y at a 5% active level (mainly DSDMAC). The product was sold in bottles of up to 5 L, which were inconvenient to carry and to store both at home and in stores. Since the formulations were 95% water, it was inevitable that concentration would evolve eventually, but the problem was not easy to solve for the following reasons:

1. To prepare stable dispersions at >7% DSDMAC meant a change in formulation and in manufacturing process.
2. The consumer had to be convinced that the new, smaller bottles contained an amount of product equivalent as the old, larger ones.

Point 1 was more difficult to achieve than point 2. Viscosities of the 3× concentrates are too high for the process used to make conventional products. Indeed, process became as important as formulation; we will look at this in more detail in Chapter 12. Table 5.5 (single actives) and Table 5.6 (mixed actives) give some examples of formulations with acceptable viscosity.

Comments

There are many formulations in the patent literature, and we cannot quote them all here.

New Generation Products. As we have already pointed out, DSDMAC is gradually being replaced by more biodegradable derivatives. Before looking at

TABLE 5.5
Ready-to-Use Rinse Conditioners at Triple Concentration (Single Active)[a]

Ingredient	(%)
Example 1[b]	
DSDMAC (100%)	12.5
Isopropanol	1.6
Diethanolamide	2
Nonionics	1
$CaCl_2$	0.3
Water, perfume, color	Balance
Example 2[c]	
DSDMAC (100%)	10
Nonionics	2
Stearic acid	4
$CaCl_2$	+
Water, perfume, color	Balance
Example 3[d]	
DSDMAC	16.6
Ethoxylated fatty amine	1.1)
Polyethylene glycol (PEG 400)	4.43
Sulfuric acid	0.85
Magnesium chloride at 40%	1
Water, perfume, color	Balance

[a]Abbreviations: DSDMAC, distearyldimethylammonium chloride; EO, ethylene oxide.
[b]*Source:* Reference 9.
[c]*Source:* Reference 10.
[d]*Source:* Reference 11.

concentrated formulations (dilute products are easier to manufacture), it is worth noting that in one Unilever patent (14), mention is made of the fact that the use of a polymer will help the softening agents considerably, including DSDMAC. Because this polymer has an amphoteric character and a molecular weight >1000, it helps the deposition of softening agents onto the cloth. This polymer is obtained by oligomerization of the following monomers:

a) cationic monomer

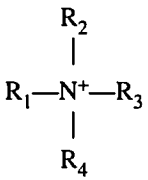
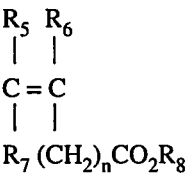


TABLE 5.6
Ready-to-Use Rinse Conditioners at Triple Concentration (Mixed Actives)[a]

Example 1[b]	
Ingredient	(%)
DSDMAC 75% (Arquat 2 HT)	14
Lanolin	2
Ethoxylated fatty acid	4
$CaCl_2$	0.05
Water, perfume, color	Balance
Example 2[c,d]	
DSDMAC	5–10
Amidoamine	5–10
Imidazoline	3.75–5.25
Electrolyte	0.05–0.4
Water, perfume, color	Balance

[a]Abbreviation: DSDMAC, distearyldimethylammonium chloride.
[b]*Source:* Reference 12.
[c]*Source:* Reference 13.
[d]The level of actives in this formulation is between 15 and 25%.

b) nonionic monomer



where R_1, $R_2 = C_{1-4}$ alkyl; R_3, $R_4 = C_{1-4}$ alkyl or alkenyl; and R_5, R_6, R_7, $R_8 = H$.

Traditional biodegradable formulations would include ester quat at 3.5% with the balance consisting of colorant, perfume, and water. Table 5.7 gives two examples of concentrated biodegradable formulations.

Fabric Softener Sheets

For many years in the United States and more recently in Europe, tumble dryers have been developing quickly. A product for this market gave a "final touch" to the whole washing process, and that is how fabric softener sheets were born. Their use gives extra softness and antistatic, and also adds a final perfume to the wash load. There are two potential problems to be avoided with softener sheets, i.e., (1) "fatty" stains caused by deposition of surfactants on laundry articles or on certain fragile parts of the machine, such as the humidity or temperature sensors, and (2) blockage of the air filter entries and exits. In addition, for such products to be effective, consumers have to be

TABLE 5.7
Examples of Concentrated Biodegradable Formulations[a]

Example 1[b] (product with 37.5% actives)	
Ingredient	(%)
Amidoamine	23.45
Diester quat	14.05
HCl	1.10
$CaCl_2$	0.55
Emulsifier	0.5
Perfume	2
Colorant	0.03
Water	Balance

Example 2[c]		
	A	B
Ester quat	5	2
Imidazoline-substituted ester	17	30
Isopropanol	—	1.5
Silicone	0.5	—
Bronopol	—	100 ppm
PEG	1.2	—
Color, perfume, $CaCl_2$, Na citrate, water	Balance	Balance

[a]Abbreviation: PEG, polyethylene glycol.
[b]*Source:* Reference 6.
[c]*Source:* Reference 7.

careful not to overload the machine, and to allow the clothes and the sheet to move freely.

Examples of formulations. The basic sheet is usually a nonwoven textile with a special texture that allows it to both hold the actives and let air through. The use of pure conditioners such as DSDMAC or quat esters is not recommended for the following two reasons: (i) they cannot be distributed uniformly throughout the wash, which might result in greasy stains on parts of the clothes that are completely hydrophobed; and (ii) they may contain traces of hydrochloric acid which can cause corrosion of certain parts of the machine. For these reasons, a cationic methosulfate is generally used (sulfuric acid is less corrosive than hydrochloric acid) together with a dispersing agent, usually a nonionic. Softener sheets act differently from softeners dosed in the final rinse of the wash cycle. In the dryer, the softener is distributed over the clothes without impregnating them, improving the antistatic effect. In general, each sheet disperses 2.5–3 g of actives or a ratio <0.1 relative to the quantity of textiles. Some raw material manufacturers have offered "ready-to-use" products (softener + dispersant), leaving only the perfume to be added. All of the biodegradable softeners we have mentioned can be used in the same way as DSDMAC to make softener sheets.

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CHAPTER 6

Hand and Machine Dishwashing Products

General: Hard Surfaces

It is probably more difficult to discuss the cleaning of surfaces other than fabrics or skin, only because of the diversity among these surfaces. Manufacturers tend to call these "hard surfaces" to distinguish them from the softness of skin or clothes. Dishwashing products are just one part of this category of detergents intended for use on hard surfaces; this group also includes products for specific rooms in the house such as the bathroom (including the tub, wash basin, faucets, shower, wall tiles), the kitchen (modern surfaces, stainless steel, china and plastic sinks), toilets, windows, and all kinds of floors.

To further complicate the formulator's task, the products have to deal with different types of soils according to the room or the type of surface on which they are to be used, implying different formulations for different uses. For example, in the kitchen, the product will have to be effective against grease (to clean stove hoods and wall tiles), burned-on stains on gas ovens or stoves, and calcium deposits on faucets and sinks. A specific product for the lavatory will have a hygiene function, which will call for bleach or something similar, or have anticalcium properties based on acids to remove deposits. A window cleaner must clean without leaving any traces—the list is endless.

This complex range is summarized in Table 6.1. While it is relatively easy for the consumer to choose a suitable dishwashing product, choosing a product that is suitable for cleaning both kitchen and bathroom may be more difficult. Of course "all-purpose" products exist, but they are usually not 100% effective on all surfaces. The consumer's choice will take into account the task at hand, i.e., the nature of soil, and the surface to be cleaned, as well as cleaning habits and lifestyles: For the same job, American consumers prefer powder abrasives, whereas Europeans prefer scouring creams or foams.

In general, however, all consumers have the same needs, i.e., reduce drudgery with products that are effective, practical, safe for the consumer (no health risks), safe for the surfaces to be cleaned, and reasonably priced. In this chapter, we will discuss dishwashing products, and in the next, other hard surface cleaners. In these two chapters and the ones that follow, it will become apparent that whether a product is formulated for hard surfaces, for clothes, or for personal care, each product represents a compromise, but a compromise that should be the best possible.

Hard Surfaces and Soiling

Hand Dishwashing

Hard Surfaces. Hard surfaces to be washed by hand include all those household articles used in the kitchen, i.e., plates, silverware, pots, glasses, and so on. These articles differ from each other and will require more or less attention depending on

TABLE 6.1
Types of Soil on Different Hard Surfaces

	Soil	Surfaces
Kitchen		
Dishes, washed by hand or machine	All food soils (variable from country to country, time factor between soiling and cleaning)	Glass, porcelain, earthenware, ceramics, plastic, stainless steel, silver, brass
Walls/counter tops	Food soil, grease	Tile, painted surfaces, cement, wood, plywood
Sinks/faucets	Calcium deposits, rust, food remains	Stainless steel, earthenware, synthetic resins, porcelain
Oven/stove	Burned-on stains	Enamel, vitreous ceramics
Floors	Dust, mud, various stains	Tile, vinyl, linoleum
Bathrooms		
Walls/flat surfaces	Calcium deposits, dust, finger marks	± as for kitchens
Wash basins/faucets	Calcium traces and scum	± as for kitchens
Showers, bath	Calcium soap, dust	
Floors	Dust	± as for kitchens
Toilet bowl	Calcium deposits, rust, germs	Porcelain
Floors	Same as for other rooms	Same as for the other rooms
Windows	Dust, finger marks	Glass

their quality. Crystal glasses, for example, are washed more carefully than ordinary glasses, and the same is true for porcelain and silverware. One of the main differences between hand and machine dishwashing is that the machine does not discriminate between different types of articles and washes everything in the same way. Table 6.2 categorizes some of the main surfaces encountered in hand dishwashing.

Soil. Apart from specific soil such as lipstick and metal traces, food accounts

TABLE 6.2
Main Surfaces Encountered in Hand Dishwashing

Glass	Ordinary glass or crystal Glass can be painted or unpainted
Porcelain	Painted under, on, or in the enamel, or hand-painted
Earthenware/ceramics	Generally painted under the enamel
Silver	Solid silver (7–8% copper), or silver plate
Stainless steel	Knives, forks, spoons
Aluminum	
Copper	
Plastics	Polycarbonate, polypropylene
Wood	

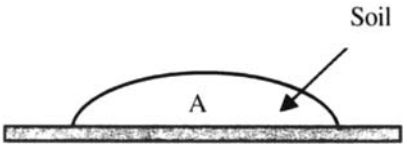


Fig. 6.1. Adherence of soil to a substrate.

for most of the soil. Its main components are: carbohydrates (sugars, starch); lipids (vegetable and animal fats); proteins (meat, milk, fish); mineral salts; additives (colorants); and all combinations of the above. The degree of difficulty in removing soil from a surface depends on the energy used; in other words, the accumulated energies of heat (water), chemicals (the detergent), and mechanical action ("elbow grease") must be greater than the energies that keep the soil together and stuck to the surface (see Fig. 6.1).

The forces vary depending on the nature of the food in question and the treatment to which the surface has been subjected (cooking, type of water, drying). The degree of cleaning difficulty is shown in a simple graph in Figure 6.2.

In this graph, couple 1 could be juice (sugar) in a glass; couple 3 could be pasta stuck to Pyrex; and couple 5 could be milk boiled in stainless steel. If the cleaning result is unsatisfactory, the consumer will make up the difference by increasing mechanical energy (using scouring pads and other products if necessary), and/or by soaking very difficult soil in a solution of hot water and detergent (thermal and chemical energy). Consumers also know that it is better to wash articles immediately; otherwise, soil removal will become more difficult as the article dries.

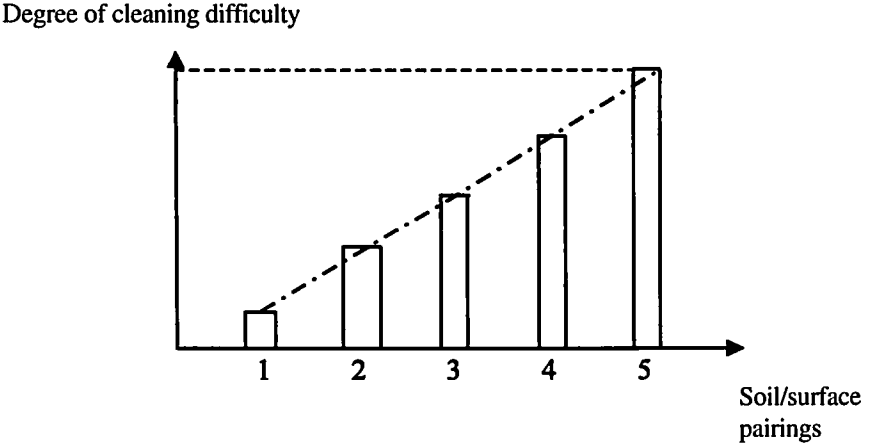


Fig. 6.2. Difficulty of soil removal as a function of soil/surface pairings.

Machine Dishwashing

Dishes. The types of surfaces that can be washed by machine are generally the same as those described for hand dishwashing, with a few exceptions, e.g., articles that could be harmed by the high pH and temperature of the dishwasher, such as sensitive metals (copper or aluminum), plastics (which can be distorted or discolored), wooden articles, or hand-painted porcelains. Some consumers do not put crystal in their machines, more for fear of "mechanical" breakage or excessive heat than of the aggressive nature of detergents. Others will not machine wash silverware despite many suitable products being available, possibly because cleaning of silver has retained something of its ceremonial character. Finally, certain kitchen articles, such as pots and pans, are too large to be washed in machines.

Soil. Here again, the types of soils are similar to those discussed under hand dishwashing, but consumers will tend to take a bit more care. For example, they may give the dishes a superficial cleaning before putting them in the machine (with paper towels or rinsing) and will generally not let residual food dry for long. Also, they may also not put very heavily soiled objects into the machine at all. In general, they know the limits of their machine and the products used. They also know that everything will be washed together in the machine, and that it is not possible for the machine to give special attention to difficult problems. In very difficult cases, a prewash will be necessary. The reader will have understood that it is a conscious choice to wash an article in the machine, but once this choice has been made, the outcome has to be impeccable in terms of performance and care for the objects washed.

Products for Hand Dishwashing

The hand dishwashing market is very different in developed and developing countries; even in developed countries, where the machine is gradually gaining ground, the traditional hand dishwashing product remains very important. Moreover, because these products are easy to manufacture, a plethora of private label brands has appeared on supermarket shelves in recent years.

Ingredients and Their Functions

A dishwashing liquid is a mixture of 20–40% surfactants, combined with other specific ingredients whose function is to increase foam, to stabilize and homogenize the formulation (hydrotope), and to provide the right viscosity. New ingredients have made their appearance more recently, generally in more high-priced brands. These include agents to improve skin care, to enhance draining, which avoids the need for drying, or to make the liquid transparent.

Surfactants. The basic parameter in dishwashing liquids is foam, which should be present throughout the wash. For the user, the first indication of product quality is

the amount of foam it makes in solution with water. As the wash progresses and more and more soil is introduced, it eventually becomes impossible to maintain foam, and the product is no longer effective. In the eyes of the consumer, this is the criterion that determines whether a product is effective; it is much more important than viscosity or the speed with which a product dissolves. This has to be kept in mind by the formulator, for it explains why formulations generally contain high levels of anionics (foaming). Nonionics, which foam little, are used in only very small quantities, mainly to control and stabilize foam and allow water to drain from the dishes more easily.

Different combinations. Traditional liquid detergents were formulated with linear alkylbenzenesulfonate (LAS), generally in combination with alkyl ether sulfate (e.g., LES, lauryl ether sulfate, which is less sensitive to hard water), and acts synergistically with LAS. Among the most commonly used LAS, the C_{11}–C_{12} chains offer good performance and foam quality in both hard and soft water. LES [C_{12}–C_{14}; 2–3 ethylene oxide (EO)], with its low Krafft point, is highly soluble in water, providing optimal synergy with LAS. The ratio of LAS to LES can vary between 80:20 and 70:30 depending on cost limitations of the formulation. The 70:30 ratio is generally recommended. Low-concentration liquids with <20% actives often contain a stabilizer/foam control agent to improve efficacy against grease. This is generally an alkanolamide.

Other surfactant systems. These include the following:

1. Systems using α-olefin sulfonate/alkyl ether sulfate (AOS/LES) are effective but more expensive. Together with amine oxide, such products will be very gentle to the skin. For AOS, C_{14} chains perform best and are relatively insensitive to hard water (1).
2. Mixtures of secondary alkanesulfonates (SAS), such as Hostapur C_{14}–C_{17} with LES, are very good for foam in both hard and soft water, and are compatible with skin and good for frequent use (2).
3. Mixtures of primary alcohol sulfates (PAS)/LES perform well but are more expensive than classical mixtures of LAS/LES. They are generally associated with alkanolamides and toluenesulfonates.

The presence of magnesium sulfate helps synergies in the LAS/LES/PAS systems if the level of Mg^{2+} is maintained at ~0.5 times the molar concentration in alcohol sulfates; the percentage of alkanolamide can be kept down to 3–4%, and the resulting formulations are more active and gentle to the skin (3). Table 6.3 summarizes the primary raw materials used and their main properties.

Other Ingredients. To make a product that is stable in storage, an agent that will help solubilize the other ingredients and control viscosity is required. Stability of a liquid in cold climates, where transport and storage temperatures can be <0°C, is a very important factor. If the product is not properly formulated, it can turn cloudy and take a long time to become clear again (on the store shelf); this will not make it attractive to consumers.

TABLE 6.3
Properties of Different Surfactants Used in Hand Dishwashing Liquids

Anionics	Properties
LAS (linear alkylbenzenesulfonate)	Low price
	Abundant foam except in hard water
	Generally good detergency
AES (alcohol ether sulfates)	Synergy with LAS (foam)
or LES (lauryl ether sulfate)	Good in hard water
	Good solubility
	Good skin properties
AOS (α-olefinsulfonate)	Good detergency
	Good skin properties
	Low foam
PAS (primary alcohol sulfates)	Good foam
	Acceptable solubility and detergency
	Less sensitive to water hardness
SAS (secondary alkanesulfonate)	Good detergency
	Good solubility
	Good skin properties
	Good foam
Nonionics	
AE (alcohol ethoxylate)	Good on greasy soil
	Insensitive to water hardness
	Low foam
APG (alkylpolyglucoside)	Good performance
	Good skin properties
	Improved biodegradability

Viscosity is also very important because it is a directly related to dosage, i.e., if the product is too viscous it is difficult to dose, requiring pressure on the bottle, and if it is not sufficiently viscous, the consumer will have the impression that it is not economical. Stability and viscosity are controlled using hydrotopes such as SXS (sodium xylenesulfonate), urea, or ethanol. Sodium, potassium, or magnesium chlorides are used to increase viscosity.

Most dishwashing liquids claim to be gentle to the skin. Many of them, however, do not contain any specific softening ingredients, relying simply on the right choice of raw materials. For example, LAS is good at removing grease from hands but, in certain cases, it can cause serious drying of skin. Most manufacturers therefore reduce or completely remove LAS from their hand dishwashing products. Three kinds of additives protect hands:

1. Protein-based additives. Proteins derived from collagen can be used, but they have a number of drawbacks (strong smell, and sometimes a brownish color); microorganisms can develop as well, resulting in discoloration and undesirable odors.

TABLE 6.4
Three Examples of an Economical Formulation[a]

Ingredient	1 (%)	2 (%)	3 (%)
LAS	14.11	15.11	13
LES (Na)	3.1	—	3
LES (ammonium)	—	7.1	—
AOS	—	—	3
Diethanolamide	2.1	—	1
EDTA	0.1	0.1	—
Na xylenesulfonate	3.1	—	—
Urea	—	2.1	3
Ethanol	—	—	1
Preservative	0.05	0.5	+
Water, perfume, colorant	Balance	Balance	Balance

[a]See Table 6.3 for abbreviations.

2. Lanolin and lanolin-derivative-based additives (4). The use of these products is not very practical because they require heat for solubilization, which complicates manufacture and increases cost.
3. Emollient surfactants. Amphoterics or zwitterionics such as CAPB (cocamidopropyl betaine) are used in combination with LES to formulate liquids that offer good wash performance and are gentle to the skin (the formulations are similar to those of shampoos, which we will examine in Chapter 9).

Examples of Dishwashing Liquid Formulations

Three types of formulations are as follows: (i) economical, with active ingredients ~20%; (ii) intermediate, with active ingredients ~30%; and (iii) top of the line, with active ingredients ~40%. Table 6.4 gives three examples of an economical formulation. Tables 6.5 and 6.6 show intermediate and premium formulations, respectively.

TABLE 6.5
Two Examples of Intermediate Formulations[a]

Ingredient	(%)	(%)
LAS	20	25
LES (Na)	10	8
Ethanol	6	6
Urea	2	3
EDTA	0.05	—
Water, perfume, colorant	Balance	Balance

[a]See Table 6.3 for abbreviations.

TABLE 6.6
Example of a Premium Formulation[a,b]

Ingredient	(%)
SAS	33
LES (Na)	7
Nonionics	2
Urea	3.5
Ethanol	2
EDTA	0.3
Water, perfume, colorant	Balance

[a]See Table 6.3 for abbreviations.
[b]*Source:* Reference 5.

Other patented formulations with specific characteristics exist. These include the use of lemon juice to mask fish smells (4) (Table 6.7); the use of dialkyl sulfosuccinates (6) to achieve better performance than with LAS/LES in soft or hard water (Table 6.8); a combination of APG®, PAS Mg and fatty alcohol ethoxylate, which yields a product that drains more easily (3) (Table 6.9); a formula for a clear liquid (7)

TABLE 6.7
Patented Formulation with a Special Characteristic: Lemon Juice[a,b]

Ingredient	(%)
LAS	29
LES (Na)	14
Lemon juice	5–20
Ethanol	5–6
Urea	5
Preservative	0.03
Water, perfume, colorant	Balance

[a]See Table 6.3 for abbreviations.
[b]*Source:* Reference 4.

TABLE 6.8
Patented Formulation with a Special Characteristic: Use of Dialkyl Sulfosuccinates[a,b]

Ingredient	(%)
Dialkyl sulfosuccinate	8.5
LES	4.5
Diethanolamide	2.5
Urea	1.5
$MgCl \cdot 6H_20$	0.5
Preservative	+
Water, perfume, colorant	Balance

[a]See Table 6.3 for abbreviations.
[b]*Source:* Reference 6.

TABLE 6.9
Patented Formulation with a Special Characteristic: Better Draining[a,b]

Ingredient	(%)
PAS (Coconut) Mg	11.5
PAS (Coconut) NH_4	1.4
Alpha-olefinsulfonate	7.4
APG®	3.7
Monoethanolamide	4.5
Tallow alcohol (18 EO)	3.4
Water, perfume, colorant	Balance

[a]Abbreviations: EO, ethylene oxide; see Table 6.3 for other abbreviations.
[b]*Source:* Reference 3.

TABLE 6.10
Patented Formulation with a Special Characteristic: A Clear Liquid[a,b]

Ingredient	(%)
LES (Na)	10.2
CAPB	1.2
APG®	2.2
SAS	10.2
Water, perfume, colorant	Balance

[a]Abbreviations: CAPB, cocamidopropyl betaine; see Table 6.3 for abbreviations.
[b]*Source:* Reference 7.

TABLE 6.11
Patented Formulation with a Special Characteristic: Dilutable[a,b]

Ingredient	(%)
SAS	66.5
LES (Na)	18.5
Nonionics (7 EO)	5
Ethanol	17.5
Preservative	+
Water, perfume, colorant	Balance

[a]Abbreviations: EO, ethylene oxide; see Table 6.3 for other abbreviations.
[b]*Source:* Reference 8.

(Table 6.10); and dilutable formulations, which are superconcentrated (70%) products and can be diluted with water to make a 20% active solution (8) (Table 6.11).

Products for Dishwashers

The dishwasher market is growing steadily. Although this development may be slow in some countries, a demand exists for machine dishwashing products, and there have been some interesting innovations (Fig. 6.3).

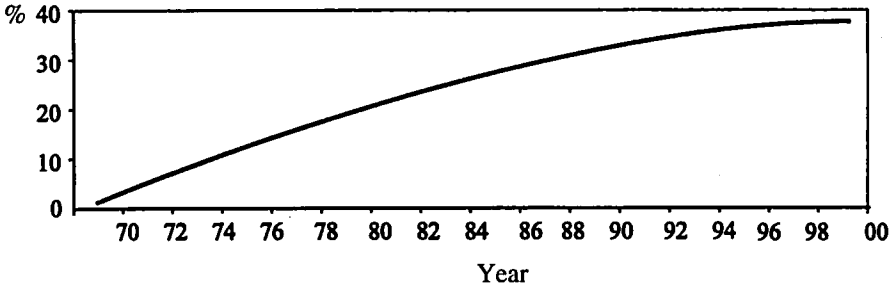


Fig. 6.3. Development of the dishwasher market in France (*Source:* INSEE).

Today in France, 38% of homes have a dishwasher, compared with 67% in the United States. Consumers are more likely to have higher expectations from a dishwasher than from a washing machine. They are prepared to pay quite a high price for a machine that will free up some time, but the result has to be perfect. Although a residual stain on a pair of jeans may be acceptable, traces of soil or other deposits on a glass after a machine wash will be rejected. Once again the formulator must attempt the impossible.

Dishwashers

Before looking at the products, it is important to understand how a European automatic dishwasher works (Fig. 6.4). Machine dishwashing depends on the following five factors:

1. The use of softened water.
2. The physicochemical action of the detergent.
3. The mechanical action as the detergent solution is thrown against the dishes.
4. The heating action of the machine.
5. The duration of these different factors.

The first factor (Fig. 6.4, part 1) is probably the most critical because the least trace of calcium on a glass will be regarded very critically by the user. Unlike washing machines, European automatic dishwashers include ion-exchanging resins, which leave very little hardness in the water (Fig. 6.4, part 8). The absence of mineral salts provides other benefits, including better removal of certain soils and very good upkeep of the machine itself (the immersion heater and the interior tank) as a result of the absence of calcium deposits. Tap water first runs through the resin tank before filling the main tank where washing takes place. Slowly, the resins become charged in Ca^{2+} and Mg^{2+} ions, releasing in exchange their own Na^{+} ions, which are not a problem. Gradually, the resins become saturated, at which point the opposite operation is needed to restore Na^{+} ions and remove the Ca^{2+} and Mg^{2+} ions—a process known as regeneration.

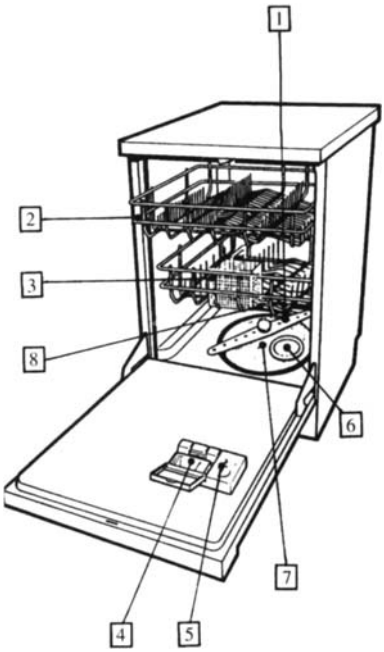


Fig. 6.4. The interior of a European dishwasher. 1, heater; 2, top rack; 3, lower rack; 4, detergent dispenser; 5, rinse aid dispenser; 6, salt container; 7, rotating spray arms; 8, container for ion exchange resins.

Comments

Water hardness in the United States is generally low (on average less than 100 ppm $CaCO_3$) and automatic washers have no provisions for ion exchange and depend on STPP for control of water hardness.

Point 2 concerns detergent formulation (Fig. 6.4, part 4), which we will discuss later. Point 3 is the mechanical action of the machine (Fig. 6.4, part 7), by which it throws detergent solution onto dirty dishes through rotating spray arms. This action is considerably weaker than the direct human contact in the hand dishwashing situation. Point 4 concerns temperature, which varies from 40 to 55 to 65°C, depending on the cycle used. The important point is not so much the highest temperature reached, but more the gradual increase in temperature, which activates the ingredients in sequential order. Point 5 depends on the program selected and includes prewashing, washing, rinsing, and drying. In the final rinse, an additional product (Fig. 6.4, part 5) is used; it allows water to drain off the dishes evenly, removing the least traces of calcium deposits. Figure 6.5 shows the wash cycle of a European dishwasher.

Comments

Again, there are major differences in machine design in the United States. Machines there have no built-in water heater and use hot water coming from a central water heater that supplies hot water throughout the house. Water temperatures in the machine are about 40–50°C.

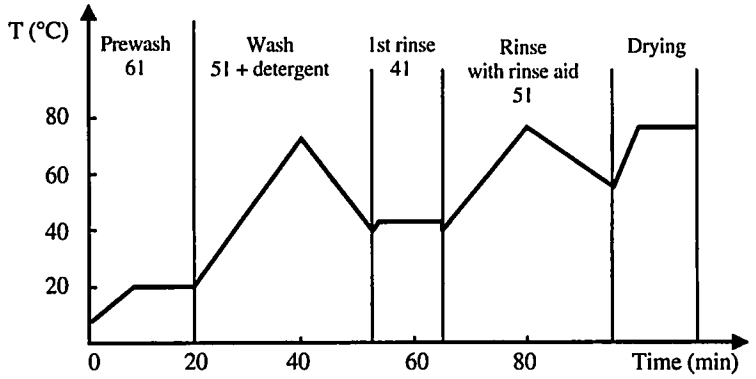


Fig. 6.5. The wash cycle in a European dishwasher.

Description of the Successive Operations. Dishwashing in a machine occurs in a succession of stages to meet specific needs; the whole operation takes place using softened water, thanks to a softener built into the machine.

Prewash. No product is needed. The dishes are sprayed with cold water by the spraying arms, removing the loose soil and beginning to soften residual food on the dishes.

Wash. Depending on the degree of soiling, this can be done at 40°C for glassware, and more often at 55 or 65°C. Water and detergent are thrown against the dishes, progressively removing all soil, thanks to the chemical action.

Rinsing. There is a first rinse in clear water, then a final rinse in hot water containing a rinse aid (part 5), which allows the water to drain evenly and to dry without leaving calcium deposits.

Drying. Drying occurs by evaporation. Throughout the cycle, the water passes continuously through different sized filters creating optimal drying conditions and removing any risk of redeposition.

Machine Developments. Like the products that support them, dishwashers are subject to developments, some of which are favorable for detergent manufacturers, others not so favorable. An example of a move in the right direction is the introduction of "enzyme cycles," which maintain a temperature of 40°C at certain times in the wash cycle in order to optimize enzyme activity. Examples of unfavorable developments include the downsizing of dosing systems (Fig. 6.4, part 4) for the detergent and the reduction in the consumption of water and electricity; the latter is very good for the environment, but it complicates considerably the task for the formulator, who has to rely on the detergent to compensate yet to deliver the same perfect result.

In summary, machine developments include lower noise levels, water consumption, and energy consumption, and smaller product dispensers while maintaining equal washing efficacy.

Three chemical products may be used, i.e., the detergent (used for each wash), the rinse product (placed in the reservoir to last for several washes), and the regenerating salt (the reservoir refilled when the water is no longer softened).

Dishwashing Products

Before looking at the different ingredients used in a machine dishwashing product, the following existing products will be examined individually: (i) conventional powders; (ii) concentrated powders; (iii) conventional liquids; (iv) concentrated liquids; and (v) tablets and pills.

Conventional Powders. First seen in the 1960s, these products have hardly changed after >30 years; they continue to represent the bulk of the market. Their efficacy is based on a mixture of tripolyphosphates, sodium metasilicate, and a bleaching agent, together with a small amount of surfactant. More recently, and for reasons of safety, metasilicate, which is classified as corrosive and is highly alkaline, is being replaced by less alkaline products such as Na disilicate, which is classified as an "irritant."

Concentrated Powders. The first powder concentrates, launched in the 1990s (Unilever, Sun Progress), are both safer (less irritating) and ecologically more attractive than conventional powders, with a dosage one-half of that used earlier. The basic raw materials are phosphates or citrates/polymers (depending on the country), disilicate, some surfactant, and, above all, a bleaching system based on perborate and tetraacetylethylenediamine (TAED), as in clothes laundering. Because of the absence of a chlorine source, enzymes can be included.

Conventional Liquids. First launched in 1986 in the United States (Palmolive Liquid, Colgate) and in 1987 in Europe, liquids now have gained ~30% of the U.S. market and 15% of the European market. The basic technology is the same as that for conventional powders, but with a lower level of pH and reserve alkalinity. The liquid form imposes the need for a structuring agent such as clay or polymers (9–11). In addition, liquids must possess rheological properties (thixotropy) which facilitate dosing, but also provide sufficient viscosity to prevent the product from running out of the machine dispenser. The advantages of liquids over powders include the following: (i) they go into solution quickly; (ii) unlike powders, they are not sensitive to humidity; (iii) they are easy to use; and (iv) they cannot cake in the dispenser (unlike powders when the packaging is not sufficiently moisture-proof).

Concentrated Liquids. To our knowledge, only one type of concentrated product is available; its uniqueness resides in the combined presence of a chlorine source and enzymes (Sun). To meet this technological challenge, the idea was to put the chlorine source into wax microcapsules with a melting point of ~46°C, which protect the enzymes in the product during storage, and releasing them to act during the wash cycle.

Tablets. These are the most recent arrivals on the market. They completely meet the needs of dishwashing machine owners who do not want to be concerned

about how much product to dose. The basic technology is very similar to that of concentrated powders, which have been compressed into tablets (12,13). In only a few years, tablets have captured 45% of the market in France, and in European countries, such as the Netherlands and Germany, they represent well over 50%.

The Different Ingredients and Their Functions. Sodium tripolyphosphate. STPP has already been discussed at length in Chapter 2 under laundering. As a complexant, STPP has a prime function in the wash process; without it, there would be a great loss of efficacy. Its main functions are as follows: (i) to form soluble complexes with the Ca^{2+} and Mg^{2+} ions in hard water; (ii) to supply a reserve of alkalinity; and (iii) to play a role in antiredeposition.

In the washing solution, most particulate oily soil and surfaces to be cleaned are negatively charged. In such situations, free calcium acts as a "bridge," fixing the soil to the surface to be cleaned. Oily soil contains a quantity of fatty acids that can combine with free calcium to form insoluble soaps, mainly on the surface of the soil, which prevents the spontaneous "roll-up" of the oily soil. Experiments have shown that free Ca^{2+} ions have a negative effect in the removal of starch and tea, and on the appearance of glassware. The explanation for this is as follows: In an alkaline environment, starch is negatively charged. Two forces must be considered: the cohesive forces between starch molecules, and the adhesive force between starch and the surface of articles. In this situation, free calcium acts like a bridge linking the starch molecules together into a gel and fixing the molecules onto the surface to be cleaned.

Tea contains polyphenol-type color bodies. The way in which tea adsorbs onto hard surfaces is not known, but we can presume that in an alkaline environment, this type of soil is negatively charged (the pK_a of phenols is ~10); thus, the free calcium can adsorb itself onto the surface to be cleaned.

During the wash, the presence of free calcium helps adsorption (or fixation) of proteins (milk) onto glasses. Their properties are therefore changed in the presence of proteins, which may explain the negative effect of calcium on the appearance of glasses. The main function of STPP in the wash solution is therefore obviously to reduce the concentration of calcium by complexing. In addition, by complexing some cations, STPP prevents them from precipitating with other anions (e.g., $CaCO_3$).

The alkalinity of a salt is its capacity to produce a high concentration of hydroxyl ions in solution (high pH). Its buffering capacity is its ability to maintain the pH within a given range despite the addition of an acid or a base. Weak acid salts/strong bases bring both alkalinity and good buffering. This is the case for STPP, but in the dishwasher, alkalinity and buffering are obtained mainly by silicate; hence the role of STPP is negligible.

In redeposition, the cations (principally di- or trivalents Ca^{2+}, Al^{3+} ions) reduce the "double layers," causing a reduction in repulsive forces between the particles (soil) themselves, or between the particles and the surfaces to be cleaned. By complexing the cations, STPP increases the antiredeposition effect. It believed that the $P_3O_{10}^{-5}$ anions can adsorb on particles, which increases their charge so that they then repel each other, resulting in a stable dispersion.

STPP has other subsidiary effects. Various studies have shown that STPP reduces critical micellar concentration of surfactants. STPP also reduces interfacial tension between oily soil and the detergent solution, causing the spontaneous "rolling-up" of the oil. The important criteria to use in the choice of STPP are as follows (14):

1. Particle shape (granulated STPP helps avoid dusting problems and reduces the risk of caking).
2. Particle size. This should be as regular as possible—neither too large nor too small (consumer preference).
3. Density. This can be based on the required product density and that of other raw materials.
4. Decomposition. STPP should contain as little pyrophosphate as possible, (free calcium in solution increases with the decomposition of STPP).
5. Hydration. The surface of the granules should contain at least 6% moisture to prevent it from hydrating during storage or in the machine distributor (caking).
6. Solubility. To obtain good performance, STPP and Na metasilicate must not dissolve at the same time; normally, metasilicate will dissolve much more quickly than the STPP.

The rate of dissolution of STPP depends on two factors, i.e., its particle size and its hydration rate (the surface of the granules should be completely hydrated and small particles should be avoided).

Sodium silicates. Metasilicate remains an important raw material today despite criticisms of its safety. There are several soluble sodium silicates, including the following:

1. Orthosilicates, Na_4SiO_4 or $2Na_2O \cdot SiO_2$, with a ratio $SiO_2/Na_2O = 1{:}2$.
2. Bisilicates or disilicates, Na_2SiO_5 or $Na_2O \cdot 2SiO_2$, with a ratio $SiO_2/Na_2O = 2$ (gradually replacing metasilicates).
3. Monosilicates or metasilicates with the general formulation $(Si_nO_3)Na_{2n}$. If $n = 1$, the formulation will be Na_2SiO_3 or $Na_2O \cdot SiO_2$ with $R = SiO_2/Na_2O = 1$. Na metasilicate is generally obtained by fusion of silicate and carbonate using a ratio of silica to alkali = 1.

$$Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 \quad \Delta H = 21.65 \text{ kcal}$$
(quartz)

The melting point is usually ~1300°C. All Na silicates have an alkaline pH; the pH is higher when the ratio SiO_2/Na_2O is low. Metasilicate (R = 1) is therefore more alkaline than disilicate (R = 2). Silicate brings hydroxyl and silicate ions into the wash solution; both play an important role in the wash process.

Fatty acids contained in oily soil are neutralized and thereby transformed into soluble soap. An increase in OH^- ions has a positive effect on the removal of soil

(electrostatic effect); at high pH, most soils and substrates are negatively charged. Repulsion therefore exists between soil/soil and soil/substrate. On the other hand, high pH discolors aluminum and attacks certain finishes. Silicate ions in the solution can adsorb at the substrate surface to form a silicate layer, which protects stainless steel surfaces present in the wash and in the interior of the machine itself from corrosion, and also protects enamel finishes on porcelain. The best performance is usually obtained at a pH of ~10. To calculate optimum amounts of silicate, we consider other factors that influence pH in the wash, namely, bicarbonate ion concentration in the tap water and the type and quantity of soil in the wash solution. The answer also lies in a thorough knowledge of domestic washing habits, e.g., dosage, water quality, and amount of soil.

Sodium carbonate. The chemistry of Na carbonate was examined in Chapter 3. In dishwashing, carbonate has two functions, namely, buffering and water softening. First, we will consider *buffering*. In aqueous solution, Na carbonate liberates hydroxyl ions according to the following equations:

$$Na_2CO_3 \rightarrow CO_3^{2-} + 2Na^+$$

$$CO_3^{2-} + H_2O \rightarrow H_2CO_3 + HO^-$$

Carbonate is therefore a source of alkalinity, provided that its concentration is sufficient. For example, a pH of 11.6 can be obtained when a solution contains 0.05 mol/L Na_2CO_3/L (5.3 g/L). However, in dishwashing formulations, it is silicate, more than carbonate, which is the source of alkalinity.

We will now consider the *water softening function.* Addition of carbonate to an STPP solution reduces the concentration of free calcium in "underbuilt" situations in which water is hard or product dosage is inadequate. The presence of carbonate has no effect on the free calcium concentration in "built" situations. To confirm the above laboratory conclusions, tests were conducted in machines under normal usage conditions, comparing the following:

- product A without carbonate
- product B with carbonate

} + a small amount of STPP → "underbuilt" situation

- product C without carbonate
- product D with carbonate

} + a normal amount of STPP → "overbuilt" situation

Results showed that "overbuilt" formulations (C and D) are clearly preferred to "underbuilt" formulations (A and B). The influence of carbonate is very weak, but it has a tendency to improve the wash in "underbuilt" circumstances (B > A). In the overbuilt situation, the use of carbonate has a rather negative effect on the appearance of glassware.

One could conclude that in theory, carbonate is a source of alkalinity (liberation of OH^- ions) and that it also plays a role in water softening by precipitating

ions that cause hardness. In practice, however, its role as a buffer is almost nonexistent because of the presence of silicate. Thus, in the case of an "overbuilt" product, part of the active ingredients can be replaced by carbonate as a "filler." On the other hand, if a lack of builder exists, it would be better to increase the STPP than to use carbonate.

Surfactants. The function of surfactants in dishwashing products is much less important than in laundering products. For application in dishwashing products, surfactants must possess the following properties: (i) an antifoam effect; (ii) low surface tension; (iii) good biodegradability; and (iv) low toxicity. In France, for example, all of the raw materials used in dishwashers must be on the "positive list" authorized by the Ministry of Health.

Two main types of surfactants are used. The first comprises EO and PO copolymers (e.g., Pluronics). They are derived from the condensation of ethylene oxide and propylene oxide and have the chemical formula HO $(C_2H_4O)_m$ $(C_3H_6O)_n$ $(C_2H_4O)_m$ H. The second group is comprised of the alcohol alkoxylates (e.g., Plurafac). An example is a straight-chain primary alcohol alkoxylate, HO $(C_2H_4O)_x$ $(C_3H_6O)_y$ $(C_2H_4O)_x$—R. Their main characteristics are summarized in Table 6.12.

We know that both water hardness and temperature reduce the CMC. But it has also been established that the CMC increases in the presence of soap (because of the saponification of oily soil in alkaline solution). In sufficient quantity, soap can significantly increase surface tension. For Plurafac, for example, it has also been found that its cloud point decreases in the presence of STPP and metasilicate, but increases when soap is added to the mixture (Table 6.13).

Nonionics in a machine dishwashing detergent have the following two functions:

1. Antifoam. Foam in the dishwasher, which is caused mainly by the presence of proteins, has a negative effect on performance because it reduces pressure from the water jets and can cause a disagreeable increase in the noise level due to cavitation of the recycling pump. Nonionics can act as antifoam agents.
2. Action on oily stains. Fatty acids in soils change into soap in the presence of silicate and STPP. These soaps are soluble and help oily soil to disperse and emulsify. However, it should be noted that triglycerides (the main ingredients of fats) are not saponified even at high pH (>11). They are eliminated from the substrates by nonionics *via* rolling-up and "solubilization" mechanisms, both described in Chapter 1.

TABLE 6.12
Characteristics of Pluronics and Plurafacs

	Pluronic	Plurafac
Surface tension at 0.1 g/L in distilled water	42–42 mN/m	30–32 mN/m
CMC (critical micelle concentration) in distilled water	~0.01 g/L	~0.01 g/L

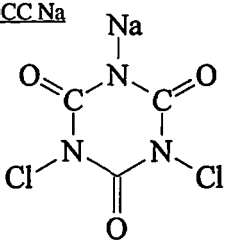
TABLE 6.13
Influence of Main Ingredients on the Cloud Point of Plurafac[a]

	Cloud point (°C)
Pure Plurafac	28
Plurafac	23.5
+ STPP (1.28 g/L)	
+ SMS (1.47 g/L)	
Plurafac	38–40
+ STPP (1.28 g/L)	
+ SMS (1.47 g/L)	
+ Soap (0.3–0.7 g/L)	

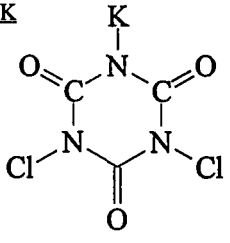
[a]Abbreviations: STPP, sodium tripolyphosphate; SMS, sodium metasilicate.

Bleaching agents. The present trend in laundry as well as machine dishwashing products is to employ a mixture of perborate and TAED; the underlying principle is described in Chapter 3. Enzymes can be used with these bleaching agents, but not with chlorine. The chlorine sources in automatic dishwashing products are sodium or potassium salts of dichloroisocyanuric acid (K or NaDCC). The chemical structures of the most widely used chlorine sources are as follows:

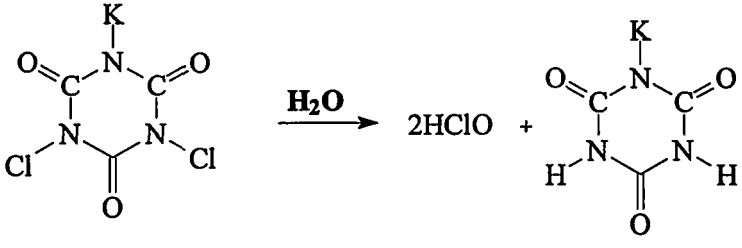
DCC Na



DCC K



In aqueous solution, ClO^- ions are liberated.



It should be noted that the species responsible for oxidation is hypochlorite.

$$HClO + OH^- \leftrightharpoons ClO^- + H_2$$

Its strong bleaching power makes possible:

- the decomposition of organic compounds (cleaning, decolorization, and deodorization) and
- the destruction of microorganisms (disinfection).

The presence of free water in machine dishwashing formulations should be avoided; otherwise, the isocyanurates hydrolyze or can solubilize the inorganic alkaline compounds (silicates), and cause a reaction with the chlorinating agent.

Other ingredients. Other raw materials that can be used in machine dishwashing are often identical with those used in laundering. TAED and perborate have already been mentioned, to which we can add amylase and protease enzymes, certain polymers, and Na citrate in nonphosphate formulations. All of these ingredients were discussed in Chapter 2; however, more must be said about enzymes and polymers, whose use in dishwashers is certain to increase in years ahead.

Considering enzymes, two important aspects (other than their efficacy) are as follows:

1. Safety in use. There is concern about potential residues on articles. Evaluations carried out in machines by a major manufacturer (Gist-Brocades) (15) under the harshest conditions, with high product dosage, little water, low temperature, and a high level of enzymes, show that residual enzyme activity on dishes is completely negligible relative to the theoretical calculations of toxicity studies (lower than 8×10^6).
2. Their future. Enzymes are certainly a raw material for the future because they can be used at low levels, which is very advantageous for concentrated products and tablets. Current developments include optimization of current enzymes, with better performance in short cycles and at low temperatures, and the introduction of new variants that act on difficult soils, e.g., oxidases on bleachable soils.

The rationale for the use of polymers is as follows. When the use of phosphates is restricted or prohibited, other water "softeners" have to be used (e.g., Na citrate or Na carbonate/bicarbonate). In general, these substitutes lack many of the qualities of STPP (excluding environmental considerations), and it is therefore necessary to use additives such as polymers. To a certain extent, polymers help to solve the problem of film forming on glass, caused by the deposition of mineral salts.

Here we discuss some specifics regarding liquids and gels. To prepare a thixotropic liquid, the different raw materials are combined with clay to form a colloid. The clay is of a smectite type (bentonite), or hectorite (9,10). Other thickening agents have been patented by Unilever, including synthetic clays (layered types such as bentonites) used at between 7 and 40% and highly pure inorganic oxides (zinc oxides, titanium and magnesium oxides). These agents (or their mixtures) make for very good finished product stability, without affecting the extent of hypochlorite decomposition during storage.

TABLE 6.14
Formulation of Conventional Powders: With Phosphates[a,b]

Ingredient	Europe (Corrosive category) (%)	United States (%)
STPP	15–35	25–35
Na disilicate	—	7–9
Na metasilicate	20–60	—
Na carbonate	0–30	25–35
Chlorine source	0.5–2.0	1–2
Surfactant	0–3	2–4

[a]Abbreviation: STPP, sodium tripolyphosphate.
[b]*Source:* Reference 16.

Examples of Formulations

Tables 6.14 and 6.15 present the formulations of conventional powders with and without phosphates, respectively. Tables 6.16 and 6.17 give the same information for compact powders. Tables 6.18 (tablets) and 6.19 (liquids and gels) complete the list of formulations.

Rinse Products

These products, called "rinse aids," could also be called "drying aids." Their function is to help water drain uniformly on the dishes during the last rinse and drying cycle, in order to give perfect drying without any traces of residue. Rinse aids are very simple to formulate. The products generally contain nonionics to lower sur-

TABLE 6.15
Formulation of Conventional Powders: Without Phosphates[a]

Ingredient	Europe (Irritant category) (%)
Na citrate	15–35
Copolymer	2.5–4
Na disilicate	8–15
Perborate monohydrate	4.5–10
TAED	1.5–3.5
Na sulfate	20–40
Na carbonate	10–30
Nonionics	0.5–1.5
Enzymes	+
Benzotriazole	+
Perfume	+

[a]Abbreviation: TAED, tetraacetylethylenediamine.

TABLE 6.16
Formulation of Compact Powders: With Phosphates[a]

Ingredient	(%)
STPP	30–60
Na disilicate	15–35
Nonionics	0.5–1.5
Polyacrylate	0–5
Na perborate	6–15
Na carbonate	0–5
TAED	0.5–4
Protease	+
Amylase	+
Lipase	+/–
Perfume	+

[a]Abbreviations: STPP, sodium tripolyphosphate; TAED, tetraacetylethylenediamine.

TABLE 6.17
Formulation of Compact Powders: Without Phosphates[a]

Ingredient	(%)
Na citrate	25–50
Nonionics	1–3.5
Polymer	0.5–6
Phosphonate	0–1
Na disilicate	15–25
Na carbonate	0–15
Na bicarbonate	0–35
Na perborate	6–20
TAED	2–7
Amylase	+
Lipase	+/–
Protease	+
Sulfate	0–25

[a]Abbreviation: TAED, tetraacetylethylenediamine.

TABLE 6.18
Two Examples of Formulations in Tablet Form[a,b]

Ingredient	A (%)	B (%)
Anhydrous STPP	35	33.6
Anhydrous metasilicate	33.7	28.8
Metasilicate · $9H_2O$	26.3	33.6
Trichloroisocyanuric acid	1	1
Anhydrous Na acetate	3	3
Calcium diphosphate · $2H_2O$	1	1

[a]Abbreviation: STPP, sodium tripolyphosphate.
[b]*Source:* Reference 12.

TABLE 6.19
Examples of Liquid and Gel Formulations[a]

Ingredient	Formula A[b] (%)	Formula B[c] (%)
Anhydrous STPP	13	—
STPP · $6H_2O$	—	28
Na silicate	5	23
Na metasilicate pentahydrate	—	15
Zeolite A	—	5
Na carbonate	5	—
Soda (50%)	1	—
Na hypochlorite	1	1
Surfactants (Dowfax 3B2)	0.8	—
Antifoam (Knapsack Lp Kn)	0.16	—
Clay (Attagel 50)	3.3	—
Clay (Laponite RD, Hectorite, Laporte)	—	0.8
Colorant, water	Balance	Balance

[a]Abbreviation: STPP, sodium tripolyphosphate.
[b]*Source:* Reference 9.
[c]*Source:* Reference 10.

TABLE 6.20
Examples of Formulations of Rinse Products

Ingredient	(%)
Nonionic (Plurafac or Pluronic)	10–25
Na toluenesulfonate or Na xylenesulfonate	0–8
Citric acid	8–15
Isopropanol or ethanol	5–10
Water	Balance

face tension and form a uniform film, and food-grade citric acid, which eliminates any residual traces of calcium. A solvent such as ethanol or isopropanol helps give a stable formula. Table 6.20 gives an example of possible formulations.

Regenerating Salt

This is extremely pure sodium chloride. Any trace of metal or anticaking agents, often found in kitchen salt, for example, could damage the ion exchange resins in the dishwasher. The main characteristic of this type of product is its granulometry, which is specifically adapted to avoid caking (absence of fine particles) and to allow the salt to dissolve progressively to optimize the efficacy of the ion exchange.

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CHAPTER 7

Other Hard Surfaces: All-Purpose Cleaners, Scourers, Bathroom Cleaners, and Window Cleaners

All-Purpose Cleaners

General

Manufacturers have always wanted to simplify the consumer's life by limiting the number of products in the home. Without returning to the days when soap was the universal product, and without confusing areas that are incompatible, such as clothes laundering and dishwashing, there are nevertheless a certain number of areas for which the use of one product only is possible, notably hard surfaces, excluding dishes. Floors, walls, windows, and modern surfaces in bathrooms and kitchens can all be cleaned with "all-purpose" cleaners, as they have come to be known (as compared to "specialist" cleaners).

Consumers want more practical products to simplify the cleaning process and often to fulfill several functions at the same time, e.g., to clean and to shine, and with less effort. The first "technological" revolution in all-purpose products came many years ago with the move from powders to liquids and with the availability of liquids more concentrated than powders. Table 7.1 summarizes today's needs.

Ingredients and Their Functions

The main function of surfactants in household cleaners is to remove grease from substrates. Table 7.2 shows surfactants classified according to their hydrophilic–lipophilic balance (HLB) value.

TABLE 7.1
Categorizing All-Purpose Cleaners by Ingredients and Their Function

Needs	Means
Better performance	More surfactants More solvents
Brilliant cleanliness (no streaks), without rinsing	Reduced quantity of electrolytes
Safer products for surfaces for skin	Neutral pH
More ecological	Biodegradable surfactants Carbonate/citrate to replace sodium tripolyphosphate Less packaging/more recycled products/refills Variants of color and perfumes as indicators of cleanliness

TABLE 7.2
Classification of Surfactants According to Their Hydrophilic–Lipophilic Balance (HLB) Value

HLB value	Surfactant function	Miscibility in water
0–5	Water-in-oil	None
5–8	Wetting agents Water-in-oil/oil-in-water	Milky dispersion
9–12	Wetting agents Oil-in-water	Microdispersions
12–15	Solubilizing detergent Oil-in-water	Clear dispersions Translucid
15–20	Solubilizing detergent Oil-in-water	Miscible (clear)

Procter & Gamble demonstrated that magnesium salts can improve performance for the removal of grease; they were first to introduce microemulsion formulations of oil/soap solutions with fatty acids as stabilizing agents and builders, together with solvents that are effective on grease (1). Among these are terpenes, which are well known for their strong smell and solvent properties; they were used in the 1980s in Mr. Clean (Procter & Gamble). The patents (2) explain that liquids generally do not include enough builders, meaning that they are not effective enough on particulate soils while at the same time they are sensitive to water hardness and often foam too much, which makes rinsing difficult. Silicones or soaps have to be added to control foam, but this causes residues on substrates (traces left after drying).

To overcome these difficulties, the patent literature covers the use of terpenes with a co-solvent to give a homogeneous solution. Examples of terpenes include α-limonene, α-pinene, and β-pinene. The polar solvent can be benzyl alcohol, for example. Subsequently, other manufacturers suggested the use of eucalyptus oils, which also contain α-pinene, and pine oils, whose main constituent is α-terpineol, which has a germicidal effect on gram-negative organisms only. Henkel (3) then showed that it was possible to increase the detergency of all-purpose liquids by using polymers combined with nonionics (in which case anionics are of no use). Water-soluble polymers include polyethylene glycols, polyvinylpyrrolidone, and other cellulose ethers. A thicker product consistency, which gives an impression of additional strength, can be obtained by the inclusion of amine oxides, which are good detergents as well as good thickening agents, at a ratio of oxide/anionic of ~94:6 or 99:1 (4).

Colgate advanced the theory that amine salts in detergents in which ethanolamine or an ethylenediamine functions as neutralizing agent, are the essential factor in avoiding traces on surfaces (5). To avoid traces, Unilever (6) suggested the use of a combination of HLB 10–15 nonionics with an ester co-polymer of styrene maleic anhydride (with isobutanol as the esterifying alcohol). Best results are obtained in formulations that do not contain electrolytes. By using an HLB 5–9.8 nonionic together with a magnesium salt of an anionic surfactant, a thick product can be obtained, one that

TABLE 7.3
Current Commercial Product Formulations[a]

Ingredient	A (%)	B (%)	C (%)	D (%)
LAS	—	0.5–1.5	—	1–2
SAS	2–4	1–2.5	3.5–5.5	—
Nonionics	0.5–1.5	2–3.5	2.5–5	2–4
Soap	—	—	—	0.1–0.5
Citric acid	2.5–4.5	—	—	—
Diethylene glycol monobutyl ether	—	—	—	1–4
Butyl diglycol or butyl carbitol				
Isopropyl alcohol	—	2–6	—	—
Polymer	—	—	3.5–5	—
Na carbonate	—	1–2.5	—	0.5–1.5
Na sulfate	—	—	1.3	—
Na bicarbonate	—	—	—	0.1–0.5
Na EDTA	—	—	—	0.2–0.4
Perfume	+	+	+	+
Water	Balance	Balance	Balance	Balance

[a]Abbreviations: LAS, linear alkylbenzenesulfonate; SAS, secondary alkanesulfonate.

is opaque and does not leave any traces. Research by companies such as Rohm & Haas is continuing today to develop polycarboxylates which are soluble in the presence of surfactants, for example, by changing their structure to facilitate incorporation into micelles. More environmentally friendly products are being sought, particularly because certain solvents are under attack. Tables 7.3 and 7.4 present examples of formulations of current commercial products and those containing terpenes, respectively.

Scourers

We have seen that consumers can use all-purpose cleaners in many different ways in various parts of the house. However, some jobs and types of stains require a stronger product; this need gave rise to detergent scourers, first in powder and then in liquid form by the mid-1970s. Scourers, whether liquid or powder, increase the "mechanical" energy needed to deal with certain stubborn stains.

Scouring Powders

Ingredients and Function. The main ingredient is an abrasive agent, which, together with low thermal energy (the product not being in solution), the chemical and physicochemical energy of the product, and quite a lot of "elbow grease," will considerably improve the cleaning performance of the product. The three following criteria are used in selecting the abrasive: (i) hardness; (ii) particle form (the more pointed the particle, the stronger is its abrasive action); and (iii) particle size (particles <2 μm will

TABLE 7.4
Examples of Formulations Containing Terpenes[a,b]

Ingredient	A (%)	B (%)	C (%)	D (%)
Paraffinsulfonate	4.5	4	—	—
LAS	—	—	5	6
Nonionics	2	—	1.5	0.5
STPP	—	—	6	—
Na citrate · $2H_2O$	3.5	3.5	—	3
Na carbonate	3	3	—	—
Na metasilicate	—	—	1	—
Orange terpene	2	2	—	—
α-Pinene	—	—	2	—
β-Pinene	—	—	—	4
EDTA	—	—	—	0.5
Benzyl alcohol	2	—	—	—
Butyl cellosolve	—	—	3	2
Hexyl cellosolve	—	3	—	—
Soap	—	—	0.05	0.5
Ethanol	—	—	—	1.5
Triethanolamine	—	—	—	2
Na cumenesulfonate	2	2	—	1
Other ingredients/water	Balance	Balance	Balance	Balance

[a]*Source:* Reference 4 (mentioned in Procter & Gamble patent).
[b]Abbreviations: LAS, linear alkylbenzenesulfonate; STPP, sodium tripolyphosphate.

not be abrasive, no matter how hard they are). The particle size range is usually from 10 to 50 μm. Table 7.5 summarizes the hardness of different raw materials on a scale from 1 to 10 (Mohs scale).

At one time, hard abrasives such as quartz were used. Subsequently, formulators have chosen raw materials in the 1–4 range of the hardness scale, and in particular, calcite. The basic formulation for a scouring powder includes the following: (i) builders

TABLE 7.5
Mohs Hardness Scale

Hardness	Raw material
1	Talc (Mg and Al silicate)
2	Gypsum (Ca sulfate)
3	Calcite (marble powder, Ca carbonate)
4	Fluorite
5	Apatite (Ca metasilicate)
6	Feldspar (K and Na silicate)
7	Quartz (sand, melted silicate)
8	Topaz
9	Corundum (alumina)
10	Diamond

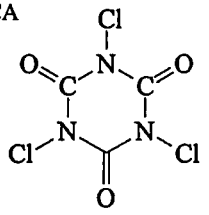
TABLE 7.6
A Simple Scouring Powder Formulation

Ingredient	(%)
Na dodecylbenzenesulfonate	0.5–8
Na orthophosphate	0–5
Sodium tripolyphosphate (STPP)	0–15
Soap powder	0–10
Na sulfate	0–2
Abrasive	55–95

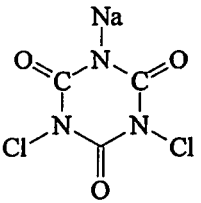
(Na or K carbonate, bicarbonates, or sesquicarbonates) with a pH of 10–12.5. In the case of builders without a buffering effect, a specific buffer was added [e.g., sodium tripolyphosphate (STPP) + Na silicate]; (ii) a water-soluble surfactant and/or soap (Na dodecylbenzenesulfonate is the most common); and (iii) the abrasive. Table 7.6 gives an example of a simple formulation.

Formulations containing bleaching agents. Certain additives, such as bleaching agents, complete these formulations, notably trichloroisocyanuric acid (TCCA) and Na or K dichloroisocyanurates (DCC).

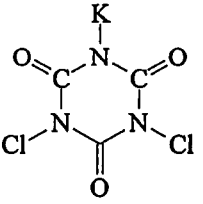
TCCA



Na DCC



K DDC



In water, the hydrolyzable N—Cl bonds liberate hypochlorite.

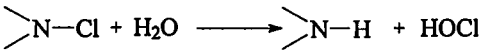


Table 7.7 gives possible bleach-containing formulations.

TABLE 7.7
Scouring Powder Formulations Containing Bleaching Agents[a]

Ingredient	(%)
Na dodecylbenzenesulfonate	2.5–5
Nonionics	0–4
Na carbonate	0–5
TCCA and/or	0.5–0.8
Na DCC or K DCC	0.8–2.5
STPP	0–10
Na orthophosphate	0–2
Abrasive, perfume	Balance

[a]Abbreviations: TCCA, trichloroisocyanuric acid; DCC, dichloroisocyanurates; STPP, sodium tripolyphosphate.

The chlorinating agents are sensitive to humidity; they can react with other organic compounds, and they can autodecompose. Research has tried to add stabilizing agents, such as certain olefins (e.g., general formulation R—CH = CHCl with a melting point of 150–300°C (7) or mercaptans (formula R—SH where R = C_{14}–C_{12}, alkyl, phenyl, or benzyl) (8) or Na anhydrous acetate (9). In addition to bleach, other ingredients may be included to improve cleaning power against specific soils and stains, e.g., calcium oxide or hydroxide, or solvents (tertiary alcohols) (10). Table 7.8 gives two examples.

There are ingredients that change color on contact with water. This is probably more useful for advertising purposes than for any real performance benefit. Green or blue phthalocyanine pigments can be used at low concentrations (0.005–0.05% by weight), which require a predispersion of the pigments in silicate, Na bicarbonate, Na silicate, and Na phosphate (11). The preparation requires care.

TABLE 7.8
Formulations of Scouring Powders with Bleaching Agents and Other Ingredients[a,b]

Ingredient	Formula A (%)	Formula B (%)
Na LAS	2.5	2.5
2,5-Dimethyl-2,5 hexanediol	—	1.5–3
Na carbonate	5–12	10–15
K carbonate	0–12	—
Na acetate	—	2–5
Ca oxide	0–0.6	—
Ca hydroxide	0.2–1	0.5–1.5
Na DCC/K DCC	0–1.5	0.8–1.5
TCCA	0–1	—
Na sulfate	—	1–2.5
Abrasive, perfume	Balance	Balance

[a]*Source:* Reference 10 (Procter & Gamble patent).
[b]Abbreviations: LAS, linear alkylbenzenesulfonate; DCC, dichloroisocyanurates; TCCA, trichloroisocyanuric acid.

TABLE 7.9
Early Scouring Powder Formulations[a]

Ingredient	A (%)	B (%)	C (%)	D (%)
STPP	11.3	13.3	16.7	0
Na dodecylbenzenesulfonate	0	5.3	3.3	8.3
Peanut oil potassium soap	1.6	0	2.7	6.7
Diethanolamide (lauric)	2.7	2.7	5	8.3
Water	Balance	Balance	Balance	Balance
Silica	25%	25%	40%	40%

[a]Abbreviation: STPP, sodium tripolyphosphate.

Scouring Creams

Scouring powders have gradually been replaced by more modern liquids, which allow more direct contact with soils. Because they already contain water, no caking problems are encountered and the products can easily be poured directly onto a cloth. Unilever was first to launch a liquid abrasive at the beginning of the 1970s. The first patents (12), published in the 1960s, included the following ingredients: (i) an alkaline phosphate (at least 8%); (ii) 0.5–3% tallow, coconut, or palm soap (Na or K) or 3–6% synthetic anionic detergent, or 1.5–8% of a mixture of synthetic detergent + soap + mono- or dialkylamide. Table 7.9 gives some formulations from that time.

Toward the end of the 1970s, Unilever (13) suggested suspending the abrasive in a three-dimensional network of tangled filaments of insoluble surfactant (such as sodium stearic, myristic, or palmitic acid at concentrations of 0.5–2% in the liquid). Table 7.10 gives the corresponding formula.

Unilever's third stage (14) was to replace this three-dimensional network by a micellar system that allowed solid particles to be held in suspension in water. This

TABLE 7.10
Formulation of a Scouring Cream with the Abrasive in Suspension[a]

Ingredient	(%)
Liquid base	
Na lauryl sulfate	1.8
Na stearate	1.5
Lauryldimethylamine oxide	0.6
Na sulfate	0.3
Na chloride	1.0
Na hypochlorite (aqueous solution)	6.0
Solid to be added to the liquid base	
Feldspar (quartz)	50
Water	Balance

[a]*Source:* Reference 13 (Unilever).

TABLE 7.11
A Scouring Cream Formulation Based on the Principle of Structured Liquids[a]

Ingredient	(%)
Na dodecyl sulfate	1.4–1.8
Alkyldimethylamine oxide (C_{12}–C_{14})	5.7–6.9
Na chloride	0–5.8
Na carbonate	0–5
Mg hydroxide	0–0.3
Ca hydroxide	0–0.3
Hypochlorite solution (15%)	7–10.5
Perfume	+
Calcite	50
Water	Balance

[a]*Source:* Reference 14 (Unilever).

is the principle underlying the structured liquids discussed at length in Chapter 4. This system is made up of surfactants, Na (C_{12-18}) alkyl sulfate or Na secondary (C_{12-18}) alkyl sulfate and a lauryl dimethylamine oxide, in certain proportions. Electrolytes are added (5–20% NaCl, for example), and possibly hypochlorite (1–3%), buffered by suspensions of calcium/magnesium oxides, and abrasive. Table 7.11 gives an example of this formulation.

Other improvements have subsequently been made to this type of technology, such as replacing nonionic surfactants by amphoteric surfactants (cocoamidopropyl dimethyl betaine) for detergency (15). Ammonia was used in place of hypochlorite (16); foam levels were optimized and rinsability was improved. Table 7.12 gives examples of such formulations.

TABLE 7.12
Improved Scouring Cream Formulations[a,b]

Ingredient	(%)
Na dodecylbenzenesulfonate	3–3.6
C_{9-11} alcohol-6EO	1–1.25
Coconut monoethanolamide	0–0.5
Na soap	0.2–0.75
STPP	0–2
Na carbonate	1–2.5
Calcite	50–55
Ammonia	0.04
Perfume	+
Preservative	+
Water	Balance

[a]*Source:* References 15 and 16.
[b]Abbreviations: EO, ethylene oxide; STPP, sodium tripolyphosphate.

TABLE 7.13
Scouring Cream Formulations with Thickening Agents[a,b]

Ingredient	A (%)	B (%)	C (%)	D (%)
Na paraffinsulfonates (C_{13}–C_{16})	1.5–3	—	—	—
LAS	—	1.5–3	—	1.5–3
Linear alcohol sulfate	—	1.5	—	3
Nonionics C_{12}–C_{14} (7EO)	—	0.2–0.8	—	0.5–1.5
Nonionics C_9–C_{11} (9EO)	0.2–0.8	—	0.5–1.5	—
α-Nonene	0.2–0.5	0.2–0.5	0.2–0.5	0.2–0.5
Na carbonate	1–4	2–4	—	2.5–4
Na citrate	1.5–4	—	—	—
STPP	—	1–3	3–5	—
Na pyrophosphate	—	—	—	3–8
Terpenes	3.5–4.5	1.5–3	3–4	3.5–4.5
Benzyl alcohol	2.5–3.5	1–2.5	1–2.5	2.5–3.5
Propanol	—	—	—	0.5–1.5
Clay (attapulgite/smectite)	—	—	3–8	—
Ca carbonate	15–25	15–25	15–25	—
Abrasive polymers	—	—	—	30–45
Natural gum	—	—	1–2.5	—
Polyacrylic acid	0.5–1	0.5–1	—	0.5–1
Water, perfume	Balance	Balance	Balance	Balance

[a]*Source:* Reference 17 (Procter & Gamble).
[b]Abbreviations: LAS, linear alkylbenzenesulfonate; EO, ethylene oxide; STPP, sodium tripolyphosphate.

The approach taken by Procter & Gamble (17) was to introduce a clay to form a colloid; this produced a viscous product in the bottle that becomes fluid when the bottle is shaken or squeezed. Later, the use of tertiary alcohols (see the section on scouring powders) increased detergency, assisted by terpene technology and a polar solvent. Table 7.13 lists four examples of formulations.

A number of other patents have now been published; in general, however, they are based on one or another of the above two technologies, i.e., Unilever's structured liquid or the Procter & Gamble method of using thickening agents, such as clays, xanthan gum, and polyacrylates.

Other Cleaners

Chlorinated Products

Hypochlorite. "Bleach," which was discovered more than two centuries ago, still has a good future, whether as a hypochlorite solution (used in Europe and developing countries where the markets are growing fast), or as a more complete product adapted to the needs of consumers in developed countries. In this chapter, we will examine the latter category. The first chlorinated products with surfactants and per-

fume appeared on European markets in the 1970s. These were high-viscosity products, which maximized contact time with the surfaces to be cleaned or disinfected. Subsequently, other forms appeared, including less viscous products sold in bottles with a trigger.

Efficacy of hypochlorite. This universal product has the following three advantages:

1. It "breaks" protein, grease, and carbohydrate molecules into smaller groups, which can then be removed by water + detergent. Hypochlorite helps detergency in this way and also stops the redeposition of soils.
2. It decolorizes most natural and synthetic colorants, as well as mildew stains.
3. It is one of the fastest acting, effective, and economical antimicrobial agents. It is therefore a very effective disinfectant for hard surfaces (e.g., kitchen or bathroom), removing soils and preventing them from becoming a breeding ground for microorganisms.

Liquid Chlorinated Products. Domestos (Unilever) is one of the main representatives of this type of product. A thickening system can be used to formulate a viscous chlorinated liquid, i.e., lauryldimethylamine oxide and a saturated soap such as Na laurate (ratio 80:20 to 60:40). This system (18) gives finished product viscosities of between 10 and 150 mPa · s at 21 s^{-1}. To formulate a yet more viscous product, either the thickening system has to be increased (and with it the cost), or an alternative system has to be manufactured "on site," using amine oxide in combination with a lauric ester (19). The resulting viscosities are between 100 and 500 mPa · s (21 s^{-1}). A further improvement on this method (20) is to include C_{12-14} alcohol-2-3EO sulfate in the thickening system to avoid a drop in viscosity during storage, particularly at high temperatures.

The weight ratios of amine oxides to soap and ether sulfate are ~65–70: 10–15:15–25, respectively. Table 7.14 gives examples of these formulations.

Properties. The cloud point of liquid chlorinated products is between 40 and 60°C. Viscosity (without isopropyl laurate) is >200 mPa · s at 21 s^{-1} initially, then

TABLE 7.14
Chlorinated Liquid Products

Ingredient	(%)
Lauryldimethylamine oxide	1–1.5
Na laurate	0.3–0.6
Isopropyl laurate	0–0.1
Na hydroxide	0.5–1
Na hypochlorite	5–12
Perfume	+
Demineralized water	Balance

210 mPa · s at 21 s^{-1} after 1 month (but passing through a peak of 300 mPa · s at 21 s^{-1}). With isopropyl laurate, initial viscosity is low (20 mPa · s), with a peak of ~270 mPa · s after ~10–12 d; then it drops again to ~240 mPa · s at 21 s^{-1} after ~1 month.

> **Comment**
> The big problem for the formulator is to find colorants and perfumes that are compatible with hypochlorite.

Toilet Cleaners

The following three types of products can be used in toilets: (i) products not permanently attached to the bowl (powders or liquids); (ii) "blocks" that are placed in the tank; and (iii) blocks that are attached below the rim of the bowl.

Products Outside the Bowl. These include powders, hypochlorite-based liquids, and acid-based liquids. Traditional powders generally contain mineral salts and give an acid reaction when in solution. Rather than use the salts as powders, they are granulated whenever possible. Adding sodium bicarbonate can produce foam in water. Detergents, oxidizing agents (Na perborate, persulfate, and trichloroisocyanuric acid) and sodium chloride (slight germicidal activity) can be added to these basic raw materials as well. Table 7.15 gives two possible formulations.

Hypochlorite-based products. These are identical with those described previously under "Chlorinated Products." Their use in toilets is quite appropriate because they are ideal germicides. By eliminating bacteria, they also eliminate odors. They also decolorize all colored organic deposits. In addition, their viscosity allows them to cling, even to vertical surfaces, and thus their efficacy.

Acid-based liquids. By destroying calcium deposits, acid liquids prevent the accumulation of stains and bacterial colonies on these deposits. The oldest of these products were formulated with highly effective hydrochloric or phosphoric acids. More recently, formulations have been "softened," because frequent cleaning has removed the need for aggressive action. For this reason, organic acids such as citric or

TABLE 7.15
Traditional Powder Toilet Cleaner Formulations

Ingredient	Formula A (%)	Formula B (%)
Na bisulfate	60–85	40–60
Na chloride	0–5	—
Na lauryl sulfate	0–1	0–2
Na sulfate	5–12	20–30
Na bicarbonate	8–15	5–12
Sulfamic acid	—	10–20

TABLE 7.16
Acid-Based Liquid Toilet Cleaner Formulations

Ingredient	(%)	(%)	(%)	(%)	(%)
Hydrochloric acid	10–20	20–30	—	25–35	—
Citric acid	—	1–4	—	—	—
Phosphoric acid	—	—	—	—	10–15
Glycol ether (solvent)	—	—	3–8	—	—
Sulfamic acid	—	—	10–20	—	—
Ammonium chloride	0.5–1.5	0.5–1.5	—	—	—
Na silicate	—	—	—	5–15	—
Nonionics	15–22	1–3	5–15	1–3	10–15
Perfume	+	+	+	+	+
Colorants	+	+	+	+	+
Water	Balance	Balance	Balance	Balance	Balance

sulfamic acids are used. Other ingredients include surfactants, solvents, thickeners, corrosion inhibitors, colorants, perfume, and abrasives. Examples of these formulations are given in Table 7.16.

To thicken an acid liquid and improve its performance while avoiding accidental product release, two types of thickening agents are available, i.e., organic and inorganic:

- We know that a formulation can be thickened by mixing ethoxylated nonionics wth the corresponding acids (21);
- viscosities of ~350 mPa · s (21 s^{-1}), which can be obtained by including methylhydroxypropyl cellulose (22); and
- xanthan gum can also be used (23).

With inorganic thickening agents, gels can be made using colloidal silica and stabilized with quaternary ammonium salts (for which the germicidal action is a "plus"). Tables 7.17 and 7.18 give sample formulations of organic and inorganic thickening agents, respectively.

TABLE 7.17
Liquid Toilet Cleaner Formulations with Organic Thickening Agents

Ingredient	(%)
Xanthan gum	0.05–0.15
Sulfamic acid	5–12
Nonionics	1.5–3
Perfume	+
Colorant	+
Water	Balance

TABLE 7.18
Liquid Toilet Cleaner Formulations with Inorganic Thickening Agents

Ingredient	(%)
Hydrochloric acid	25–35
Na chloride	5–8
Alkyldimethylethylammonium chloride	0.2–0.6
Colloidal silica	3–5
Perfume	+
Water	Balance

Blocks for the toilet tank. These blocks are usually totally immersed and "treat" the water before it goes into the bowl. The major problem with this type of product lies in the choice of process to make them, i.e., extrusion, compression, or molding, and also whether to hold the product in the tank—freely or in a special container. A block that floats freely in the water must have limited solubility. Examples of the simplest formulations (blocks in containers) are given in Table 7.19.

Unlike other products, toilet blocks contain very high levels of colorants (several %) and perfume (≥10–15%). Several Procter & Gamble patents (24) disclose methods for increasing the life of a block using Na carbonate and coconut fatty alcohols. Examples of formulations are given in Table 7.20.

Free-floating blocks in the tank. The speed at which the block dissolves can be controlled by a balanced combination of hydrophobic and hydrophilic components, and the surface of the block can be "gelled" with the use of carboxymethylcellulose. The formulations in Table 7.21 include a disinfectant (hypochlorite) and perfume (25).

Blocks for Attachment to the Toilet Bowl. These blocks are held in a plastic grill-like basket, which is placed under the rim of the bowl where it is flooded, thus liberating a small amount of product each time the bowl is flushed. Their main functions are to clean and to give off a pleasant fragrance. Ingredients include perfume (5–10%), surfactants to prevent calcium deposits and provide foam, colorants, builders (STPP), and other ingredients such as sodium sulfate to reduce cost. Blocks can be manufactured by molding or extrusion.

TABLE 7.19
Formulations of Blocks for the Toilet Tank

Ingredient	(%)	(%)
Na paraffinsulfonate	70–85	—
Hypochlorite (Ca/lithium)	—	60–70
Chlorides	1.5–5	20–35
Sulfate	—	5–15
Colorant	+	+
Perfume	+	+

TABLE 7.20
Formulations of Longer Lasting Blocks for the Toilet Tank[a]

Ingredient	(%)
Mg lauryl sulfate	50–65
Na carbonate	1–3
Na sulfate	10–20
Coconut fatty alcohol	4–8
Na chloride	0.2–0.5
Colorant	+
Perfume	+
Water	Balance

[a]*Source:* Reference 24 (Procter & Gamble).

Molding. The mixture is heated to 60°C or more, then cooled in molds. This is the oldest process, though it has two major drawbacks: (i) a maximum of only 15% of anionics can be used, this ingredient is both inexpensive and foams well (ideal characteristics for this type of product); and (ii) a batch manufacturing process is needed.

Extrusion. This method allows the use of up to 80% anionics. The major problem with this method is that products containing >60% anionics are sensitive to humidity, with the risk that the product will turn into a sticky mixture. The manufacturing process has to be exact (slow addition of small quantities of water in the pulverization step), the temperature has to be watched, and homogenization has to be perfect after extrusion. Tables 7.22–7.24 give examples of a molded product, a specialty product, and an extruded product, respectively.

TABLE 7.21
Formulations of Free-Floating Blocks for the Toilet Tank[a,b]

Ingredient	A (%)	B (%)	C (%)	D (%)
Ethoxylated cetyl stearyl alcohol (6 EO)	80–95	—	35–55	35–55
Ethoxylated monoethanolamide (coconut)	—	25–35	—	—
Diethanolamide (coconut)	—	10–25	—	—
Na dodecylbenzenesulfonate	3–8	—	—	—
Na isooctylbenzenesulfonate	—	—	35–55	—
Ethoxylated dodecyl alcohol (50 EO)	—	—	—	35–55
Ethoxylated tallow alcohol (50 EO)	—	40–60	—	—
2,4,4-Trichloro-2-hydroxy diphenyl ether	—	—	3–8	1–4
Ca hypochlorite	—	3–8	—	—
Colorant	+	+	+	+
Perfume	—	—	—	+

[a]*Source:* Reference 25.
[b]Abbreviation: EO, ethylene oxide.

TABLE 7.22
Formulation of a Molded Block Product

Ingredient	(%)
Alkanolamide	15–35
Ethylene oxide/propylene oxide copolymer	50–65
Na dodecylbenzenesulfonate	0–10
Na bicarbonate	0–25
Perfume	+
Paradichlorobenzene	3–6

TABLE 7.23
A Block Formation with Added Calcium Chloride[a,b]

Ingredient	(%)
Alkyl ether sulfate C_{12-16}-3EO	19–21
Polyethylene glycol (MW 8500)	17–37
Monoethanolamide (coconut)	0–10
Calcium chloride	3–4
Paradichlorobenzene	20–50
Colorant	+
Perfume	+

[a]*Source:* Reference 26 (L'Oreal) suggests the addition of calcium chloride to avoid free water in the mixture.
[b]Abbreviation: EO, ethylene oxide.

Window Cleaning Products

Even more than for other cleaning products, the efficacy of a window cleaning product can be judged immediately from any traces left on glass or mirrors. These products are sold in liquid form (for the very good reason that the formulations contain a high level of water!) and are packed in bottles with a trigger for greater ease of use. The high water levels in these formulations make it unnecessary to dilute them with tap water, which could cause bad results (traces). The product has to wet the surface to be cleaned properly, and then it has to dry without forming large drops (at >25 μm, drops will diffract visible light when they dry, leaving visible streaks and stains). The wetting effect is achieved by the surfactant, whereas the cleaning itself is performed by a solvent that has to be dosed precisely to avoid damage to painted surfaces, for example.

The Choice of Surfactants. The choice of surfactants is important. Products such as ethoxylated tallow alcohol-18EO can help avoid traces; others such as primary linear alcohol C_{9-11}-5EO may leave limited traces; secondary linear C_{14-15} alcohol-7EO will leave traces, and primary linear C_{12-14} alcohol-3EO will be disastrous. Solvents (0.1–15% maximum), such as isopropanol or glycol ether, can be used. Table 7.25 gives possible formulations.

TABLE 7.24
Example of an Extruded Block Product[b]

Ingredient		(%)
Monoethanolamide (coconut)	(1)[c]	18
Ethylene oxide/propylene oxide copolymer		10
Na sulfate	(2)[c]	30–40
Na LAS		62
Na PAS		—
Na pyrophosphate	(3)[c]	10
Polyethylene glycol		—
Colorants		+
Perfume		+

[a]Abbreviations: LAS, linear alkylbenzenesulfonate; PAS, primary alcohol sulfate.
[b]*Source:* Reference 27.
[c](1) Alkanolamides are foam stabilizers; (2) sulfate reduces the cost of the formula; (3) phosphates reduce limestone.

Improvements. The use of a water-soluble substance that leaves an invisible film may provide anticondensation properties on the treated surface. This substance will prevent water from condensing into innumerable drops by forming an even layer on the glass. An example of such a substance is polyethylene glycol (PEG) (28). Certain high-molecular-weight (20,000) PEGs are not just lubricants: They have a greater affinity for glass than for the oily soil/dust; as a result, they facilitate the transfer of the soil onto the cleaning cloth and reduce the risk of leaving traces (29). Clorox (30), in one of their patents, described how polyvinyl alcohol (or polyvinyl alcohol + cationic polymers) can be used to formulate products that drain evenly from the surface of glass. For example, a mixture of trimethylolmelamine + polyvinyl alcohol can be used, which is catalyzed by acid to form a polymer with the following structure:

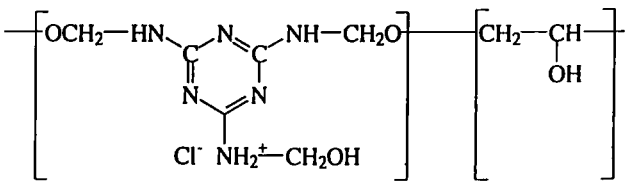


TABLE 7.25
Window Cleaner Formulations, Including Surfactants and Solvents[a]

Ingredient	(%)
Tallow alcohol-18EO	0.05–1.5
Isopropanol	5–15
Ammonia	to adjust the pH to ~10
Deionized water	Balance

[a]Abbreviation: EO, ethylene oxide.

TABLE 7.26
Formulation of a Window Cleaning Formula for Even Draining

Ingredient	(%)
Trimethylolmelamine	0.1
HCl 38%	0.04
Polyvinyl alcohol	0.4
Nonionics	0–0.5
Water	Balance

TABLE 7.27
Formulation of a Window Cleaning Product with Polymers of Acrylic Acid[a]

Ingredient	(%)
Wetting agent (e.g., Fluorad FC-120, 3M)	0.01
LAS acid	0.25
Ammonia	0.20
Isopropanol (solvent)	5.00
Propylene glycol methyl ether (solvent)	2.00
Carbopol EDT 2623[b]	0.10
Deionized water	Balance

[a]Abbreviation: LAS, linear alkylbenzenesulfonate.
[b]*Source:* Reference 31 (Goodrich).

The theory is that cationic structures fix themselves onto the Si-OH groups of glass. Because the polymer is hydrophilic, draining is even. Table 7.26 gives a sample formulation.

Other polymers, such as Goodrich's "Carbopol" (31), can improve the performance of window cleaning products. Carbopols are high molecular weight cross-linked polymers of acrylic acid. They act as agents with the following tasks:

(i) to thicken;

(ii) to keep solid particles in suspension; and

(iii) to stabilize certain liquids.

Table 7.27 gives an example of one formulation. The presence of Carbopol in the formulation allows droplets of the product to adhere to the window surface. It provides better contact between the detergent and the window, and makes it easier for the consumer to use.

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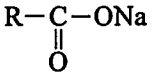
CHAPTER 8

Skin Care Products

Toilet Soaps

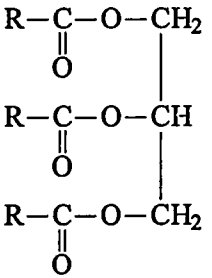
Raw Materials

In this discussion, we will use the following formula for soap:



where R is the total number of carbon atoms. In general, this varies between 6 and 20 (two by two). There are also fatty acids whose structure includes one or several double bonds. For example, the most widely used unsaturated fatty acids are those containing 18 carbon atoms in total.

Fatty matter and oils, whether animal or vegetable, are made up of *triglycerides,* which are compounds formed from three molecules of fatty acid and one molecule of glycerol. Their formula is as follows:



"Glycerol" is the name of a pure product. "Glycerine" is the name given to all impure forms of glycerol (e.g., glycerol in solution). Fatty acid chains of triglyceride can be either all of the same or of different length, which is characteristic of animal and vegetable fats. This does not matter in the case of soaps because the fatty acids are separated from glycerol; in some industries, however, particularly the food industry, the type of molecule (fatty acid composition) will determine the physical properties of the finished product (chocolate or margarine, for example).

Raw Materials Used in Soap Making. The main raw materials include tallow (beef and sheep) and coconut oil. The fruit of the coconut tree is much larger than the fruit of the palm tree. The coconut is green, becoming brown on drying. It is the nut of the fruit that is used to make oil (Fig. 8.1). Areas of cultivation include the Solomon Islands and the Philippines.

Fig. 8.1. Photograph of the coconut tree and coconuts.

Other raw materials include palm oil, which is obtained from the skin of the palm fruit, and palm kernel oil, which is obtained from the kernel of the palm fruit. Areas of cultivation include Colombia, the Ivory Coast, Ghana, the Congo, Thailand, and Malaysia (Fig. 8.2).

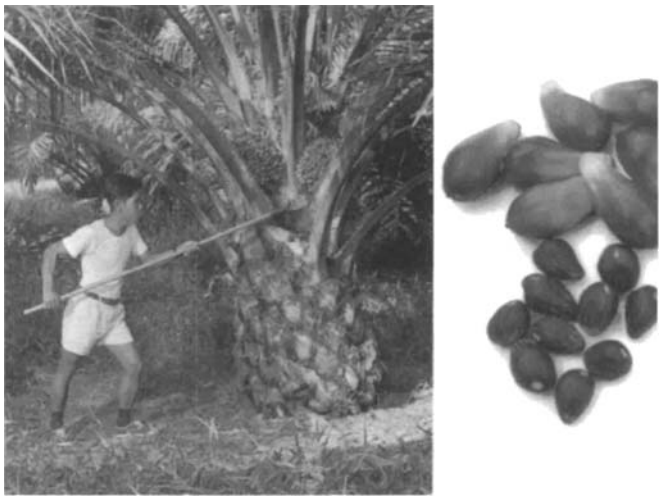


Fig. 8.2. Photograph of the palm tree and its fruit.

In Europe and in the United States, a mixture of tallow and coconut oil is generally used. Palm oil and palm kernel oil are used more frequently in the producing areas, such as Africa and Southeast Asia. Each fat is made up of fatty acids of different chain lengths (summarized in Table 8.1). The table shows that coconut and palm kernel oil are rich in C_{12} (few long chains); tallow and palm oil do not contain C_{12} chains, but a mixture of longer saturated and unsaturated chains.

Soaps are generally made from the following mixtures: tallow/coconut, tallow/palm kernel oil, palm oil/coconut, and palm oil/palm kernel oil, with 10–40% of coconut or palm kernel oil (usually ~20%) and 60–90% of tallow or palm oil. Taking as an example an 80:20 mix of palm oil and coconut, the soap produced will have a mixture of fatty acids split approximately as shown in Table 8.2.

The choice of a specific mixture will affect the quality of the final soap. For example, short-chain fatty acids are more soluble; they yield soaps that are more foaming, more irritating to skin, and that wear faster. A compromise must be found to obtain a mixture which satisfies the desired performance/cost criteria.

Preparation of Raw Materials

Prior to utilization in making soap, the untreated raw materials go through the twin processes of bleaching and deodorizing.

Bleaching. The first step in bleaching oils is vacuum drying at high temperature (90°C). The vacuum helps to avoid oxidation and consequent deterioration. Once the water has been removed, bleaching earth is added in the form of a natural clay called montmorillonite. Its granulometry provides a very large exchange surface of ~150–300 m^2/g! When this clay is exposed to dilute acid, either before drying or during bleaching of the oil, some of its aluminum atoms are dissolved, leaving "holes" in the structure. Impurities such as dust, color, and various odors in the oil are absorbed into the holes. This stage is completed by adding 5% of bleaching earth to the dried oil. The mixture is agitated at 90°C for 15–30 min. After slight cooling to 70°C, which reduces the solubility of certain contaminants, the mixture is pumped through filter presses.

Deodorizing. To obtain a perfect oil of almost edible quality, the next operation uses steam under vacuum to remove all odors that could give the finished product an unpleasant smell (rancidity). The pure oil is now ready to be transformed into soap. The soap-making process is described in Chapter 12. Here we will deal only with the principles of converting fats into soap.

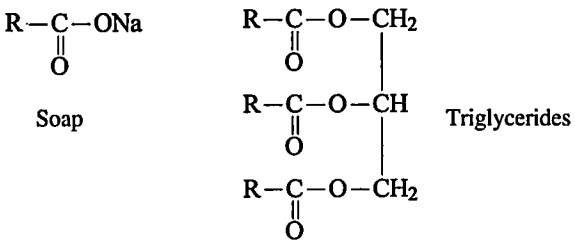


TABLE 8.1
Average Composition of the Main Fats Used in Soap Making

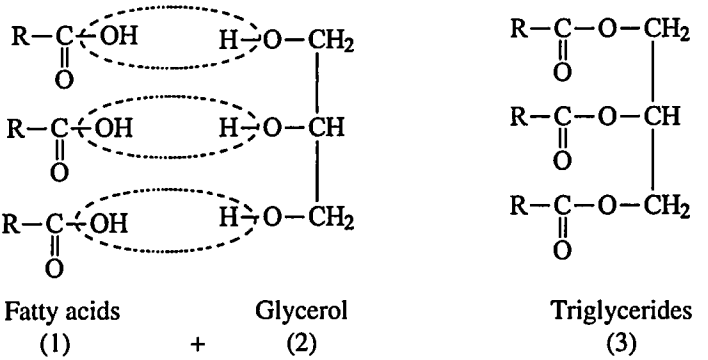
Chain length (average)	$<C_{10}$ (%)	C_{10} (%)	C_{12} (%)	C_{14} (%)	C_{16} (%)	C_{16} (%)	C_{16} with 1 =[a] (%)	C_{18} (%)	C_{18} with 1 = (%)	C_{20} with 2 = (%)	C_{20} with 1 = (%)	C_{20} Saturated (%)	C_{20} Unsaturated (%)
Common name	—	Capric	Lauric	Myristic	Palmitic	Palmitoleic	Stearic	Oleic	Linoleic	Arachidonic	Gadoleic	—	—
Coconut oil	9.5	6	47	18	9.4	0.1	2	5.5	2.5	0	0	0	0
Palm kernel oil	3.5	3	47	16.2	8.6	0.2	2.3	16.1	3.1	0	0	0	0
Tallow	0	0	0	3.4	25.6	4.7	22.3	38.4	3.2	0.5	0.5	0.5	0.1
Palm oil	0	0	0	1.4	56.9	0.4	5.1	28.5	7.2	0.1	0.1	0.1	0.1

[a]1 = indicates one double bond; 2 = indicates two double bonds.

TABLE 8.2
Fatty Acids for an 80:20 Mixture of Palm Oil and Coconut

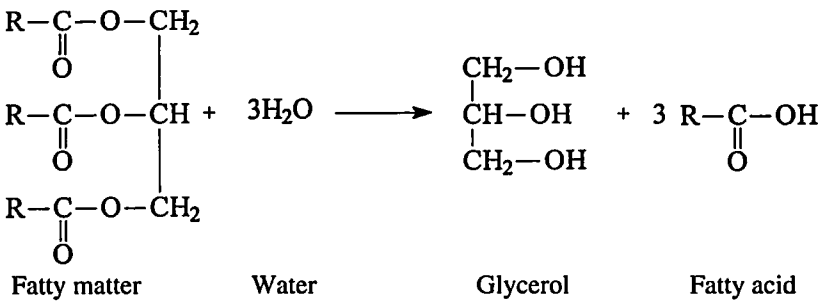
Chain length	$<C_{10}$	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}	C_{18} 1 =	C_{18} 2 =
(%)	2	1.3	9.5	4.4	36.6	4.6	32.5	9
	Short-chain saturated fatty acids			Long-chain saturated fatty acids			Long-chain unsaturated fatty acids	

To understand the reaction that will make soap and glycerol from triglycerides, we list below the structure of three essential molecules:



The difference between (3) and (1) + (2) is three molecules of water. It would suffice to insert three water molecules into the triglyceride molecular structure to "break up" the triglyceride into three fatty acid molecules and one glycerol molecule. The fatty acids are then neutralized with caustic soda to give soap.

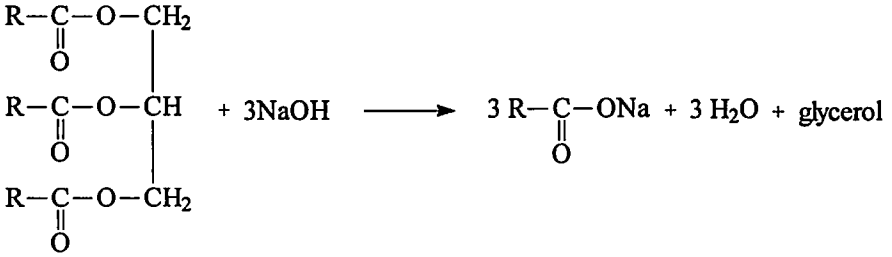
There are two ways to make soap. The first way is to heat water and fats to a high temperature under strong pressure (250°C at 50 atm).



The reaction takes place using an excess of water to separate glycerine (glycerol + water) from the insoluble fatty acids. The fatty acids are then purified by distillation

for use by the soap maker (neutralization of fatty acids with caustic soda). The manufacture and purification of fatty acids constitutes a difficult industrial process that can be accomplished only by manufacturers of fats and their derivatives.

The second process uses less energy because only 100°C is required at atmospheric pressure. The fats are boiled directly with a caustic soda solution, and the fatty acids formed react immediately to form soap.



Glycerine must then be separated from soap by a complex operation because the solution is relatively well mixed. Nevertheless, this is the process generally used by the large soap companies.

Direct Manufacture of Soap from Fats (Direct Saponification). Figure 8.3 outlines the different stages for converting fats into soap. The mixing step can be conducted either with bleached and deodorized oil or, preferably, with crude oil which is bleached and deodorized after mixing.

Bleaching/deodorizing. This stage was described under "raw materials." Contaminants such as carotene, blood, mucilage, or chlorophyll are removed from the oil itself, along with external impurities such as water, rust, or dust.

Saponification. The manufacture of soap paste (saponification) is done in the same way; the mixtures of soap, water, and electrolytes differ greatly depending on their relative concentrations. Different forms can coexist (known and defined as "phases"). In particular, we can distinguish the following:

(i) the *niger* (low concentrations of soap and electrolytes), an isotropic solution;

(ii) at higher concentrations of soap and low electrolyte concentrations, *neat soap*, which becomes "household soap" after cooling; and

(iii) *crude soap*, resulting from a phase in equilibrium produced at high concentrations of NaCl.

To express the percentage of fatty acids in a soap, the following calculation is used: Given pure fatty acids (FA) with a molecular weight (100% FA) = M_1 and pure soap corresponding to a molecular weight of M_2, the percentage of fatty acids in the soap will be as follows:

$$M_1/M_2 \times 100 \times \% \text{ pure soap in the product}$$
given that $M_2 - M_1 = 22$.

$$R-COO-(H) \longrightarrow R-COO-(Na)$$
$$-1 \qquad +23$$

For example, if $M_1 = 256$ and $M_2 = 278$, the anhydrous soap will contain $256/278 \times 100 = 92\%$ fatty acid. A 60% soap will contain $60/100 \times 256/278 \times 100 = 55.3\%$ fatty acids.

Washing. The next stage separates glycerine from soap, based on the principle that glycerol is soluble in brine (a salt solution), whereas soap is not. Washing also eliminates most colored impurities. Washing is done by mixing soap with a given volume of brine, using steam jets for agitation. After a few hours at rest, the soap rises to the top of the kettle, and the glycerine/brine mixture sinks to the bottom. This operation is repeated three times, on average, using cold brine to remove all the glycerine from the soap (the mixture brine + glycerine is called spent lye).

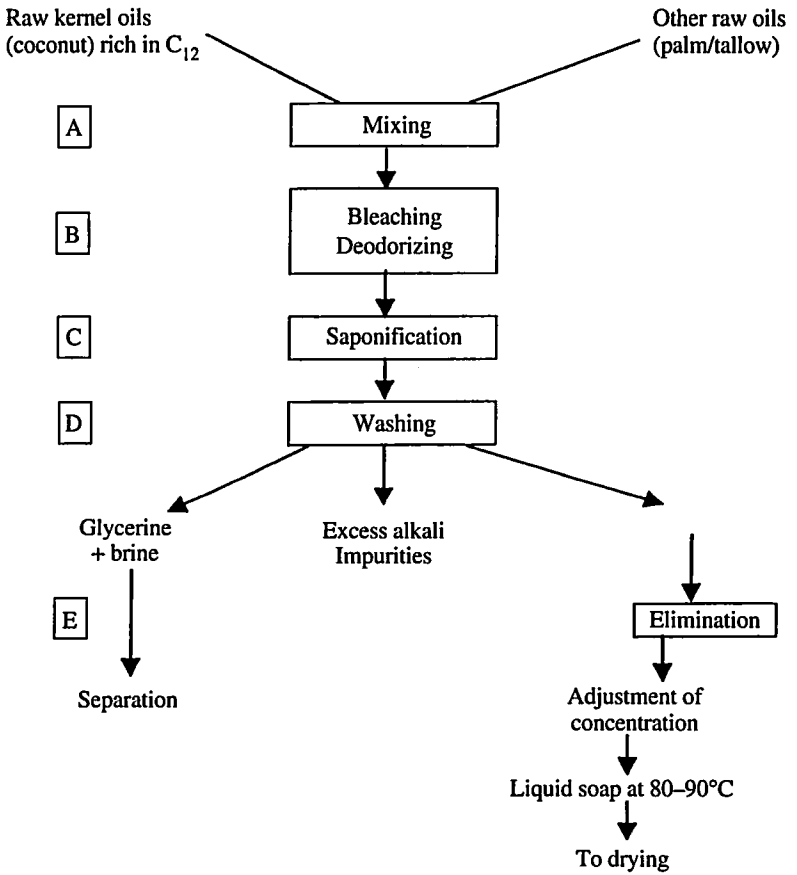


Fig. 8.3. Different stages in making soap by direct saponification.

Dilution. The recovered solution of brine + glycerine (spent lye) is sent for evaporation to recover glycerine for sale and salt for reuse.

Fitting. At this stage, the soap still contains a lot of salt that would harm its performance if left untreated. The finishing process reduces the amount of salt, removes residual colored impurities, and concentrates the soap solution. The process consists of vigorously mixing the soap solution with a given amount of dilute caustic soda. Depending on the amount of NaOH, this yields the following:

(i) a top layer of neat soap (63% fatty acids); and
(ii) below, either a mixture of water-salt-caustic-impurities (without soap) or a niger containing up to 25–30% of soap, salt, caustic, and impurities.

In modern soap making equipment (Mazzoni, Ballestra) this operation is part of the process and is no longer needed as a separate step.

Soap Making by Fatty Acid Neutralization. As we have already seen, this method is less common than the one described above. Its disadvantages include its cost (stainless steel equipment) and the fact that it produces very large quantities of fatty acids that only large manufacturers can handle. It also has considerable advantages. It is simple (see Fig. 8.4); there is no need for the washing and finishing steps; and it is flexible, particularly because the fat charges can be changed quickly.

Drying of Soap Paste

The paste obtained by one or the other of the processes described above is dried in a vacuum evaporator. The solution is heated to 140°C under pressure (2–3 atm), and then flash-dried in a vacuum chamber (~40 mm Hg). Under these particular conditions, the soap does not boil, but when the superheated steam reaches the vacuum

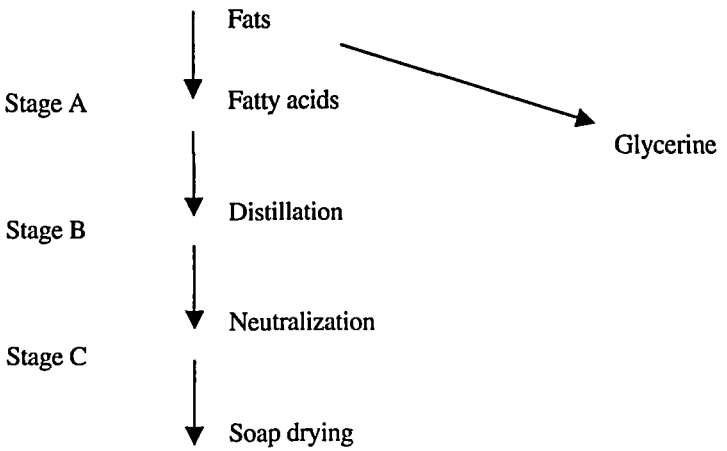


Fig. 8.4. Manufacture of soap by neutralization of fatty acids.

chamber, it boils instantly. The steam produced is extracted by the vacuum system, leaving dried soap at a temperature of ~50°C and still containing ~12–14% water. The lower part of the vacuum chamber consists of an extruder, for making soap "noodles" which are subsequently compressed and shaped into bars of soap.

Domestic "Household Soap". The old household soap was simply a 63% fatty acid neat soap that was cooled and cut into bars. Today, regardless of the type of soap, the process consists of drying by evaporation under vacuum, but under different conditions. Because soap contains more water, the temperature has to be quite low to be able to extrude and cut the soap without problem. To achieve this, a vacuum of 15–20 mm Hg is generally used.

Superfatted Soaps. To improve the foam and feel, soap can be "superfatted" by adding "free" fatty acids (not already present in the soap itself). Moreover, these free fatty acids will neutralize any residual caustic soda. The percentage of free fatty acids is usually ~5%, added into the soap paste under high pressure and before flash-drying.

> **Comments**
> In the same way, preservatives and antioxidants (sequestrants) can be injected into the soap to avoid negative effects from machinery. For example, the presence of copper or iron can cause discoloration and unpleasant smells (catalytic oxidation).

Formulation

Classical Toilet Soaps. Table 8.3 gives formulations of toilet soaps found in the trade.

TABLE 8.3
Formulations of Classical Toilet Soaps

	Non-superfatted soap (%)	Superfatted soap (%)
Nominal composition of fats	80–20 (palm/palm kernel)	65–35 (tallow/coconut)
Na soap	83–88	80–85
Free fatty acids	—	4–6
Preservatives		
Na EDTA	0.015–0.030	0.015–0.030
EHDP[a]	0.010–0.025	0.010–0.025
Orthophosphoric acid	0.1–0.2	0.1–0.2
Colorants	+	+
Opacifiers (titanium oxide)	0.1–0.7	0.1–0.7
Brighteners	+	+
Perfume	+	+
Water, salts	Balance	Balance

[a]EHDP, ethanehydroxydiphosphonates (e.g., Dequest 2016, Solutia).

Specific Soaps. We have already discussed classical household and toilet soaps, and superfatted soaps. Other types of soaps include the following:

1. Soap flakes, obtained by forcing soap chips through a rolling mill to form a fine film that is then broken into flakes.
2. Soft soap is a specific physical balance of potassium and unsaturated oils.
3. Liquid soaps (for dispensers). A selection of raw materials and additives can be used to make a concentrated but viscous liquid.

We will look in more detail at two special kinds of soaps, i.e., transparent soaps and germicidal soaps.

Transparent soaps. The basic principles involved in manufacturing a transparent or translucent soap on a normal production line are as follows:

(i) all raw materials should be as pure as possible;
(ii) no opacifying additives should be used;
(iii) certain conditions must be rigorously observed [saponification indices; the titer (melting range) of the fats; the percentage of electrolytes; drying and, in particular, temperature throughout the process (≈ 35°C)];
(iv) crystallization inhibitors must be added (sugar solutions, polyols, glycerine); and
(v) resin and/or castor oil is added to the fatty acid mixture.

Soap is opaque because soap molecules form long filament-shaped structures, particularly if the cooling process is long. By observing the conditions above, these structures will not form and crystallization will not take place. Two processes have been developed by Henkel (1) and Unilever (2), respectively.

In the Henkel process, a mixture of fatty acids is used (tallow/coconut/castor oil), which is saponified using pure caustic soda in the presence of resin to avoid the formation of crystals. The hot soap is cooled from ~100 to 20°C in a few seconds, and cold is maintained for the rest of the process (milling, extrusion, and so on).

A different technique using a classical manufacturing process without adding sugar, alcohol, or resins is described by Lever U.S. The process uses neat soap with its alkalinity reduced to ~0.03% by adding coconut fatty acids. Drying to ~20% humidity is followed by cooling on rollers, at ~27°C. The chips are mixed with water containing salt to obtain 22% water and 0.4% salt, and the temperature reaches 38.5°C. Rolling and vacuum extrusion, performed at <38°C, result in a water content of 19.8%.

It can be seen from these two examples that the production of a transparent soap requires great care in the process.

Other processes. Transparent soaps can also be produced without using classical processes, e.g., by mixing tallow and coconut oil, which is filtered at 80°C, and then adding castor oil. A mixture of caustic soda and alcohol is introduced and mixed with the oils, then cooled to <75°C until saponification is complete. After a certain rest time, glycerine is added with a sugar solution at 80°C. The addition of coconut oil reduces the free alkali (<0.15%); colorants and perfume are then added at <60°C. The mixture

TABLE 8.4
Formulation of Transparent Soaps

Ingredient	(%)	
Na soap	65–78	80 tallow:20 coconut in the charge
Polyethylene glycol	8–15	
Glycerol	2–10	
Free fatty acids	2–5	
Preservatives	+	
Colorants	+	
Perfume	+	
Water, salts[a]	Balance	

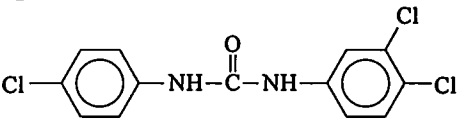
[a]<0.2% NaCl.

is poured into molds and dried quickly. Table 8.4 gives an example of the formulation of transparent soaps.

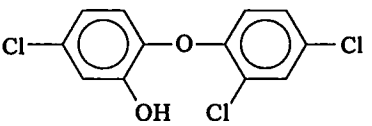
Antibacterial soaps. These are produced with the use of antibacterial agents such as Irgasan DP300 (Ciba-Geigy) or 3,4,4′-trichlorocarbanilide (TCC). TCC tends to be used less frequently because it can form trichloroanilines, which cause skin problems. For this reason, soap containing TCC cannot be recycled using heat. Irgasan DP300 has other disadvantages in that it tends to develop color under light. This phenomenon can be reduced by the presence of free alkali. Antibacterial soap formulations available in the trade are given in Table 8.5.

The chemical formulations of germicides are as follows:

TTC: 3,4,4′-trichlorocarbanilide
Empirical formula: $C_{13}H_{14}Cl_3N_2O$
Structure:



Irgasan DP300 (Ciba-Geigy): 2,4,4′-tricholoro-2′-hydroxydiphenyl ether
Empirical formula: $C_{12}H_7C_{13}O_2$
Structure:



Detergent Bars

The Main Ingredients and Their Functions

The main ingredients in detergent bars and their functions are listed in Table 8.6. The principal advantages of these bars are that, unlike toilet soap, they are not sensitive to calcium in hard water and they leave a certain feeling of softness on the skin (like shower gels and bath foams).

TABLE 8.5
Formulation of Germicidal Soaps[a]

Ingredient	A (%)	B (%)	C (%)
Nominal composition	Antibacterial = TCC + Irgasan 80:20 or 75:25 tallow/coconut palm/palm kernel	Antibacterial = TCC 80:20 or 75:25 palm/ coconut	Antibacterial = Irgasan 80:20 or 75:25 tallow/coconut palm/palm kernel
Na soap	75–85	80–85	85–88
Preservatives			
EDTA acid	0.01–0.05	0.01–0.05	0.02–0.05
EHDP acid	0.01–0.05	0.01–0.05	0.02–0.05
Orthophosphoric acid	0.005–0.015	0.005–0.015	0.1–0.2
Antibacterials			
TCC	0.1–0.5	0.03–0.1	—
Irgasan DP 300	0.1–0.5	—	0.1–0.5
Colorants	+	+	+
Perfume	+	+	+
Brighteners	+	+	+
Titanium oxide	+	+	+
Water, salts	Balance	Balance	Balance

[a]Abbreviations: TCC, 3,4,4'-trichlorocarbanilide; EHDP, ethanehydroxydiphosphonate.

Examples of Formulations

Examples are given in Table 8.7.

Comments

Antimicrobials can also be incorporated into detergent bars. As for toilet soaps, TCC and/or Irgasan DP300 can be used. Differently shaped bars can be made using the same finishing processes as toilet soaps, i.e., a manufacturing line including hoppers, mixers, plodders/extruders, and stamping presses with different molds.

TABLE 8.6
Main Ingredients in Detergent Bars and Their Function[a]

Ingredient	Function
Na cocoyl isethionate	Active (foam and cleaning)
Na linear alkylbenzenesulfonate	Speed and volume of foam
Anhydrous soap	Gives a creamy feel to the foam/plasticizer
Na isethionate	Hardener
Na stearate	Hardener
Stearic acid	Plasticizer, softness
Titanium oxide	Opacifier, whiteness
Mineral oil	For marketing, e.g., "bath oil"

[a]*Source:* References 3–5.

TABLE 8.7
Sample Formulations of Detergent Bars[a]

Ingredient	(%)
Na cocoyl isethionate	44–60
Na alkylbenzenesulfonate	0–2
Anhydrous soap	7–8
Na isethionate	2
Stearic acid	15–19
Na sulfate	5
Preservative + complexing agent	+
Titanium oxide	0.2
Water, perfume	Balance

[a]Unilever patents.

Bathroom Products: Shower Gels and Bath Foams

The First Products

Adding products to the bath is not new. Everyone can recall "bath salts," which were still in fashion not so many years ago. They colored and perfumed the water, making washing easier and softening the water. Their formulations are simple and include water softeners (sodium tripolyphosphate together with sodium sesquicarbonate to buffer the high alkalinity). Examples are given in Table 8.8.

These products are quite useful because they soften the water and thus improve the efficacy of soap. They also perfume the bath. Because of their alkalinity, they can be irritating to sensitive skin. There are more sophisticated versions with foam, and some even contain surfactants. Table 8.9 provides an example.

Bath oils have also been known for a long time. These can be divided into immiscible oils/nonemulsifiable in water and miscible/emulsifiable products. The first type, which is relatively rare, can be made by mixing castor oil with ethanol to make it fluid. A possible formulation is 30–80% castor oil, 10–60% ethanol, with the pres-

TABLE 8.8
Formulations of Early Bath Additives[a]

Ingredient	A (%)	B (%)	C (%)
STPP	45–55	45–55	—
Na sesquicarbonate	45–50	—	75–90
Na chloride	—	45–55	—
Borax	—	—	5–20
Perfume	+	+	+
Colorants	+	+	+

[a]Abbreviation: STPP, sodium tripolyphosphate.

TABLE 8.9
Bath Additives with Additional Ingredients

Ingredient	(%)
Na bicarbonate	40–50
Tartaric acid	35–45
Na hexametaphosphate	8–15
Carboxylmethylcellulose	1.5–3
Na lauryl sulfate	2.5–7
Perfume	+

ence of perfume and colorants. The bath oil is mixed with water using tap pressure; then a film floats to the surface and transfers itself to the skin during the bath. Synthetic esters, such as isopropyl myristate or palmitate, or butyl stearate, can also be used; all are easy to perfume and color. A possible formulation is ≥90% isopropyl myristate, 5–10% perfume, and colorant.

A second more popular type contains surfactants and water softeners. Originally, this type contained mainly sulfated oils (castor/soy, from 50 to 90%). More recently, a new generation of bath products has been launched.

Current Products: Shower Gels/Bath Foams

These products are very similar to shampoos, which will be discussed in detail in Chapter 9. There are two categories of shower/bath products, differentiated by users' preferences, i.e., whether or not they prefer the feeling of a fatty product that leaves the skin slippery after the bath or shower. The products in the first category, which do not contain soap, are favored in Europe and the United States; products in the second category are favored in Asia and contain soap. Table 8.10 gives two possible formulations.

TABLE 8.10
Formulation of Non-Soap Shower Gels/Bath Foams[a]

Ingredient	A (%)	B (%)
Na isethionate	9	5
Lauryl ether sulfate	—	2
Coco betaine	6	—
Cocamidopropyl betaine	—	8
Silicone oil	5	5
Jaguar C-13-S	0.1	0.1
Preservative	+	+
Perfume, water	Balance	Balance

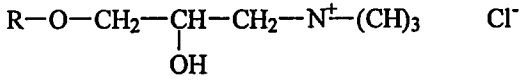
[a]*Source:* Reference 3.

TABLE 8.11
Formulation of Shower Gels/Bath Foams with Soap

Ingredient	Transparent base (%)	Opaque base (%)
Myristic acid	5–8	5–8
Lauric acid	5–8	5–8
Oleic acid	2–4.5	2–4.5
Glycerine	10–15	10–15
NaOH 45%	7–10	7–10
Formaldehyde	0.05–0.25	0.05–0.25
Cocoamidopropyl betaine	12–20	12–20
Silicone (emulsion) 60%	—	2–6
Na EDTA	0.05–0.15	0.05–0.15
BHT[a]	0.02–0.07	0.02–0.07
NaCl	+	+
Colorants	+	+
Perfume	+	+
Water	Balance	Balance

[a]BHT, butylated hydroxytoluene, is an antioxidant; its chemical structure is given in Chapter 9.

Jaguar C-13-S, present in these formulations, is a cationic guar gum derivative; it is guar hydroxypropyltrimethylammonium chloride with the following formula:



where R is a polysaccharide residue.

The second category of products contains the same ingredients as above but with soap in addition (myristate, oleate, laurate). Table 8.11 gives two different formulations.

References

1. Henkel, German Patent DE 574,927.
2. Unilever, U.S. Patent US 2,970,116.
3. Helliwell, J.F., Unilever, World Patent WO 9,403,151.
4. Madison, S.A., M. Massaro, G.B. Rattinger, and C. Wenzel, Unilever, World Patent WO 9,514,661.
5. Cherrey, M., D. Filiciano, and S. Wivell, Chesebrough Ponds, U.S. Patent US 5,441,671.

CHAPTER 9

Hair Care Products

Before considering the products themselves, some general points must be made about hair and its care.

The Problems of Hair

Introduction to the Structure of Hair

Shampoos are intended to clean hair. Hair grows from a tiny pit in the skin of the scalp, called the hair follicle (see Fig. 9.1).

Hair has two parts: (i) the bulb, flared at the bottom, enclosing the root (dermal papilla), which is rich in blood vessels; and (ii) the shaft, which is made up of three concentric layers. From the center out, they are the medulla, the cortex, which is the main component of hair, and the outer cuticle, made up of keratin. This is a scleroprotein consisting of a large number of amino acids, the main one being cysteine. The cells in the lower third of the hair follicle produce the keratin. The three layers are surrounded by two sheaths and an amorphous substance, which is a vitreous membrane (Fig. 9.2).

Each hair goes through three phases as follows:

1. Growth, which lasts about 3 years (anagan phase).
2. Transition, which lasts about 3 weeks, during which time the follicle is inactive (catagan phase).
3. Rest, when the dead hair falls out, pushed by a new young hair in its first phase (telogan phase) (Fig. 9.3).

Hair grows ~0.35 mm/day. It grows more quickly in summer than in winter, at night than by day, and women's hair grows more quickly than men's. Humans have between 100,000 and 150,000 hairs. In young people, 85% of the hair is in the growth

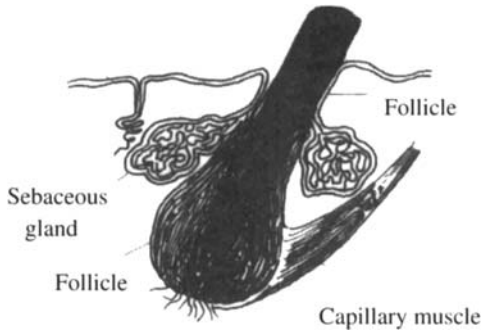


Fig. 9.1. Hair follicle.

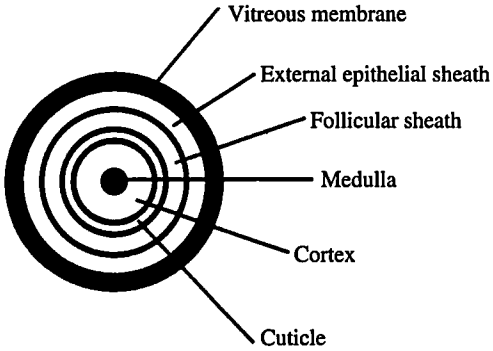


Fig. 9.2. Cross-section of a hair.

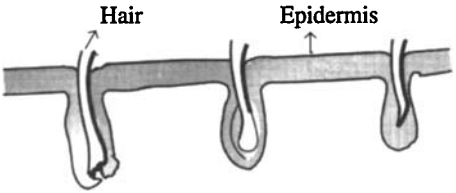


Fig. 9.3. The life of a hair.

phase, the number of dead hairs increasing with age. Loss of 50–100 hairs per day is normal. The total area of hair on a woman's head is between 4 and 8 m^2. This is the area that has to be cleaned, bearing in mind that hair's porosity can vary depending on exposure to the sun, the weather, and various chemical agents.

Hair Problems

If we examine a long hair in its entirety, we observe the following four conditions:

1. Near the root, the hair is new, thus it is in good condition. The ridges of the cuticles are even, completely covering the cortex (Fig. 9.4).
2. Five centimeters from the root, the hair is already older, and has been subjected to the effect of combs, brushes, and drying. The ridges of the cuticles are damaged and broken (Fig. 9.5).

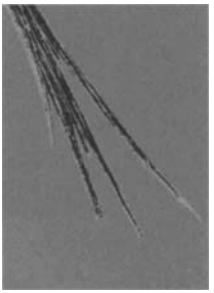


Fig. 9.4. A hair near the root.

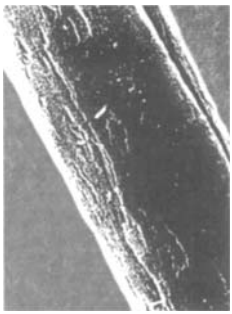


Fig. 9.5. A hair 5 cm from the root.

3. Toward the end of the hair, most of the cuticle has disappeared for the "mechanical" reasons given above and also as a result of exposure to chemicals or ultraviolet (UV) light. The cortex is now exposed (Fig. 9.6).
4. The end of the hair is in several parts; all of the cuticle is gone, the cortex is completely exposed and is easily broken (Fig. 9.7).

Other explanations for the fragility of hair include dirt and dandruff.

Hair Soil. Soil on hair is varied and comes from many sources. Sebum and its derivatives are the main components. Figure 9.8 shows the sebaceous gland that secretes sebum into the follicle.

The amount of this secretion changes with age, starting at a low level during childhood, increasing during adolescence, reaching its maximum in adulthood, and decreasing thereafter with age.

Other sources of soil include keratin debris from flaking of the scalp; proteins; organic and inorganic compounds from sweat; dust from the atmosphere; and remains from hair care products, including hair spray, gels, and other hair preparations. Sebum traps dust and debris from all sources and is the determining factor in the removal of soil from hair. Hair lipids constitute a complex mixture that changes according to sex, age, diet, and the seasons. The lipid mixture is subject to chemical changes, such as hydrolysis and oxidation, which change physical properties of the lipids, such as their consistency or their polarity. These are important factors in their capacity to resist removal.

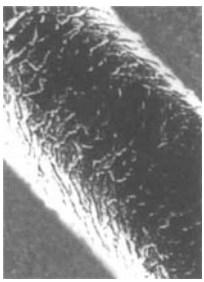


Fig. 9.6. Toward the end of a hair.

Fig. 9.7. The end of a hair.

Comments

Seborrhoea (a term used by dermatologists) refers to hypersecretion from the sebaceous glands. It occurs on the scalp, which takes on an oily appearance. Seborrhoea is somewhat responsible for the condition referred to as greasy hair. The cosmetic consequences are serious, as indicated in the following:

(i) hair becomes greasy too quickly;
(ii) greasy hair soils quickly through the accumulation of dust;
(iii) hairstyles do not last; and
(iv) peroxidation of sebum creates unpleasant odors.

Dandruff. It is normal for superficial cells from the horny layer (stratum corneum) of skin to deteriorate and cause numerous tiny fragments of keratin or invisible flakes (squama). Flaking becomes abnormal if visible flakes (dandruff) form. These flakes, grey or brownish in color, appear in the hair and fall onto clothes. The flakes can be washed away quickly, but they reappear very quickly. This condition is referred to as dry scalp, or dandruff. Dry scalp is related to age, i.e., it begins at puberty, accelerates to the age of 20–25 y, and then diminishes. It is more common in winter than summer, and 10–15% of the population (men and women) suffer from the problem.

The causes of dry scalp are not entirely clear. There are two possible explanations:

1. Fragility of the scalp, which causes abnormal flaking. In other words, if the surface layer of skin renews itself too quickly, there is greater cell loss, and the outcome is dandruff.

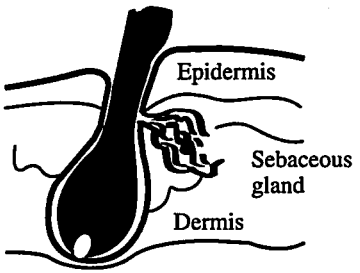


Fig. 9.8. The secretion of sebum by the sebaceous gland.

2. Abnormal proliferation of microbes and/or yeast because the scalp shelters an abundance of germs from the environment. These germs belong to three groups, i.e., aerobic and anaerobic bacteria, and, above all, yeasts (*Pityrosporum, P. ovale,* and *P. orculare*). Because the scalp is full of glands that secrete abundantly, it is a perfect environment for the growth of microorganisms. But these specific conditions seem to suit only *P. ovale*, which represent 75% of the microflora among dandruff sufferers, compared with 45% on normal scalps.

Shampoos

Ingredients and Their Function

The main job of a shampoo is to wash hair, i.e., to remove soils such as dust, grease, and the other dead cells discussed above. But a shampoo must have certain other properties to be competitive in the marketplace. Specifically, it must:

(i) dissolve easily whatever the water hardness, without forming precipitates;
(ii) clean well (in all water hardnesses) without excessive removal of oil (implying a surfactant that emulsifies well and has less pronounced wetting action);
(iii) leave hair supple, soft, easy to comb, and with less static;
(iv) foam quickly and abundantly (consumer need), but rinse away easily and not cause irritation (except very momentarily) if in contact with the eyes;
(v) perform well at neutral or slightly alkaline pH;
(vi) have a pleasant fragrance;
(vii) be nonirritating to the hands;
(viii) be nonirritating to the scalp;
(ix) be attractive in appearance (color, pearlescence, and a good viscosity); and
(x) (of course) be reasonably priced.

Certain shampoos are designed to help solve specific problems mentioned above, therapeutic and antidandruff shampoos, for instance. Meeting these different needs requires rigorous selection of raw materials, which is the next topic to be discussed.

Surfactants. In Chapter 1 we looked at the different surfactants used in detergents and personal care products, their physicochemical properties, and how they work. For more details of chemical structures, the reader should therefore refer to that chapter. Here we summarize the surfactants most frequently used in shampoos, along with their advantages and disadvantages. Clearly, no raw material is ideal, and none will meet 100% of the requirements. Nevertheless, good quality shampoos can be made from a variety of surfactants combined with additives. Table 9.1 gives an extensive listing of shampoo surfactants and their characteristics.

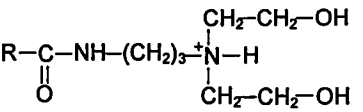
In this table, we present many types of surfactants, each with its own well-defined characteristics. Some manufacturers generally use only two kinds of surfactants, i.e., the main surfactant and a cosurfactant. Table 9.2 lists the characteristics of the most

TABLE 9.1
Shampoo Surfactants and Their Properties

Surfactant	Properties
Anionics	
Soaps	*Advantages*
	Inexpensive
Inorganic (Na, K)	Very little risk to eyes
Organic (alkanolamines)	Do not remove grease excessively
	Leave hair soft and manageable
	Good detergency and good foaming properties in soft water
	Disadvantages
	Alkaline solutions (dermatological problems)
	Sensitive to calcium, i.e., cleaning properties and foam reduced in hard water; calcium soap deposits = dull hair
Sulfonates	
Linear alkylbenzenesulfonate	*Advantages*
	Good degreasing (→ 3–4% for special "greasy hair" shampoos)
	No alkaline hydrolysis (sulfonic acids are strong)
	Inexpensive
α-Olein sulfonates	*Advantages*
	Good stability at low pH
	Good tolerance to hard water
	Foam well in the presence of sebum
	Low cloud point
	Good solubilization properties
	Little color
	Little odor
	Generally not irritating to skin
Sulfosuccinates	*Advantages*
	Good detergency
	Good foaming properties
	Very mild on the skin
	Nonirritating (eyes)
	Disadvantages
	The ester group tends to hydrolyze
	Best used at a pH of ~6.5
Acyl isethionate	Properties comparable to sulfosuccionates
	Same problems of stability
	Poor solubility in cold water, used for opaque shampoos
Sulfoalkylamides of fatty acids	*Advantages*
e.g., *N*-acyl taurides	Foaming
	Good dispersion of calcium soaps
	Same feel as soap-based formulations

Continued

TABLE 9.1
(Cont.)

Surfactant	Properties
Sulfates	
Alkyl sulfates Primary alcohol sulfate	Long chains = good detergency, good emulsifying, and solubility
Alkyl ether sulfates *n* between 2 and 3 Lauryl ether sulfate	When *n* (EO) is low, solubility R: $C_{12} - C_{14}$ diminishes in cold water Good foaming properties Good tolerance on skin
Diglycolamide sulfates	The sulfated diglycolamides are not unstable in aqueous solution and can be used in shampoos
Carboxylates	
Salts of *N*-acyl amino acid e.g., *N*-acyl sarcosinates	Good foaming properties Good detergency More soluble than soap in hard water Not irritating to hair or skin Give hair and skin a soft feel
Polyoxyethylene carboxylates	Satisfactory detergency Good dispersion of calcium soaps Easy to rinse Same properties as *N*-acyl amino acid salts High *n* = compatibility with cationics Soluble in weak pH Foam less than lauryl ether sulfates
Cationics	Condition hair after washing Behave like flocculants (poor detergency) Physiologically active and irritating. Irritation is minor with long-chain amino esters carrying many hydroxyl groups, 
Amphoterics and dipolar surfactants e.g., Sulfobetaines	Strong substantivity (used in shampoos for grey or dyed hair) Amphoterics and zwitteronics are less toxic and less irritating than cationics. They are usually combined with other surfactants (anionic and nonionic) to make mild shampoos (for babies).

Continued

TABLE 9.1
(Cont.)

Surfactant	Properties
Nonionics	
Alkanolamides	
e.g., Monoethanolamide	Increase foaming effect Stabilize alkyl sulfate-based formulations
or diethanolamide	Stearic acid ethanolamide, used as a pearlescent thickener Oleic acid ethanolamide, also used for its conditioning effect
Polyethoxylated derivatives	
e.g., Ethoxylated fatty alcohols	Good detergent properties (low foam $n = 2 \times 3$ of the number of C in R. When n is high, irritation is reduced).
Fatty acid polyglycol esters	Fatty acid polyglycol esters are the basic ingredients of baby shampoos, being very mild. They reduce irritation to a minimum because of anionic surfactants used in combination with ether sulfates and betaines. Extremely compatible with skin Exceptional foaming properties
$R\text{–}COO(\text{–}CH_2\text{–}CH_2\text{–}O)_n\text{–}H$	
Amine oxides	
(semipolar compounds)	Multifunctional
Cationics mainly in an acid environment	Stabilize foam Regulate viscosity Have a conditioning effect Potential anti-irritant

used surfactants. Other manufacturers use many types of surfactants chosen from the long list in Table 9.1.

Conditioning Agents. As we saw above, some surfactants have a strong degreasing effect on hair and also on hands, which is not a good feature for shampoos. In addition, the surfactant tends to adsorb on hair, making it brittle and difficult to style. Special ingredients, which we will discuss below, are available to counteract these effects.

Lanolin. Lanolin and its derivatives, as well as cetyl alcohol, produce good results at low incorporation levels; (if the level is >2%, the foaming properties of the shampoo are affected).

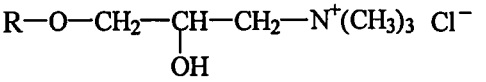
Lecithin. Lecithin can also be used at low levels. Egg and egg yolks, which contain lecithin, cholesterol, and proteins, are also used. They protect (colloidal) and act as conditioners.

Cationic polymers. These include homopolymers and cationic copolymers obtained by copolymerization of a vinyl monomer carrying a quaternary ammonium group or a quaternized amine with another water-soluble monomer, such as acrylamide or methacrylamide. The most frequently used polymers are those derived from

TABLE 9.2
Characteristics of the Most Widely Used Surfactants

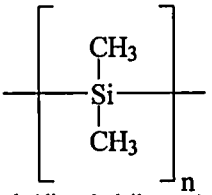
Main surfactant		Cosurfactant	
Example	Characteristic	Example	Characteristic
Lauryl ether sulfate (LES)	Nontoxic Good detergency Good foaming properties Low irritation Little/no color Little/no odor Easily available Moderate cost	Cocamido-propyl betaine (CAPB)	Increases foam in the presence of soil Increases viscosity Improves softness (slight effect) Decreases dryness of skin

guar gum, such as guar hydroxypropyltrimethylammonium chloride (sold under the name Jaguar C-13-S, C17, and so on); its formula is as follows:

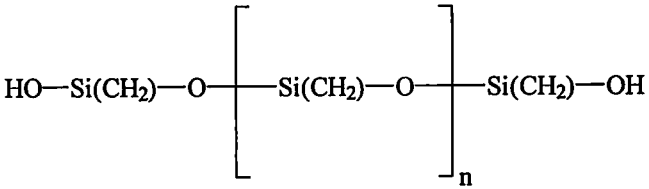


where R = a polysaccharide residue.

Silicones. These include high-molecular-weight (>200,000) polydimethyl siloxane and dimethicones.

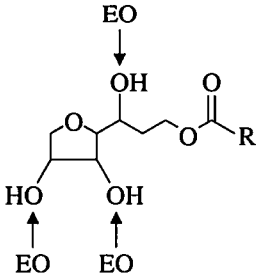


Poly(dimethylsiloxane)



Dimethicone

Certain mild surfactants can also be used as additives, such as sorbitan polyoxyethylene monostearate (e.g., Tween 60).



These conditioning agents seem to be effective because they adsorb on hair more rapidly than alkyl sulfate or alkylarylsulfonates. If these anionics were adsorbed first, they would prevent the conditioning agents from adsorbing. Other theories state that conditioning agents attach themselves during rinsing (strong dilution), or that they surround the surfactant micelles.

Therapeutic Agents. Some formulations include ingredients to correct hair and scalp abnormalities, such as greasy hair. In this paragraph we will deal mainly with dandruff (see above).

Antidandruff agents. Three possible ways of dealing with dandruff are:

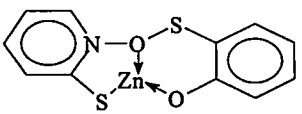
(i) reduce the speed of renewal of the cells;

(ii) inhibit the growth of yeast, which seems to be responsible for the production of flakes (*P. ovale*), as seen earlier;

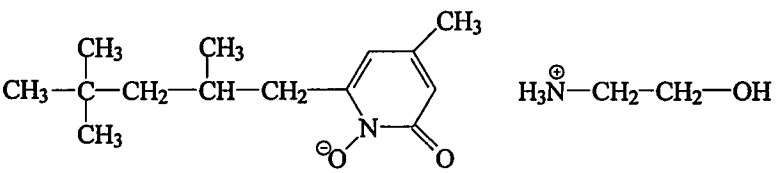
(iii) reduce the amount of free fatty acids on the scalp because these are an ideal environment for microorganisms, including yeasts.

With respect to (i), it might be possible to strengthen the horny layer (stratum corneum) of skin to limit flaking. In this case, the use of keratolytic products such as sulfur or selenium sulfur could give good results. However, these products can also cause thinning of the horny layer, leading to a greasy condition favorable to microorganisms. It should also be noted that selenium disulfur, which is relatively toxic, is usually used in shampoos sold in drugstores. For (iii), shampoos for greasy hair can be used; we will consider these a little later. Germicides are used to reduce the growth of microorganisms, including the yeast *P. ovale*. The most common include zinc pyridinethione (ZnPTO) and piroctone olamine (Octopirox).

The latter is usually preferred to ZnPTO, which can cause stability problems at low temperatures, and also toxicity. Piroctone olamine is more soluble in surfactants, not very toxic, easy to use, and stable. However, it costs more than ZnPTO.



Zinc pyridinethione

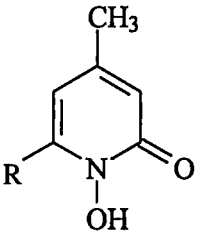


Piroctone olamine

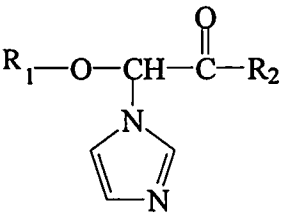
Other derivatives mentioned in the patent literature include:

(i) pyridinethiol *N*-oxide or *N*-hydroxypyridinethione and their insoluble salts;
(ii) hydroxypyridone derivatives;
(iii) imidazolylketone derivatives; and
(iv) selenium sulfide.

The structures of (ii) and (iii) are as follows:



Hydroxypyridone derivatives

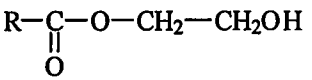


Imidazolylketone derivatives

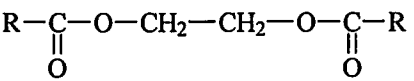
Other Ingredients. Other ingredients can either improve the physical aspects of the product, such as viscosity, pH, stability, or preservation, or make the products more attractive to the consumer (e.g., color, appearance, or perfume).

Opacifiers and pearlescing agents. These are generally long-chain alcohol sulfates such as sodium cetyl sulfate (C_{16}). Others include the following:

(i) poorly soluble alkanolamine salts of saturated fatty acids, C_{18} or higher;
(ii) fatty alcohols (tallow, cetyl, and steryl alcohols), which are good for conditioning, but reduce foaming properties;
(iii) vinyl ethylene or styrene polymer emulsions; and
(iv) esters of ethylene glycol, propylene glycol, or glycerol. Of these, the most frequently used are glycol monostearates (GMS) and ethylene glycol distearates (EGDS) as shown below:



GMS



EGDS

Thickening agents/viscosity regulators. Inorganic electrolytes, e.g., NaCl, are used as are soluble cellulose derivatives, i.e., carboxymethylcellulose, methylcellulose, hydroxymethyl-, or hydroxyethylcellulose. These derivatives thicken opaque formulations and can have other functions, such as conditioning, foaming, and

antiredeposition. By leaving a thin film after rinsing, they help to untangle hair. Carboxyvinyl polymers sold under the name Carbopol (B.F. Goodrich Chemical) can be very good thickening agents, particularly in the presence of ethoxylated fatty alcohols. They give a creamy foam and prevent separation of silicones or silicone emulsions, particularly when the product is stored in heat.

A desired product consistency can also be obtained by mixing certain surfactants. For example, a shampoo based on triethanolamine alkyl sulfate can be thickened by adding the corresponding ammonium salt. Finally, viscosity can also be adjusted with the use of ethylene glycol, glycerol, and polyethylene glycols (PEG) of various molecular weights.

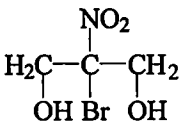
Foam stabilizers. As already mentioned in Chapters 1 and 4, alkanolamides, and in particular the mono- and dithanolamides, are very good foam stabilizers. These products add density, a creamy feel, soapiness, and stability to the foam of the main surfactants. Moreover, they can change the rheological properties of the formulation; finally, they bring a certain synergy to the detergency of fatty alcohol sulfates.

Vitamins. Vitamins A, B, C, and E are used most. All of these vitamins, and vitamin E in particular, help control oxidation/reduction and can help blood circulation in the scalp.

Preservatives and antioxidants. Preservatives stop mold formation and fermentation. Making the right choice of preservatives is important for the following reasons:

(i) their efficacy must not be inhibited by surfactants;
(ii) they must be stable and not lose their activity too quickly;
(iii) some preservatives can be irritants; and
(iv) others, such as phenolic compounds, give a "brownish" color.

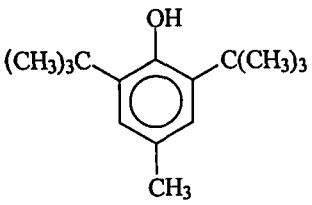
Formaldehyde, which acts at low concentrations on a wide spectrum of organisms, is still the most widely used today. However, it can cause compatibility problems with certain additives, and its use is prohibited in some countries for environmental reasons. Many other preservatives can be used, such as *p*-hydroxybenzoic acid, sorbic acid, and hydroxyquinoline sulfate; the product most widely used to replace formaldehyde is Bronopol (2-bromo-2 nitropropane 1-3 diol), which has the following structure:



Comments

Liquid and gel products can be contaminated by yeasts and microorganisms when the level of surfactants is low and the production unit is not well disinfected. This is particularly true of dishwashing liquids with <20% actives, fabric conditioners, shampoos, toothpastes, shower gels, and bath foams. Preservatives should be used for these products to avoid the development of mold and bacteria. In addition, the greatest care should be taken to disinfect the production line, as we shall see in Chapter 12.

Antioxidants. Butylated hydroxytoluene (BHT, 2,6-di-*tert*-butyl-*p*-cresol) is frequently added as an antioxidizing agent to prevent oxidation by catalytic traces of transition metals contained in certain raw materials. Its chemical formula is as follows:



Sequestering agents are also used to prevent the formation of insoluble soap (Ca and Mg) during the rinsing step. EDTA is the most widely used. These compounds can also complex trace metals (Cu, Co), which catalyze the oxidation of ingredients.

Colorants and perfume. These are chosen based on qualitative criteria, but must also be compatible and stable with other ingredients. In shampoos for sensitive skin, particularly baby shampoos, the perfume should not contain irritants. The different ingredients and their functions discussed above are summarized in Table 9.3.

TABLE 9.3
Principal Ingredients of Shampoos and Their Functions

Function	Ingredient
Detergency	Mild surfactants: Na-, Mg-, NH_4 lauryl ether sulfate (LES), Na-Mg cetyl ether sulfate, Na sulfosuccinate
	Extra mild surfactants (nonionics), e.g., polyethoxylated sorbitan ester
	Cosurfactant: amphoterics, zwitterionics, e.g., cocamidopropyl betaine (CAPB)
Conditioning	Surfactant/amide/glycol soap agents
Aids deposition of conditioners	Cationics
	Cationic polymers
	Silicones and derivatives
Therapeutic effect	
Dry hair	Oil, fatty alcohols, proteins
Greasy hair	Proteins, vitamins
Antidandruff	Antimicrobials/keratolytic agents
Silicone stabilizer	Carboxyvinyl polymer
Pearlescent effect	Ethylene glycol distearate
Thickening	
Preservative	Formalin, Bronopol
Antioxidant	Butylated hydroxytoluene (BHT), EDTA
Viscosity	Salts (e.g., NaCl), glycol, polyethylene glycol
pH	NaOH/acid

Formulation Examples

It is important to repeat that many formulation patents are given in this book. These patents concern one or two new raw materials used in the product, but to ensure full protection of the invention, the formulations given include details over a wide range of all of the other groups of ingredients, from surfactants to conditioning agents, including even minor compounds such as stabilizers. For example, for a new surfactant described in the invention, every possible cationic, from silicones to cationic polymers, and every imaginable monomer are mentioned. Similarly, for a new polymer described in a patent, all possible combinations with surfactants and additives already described in other patents, are also covered. The greatest care should be taken to check patents before using a product, to avoid all risk of infringement. We would like to emphasize that most of the examples of formulations given in this book are taken from the original patents.

Examples of Classical and Conditioning Formulations for Normal Hair. Classical formulations for normal hair usually contain between 12 and 16% anionic surfactants and cosurfactants (amphoterics or zwitterionics). If an opaque/pearlescent product is desired, GMS or EGDS is added. Tables 9.4 and 9.5 give examples of classical formulations and conditioning shampoos, respectively. The latter are ideal for dry hair given that they contain conditioning agents, which give a softer, less dry feeling. Known as "2 in 1 shampoos," these shampoos have taken a very important place in the market and are the subject of numerous patents.

There are other approaches. One involves the use of a mild surfactant with a styling agent (hydrophobic polymer), dispersed in a volatile polar solvent (hydrocarbon). The mixture of styling agent and solvent gives rise to particles 0.1–100 μm in size. These particles deposit easily on hair during washing. After drying, the solvent evaporates, leaving a deposit of styling agent, which gives the hair the desired effect. Table 9.6 gives an example of a patented formulation (1).

TABLE 9.4
Classical Shampoo Formulations for Normal Hair[a]

Ingredient	A (Transparent) (%)	B (Opaque) (%)
Surfactant (LES)	10–15	10–15
Cosurfactant (CAPB)	2–4	2–4
Mono- or diethanolamide	0–1	0–1
Stabilizing opacifiers	0	0.5–2
Antioxidants	+	+
Preservatives	+	+
Viscosity regulators	–/+	–/+
Ingredients to adjust pH	–/+	–/+
Perfume, colorant, water	Balance	Balance

[a]Abbreviations: LES, lauryl ether sulfate; CAPB, cocamidopropyl betaine.

TABLE 9.5
Shampoo Formulations with Conditioners[a]

Ingredient	(%)
LES	10–15
CAPB	1–4
Silicone emulsion	0–1.5
Carboxyvinyl polymer (Carbopol)	0–0.3
Ethylene glycol stearates	0.5–1.5
Guar hydroxypropyltrimethylammonium chloride	0.1–0.5
Perfume	+
Formaldehyde	0.05–0.15
BHT	0.025–0.06
NaCl	0.5–1.5
Colorants	+
Citric acid/NaOH	+/– to adjust pH
Water	Balance

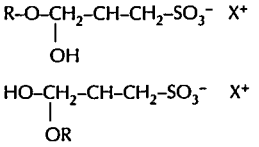
[a]Abbreviations: LES, lauryl ether sulfate; CAPB, cocamidopropyl betaine; BHT, butylated hydroxytoluene.

A second approach (2) uses a nonionic dimethicone polymer together with a cationic polymer to help deposition. Examples of patented formulations are given in Table 9.7. Trials have shown that formula 1 is equal to formula 2 and better than formula A.

TABLE 9.6
Shampoo Formulation with Mild Surfactant and Styling Agent[a,b]

Ingredient	(%)
Alkyl glyceryl ether sulfonate[c]	14
Polymer gel/solvent mixture[d]	6
Monosodium phosphate	0.3
Glycol distearate	2
Monoethanolamide (copra)	0.7
Pentaerythritol PEG tetrastearate	0.4
Cetyl alcohol	0.42
Stearyl alcohol	0.18
Polyquaterterium 10	0.30
DMDM hydantoin	0.37
Water	Balance

[a]*Source:* Reference 1.
[b]Abbreviations: PEG, polyethylene glycol.
[c]The chemical formula is as follows:



or

[d]Solvent: Hydrocarbon or di- (C_5–C_7) alkyl ether.

TABLE 9.7
Shampoo Formulations with Nonionic and Cationic Polymers[a]

Ingredient	1 (%)	2 (%)	A (%)
LES (2 EO)	16	16	16
CAPB	2	2	2
Deposition polymer	0.1	0.1	0.1
Dimethiconol polymer emulsion (60%)	3.2	—	—
Silicone surfactant emulsion (50%)	—	3	—
Silicone emulsion obtained by strong mechanical action	—	—	4
EGDS	1.5	—	1.5
Carbopol 980	—	0.4	—
Water	Balance	Balance	Balance

[a]Abbreviations: LES, lauryl ether sulfate; EO, ethylene oxide; CAPB, cocamidopropyl betaine; EGDS, ethylene glycol distearate.

Shampoos for Greasy Hair. For these shampoos, a mixture of surfactants is used. This will give sufficient detergency to remove fatty deposits and soil, which is trapped in abundance by fats, without being irritating to the scalp. The seborrheic scalp has an uneven fragile surface, which is very sensitive to stimulation (for example, excessive massage). For this reason, it must be treated with much care. Examples of treatment include free fatty acids. Used at low concentrations, these can delay the transfer of sebum from scalp onto the hair. Proteins (gelatin or casein) can absorb sebum and make it more waxy to reduce sensitivity to the seborrheic condition. A L'Oréal patent (3) suggests the use of nonionics derived from polyglycerol, which foams and cleans well, and delays considerably the reappearance of the greasy condition, without requiring other antigrease agents. Some additives could be used in these formulations to improve their efficacy. Table 9.8 gives an example of formulations for greasy hair.

TABLE 9.8
Shampoo Formulations for Greasy Hair[a]

Ingredient	(%)
Na or NH_4 LES	8–14
CAPB	2–4
Mono/diethanolamide	–/+
Opacifier (GMS or EGDS)	0–2
Specific ingredients	—
Protein hydrolyzates, egg	0.05–0.1
Preservative (Bronopol)[b]	+
Antioxidant (BHT)	+
Perfume, water	Balance

[a]Abbreviations: LES, lauryl ether sulfate; CAPB, cocamidopropyl betaine; GMS, glycol monostearate; EGDS, ethylene glycol distearate; BHT, butylated hydroxytoluene.
[b]Eggs are incompatible when formol is used as a preservative.

TABLE 9.9
Shampoo Formulations for Dry Hair[a]

Ingredient	(%)
Na or NH_4 LES	8–14
Polyoxyethylated sorbitan ester	0–1
CAPB	2–4
Mono/diethanolamide	–/+
Opacifier (GMS or EGDS)	0–2
Specific ingredients	
Olive oil, almond oil	0.05–1.0
Protein hydrolyzates	0.05–0.1
Fatty alcohols (cetyl or stearyl)	0.1–0.4
Vitamins	0–0.2
Preservatives/antioxidants	+
Perfume, water	Balance

[a]Abbreviations: LES, lauryl ether sulfate; CAPB, cocamidopropyl betaine; GMS, glycol monostearate; EGDS, ethylene glycol distearate.

Shampoos for Dry Hair. A mixture of surfactants and other additives is used. Once adsorbed on hair, it can compensate for some of the inadequacies of nature. Possible additives include the following:

(i) organic fatty acids (oleic, stearic) to prevent the removal of amino acids and oligoproteins (whose disappearance is part of the deterioration process of hair);
(ii) fatty alcohols (lauric, myristic, oleic);
(iii) natural triglycerides (almond, corn, and olive oils);
(iv) fatty esters (glycol stearate or oleate); and
(v) protein hydrolyzates (collagen, gelatin, casein).

Table 9.9 gives an example of such formulations.

Baby Shampoos. The essential requirement of these shampoos is that they be nonirritating to hair, scalp, and particularly eyes. A lower level of surfactant is used and the ratio of surfactant to cosurfactant is changed. Very mild surfactants can be used such as sulfosuccinates or polyoxyethylated sorbitan ester. An example of a formulation for baby shampoos is given in Table 9.10.

Antidandruff Shampoos. As we have seen, specific ingredients are used. These are either bacteriostats or fungistats to avoid proliferation of bacteria and yeasts (*P. ovale*) or keratolytic products, such as selenium sulfide (used in pharmaceutical preparations) or salicylic acid, to strengthen the stratum corneum and limit flaking. Table 9.11 gives examples of formulations.

Comments
Conditioning systems, such as those mentioned for "2 in 1 shampoos," can be added to the formulations for antidandruff, greasy and dry hair, and baby shampoos.

TABLE 9.10
Formulation of Baby Shampoos[a]

Ingredient	(%)
Na or Mg LES (2, 6, or 8 EO), or Na, Mg oleyl ether sulfate or Na sulfosuccinate	5–7
Polyoxyethylated sorbitan ester	0.5–1
CAPB	3–4
Preservatives/antioxidants	+
Perfume, water	Balance

[a]Abbreviations: LES, lauryl ether sulfate; EO, ethylene oxide; CAPB, cocamidopropyl betaine.

Dry Shampoos. This type of product is a special case since it is not based on surfactants. The product is applied directly to the hair in dry powder form where it is left for some minutes before being brushed off. Three ingredients typify this kind of product:

(i) the first absorbs grease (rice or cornstarch);
(ii) the second has an abrasive character to eliminate soil (different kinds of earths); and
(iii) the third is an alkali (Na carbonate, borax).

Conditioning Products

In the 1960s, these products were used only in salons; however, they have now grown into large markets in most developed countries, and particularly the United States. They are best used when the hair is long and dried with an electric hair dryer. They provide the following benefits:

(i) supple hair, when damp;
(ii) easy untangling, when damp;

TABLE 9.11
Formulation of Antidandruff Shampoos[a]

Ingredient	1 (%)	2 (%)	3 (%)	4 (%)
LES	10–15	10–15	10–15	10–15
CAPB	1–2	1–2	1–2	1–2
Antidandruff agents				
Antimicrobials				
Piroctone olamine	0.05–0.15			
Zinc pyridinethione		0.05–0.15		
Keratolytics				
Selenium sulfide			2	
Salycilic acid				2
Opacifers, preservatives	Balance	Balance	Balance	Balance

[a]Abbreviations: LES, lauryl ether sulfate; CAPB, cocamidopropyl betaine.

(iii) easy brushing, when dry;
(iv) shine, silkiness, and volume; and
(v) protection, particularly for the ends of the hair.

Formulation Principles

Conditioning products can be divided into two groups, the classics (without thickening polymers) and conditioners with thickening polymers.

Basic Ingredients. In both cases, the conditioning product contains a cationic surfactant and a fatty alcohol as basic ingredients. The cationic adsorbs easily on hair (negatively charged) and produces a light conditioning effect that helps particularly in dry or wet combing. Its main drawback is that it can irritate eyes. Addition of a fatty alcohol improves both the safety and the functional aspects of cationic solutions, because mixed bilayers are formed, which are dispersed in the aqueous phase. This lamellar phase has the following three functions:

(i) it helps deposit active product on hair more effectively;
(ii) it reduces irritation because the cationic reduces the concentration of free monomer;
(iii) it increases the suspension capability;
(iv) the network formed is an effective system for maintaining suspension and gives rise to a stable product.

Other Ingredients. These include polyethylene glycol, which can be used as a humectant, hydroxyethylcellulose, a nonionic polymer that acts as a thickening agent and makes the product easier to handle during processing, and electrolytes, because the viscosity of formulations without hydroxyethylcellulose is strongly affected by the presence of electrolytes dissolved in process water. Table 9.12 gives examples of formulations.

TABLE 9.12
Formulations of Conditioners

A. Conditioning agents[a]		B. Thickening and pearlescent agents[b]	
Ingredient	(%)	Ingredient	(%)
Cetyltrimethylammonium chloride (CTAC)	0.5–1.2	Monostearate glycerol	0.5–1
Cetyl/stearyl alcohol	1.5–3	Stearyl stearate	0.3–0.7
Poly(dimethylsiloxane) (>5000 cps)	0.5–2.5	Cetyl palmitate	0.3–0.7
		Paraffin	0.5–1.5
		Hydroxyethylcellulose	0.7–1.5

[a]For A, concentrations can be varied depending on the desired effect.
[b]For B, a formula can contain one or several thickeners.

TABLE 9.13
Formulations for Intensive Care Conditioners

Ingredient	A (%)	B (%)
CTAC[a]	0.8–1.2	1–1.5
Cetyl/stearyl alcohol	2–3	2–4
Cetyl alcohol	0.5–1.5	—
Paraffin	—	0.5–1.5
Stearyl stearate	1.5–3	—
Hydroxyethylcellulose	1–2	—
Hydroxypropylmethyl cellulose	—	1–2
Poly(dimethylsiloxane) (>5000 cps)	0.5–1.5	—
Preservatives	+	+
Perfume	+	+
Colorants	+	+
Water	Balance	Balance

[a]Abbreviation: CTAC, cetyltrimethylammonium chloride.

Special Conditioners. Conditioners can contain some of the effects mentioned under shampoos (e.g., conditioners for "intensive care" or antidandruff). The intensive care conditioners are classical conditioners that have been enriched with fatty alcohols. Two examples are given in Table 9.13.

For antidandruff conditioners, piroctone olamine is almost insoluble in a conditioner base. Below its solubility limit, this ingredient separates. Above this limit, it is present in a solid state, in which it can deposit effectively on hair and scalp. The major problem with piroctone olamine is a yellowish discoloration that can occur as a result of an interaction with UV light. This makes the use of opaque bottles or UV absorbers necessary. Piroctone olamine can also interact with the perfume and with iron. This type of formulation is therefore quite difficult to develop.

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2. Murray, A.M., Unilever, World Patent WO 9,509,599.
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CHAPTER 10

Oral Care Products: Toothpastes

The Human Mouth

The mouth contains teeth, the oral mucous membrane or cheeks, tongue, and gums, known as the fixed parts, and saliva, the moving part. The fixed parts are continuously bathed in a flow of saliva. Teeth are rooted in the alveolar ridge. The part of the tooth above the gum, the crown, is protected by a layer of enamel, a hard substance without living cells. Like bone, it is made from an organization of hydroxyapatite crystals (a form of calcium phosphate) that can be up to 1 mm thick. Dentin is a less rigid enamel, containing 20–30% living cells. The root dentin is covered by a more or less rough substance, cementum, to which the fibers of the periodontal ligament are attached. The neck is the meeting point between the enamel and the cementum, and is usually covered by gingival mucus. The heart of the tooth is the living pulp, which contains blood vessels and nerves. Figure 10.1 shows the structure of a tooth.

Saliva is constantly renewed, produced by glands in the cheeks and the back of the mouth. Saliva is essential for lubricating and protecting the gums. It is made up of proteins, many of which contain carbohydrates; these give the saliva a viscous consistency and allow it to cover the whole mouth with a film of proteins (the pellicle). Bacteria can attack teeth only after they have adhered to this film. Saliva also contains calcium and phosphate to keep the enamel surface healthy, certain enzymes, bacteria, and antibacterial substances.

Principal Dental Problems

To know what is required of a toothpaste, we need to know the problems it confronts.

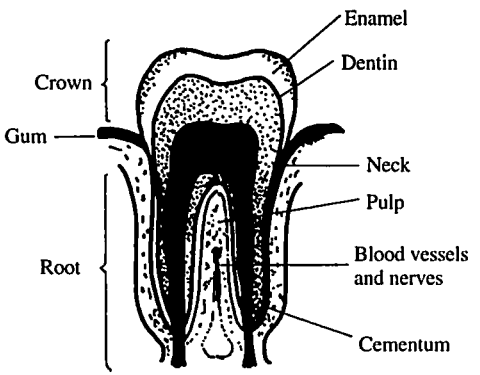


Fig. 10.1. Structure of a tooth.

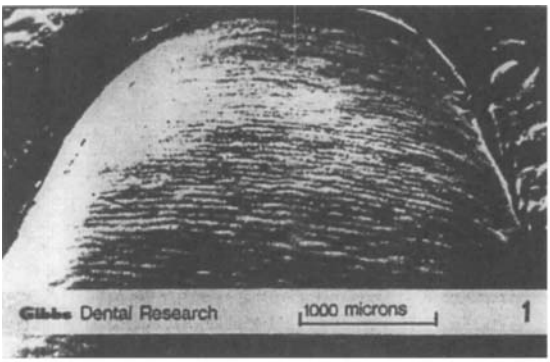
Dental Plaque

This is a whitish substance that collects on teeth and gums, and is removed by brushing.

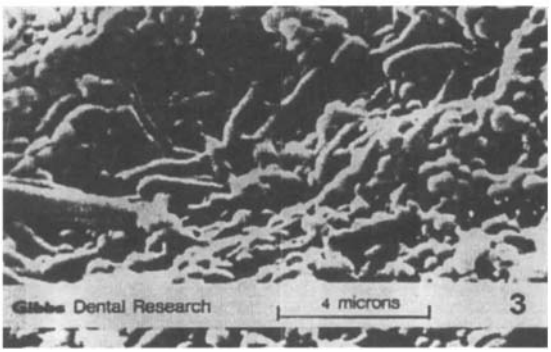
Most dental problems are related directly to dental plaque. About 70% of plaque is made up of millions of bacteria, which lodge in a mass of insoluble carbohydrate (the matrix, synthesized by bacteria). (See photos, Fig. 10.2.) Plaque starts with a deposit of salivary mucus on teeth. Mucus contains aerobic bacteria that need oxygen to grow. With time, anaerobic bacteria appear; these are the principal cause of problems related to plaque.

Gum Problems

Poor dental hygiene allows the formation of plaque, causing gingivitis or inflammation caused by toxins produced by the bacteria. With time, the gum recedes, the fragile root dentin is exposed, and, finally, the tooth will fall out.



A clean tooth



Dental plaque

Fig. 10.2. Photographs of teeth with and without dental plaque.

Tartar

Tartar is calcium phosphate from saliva that deposits on plaque. Saliva is supersaturated in calcium phosphate. Calcium phosphate crystals therefore precipitate easily. Tartar is strongly attached to the tooth surface and cannot be removed by simple brushing.

Sensitive Teeth

Gums, receding with age, expose first the root dentin (under the protective layer of enamel) and then the pulp. The nerve cells of the pulp are then exposed to outside stimulation (heat, cold), causing discomfort. Dentin can also be exposed by excessively hard brushing, which causes the gum to retreat.

Stains

Dyes that adhere to enamel cannot be removed by simple brushing with water. Toothpaste must contain a soft abrasive, which does not attack the enamel or the dentin.

Bad Breath (Halitosis)

Compounds containing sulfur, called thiols, are produced by the bacterial metabolism responsible for halitosis, or bad breath. Advanced caries can also contribute to bad breath. Regular brushing with an antiplaque and anticaries toothpaste is essential for solving this problem. Some products contain specific ingredients, such as zinc, which react with thiols.

Caries

Caries are holes in the enamel. Once the pathology is established, teeth suffer irreversible damage and can cause pain and discomfort. Left untreated, the tooth will ultimately be destroyed completely.

Dental caries result from a process that destroys the local structure of the tooth. Organic acids demineralize enamel, liberating enamel ions such as calcium, phosphate, carbonate, magnesium, fluoride, sodium, and other trace elements.

The presence of acid-forming bacteria is the necessary condition for the process (all bacteria capable of transforming sugars into acids are cariogenic). These bacteria, known as *Streptococcus mutans*, are highly acidogenic and significantly increase the risk of caries.

Acids which attack the enamel are produced by fermentation of carbohydrates in food by the bacterial flora that has accumulated in dental plaque. These carbohydrates come from different sources such as sucrose or fermentable carbohydrates. The acid can also come from beverages.

Factors that influence the activity of acids on enamel include the length of time food remains on the tooth surface, the quantity of acids, and their capacity to

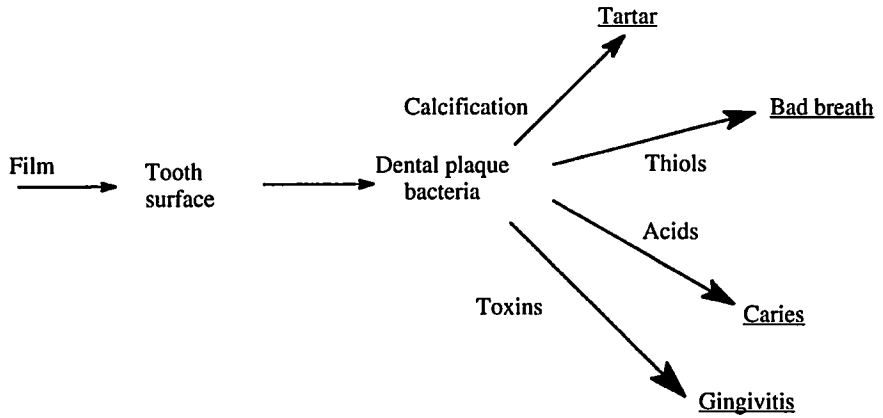


Fig. 10.3. Diagram of dental problems.

favor the formation of dental plaque. Caries will begin to develop only when the following conditions are met:

(i) a vulnerable tooth;
(ii) the presence of fermentable carbohydrates;
(iii) the presence of acid-forming bacteria (*S. mutans*);
(iv) sufficient time for demineralization to take place; and
(v) insufficient time for, or strength of, remineralization.

Normally, saliva plays a protective role, i.e., it buffers the flow of acid on the tooth surface (1), has certain antibacterial properties, and provides elements that participate in the remineralization of dental tissue (such as calcium, phosphorus). But saliva alone is not enough. Good oral hygiene, in particular the use of fluoride toothpaste, is essential if caries are to be avoided, as we shall see in due course. Figure 10.3 summarizes dental problems.

Main Ingredients and Their Functions

A toothpaste must fulfill two primary functions. First, it must clean teeth and refresh the mouth ("cosmetic function"). Second, it is the vehicle for certain therapeutic agents (e.g., fluoride against caries).

Water and Humectants

Water dissolves and dissipates the therapeutic agents, detergents, thickeners, and sweeteners. Humectants permit a reduction in the percentage of water in the formulation, which helps preserve the product to some extent, and reduces drying out (if the cap is left off, for example). The humectant therefore plays a small role in the appearance of the toothpaste, and gives a slight shine. The products used are listed in Table 10.1.

TABLE 10.1
Products Used as Humectants and Alcohols in Toothpastes

Mild and refreshing sorbitol (solid): $HOCH_2[CH(OH)]_4\ CH_2–OH$
Mild glycerol, which gives a feeling of warmth (liquid): $HOCH_2CH(OH)\ CH_2OH$
Alcohols
Ethanol: $CH_2–CH_2OH$
Ethylene glycol: $HOCH_2–CH_2OH$
Propylene glycol: $CH_3–CHOH–CH_2OH–CHOH–CH_3$
Glycerol (given above)
Sorbitol (given above)
Polyethylene glycol: $—[CH_2–CH_2O]_n—$

Surfactants

In toothpaste, surfactants help clean teeth by removing food residues and plaque, provide the foam that consumers want, and dissolve and disperse flavors that are insoluble in water (formation of micelles in which the flavors are dissolved).

Here also, two ingredients predominate, i.e., sodium lauryl sulfate and sodium alkylbenzenesulfonate. A good quality and quantity of foam is obtained by mixing two products:

$$\underset{\text{Sodium lauryl sulfate}}{CH_3—(CH_2)_{11}—SO_4^-Na^+} + \underset{\text{Sodium alkylbenzenesulfonate}}{CH_3—(CH_2)_{11}—CH_6H_4SO_3^-Na^+}$$

Abrasives

The abrasive contributes to ensuring the right viscosity and provides cleaning by abrasion of the stained/colored firm on the tooth surface. The three abrasives most frequently used are:

- silica (SiO_2), amorphous;
- calcium carbonate ($CaCO_3$, calcite or aragonite); and
- alumina (aluminum hydroxide), $Al(OH)_3$.

Other abrasives include:

1. Dicalcium phosphate dihydrate: $CaHPO_4 \cdot 2H_2O$
2. Dicalcium phosphate: $CaHPO_4$
3. Insoluble metaphosphate: $(NaPO_3)_x$
4. Calcium pyrophosphate: $Ca_2P_2O_7$

These ingredients should not harm either enamel or dentin, but must be effective in removing colored stains. Their efficacy depends on their hardness, particle size, and

TABLE 10.2
(Mohs scale) Comparison of Dental Abrasives and Tooth Hardness

Abrasive			Tooth		
Amorphous silica	Alumina	Ca carbonate	Enamel	Dentin	Tartar
5	2.5–3.5	3–4	4–5	2–2.5	3

concentration in the finished product. Table 10.2 shows a comparison of abrasives and tooth hardness.

This table shows that, in fact, only dentin, which is softer than enamel, has to be taken into account in the choice of an abrasive. Industry standards that reflect this concern have been defined, i.e., abrasiveness is defined as the quantity of dentin abraded under standard conditions—dentin abrasion value (DAV). The abrasive also contributes to the viscosity of toothpaste, particularly at high concentrations (>30%). The choice of abrasive also depends on the choice of therapeutic agents (because incompatibilities exist) and whether the desired product is opaque or transparent.

Comments

Precipitated calcium carbonate, in addition to its abrasive properties, has other interesting qualities. It buffers the pH of saliva, which contributes to the prevention of caries. After brushing with a toothpaste containing calcium carbonate, the compound is suspended in the saliva where it works as a pH buffer. The suspended particles then adhere to certain cavities in the tooth structure and in the plaque. From there, a progressive liberation and dissolution into saliva takes place which thus prolongs the buffering effect (2).

Thickeners

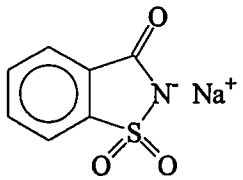
Thickeners help to avoid sedimentation of abrasive and bring rheological properties to toothpaste, such as facilitating flow from the tube while ensuring that it remains firmly on the brush. Thickeners structure the liquid phase of the product, holding the abrasive in suspension. This structure disappears when pressure is applied to the tube, only to reform when the pressure stops (thixotropy). Either organic or inorganic thickeners can be used. Among organics are polymers such as sodium carboxylmethylcellulose (SCMC) and xanthan gum. SCMC is available in many forms with different thickening abilities and electrolyte tolerance. Xanthan gum is a high molecular weight natural polymer, obtained by the fermentation of glucose by *Xanthomonas campestris*. It has some advantages over SCMC, including better mouth feel, better electrolyte tolerance, resistance to microbial deterioration, and good stability over time. The main inorganic thickeners used are silicas (fumed, precipitated, gels) and also certain clays (laponite or hectonite).

Structurants

Polyethylene glycol (PEG) is sometimes used to structure and solubilize both the flavor and the surfactant.

Sweetening Agents

These make the product more acceptable in terms of taste, by masking the bitter taste of some ingredients in the formula. Historically, sugar was used as a sweetening agent! Ingredients used today are nonfermentable, which helps avoid caries; the most commonly used is saccharin (sodium salt of *o*-sulfobenzimide). Its chemical structure is as follows:



Opacifiers

Titanium dioxide (TiO_2) is added to white opaque toothpastes to improve whiteness and to vary the shade of a colored product.

Colorants

Colorants must meet safety, stability, and cost norms. Generally, they are therefore food-grade constituents and can be soluble or insoluble (pigments). It is sometimes possible to add small quantities of color stabilizers such as magnesium sulfate.

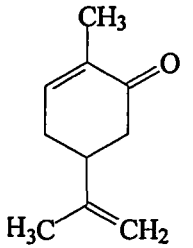
Stabilizers and the Adjustment of pH

Previously, alumina-based toothpastes were packed in nonlacquered aluminum tubes. Stabilizers were added to avoid chemical reactions between product and pack, using sodium dihydrogen phosphate (NaH_2PO_4), which is still used today, but to stabilize the pH rather than prevent interactions. (Tubes today are of better quality, whether lacquered or plastic.) Zinc citrate is also used as a buffer, reducing pH to neutral. It should not be used together with phosphates because it forms insoluble zinc phosphate salts. To raise the pH of formulations containing high sorbitol levels, trisodium phosphate (Na_3PO_4) can be used. For reasons mentioned above, this cannot be used with zinc citrate, in which case, sodium hydroxide should be used to adjust the pH.

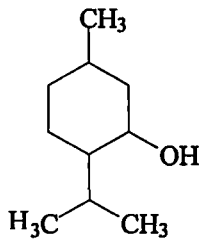
Flavors

The taste of a toothpaste is critical for the consumer. Apart from very specific exceptions, such as flavors for children, the range of flavors is very limited, i.e., 80% of

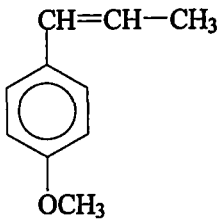
tastes are based on mint, peppermint, or a mixture of the two. Most of the remainder is methyl salicylate from the gaultheria plant. In some countries, there are variations from these norms, e.g., fruity notes in Japan, aniseed in the Mediterranean, and spicy notes in South America. Mint/peppermint oils together with menthol account for 60–80% of flavor bases for toothpastes. The flavor sources are either natural or synthetic. Some toothpaste flavor formulations are as follows:



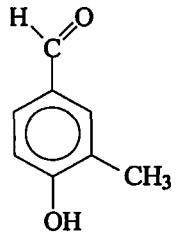
Spearmint (carvone)



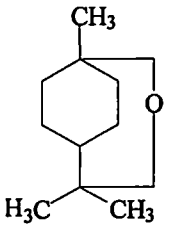
Menthol



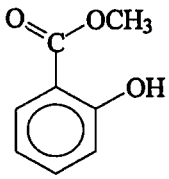
Anethole



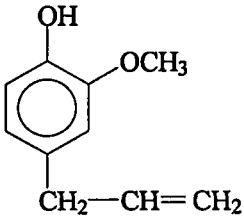
Vanillin



Eucalyptus (eucalyptol)



Wintergreen (methyl salicylate)



Clove (eugenol)

Preservatives

As explained previously, the humectant helps in the preservation of the product, but in formulations with little water, other products can be added that inhibit mold and growth of bacteria. These include formaldehyde, sodium benzoate, potassium sorbate, and *p*-methyl benzoate. Sodium benzoate and potassium sorbate are used at pH < 5.5 because they are more effective in their unionized form. *p*-Methylbenzoate, however, is more effective when the pH is close to neutral.

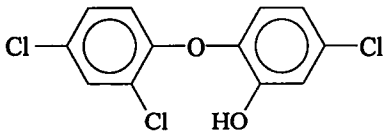
Therapeutic Agents

Antitartar. Pyrophosphate salts (anion = P_2O^{4-}) have been the standard ingredient, usually in a mixture, such as tetrasodium pyrophosphate (poor solubility at low temperatures) with potassium tetraphosphate (better solubility, but salty taste).

Desensitizing Agents. The first agent to be authorized was strontium, but this also has a salty taste and is not compatible with fluorides. The next generation was strontium acetate, with a less salty taste and better compatibility with fluoride. Potassium salts (chlorides, nitrates, citrates) are the most widely used today; they are compatible with fluoride and have a neutral taste.

Antiplaque Agents. There are two main groups:

1. Antimicrobials with a metallic ion. This class includes salts of zinc (water soluble), copper, or tin. Zinc salts, particularly zinc citrate, are the most widely used in toothpastes. In the literature, sources of the zinc ion include zinc chloride, zinc sulfate, or zinc thiocyanate, for example.
2. Organic antibacterial agents. Among organic antimicrobials, the best known is chlorhexidine digluconate, but it has a bitter taste and stains teeth; it has not been very successful in toothpastes. On the other hand, Triclosan (Irgasan DP 300, Ciba-Geigy) is widely used:



Some authors think that the use of only one bactericide in a toothpaste is less effective than the combination of two, such as zinc citrate and Triclosan. Plaque reduction is improved and gingivitis is retarded.

Anticaries. There are a certain number of options to control and reduce dental caries, the greatest problem in tooth care. Use of fluoride salts is one of the most effective methods (3). The action of fluoride can be explained by the following:

(i) its antimicrobial function;
(ii) the interaction between fluoride and enamel to form a fluorinated hydroxyapatite compound (fluoroapatite) that is more resistant to acid than enamel on its own;
(iii) its "repairing" effect in forming calcium and phosphate which remineralize the tiny lesions in which caries begin.

It is well known that fluoride inhibits bacterial growth, but the concentration required to be effective is far higher than the amount delivered in a toothpaste (4). The generally accepted explanations for the efficacy of fluoride are the last-mentioned points above, i.e., the formation of the fluorinated hydroxyapatite compound, which is stronger against acids (3), and the inhibition of demineralization of enamel (5). The therapeutic efficacy of fluoride would therefore appear to be due to a reduction in solubility of enamel and to the remineralization of areas under attack. Remineralization of enamel is the consequence of adsorption of fluoride onto the enamel surface (6). The remineralized lesion is arrested, neither increasing nor decreasing with time (1). Incorporation of fluoride into the matrix gives rise to fluorinated hydroxyapatite, which is stronger than enamel (7).

The correct use of a fluoride toothpaste provides a fluoride concentration sufficient to prevent caries from forming, or to cure them. A concentration of 0.01–0.02 ppm fluoride is sufficient to form fluorinated hydroxyapatites, which reduce enamel solubility and help to fix calcium onto the caries (remineralization) (8,9). People usually brush their teeth 1–3 times per day. If a fluoride toothpaste is used, the level of fluorine in saliva is twice as high as that for users of nonfluoride toothpaste. This is due to the fact that the fluoride is adsorbed at different parts of the mouth after brushing and is then gradually released into saliva (4).

The elimination of free fluoride occurs in two phases as follows:

(i) after brushing, the concentration falls quickly to ~0.08 ppm of fluorine after 30 min;
(ii) in a second phase, the concentration falls more slowly to an almost stable level of 0.02 ppm of free fluoride between two brushings. A well-formulated product will ensure a level of free fluoride in saliva of >0.02 ppm for several hours (4).

In the 1940s, Na fluoride was the first fluorine salt to be incorporated into a toothpaste, following a successful reduction in caries after fluoride had been added to water. However, in this form, insoluble calcium formed in the presence of carbonate in the formulations, and clinical efficacy was in fact nonexistent (later, fluoride and more recently, silica continue to be used in calcium pyrophosphate–based formulations). The first fluoride to be used effectively in a toothpaste was stannous fluoride (SnF_2); however, this gave rise to manufacturing process problems because it required acid conditions. Moreover, its instability sometimes caused yellow/brownish discoloration of the teeth.

The literature mentions the following sources of the fluoride ion: sodium fluoride, potassium fluoride, lithium fluoride, aluminum fluoride, zinc fluoride, sodium monofluorophosphate, acidic fluorophosphate, ammonium fluoride, titanium tetrafluoride,

and amine fluoride. In practice, the compounds that provide the fluoride ion are sodium fluoride, monofluorophosphate (Na_3PO_3F), and sometimes certain amine fluorides. Every year, the World Health Organization issues a world map of caries in 12-yr-olds, which clearly reflects eating habits (Fig. 10.4).

In the 1970s, these data indicated a highly negative trend in industrialized countries, in contrast to the situation in developing countries. Since that time, however, there has been a clear, and sometimes marked, reduction of caries in almost all industrialized countries as a result of preventive programs, while in developing countries, the situation has deteriorated because of a lack of programs. In France, for example, a July 1998 decree requires all 15-y-old adolescents to visit the dentist, with any necessary dental work to be paid for by the government. Previously, a dental visit by school age children was only recommended without strict follow-up.

Good dental hygiene helps to remove plaque and to prevent problems such as gingivitis, periodontal disease, and caries. However, subsequent studies (10) have shown only a weak relationship between dental plaque and caries. This is why simply removing plaque through regular brushing is not enough to eliminate caries. The toothpaste should also include specific anticaries ingredients. Fluorides have been studied in detail, particularly by the large manufacturers, who have conducted long-term research programs on subject groups. The conclusions are clear: brushing teeth will not reduce caries unless the toothpaste contains fluoride. The statistics speak very clearly (11). In a 3-year study of the effect of fluoride toothpastes on the prevention of caries, the annual numbers were as follows:

(i) toothpaste with fluoride, 4.40;
(ii) toothpaste without fluoride, 8.32;
(iii) control (no specific instructions), 8.96.

In Norway, for instance, the number of caries in children declined dramatically with the introduction of fluoride toothpastes (Fig. 10.5).

Use of fluoride toothpaste is therefore the primary way to fight caries. Other factors seem to be relatively unimportant. For instance, limitations of sugar consumption and other foods that could give rise to carbohydrates have very little effect on the elimination of caries (12). Table 10.3 summarizes the main ingredients in fluoride toothpastes and their functions.

Examples of Toothpaste Formulations

Formulations cited in the patent literature are numerous. Those that follow are intended to illustrate different points, and are far from being exhaustive.

Opaque Formulations

In the example in Table 10.4, sodium fluoride is the source of fluoride ion (anticaries) and zinc chloride is the antimicrobial (13). The example in Table 10.5 con-

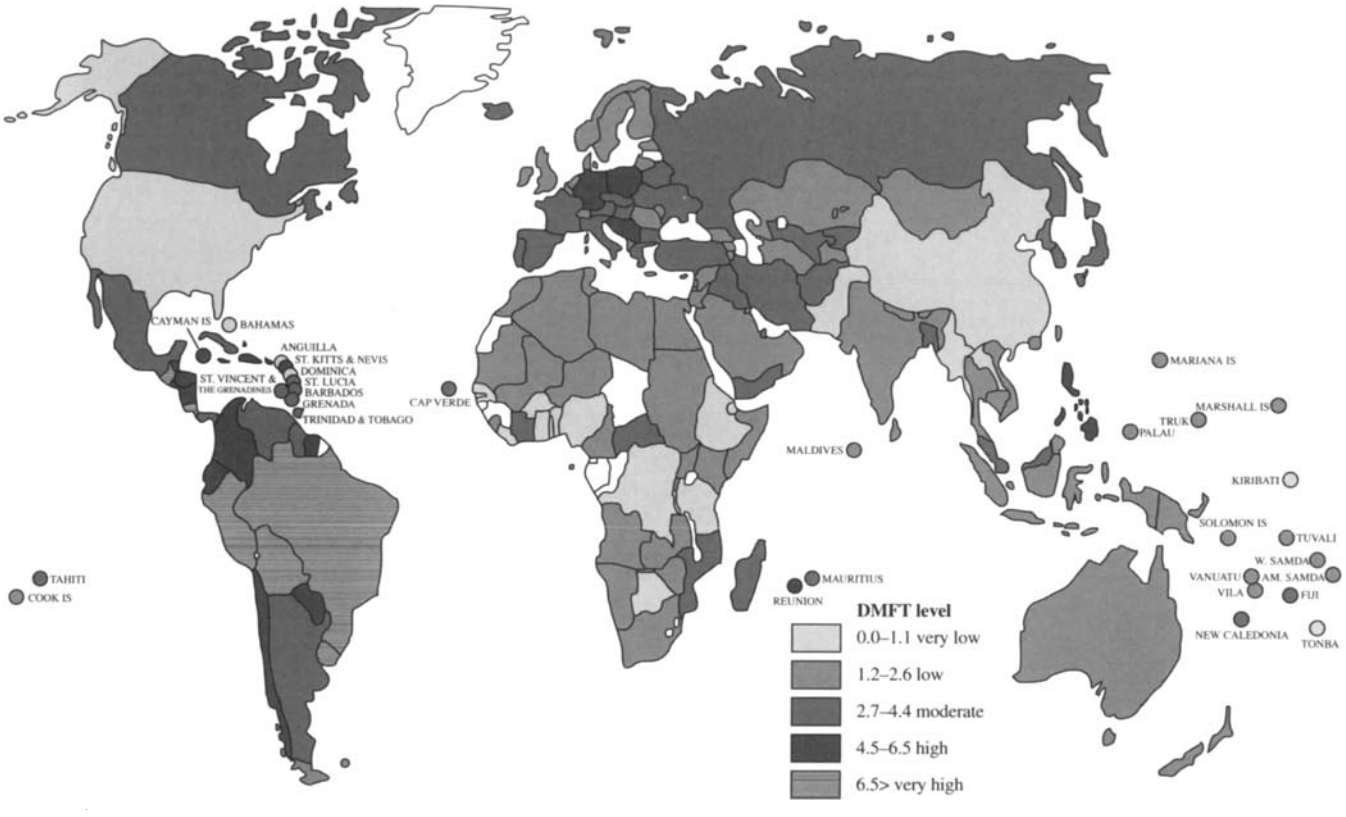


Fig. 10.4. Occurrence of dental caries in 12-y-olds worldwide (1993 data). *Source:* World Health Organization.

TABLE 10.3
Main Ingredients of Fluoride Toothpastes and Their Functions[a]

Ingredient	Function
LAS, PAS	Detergent, foam
Sorbitol, glycerol	Humectant
Amorphous silica, precipitated carbonate, alumina, calcium phosphate	Abrasive
Cellulose derivatives, xanthan gum, silica gels	Thickeners
Saccharin	Sweeteners
Titanium dioxide	Opacifier
Mint and peppermint oils	Flavor
Formaldehyde, sodium benzoate	Preservatives
	Therapeutic agents
Fluorine derivatives	Anticaries
Pyrophosphate	Antitartar
Antibacterial (zinc salt or Triclosan)	Antibacterial (plaque, gingivitis, bad breath, periodontal disease, caries)
Strontium acetate, potassium salts	Sensitive teeth

[a]Abbreviations: LAS, linear alkylbenzenesulfonate; PAS, primary alcohol sulfate.

tains sodium monofluorophosphate as the fluoride source, combined with two antimicrobials (14).

Formulation for a Transparent Toothpaste

Transparent toothpastes are obtained by modifying the refractive indices of the liquid and solid phases. Examples of refractive indices for different materials are given in Table 10.6.

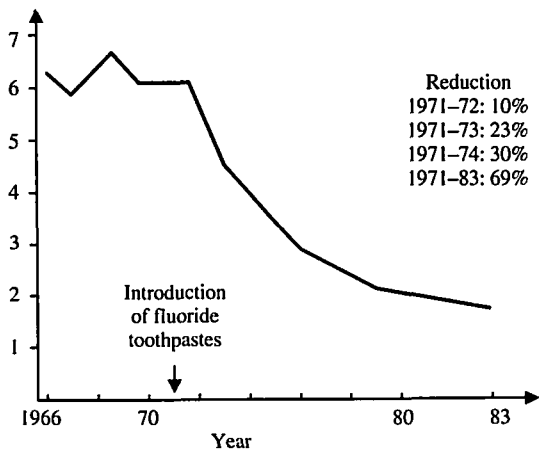


Fig. 10.5. Development of caries in children in Norway after the introduction of fluoride toothpastes.

TABLE 10.4
Opaque Toothpaste Formulation with Sodium Fluoride[a]

Ingredient	(%)
Na fluoride	0.22
Zinc chloride	2
Sorbitol (70%)	35
Glycerol	10
Hydrated silica	23
N-ethyl cocoyl taurate	3.75
Xanthan gum	1
Hydroxyethylcellulose	1
Na gluconate	0.80
Titanium dioxide	0.80
Na saccharinate	0.7
Saccharin	0.10
Na benzoate	0.20
Flavor	1.3
Demineralized water	Balance

[a]*Source:* Reference 13.

It can be seen that by adding small quantities of sorbitol (70%) syrup in water or glycerol, it is possible to obtain the same refractive index as silica. The graph in Figure 10.6 shows how light is passed on through a suspension of silica in a mixture of water/sorbitol as a function of the refractive index. When the refractive index of silica is the same as the liquid phase, the light passed through is maximum, and the mixture is transparent.

Tables 10.7 and 10.8 give two examples of transparent formulations. In the second example, inclusion of soluble zinc salts as antimicrobials can cause crystals

TABLE 10.5
Opaque Fluoridate Toothpaste Formulation with Two Antimicrobials[a,b]

Ingredient	(%)
Alumina trihydrate	50
Sorbitol (70%)	27
Na PAS	1.88
Na LAS	0.63
SCMC	0.8
Zinc citrate dihydrate	1
Triclosan	0.5
Na monofluorophosphate	0.85
Flavor	1.2
Na saccharinate	0.18
Formaldehyde	0.04
Demineralized water	Balance

[a]*Source:* Reference 14.
[b]Abbreviations: PAS, primary alcohol sulfate; LAS, linear alkylbenzenesulfonate; SCNC, sodium carboxymethylcellulose.

TABLE 10.6
Refractive Indices for Various Materials

Material	Index
Silica	1.45–1.46
Alumina	1.52–1.55
Carbonate	1.148–1.168
Sorbitol (syrup)	1.455–1.461
Glycerol	1.4729
Water	1.333

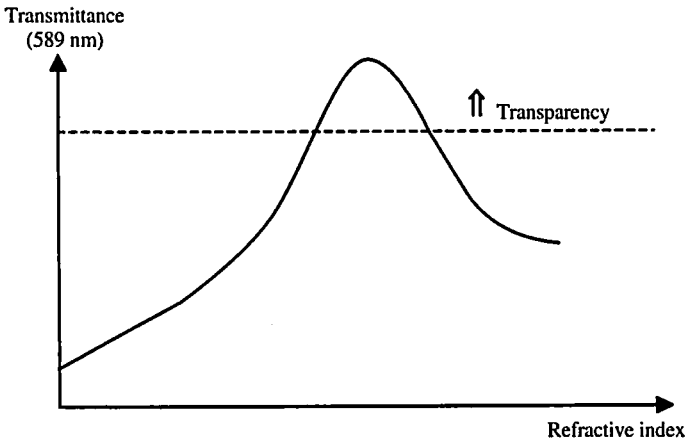


Fig. 10.6. Transmittance as a function of refractive index.

TABLE 10.7
A Transparent Toothpaste Formulation[a,b]

Ingredient	(%)
Glycerine (99.5%)	9.95
Sorbitol (70%)	33.88
SCMC	0.4
Carrageenin	0.4
Na fluoride	0.243
Na saccharinate	0.3
Poly(vinyl ether/maleic anhydride)	2.00
Caustic soda (50%)	0.6
Precipitated silica	22
Na PAS	1.5
Flavor	1
Triclosan	0.3
Water	Balance

[a]*Source:* Reference 15.
[b]Abbreviations: See Table 10.5.

TABLE 10.8
Transparent Toothpaste Formulations with an Added Amino Acid[a,b]

Ingredient	(%)	(%)
Sorbitol (70 %)	58.59	58.95
Polyethylene glycol (MW 1500)	5	5
Na monofluorophosphate	0.8	—
Na fluoride	—	0.33
Na PAS	1.7	1.7
SCMC	0.5	0.5
Saccharin	0.2	0.2
Colorant	0.012	0.012
Flavor	1.1	1.1
Zinc sulfate heptahydrate	0.686	0.686
Glycine	0.3584	0.3584
Water	Balance	Balance

[a]*Source:* Reference 16.
[b]Abbreviations: See Table 10.5.

to form in a transparent toothpaste. A Unilever patent (16) shows that the use of an amino acid (preferably glycine) prevents this problem.

The examples in Tables 10.7 and 10.8 contain both antimicrobials and anticaries agents. Products sold in the trade will generally contain only the anticaries agents for reasons of cost. For a toothpaste to be effective against caries, it is not enough simply to add fluoride salts. It is vital that all ingredients be stable during the life of the product. It is not unusual to find products in the trade (particularly those manufactured in Third World countries) that have lost fluoride activity. Large brand manufacturers have the advantage of knowing how to keep anticaries agents stable, e.g., by choosing the right raw materials and manufacturing processes and using stabilizing systems. In addition, manufacturers are constantly improving the anticaries efficacy of their products through research. An example is the search for yet more effective fluoride compounds such as alkylamine fluorophosphates (17) or combinations of fluoride compounds with other agents such as silicones (to help adsorption of fluoride on teeth) or a mixture of fluoride salts with glucoside (xylitol), which has improved anticaries properties (18).

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CHAPTER 11

Product Performance Evaluation

Performance Tests of Laundry Detergents

Laboratory Tests

Detergents, both powder and liquid, are tested under standard laboratory conditions to fine-tune a formulation before more extensive tests in washing machines. In this section, we will discuss test cloths and washing procedures.

Test Cloths. Test cloths are used by detergent manufacturers and also by independent laboratories. Large pieces of fabric—cotton, polyester, or polyester/cotton—are soiled in a standard manner in large baths of various ingredients. After drying, the fabric is cut into test-sized cloths of ~15 × 15 cm^2, for use in the laboratory or in machines. Each test cloth is specific for one stain to test the different ingredients in a detergent and to examine each piece of the puzzle for the following effects: general detergency, enzyme efficacy, and bleaching effect. The difference in whiteness is measured before washing (initial reflectance) and after (final reflectance) with the use of a reflectometer (e.g., Elrepho, Hunter, Gardner). Cleaning efficacy is given by $\Delta R = R_f - R_i$ (see below for machine evaluation). A test cloth is good for one wash only; thus, there is no cumulative effect. Of course, a test should be conducted several times under identical conditions to compare one product with another. Typical test cloths are listed below.

1. "Krefeld" test cloths. Supplier: WFK Krefeld e.v., 4150 Krefeld, Adlerstrasse, 14, Germany. These cloths can be used at all temperatures. They are sensitive to the type of surfactant used, but less so to the quantity.
2. "EMPA" test cloths. Supplier: EMPA Eidgenoessische Materialprüfungs und Versuchsanstalt, 9001, St. Gallen Unterstrasse, 11, P.O. Box 977, Switzerland. Types of test cloths include EMPA 101, general detergency; EMPA 111 and 116, very sensitive to proteolytic enzymes; EMPA 112, sensitive to enzymes (particularly amylases); EMPA 114, sensitive to bleaching agents, particularly at low temperatures (and to a lesser extent to detergency in general).
3. "Center for Test Materials" (CFT) test cloths. Supplier: CFT, Stoomloggerweg 11, 3133 KT Vlaardingen, Holland. This center provides a variety of cloths. The main ones include the following: AS 8, for tests at >60°C, measuring detergency; AS 9, for tests at <60°C (detergency); PC 9, same soil as AS 9 but for polyester/cotton (low temperature); AS 10, measures enzymatic effect and detergency; PC 12, measures enzymatic effect and detergency at low temperature; BC 1, tea stain to measure bleaching effect.

TABLE 11.1
How Test Cloths Are Used

	Low temperature wash	High temperature wash
Detergency	AS 9, PC 9, EMPA 101 Krefeld WK 106	AS 8 Krefeld WK 106
Enzymate effect	AS 10, PC 12	
Protease	EMPA 111 and 116	AS 10, EMPA 111 and 116
Amylase	EMPA 112	EMPA 112
Bleaching (wine, tea, coffee)	EMPA 114, BC 1	EMPA 114, BC 1
Redeposition	Cotton or white polyester/cotton	White cotton
Fluorescent whitening	Cotton or polyester/cotton White, nonbrightened cotton	Nonbrightened white cotton

4. "Scientific Services" test cloths. Supplier: Scientific Services S/D Inc., 41 Main Street, Sparrow Bush, NY 12780. This laboratory supplies test cloths printed with dust/sebum and clay for general detergency as well as a variety of individual stain cloths (blood, cocoa, used motor oil, etc.).

Clean cloths. In addition to the above test cloths, other types of cloth are added to the test load to complete the evaluation of a product. These include clean cloths, called "monitors," which are used for several wash cycles to measure the following: (i) redeposition (white cloth: cotton, polyester, polyester/cotton); (ii) brightening effect (nonbrightened at the start, and accumulating fluorescent whiteners); (iii) dye transfer from a colored load to white cloths that pick up dyes dissolved in the wash liquor. Some cloths can be used to measure color loss over a number of washes. Generally, test cloths do not react to only one ingredient or family of ingredients in a detergent. Table 11.1 gives a summary of the usage of different test cloths. It is important that the formulator be perfectly familiar with the different possibilities so as to use them effectively.

Washing Protocols. The most commonly used piece of machinery consists of a battery of mini-machines working simultaneously, at the same temperature, with the same agitation for the same length of time (Terg-O-Tometer). It consists of a series, e.g., six stainless steel pots, placed in a water bath at a controlled temperature (Fig. 11.1).

In this manner, six experimental products can be tested simultaneously. The test methodology takes into account the following:

(i) wash and rinse water hardness;
(ii) wash temperature;
(iii) cloth/liquor ratio (quantity of test cloths/wash water);
(iv) type of test cloth;
(v) product dosage (usually 1.5–2.5 g/L);

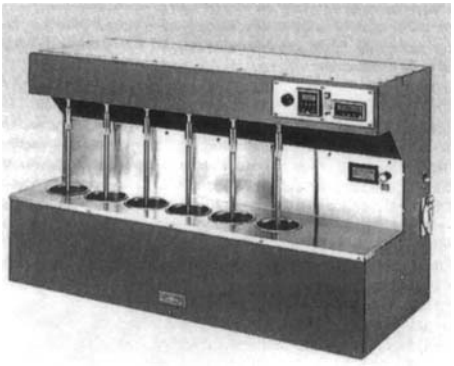

Fig. 11.1. Terg-O-Tometer.

(vi) time the product takes to go into solution (e.g., 2 min);
(vii) duration of the wash; and
(viii) duration of the rinse.

Tests are conducted as follows:

1. Equal volumes of water are placed in each pot.
2. The water is heated to the desired temperature and agitated.
3. The products are allowed to dissolve for a fixed period of time.
4. The cloths are placed into the solutions.
5. The cloths are washed for a fixed period of time, e.g., 10 min.
6. The process is stopped and the pots emptied.
7. The cloths are rinsed (for 1, 2, or 5 min, for example).
8. The cloths are dried.

Although results do not vary much, it is recommended that the operation be repeated three to five times, the ideal being six, using each of the pots once. This test, which is far from real wash conditions, at least allows a rapid evaluation of the strengths and weaknesses of one product relative to another and allows the formulator to direct the research in one direction or another, e.g., to increase detergency if the surfactants are inadequate, or to adjust bleaching or redeposition properties.

Tests in mini washing machines (Calor type) can help with the study of long-term effects after many washes, bearing in mind again that such conditions are still far from reality and are valid only for assessing the relative performance of comparable products. For example, we can study redeposition after 5, 10, 15, or 25 mini-washes, or the build-up of brighteners starting with untreated cloths.

Tests in Experimental Laundry Centers

Norms do exist in this area because these tests are often internal to a given company. Some research laboratories employ their own evaluation methodologies and some

even make their own test cloths. We will give an idea of one of the test methods for product evaluation, given that similar test methods are used by independent laboratories, such as the Technical Centre for Colouring and Cleaning in Lyon, to compare different products.

We have already seen that laboratory tests can be used to compare the main characteristics of one product with those of another, but they are not representative of the real usage conditions. The next stage after laboratory evaluation is therefore evaluation in washing machines. At this stage, the formulator will want to compare the efficacy of the test product with a reference formulation or a competitive product. Washing machine tests, which are very close to real household conditions and rich in various performance measures are one of the main steps in the development of a new product.

Before looking at this in more detail, we should first look at the missing element in the washing process (after the detergent, the washing protocol, and the water, which we have already discussed), that is, the washing machine. We will examine three parts of this process, i.e., the washing machine, soiled clothes and wash loads, and product evaluation.

Washing Machines: Description and Operation. There are various types of washing machines. All use the same principle of supplying the following additional energies to work with the detergent:

1. Mechanical energy through rotation of the drum. This should vary depending on the type of fabric. Thus, wool should be treated with care, whereas cotton requires strong action; we can all visualize the beating sticks required in times past.
2. Thermal energy, i.e., cold water heated by electricity or hot water direct from the tap, as in the United States.
3. Kinetic energy, i.e., the length of agitation will have a direct effect on the results. Similarly, a pause in the rise in temperature will allow the enzymes in the detergent to exert an optimal effect (biological energy).

There is thus a high degree of complementarity between the machine and the detergent. For this reason, they have to be fine-tuned to work together on a number of criteria including the following:

(i) foam levels (link between the detergent and the type of agitation by the machine);
(ii) detergent dosing, i.e., the design of the detergent dispenser (European machines only), incoming water pressure and temperature; the product must empty easily from the dispenser without leaving residues, whatever the temperature, which can vary from a few degrees in winter (2–3°C) to 18–20°C or more in summer; and
(iii) optimal use of different detergent ingredients. If a particular design of the drum prevents all of the detergent from going into solution, the result will be suboptimal.

Some detergents, such as concentrated powders or isotropic liquids, cannot be used in normal machine dispensers. In these cases, different dosing mechanisms are used, such as dosing balls or direct dosage into the drum, allowing the detergent to go into solution progressively. A final criterion in this relationship between the product and the machine is the level of risk that the detergent will corrode the enamel tank (gradually being replaced with plastic). The formulator must therefore keep all of these variables in mind in incorporating specific agents.

How washing machines work. Machines have worked on a similar principle for generations, but not without evolving. Today, thanks to "fuzzy logic," some machines can adapt washing conditions to the weight of laundry or to the degree of soiling. The general principles include the following:

1. Water: In Europe, the machines require ~17 L of cold or hot water.
2. Addition of detergent: This takes place *via* a drawer-type dispenser (or other) or *via* an appropriate dosing system (e.g., a ball).
3. Agitation has three levels:
   (i) gentle agitation (5-s sequences with 10-s rest), or rocking motion (wool), and a high water level;
   (ii) normal, a medium water level and average agitation (5-min wash and 10-min rest); and
   (iii) high, a low water level and normal agitation (for 10 min with 5-min rests)
4. Temperature: Water is heated by an immersion heater in the tank. In general, the temperatures are: cold, 30, 40, 60, and 90°C (although often there is a thermostat that can be regulated). United States machines offer three temperatures: cold (ambient), warm (about 90°F), and hot (about 125°F). These temperatures are generated by the appropriate ratios of hot (from the central water heater) and cold (tap) water.
5. Rinsing and spin-drying: Today, most machines use three or four spins to dry, at regulated speeds between 0 to 1000 or even 1200 cycles/min. Between each of the three or four rinses (24 L of water), the spin cycle helps to eliminate most detergent residues. The final spin should leave the laundry ready for drying. At some stages, chlorine bleach (which is going out of fashion) is added to the rinse water, and softener is added in the last rinse.

Certain types of machines are illustrated in Figure 11.2. In Europe, there are front-loading machines (with a porthole) and top-loading machines (particularly in France). These are drum machines. In the United States and Japan, machines are loaded from the top. In the United States, the machines are equipped with agitators, while in Japan they agitate with pulsators. Machines in Europe are smaller than those in the United States, particularly the top-loading machines. Because of their design, some machines can cause loss of part of the detergent used; this is mechanical loss (Fig. 11.3). Some of the powder can flow along the frame of the tank (where it is ineffective) to end up in inaccessible parts just before the evacua-

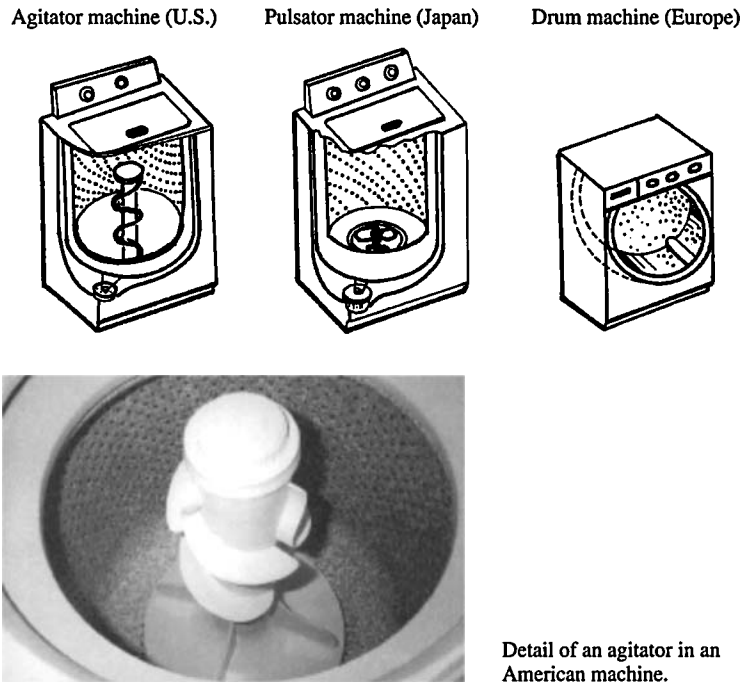

Fig. 11.2. Different types of machines.

tion pump. This same phenomenon is encountered when isotropic liquids are placed into the dispensing unit.

Soiled Cloths and Machine Loads. In machine tests, laundry is sorted into loads, made up of standard test cloths, stained cloths, and soiled laundry.

Standard test cloths. Standard test cloths are those we discussed above in the context of laboratory tests (e.g., AS 8 or EMPA). Clean cloths are included to

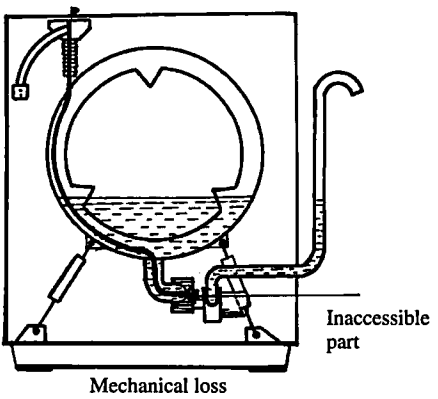

Fig. 11.3. Mechanical loss.

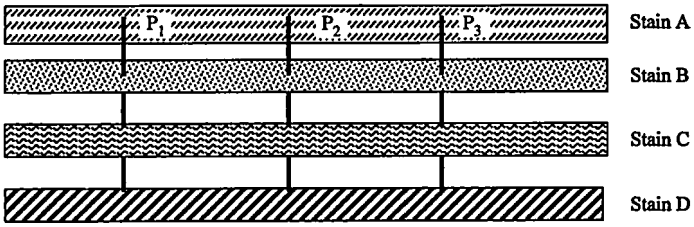

Fig. 11.4. Preparation of stain strips.

study specific aspects. They go through several washes to measure redeposition (white cloth, e.g., cotton, polyester, polyester/cotton), the fluorescent whitening effect (nonbrightened at the start), dye transfer from colored clothes to whites that pick up the dye in the wash solution. Some colored cloths can be used to measure color loss as a function of the number of cumulative wash cycles. Finally, cotton cloths can be included to measure mineral incrustation and terry toweling can be included to evaluate softness after several washes.

Stain cloths. To complete development, the formulator must evaluate a product on as many criteria as possible. This is why a whole battery of soils has been created for addition to the test washes. These soils are applied to white cotton, for example, which has been prewashed several times to remove all finishes that might make stain removal easier. Each detergent manufacturer will have particular tests, e.g., dissolved (tea or coffee), or they may be applied directly (e.g., lipstick, makeup, or fruit stains). As a general rule, to control this particular variable, a large stain that can be cut into several pieces is preferred, depending on how many comparisons are to be made. For example, for three test products, "monitors" are prepared as shown in Figure 11.4. The cloth is cut into four strips, each with four identical stains, and aged before the test. Strip 1 is put into the machine with product P1, strip 2 with product P2, and the last will be washed with P3. Strip 0 will be the control, which is not washed. Another approach is to make a large circular stain cut into fourths, each fourth being washed with a different product (Fig. 11.5).

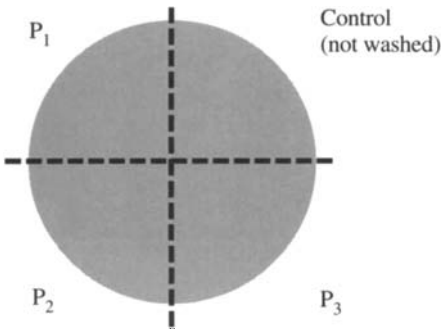

Fig. 11.5. Preparation of stains.

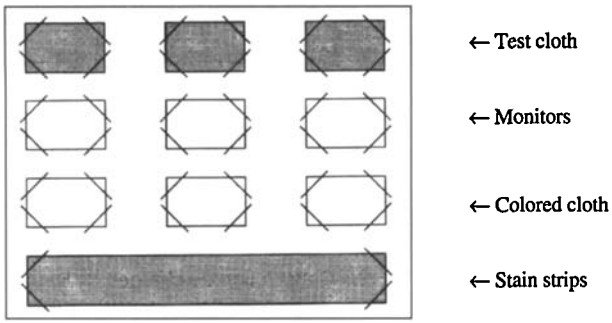

Fig. 11.6. Arrangement of test cloths and stain cloths to be loaded into the machine.

Comments

The different stain cloths (or stain strips), along with the test cloths and monitors, are usually pinned to an article such as a hand towel, to prevent them from rolling into a ball and distorting the results. Figure 11.6 shows how the cloths are arranged. In this way, contact between the wash solution and the cloths will be optimal.

Naturally soiled clothes. Test Method 1: Identical loads can be prepared in different ways. The first test method is the general one and involves differing test loads of dirty clothes. Numerous families are recruited to supply dirty laundry (Fig. 11.7). Very lightly or heavily soiled articles are removed, to keep each of the loads balanced (Fig. 11.8). After sorting, the remaining items are divided into balanced wash loads in terms of soiling and weight (Fig. 11.9). This protocol of sorting clothes is complicated

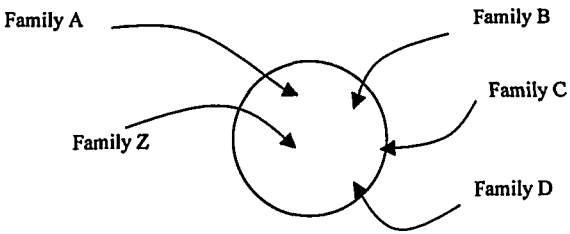

Fig. 11.7. How wash loads of dirty clothes are made up.

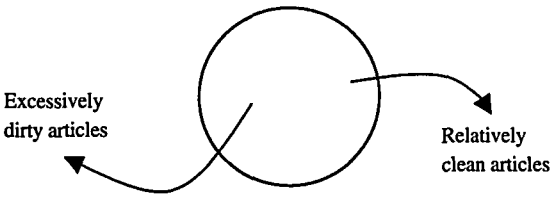

Fig. 11.8. Sorting the wash.

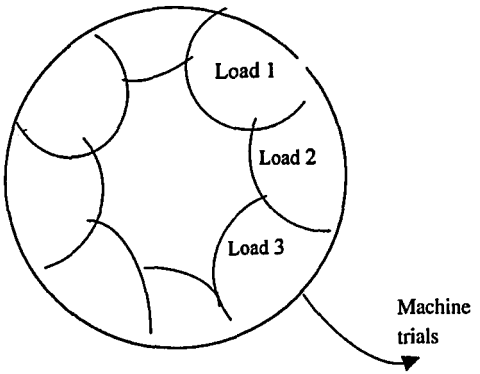

Fig. 11.9. Making up wash loads of dirty clothes.

because a large quantity of items is needed at the beginning to be able to make up the number of balanced loads required for statistically valid results.

Test Method 2: This is the split-articles test. In this case, the number of families involved is small. Each family is asked to supply clothes that have been worn; similar articles, supplied by the laboratory, are cut in two to compare two detergents. In this way, soiling is perfectly balanced between washes (Fig. 11.10).

Test Method 3: This is the wash-and-wear test. In this test, families are supplied with articles which they use and return for washing with product X by the formulator, who then returns the clothes for wearing, and so on. This test method allows a comparison of detergents on various fabrics and articles over a long period of time, with the same articles always washed in the same detergent.

Product Evaluation. Before all tests, an experimental plan should be drawn up according to the general scheme in Table 11.2, using the following procedure:

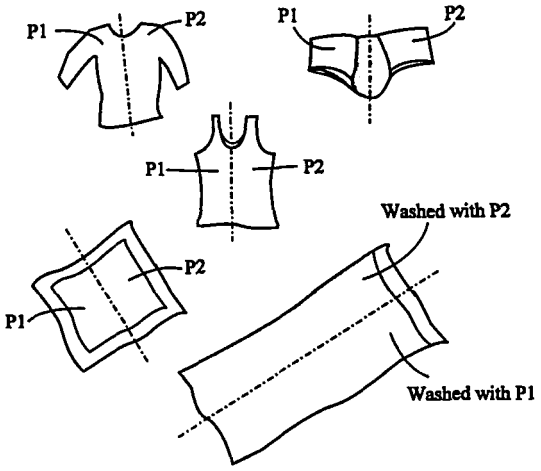

Fig. 11.10. Splitting of soiled test articles.

TABLE 11.2
Sample Plan for Product Evaluation of Laundry Detergents

Product P1	Wash #	1	2	3	4	5	6	7	8	9	10	15	20	25	50
Test cloths	AS 12	X	X	X	X	X	X	X	X	X	X	X	X	X	
	AS 8	X	X	X	X	X	X	X	X	X	X	X	X	X	
	AS 10		X	X	X	X	X	X	X	X	X	X	X	X	X
	EMPA 114	X	X	X	X	X	X	X	X	X	X	X	X	X	
	BC1		X	X	X	X	X	X	X	X	X	X	X	X	X
Stains	Stain 1	X	X	X	X	X	X	X	X	X	X				
	Stain 2	X	X	X	X	X	X	X	X	X	X				
	Stain 3	X	X	X	X	X	X	X	X	X	X				
	Stain 4	X	X	X	X	X	X	X	X	X	X				
	Stain 5	X	X	X	X	X	X	X	X	X	X				
Soiled laundry 1-cycle wash	Redeposition and/or Fluorescence	X	X	X	X	X	X	X	X	X	X	X	X	X	
Test cloths Multicycle washes	Redeposition and/or Fluorescence	X				X									
		X									X				
		X										X			
		X											X		
		X												X	
	Incrustation	X												X	
	Softening evaluation	X													X
	Colored cloths	X									X				
		X												X	
		X													X

For a given product, the artificially soiled test clothes will be used in the first 25 wash cycles, and stains in the first 10 wash cycles only. Redeposition and fluorescent whitening will be measured after one wash cycle (average of 25 measures) and cumulatively after 5, 10, 15, 20, and 25 wash cycles. Mineral incrustation (ash levels) will be determined after 25 and 50 successive cycles.

Only one water hardness will be studied [e.g., 25° French (FH)], and this will determine dosage. Additives will include chlorine, softeners, and so on. Before starting the test, the prototype formulations and the reference product should be checked to ensure that they have the expected composition (e.g., actives level, bleaching agents, or enzymes) and that their physical characteristics are correct (e.g., speed of dissolution). Competitive products will usually be purchased in the trade and analyzed.

In this type of evaluation, it is important to use a selection of washing machines representative of the market being studied (different manufacturers and models). Let us assume that the products are to be tested in a brand X machine. If four products are being used, four similar model X machines will be needed (usually purchased at the same time). It is not essential that they be identical because the test products will be used in all of the machines the same number of times. For example, if the available machines are M1, M2, M3, and M4, products will be rotated in the different machines as shown in Table 11.3. Machine parameters such as length of cycle, temperature, and water in and out, are checked continuously to expose any technical problems quickly.

If the test is an all-temperature detergent, the study should be conducted at low, medium, and high temperatures. If the 90°C cycle without prewash is used, this will determine the type of cloth to use (no polyester or cotton/polyester), and more particularly a load of 4–5 kg cotton or 2–2.5 kg synthetics. Ideally, tests should be conducted using normally soiled domestic clothes, in other words, under real user conditions.

Performance measures on test cloths. Washing performance is measured instrumentally and by visual observation. Here we will discuss reflectance and fluorescence. We have already mentioned the reflectometer, which is used to measure the whiteness of soiled test cloths and white monitors. Different instruments can be used to measure reflectance on cloth (Elrepho, Gardner, Hunter). Whiteness is determined by measurement of the reflectance accross the spectrum. Specific measurements can be taken at a given wavelength using the tristimulus filters, e.g., flu-

TABLE 11.3
Rotation of Products in Machines

	M1	M2	M3	M4
1st wash	P1	P2	R1	C1
2nd wash	P2	R1	C1	P1
3rd wash	R1	C1	P1	P2
4th wash . . . and so on	C1	P1	P2	R1

orescence, color, on articles (effect of dye transfer or color fading). For example, in the fluorescence reflectance is measured at a given wavelength (for example, 460 nm) and is divided into total *RT* reflectance [reflected light + fluorescence emitted by the fluorescent whiteners on the cloth, excited by ultraviolet (UV) light], and true *RV* reflectance (excluding UV), which is obtained by placing a filter in the beam of incident light to filter the UV light. The fluorescence of a cloth (*F*) is equal to $RT - RV$.

Most evaluation tests use test cloths. In all cases, the comparison method among products is the same and involves measuring cloth reflectance before and after washing as follows:

1. Measure cloth reflectance before washing. Cloths should come from the same bolt of cloth. About 10 readings on the reflectometer are enough to obtain the average reflectance before washing (initial reflectance, R_i). Generally, the measurements are done on test pieces of 10×10 cm^2 folded in four (the area measured by an Elrepho-type reflectometer is a 30-mm diameter circle). On unwashed cloth, reflectance is generally measured excluding UV (real reflectance). A reading of 100% is perfect white, and 0% is perfect black.
2. Measure cloth reflectance after washing with the different test products. Since artificial soiling is not removed evenly, four measurements should therefore be made on each test cloth to obtain a value that is representative of the whole cloth in a given wash (final reflectance, R_f). The efficacy of a product is expressed by $R_f - R_i$, commonly called ΔR. Thus, for an experiment including 10 repeat washes, each ΔR for product P1 will be compared with the ΔR of product P2 to complete a study with statistically valid results (statistical methods are dealt with in Chapter 17).

Unsoiled cotton, polyester, or polyester/cotton are the most common white fabrics for measuring redeposition. These white cloths tends to grey with an increasing number of wash cycles as a result of cumulative pick-up of soil suspended in the wash liquor. In contrast to soiled test cloths, the reflectance of white cloths will be reduced over successive washes. This gives the following relationship: % redeposition = f (number of washes). Over successive washes, the fluorescent whitening agents on cloth and increase the whitening effect. The dye transfer effect is measured using tristimulus filters on the Elrepho.

Evaluation of stain removal. The same stains, washed with different products, are usually compared by a panel of 10 trained examiners who view the washed articles in conditioned light (artificial daylight) to avoid uncontrolled external influences. The panelists grade the stains while simultaneously ranking the products among themselves. Stains are graded by a score relative to a pre-established standard, e.g., 1 = 100% residual stain; 5 = the stain has disappeared completely. (Some people prefer to judge the results by the tristimulus measurements.) Grading is used to determine the best product, using statistical methods that we will discuss in Chapter 17.

General detergency on naturally soiled articles. To prepare equivalent lists, a large quantity of soiled laundry is needed. The personnel who sort the laundry are specially trained, and the procedure is as described above for soiled test cloths. If products are to be tested in parallel, four identical loads are prepared simultaneously.

After washing, the wash loads are evaluated visually by specialists who are capable of judging the nuances, size, and intensity of residual stains and soiling. Paired comparisons are also possible, using a panel of judges to compare the results obtained with different products. The panel may also assign a relative detergency score (a percentage) for each article and then average out the entire wash load to obtain a final score.

In the split-article test, trained judges compare the half of an article washed with product P1 directly with the other half washed with product P2, all articles being viewed under conditions of artificial light.

In the wash-and-wear test, worn articles A1 are compared after washing in product P1, with articles A2 washed with product P2. Articles A1 are always washed with P1, articles A2 are always washed with P2. A minimum of 10 wash cycles is required before the results become significant.

Softness evaluation. This test method requires either ~10 trained panelists or a larger panel of 25 nonspecialists. The test fabric is usually terry toweling, which is evaluated after 25 or 50 washes. A grading from softest → least soft is established. A score can also be given relative to control cloths that are more or less soft.

Performance Tests of Fabric Softeners

Various test methods that should give an objective measure of softness have been developed, but none is really satisfactory. The formulator generally must use a panel of trained technicians for making softness evaluations. The test method is comparable to that described above. It consists of classifying samples of toweling from the softest to the harshest or comparing these samples with a standard series. The standard series has been washed under controlled conditions and softened to varying degrees to provide a range of softness (Table 11.4). The use of such a reference range, in addition to the grading exercise, allows products to be tested at different times with the condition that the parameters for preparing them and the cloth are kept constant.

TABLE 11.4
Reference Range

	(%)		(%)
Extremely soft	100	Average	50
Very soft	90	Slightly harsh	40
Quite soft	80	Harsh	30
Soft	70	Very harsh	20
Slightly soft	60	Extremely harsh	10
		Completely harsh	0

Performance Tests of Dishwashing Liquids

The performance of a dishwashing liquid is evaluated on two main parameters, i.e., quantity and stability of the foam during the wash. To evaluate foam, a number of parameters are important, including the following:

(i) the nature of the soil;
(ii) the uniformity of soiling on the test plates/dishes;
(iii) water temperature;
(iv) water hardness;
(v) product concentration; and
(vi) the precise determination of the moment at which there is no more foam (% of the surface not covered).

The test generally consists of washing a certain number of dishes that have been previously soiled. The exact soils, their quantity, the time they have been allowed to dry on the dishes, and the conditions of drying must be defined. The foam level is measured at regular intervals, and the number of dishes washed is counted until there is no foam left. The operation is usually carried out by about three trained operators to obtain an average that takes into account the individual habits of each operator.

Performance Tests of Other Hard Surface Cleaners

Evaluation of All-Purpose Cleaner Performance. To evaluate the performance of an all-purpose cleaner, the manner of application and the mechanical energy applied must be simulated. A Gardner Straight Line Washability Apparatus is often used. The cleaning head of the machine is wet with a solution of the test product. The head moves back and forth on the chosen substrate, which has been previously soiled uniformily with grease, oil, or various other soils. After a given number of passes, the cleanness of the surface is evaluated by panelists who compare different products. The increase in reflectance of the cleaned substrate is also measured using a reflectometer. Other more sophisticated machines (e.g., circular action machines) for testing are available, usually based on the same principle.

Scouring Powder and Liquid Performance Tests. To evaluate a scourer, whether liquid or powder, two parameters should be taken into account, i.e., the types of surfaces usually cleaned and the types of soiling and stains normally encountered. Many combinations are possible, and each manufacturer will have unique test methods preparing the test soil. Surfaces can include tiles, formica, paintwork, glass, linoleum, porcelain, or enamel. Stains and soils may include an oily soil, rust, dust, or food soils, such as tea, coffee, burned milk, or calcium deposits.

Trained panelists can be used to test product performance; for example, clean a stainless steel sink in a given time and then judge performance in terms of the overall

result, how well the product rinses, in how much time, and whether it has left particulate traces. A machine such as the Gardner apparatus referred to previously is used to measure the abrasive effect of the product by passing a sponge loaded with the product over a surface a given number of times. This machine can also be used to do comparative performance tests, with the test surfaces evaluated by panelists or optically. Some manufacturers also have special tests to assess product feel because solid particles should not be unpleasant to touch. This is why their shape and size are important.

Performance Evaluation of Personal Care Products

Toilet Soap

General Performance. Several panelists wash their hands several times a day with the different test products. Criteria include the following:

(i) the amount of foam;
(ii) the appearance of the foam;
(iii) the effect of the product on skin, during and after washing, i.e., mildness or harshness;
(iv) the perfume during use and for some time afterward;
(v) rate of use-up; and
(vi) defects in the soap, e.g., mush, cracking, or hard bits.

Antimicrobial Soap Effectiveness. For the "hygiene" effect, two of the tests used to measure actual antimicrobial effect are as follows:

1. Bacterial contact time (BCT). This test is used to show how long the antimicrobial takes to destroy 99.9% of test microorganisms. A given quantity of these microorganisms is introduced into the soap solution; then a sample is removed every 15 s during min 1, and then every minute for 5 min thereafter. After incubation, the colonies are counted.
2. Finger imprint test. The main benefit of antimicrobial in a soap is that it is deposited on the skin after use, and inhibits growth of antimicrobial bacteria in pores and follicles as well as those from contact with the outside or the environment. In the test, hands are washed and then placed in contact with a gel containing selected bacteria. If the bacteria fail to grow in the contact area, the antimicrobial effect is present.

Shower Gels and Bath Foams

Among the different test methods used, one is the subject of World Patent 9,403,151 (1). Volunteers wash one of their arms with 0.5 g of control product using their free hand. After rinsing for 10 s, the arm is wiped with an absorbent paper of the Sopalin type. After this wash, the panelist uses the test product. Ten seconds after drying, a

transparent adhesive tape 25 mm wide is placed on the area that has just been washed and is held under constant pressure of 85 g/m^2 for 30 s. The silicone softening agent contained in the product is transferred from the skin to the tape. The quantity of silicone transferred is then determined using different techniques, one such being X-ray fluorescence spectrometry. This method allows a comparison of the efficacy of the different test products as a function of the amount of silicone absorbed.

Shampoos

One of the main criteria in studying a new shampoo is its application to hair. To examine this, experienced professional hairdressers are often asked to assess the main attributes of the new product. Subsequently, panels and consumer tests are used to refine the assessment. But as always for a detergent product, laboratory tests can be used to clear the way.

Laboratory Evaluation. The main parameters are:

1. Foaming properties. A number of techniques have been developed to reproduce the rubbing motion of hands on the scalp, for example, a "screening test" using household food mixers for new formulations. The main difficulty is obtaining good reproducibility of the test in terms of time, speed of agitation, or foam temperature. A standard soil, taken from the scalp, for instance, can be added. This test method correlates with measurements taken *in vivo* for the amount of foam, but not for its viscosity or specific volume. Other similar test methods exist, but they all have the same disadvantages as those mentioned above.
2. Detergency. The classical procedure is to immerse a soiled surface in a test solution under precise conditions in terms of duration, temperature, and degree of agitation. The soil itself poses problems. Some authors recommend lanolin (from wool), or certain types of sebum. The substrate can be cloth, for example.
3. Cosmetic properties. Test methods have been developed to measure ease of brushing and combing, but interpretation is not always easy.

Real-Life Evaluation and Criteria Involving the Senses. As we have just seen, nothing can replace direct evaluation on real hair. A comparison is usually made; each half of the head is washed simultaneously by two trained technicians, using a reference shampoo and an experimental product, respectively. The head is washed twice, with a rinse between washes. Factors tested include foaming properties and quantity of foam (e.g., volume, softness, creamy appearance, density, or ease of rinsing); ease of use; detergency; cosmetic properties; speed of drying; and, on dry hair, ease of brushing, shine, body, and condition of the ends. Some of these criteria can be tracked for several days after use of the product; it is also important to study the cumulative effect over a number of washes, particularly for oily hair or antidandruff shampoos (for which prototypes should be tested on many different kinds of hair).

Comments
Skin and eye irritation tests are also done; these will be discussed in Chapter 19.

Dentifrices

Various test methods can be used to measure dentifrice efficacy, for example, of an anticaries agent. Two examples are laboratory tests and clinical tests.

Laboratory Tests. The principle is to measure the solubility in acid of hydroxyapatite (HAP), which is the constituent of enamel. The lower the solubility, the greater the resistance of enamel to attack by acid. In the test, a HAP powder that has been treated with fluoride compounds is contacted with the acid for a time *t*. After filtering and drying, the residual of HAP is weighed to determine solubility compared with that of an untreated HAP control. The difference in the degree of solubility of the two products gives the efficacy of the anticaries system tested. Instead of HAP, extracted teeth can be used in the same manner as described above.

Clinical Tests. In Chapter 10 we mentioned the Unilever test method of evaluating the efficacy of a fluoride toothpaste, which was used in Norwegian schools for a 3-y period. Similar clinical tests have been conducted by other organizations, including the following example carried out by Goupil Laboratories (2). A toothpaste formulation was tested in parallel with other control formulations on patients with caries. The panelists brushed twice a day for 2.5 min each, once in the morning and once in the evening before bed. The study was conducted on children from ages 8 to 14 years living in boarding schools (ensuring daily controls) and lasted for 3 years. Dental surgeons regularly checked for caries using the DMF index (also used by the World Health Organization), a set of criteria in which D = decayed (caries), M = missing, F = filled.

The difference between the DMF index at the end of the test and the DMF initial measurement gives the increase in caries. From this definition, a large positive difference corresponds to a significant increase in the number of caries at the end of the test compared with the original measurement. A small increment means a slight increase in the number of caries at the end compared with the beginning. The results of clinical tests can be expressed as either an increase, i.e., (DMF tooth index at the end of the test – DMF tooth index at the initial measurement) or as a percentage in the reduction of caries, i.e., (test product increment – control product increment)/control product increment × 100.

References

1. World Patent WO 9,403,151.
2. Goupil, European Patent EP 0138,705.

CHAPTER 12

Manufacturing Processes

Introduction

This chapter will give some examples of the manufacturing process for the products discussed in previous chapters. We will not go into great detail because each large manufacturer has particular secrets and know-how that make a difference in the final product. For example, the simple application of a well-known process, such as spray-drying a conventional powder, will not always result in a product with little sodium tripolyphosphate (STPP) breakdown, good flow properties, and satisfactory behavior in the washing machine.

The examples given here are often taken from patents. In addition, certain raw material suppliers provide advice on the best way to incorporate their materials into a product. Machinery suppliers also develop their own manufacturing processes to help sell complicated machinery, sometimes on a "turnkey" basis (e.g., installation of a conventional or concentrated powder line, equipment for the manufacture of toilet soap from A to Z, or toothpaste manufacturing machinery).

Detergent Powder Manufacturing

Powder Detergents

Conventional Powders. Traditional detergent powders are manufactured in three stages:

1. Preparation of a mixture of liquid and solid raw materials (the "slurry"), which can stand high temperatures, and which is then atomized ("spray drying").
2. The "base powder" thus produced is allowed to cool before the more sensitive ingredients are added, i.e., "postdosing."
3. The final powder is packed.

Slurry making and spray drying. The mixture is obtained by addition to water of raw materials such as phosphates or zeolites, carbonate, surfactants, polymers, or brighteners. Certain precautions must be taken; for example, fatty acids/sulfonic acid should be neutralized separately in a mixer before introduction into the slurry. The mixture is agitated strongly to obtain good homogenization before it is sent to a second mixer where the inorganic salts (Na sulfate, carbonate, and, of course, STPP) are hydrated for a set period of time. The mixture is then pumped under high pressure through calibrated nozzles at the top of the spray tower, and drops through a countercurrent flow of hot air (~400°C). Small particles 500–700 μm in

size are formed and constitute the base powder, which cools gradually as it is transported in the open air, and is then stored in a silo.

These are obviously no more than general principles. Each manufacturer has a particular know-how for slurry making and powder blowing, covering variables such as temperature, residence time, or water content, with the aim of minimizing STPP breakdown, obtaining good physical properties of the product such as:

(i) good powder flow;
(ii) granulometry;
(iii) stability during storage (e.g., no caking); and
(iv) good dispersion from the washing machine dispenser.

Figure 12.1 shows the basic principles of manufacturing a conventional powder.

Postdosing. Sensitive ingredients such as enzymes, perborate, tetraacetylethylenediamine (TAED), antifoams, or perfume must be added at <35°C to avoid decomposition. The finished powder thus obtained is an intimate mixture thanks to the utilization of mixers (e.g., fluidized bed).

Comments

Handling of enzymes requires special safety precautions to avoid all risks to workers in contact with them. In particular, enzyme dust should be avoided. More details concerning the handling of enzymes will be given in Chapter 19.

Packaging. The product obtained after mixing is then put into packets, boxes, or drums equipped with a dosing system.

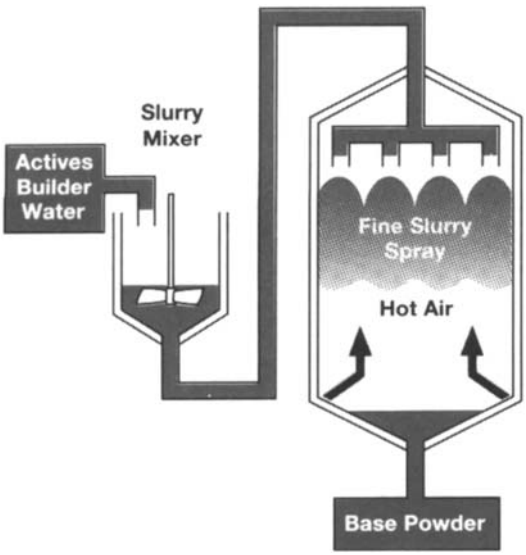

Fig. 12.1. Powder manufacture. Figure reprinted with permission of Lever Europe.

Concentrated Powders. There are two ways to manufacture concentrated powders: densification of a blown powder or densification and granulation from raw materials without atomization (nontower route, NTR).

Densification of a blown powder. A number of processes are available, one of which we have already mentioned in Chapter 3 (1). Another is described in two patents (2,3) that explain how to make a concentrated powder in two steps. In Step 1, the powder is crushed at high speed in a mixer/granulator for a short period of time (5–30 s) to reduce the porosity of the particles. These particles can be reshaped. At this stage, liquid components such as nonionics can be added to increase the content of the product surfactant. Mixer/granulator types include the Lödige Recyler CB 30, the Schügi granulator, or the Drais K-TTP 80. After Step 1, the porosity of the powder still remains high. In Step 2, the powder is transferred to a second mixer/granulator where it is processed in a similar manner for 1–10 min, but at slower revolutions. During this stage, the porosity is further reduced, and dispersible solid particles, such as zeolite, carbonate, and amorphous calcium silicate, can be added. Addition of these particles helps prevent agglomeration and ensures good flow properties of the powder. Mixers used in this second phase are the Lödige Ploughshare or the Drais KT type. Next, the powder is transferred to the postdosing station where sensitive ingredients such as perborate, TAED, and antifoam granules are added.

This process can achieve far higher densities (700–750 g/L) and higher active levels (20% higher) while retaining good physical properties such as granulometry and flow properties. Figure 12.2 is an example from a Unilever patent (3).

Nontower route (NTR). Considerable literature exists concerning this process, as well as many patents (4–6), and publications from equipment suppliers such as

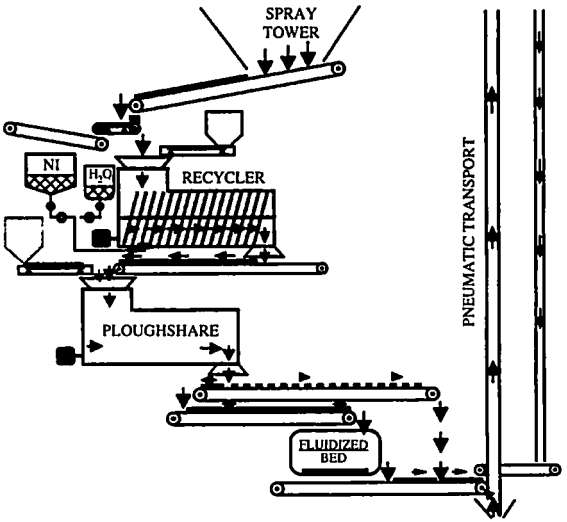

Fig. 12.2. Concentrated powder made from a blown powder. NI, nonionic.

Ballestra who offer turnkey plants. This process has many advantages as follows:

(i) even higher densities (0.8–0.9 g/L) can be obtained;

(ii) a wider range of surfactants, e.g., nonionics, primary alcohol sulfate (PAS), or alkylpolyglucoside (APG®) can be used;

(iii) energy consumption is decreased; and

(iv) equipment costs are lower. The major drawback lies with the solid components, particularly builders, which must have high absorption capabilities for the liquid components of the formulation.

It is not possible to discuss here all of the methods used; we will give one example (2) from among the many that are mentioned in the patents. Like the process described above for the densification of a blown powder, this process consists of two main steps. Step 1 involves the preparation of an anionic surfactant by neutralization of its precursor acid with a soluble alkaline inorganic salt in a high-speed mixer. Processing time is very short, i.e., only 5–10 s. The soluble inorganic salt can be carbonate or bicarbonate, or sodium silicate. The anionic precursor can be the acid form of linear alkylbenzenesulfonate (LAS), α-olefinsulfonate (AOS), or primary alkyl sulfate (PAS). The final mixture contains other ingredients, such as nonionics, fatty acids, builders, antiredeposition agents, and fluorescent whitening agents. In this manner, one obtains malleable granules with low water content. Their porosity remainds high at this stage.

In Step 2, the granules are transferred to a second granulator which operates at a lower speed. The time in process is longer, i.e., 1–10 min. During this step, porosity is reduced, increasing the density of the granules, which are then transferred to a fluidized bed for cooling. These granules form the base to which are added heat sensitive ingredients such as enzymes and bleaching agents in the post-dosing operation. One possible NTR process is shown in Figure 12.3. The mixer/granulators include those from Lödige, Eirich, Drais, and Ballestra.

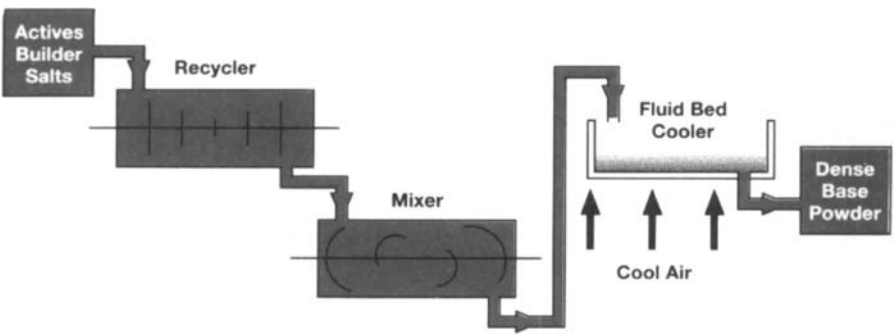

Fig. 12.3. Nontower process. Figure reprinted with permission of Lever Europe.

Comments

Certain powdered ingredients cannot be post-dosed as such onto the base powder, for a number of reasons:

1. The physical properties of the powder and its behavior will be changed. For example, postdosing of sulfate or carbonate that is too fine will result in caking and poor dispersibility in the washing machine dispenser.
2. Some ingredients such as powdered enzymes, TAED, and antifoams, are not storage-stable unless they are encapsulated or granulated.
3. For enzymes, several methods of encapsulation were mentioned in Chapter 2.

For TAED, which is not very soluble, a small particle size is required to ensure that it dissolves as soon as the powder enters the wash solution. Powdered TAED cannot be used because, in contact with perborate and free water in the detergent product during storage, it forms peracids with a resulting loss of performance. TAED must therefore be granulated to minimize contact with perborate and the resulting perhydrolysis or hydrolysis. The granules must break up quickly in the wash solution to liberate and dissolve the TAED quickly. Granulation processes are part of the specific know-how of the manufacturers.

Other Powders

Manufacture of Machine Dishwashing Powders. The process is simple and is carried out in a mixer which does not crush the powder and cause dust. After the nonionic liquids are dosed onto the base formulation (STPP or citrate + carbonate), the other ingredients are added until a homogeneous mix is obtained. The mixers mentioned above to manufacture concentrated powders can be used.

Manufacture of Scouring Powders. Scouring powders are easy to make because they are dry-mixed. Liquid surfactants and perfume are generally sprayed onto (part of) the abrasive, and then the remaining solid ingredients are added. A slow-speed mixer is used to avoid damaging the particles and creating dust. For safety reasons, silica is no longer used; this abrasive can also scratch the surfaces being cleaned.

Manufacture of Liquids

Most liquids are made with premix tanks, mixers with different agitators, and so on. To simplify, we give an example of a line for manufacturing liquid detergents in a batch process (Fig. 12.4). Every line is a bit different, with various pumps, intermediate tanks for the preparation of premixes, agitators with blades or variable speed turbines, and explosion-proof motors. However, these lines do not differ greatly from one another. For simpler liquid products, there are continuous lines such as the one shown in Figure 12.5.

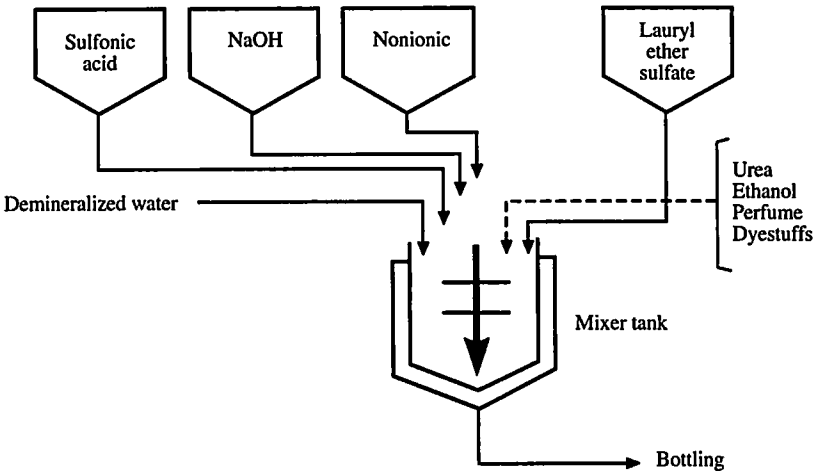

Fig. 12.4. Line to produce liquid products.

Liquid Detergents

Manufacture of Isotropic Liquid Detergents. The process is simple. In a temperature-controlled first mixer, fatty acids and sulfonic acids are neutralized. This is followed by cooling and mixing with the rest of the formultion (e.g., alcohol, enzymes, perfume, or colorants) in a second mixer. The order in which the raw materials are added has an effect on the stability of the finished product. For each formulation, the order of addition must be studied in order to achieve the best stability.

Structured Liquids. Structured liquids impose more constraints because of the number of variables that affect product stability. These include the order of addition of raw materials, the water temperature, and the speed of mixing. We give here an example from the Unilever patents (7,8). Water is pumped into the main mixer and agitated. In the secondary mixers, soaps or sodium carboxymethylcellulose (SCMC) are prepared if required. Sodium silicate, SCMC, Na LAS, K oleate, and optical fluorescent whiteners are added to the main mixer, still with moderate agi-

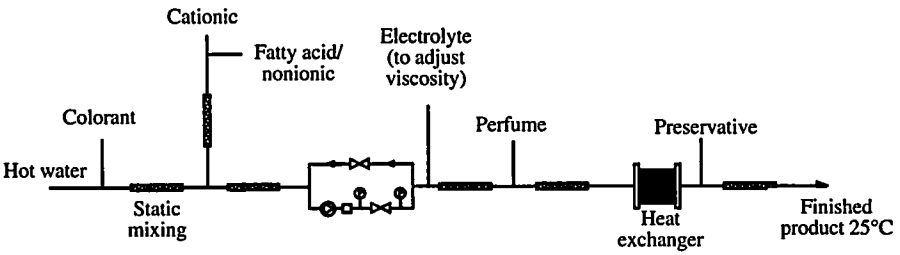

Fig. 12.5. Continuous line to produce liquid products.

tation, and the mix is heated to ~60–70°C. When this temperature is reached, heating stops, STPP is added, and agitation continues until the mixture is homogeneous. Then, nonionics are added and the mixture is cooled with continued stirring until the temperature drops to 30–35°C. Finally, the missing water is added (e.g., water lost by evaporation during the process) along with perfume, silicone, and enzymes. For nonphosphate liquids, deflocculation polymers are added after the zeolite. An alternative is to prepare a mixture of polymers and surfactants to be added into the mixer, as is done for liquids with STPP.

Manufacture of Liquid Scourers

This process is very similar to that described for structured liquid detergents with slight changes, such as the following:

(i) phosphate at twice its weight in hot water is added during mixing and the solution is cooled to 43–45°C;

(ii) the surfactants are dissolved in the rest of the hot water and then cooled before addition of alkanolamide; and

(iii) the two premixes are combined, and an abrasive is added along with the other ingredients (e.g., perfume).

Manufacture of Fabric Softeners

The manufacture of dilute fabric softeners is relatively simple. The colorants are added first to hot water at 70–75°C in a mixer, followed by the preheated cationics in liquid paste form. Agitation is strong for some time to obtain a homogeneous dispersion, which is then cooled to 25–30°C. Finally, Formol is added, followed by perfume and possibly a solution of $CaCl_2$ and acid to adjust viscosity and pH.

The production of a concentrated conditioner is more complicated, particularly if distearyldimethylammonium chloride (DSDMAC) is used. One method is given below as an example (9). The cationic is heated above its Krafft point, added to hot water containing certain quantities of electrolytes, and strongly agitated in a mixer. The nonionic is then added to control the viscosity. The new mix is then cooled quickly to below its Krafft point, still under agitation. Volatile ingredients such as perfume and preservative are then added to the mixture. Nonvolatile compounds such as colorants can be added at any time during the process.

Another method (10) can be used to manufacture a superconcentrate >35% ester quat. Two cationic compounds are used. They are heated and mixed together to form a paste system which is held at ~70°C. This mixture is added to water containing polyethylene glycol (PEG) and hydrochloric acid. A thick emulsion is formed, to which a $CaCl_2$ solution is added. Perfume is added to this mixture in the form of a perfume/water/nonionic emulsion. The new mixture is cooled to 30°C, still under agitation. Colorant and sometimes a preservative is added at this stage. This gives a final product with a viscosity of ~1400 mPa · s.

Manufacture of Dishwashing Liquids

This is a simple process, which can be summarized as follows:

Sulfonic acid
↓
Neutralization (by NaOH/KOH/NH_4OH in solution)
↓
Adjustment of pH (alkali or acid)
↓
Introduction of nonionic/lauryl ether sulfate (LES)
↓ ← Adjustment of viscosity: salts (for ↑)
Cooling solubilizers (for ↓)
↓ (hydrotopes)
Introduction of colorants, preservatives, and perfume

Some precautions must be taken as follows:

(i) slow agitation during the neutralization stage;
(ii) cooling of the main mixer to avoid exceeding a certain temperature during neutralization;
(iii) pH should be neutral before adding the nonionic component (unstable in an acid environment).

Viscosity control. In the worst of cases, the addition of too much salt will cause "salting out" of the organic components, and at best will raise the cloud point so that the product would start turning milky at undesirably high temperatures. Hydrotopes can be added directly to the water before the other ingredients. The function of the hydrotopes is not only to adjust the viscosity but also to influence the cloud point, or stability at low temperatures. Alcohols should be added after neutralization and before addition of the ether sulfates. The use of preservatives is recommended. That choice varies by country, depending on legislation.

Manufacture of Shampoos

The manufacture of shampoos may appear simple. To a certain extent this is true, but to avoid instability does require the greatest care, particularly in the order of addition of the ingredients, the duration, and the speed of mixing. Each manufacturer has a unique know-how, and a large variety of processes exists. The most common method, found in the publications of raw material producers, is as follows:

1. Prepare the various premixes in the secondary mixers, e.g., the ethylene glycol monostearate (EGMS) or ethylene glycol distearate (EGDS) opacifier emulsion; perfume + polymer + preservative.
2. Add the surfactant (for example, LES) to hot water in the main mixer while agitating strongly.

3. Addition of the different premixes should be in a well-defined order, specific to each manufacturer, in order to obtain the right stability in the final product.
4. Sensitive ingredients should be added once the mixture has cooled down to <30°C.

> **Comment**
> When an 80% active LES is diluted, the resulting solution becomes viscous and can give rise to agglomerates that are very difficult to dissolve. It should therefore be introduced into the mixer, together with water, using a pump with a high shear rate. The cosurfactant, cocoamidopropyl betaine (CAPB), should be added in the cold.

For illustration, we cite here an example from the Procter & Gamble patents (11) of the manufacture of a conditioner. All ingredients except the preservative, perfume, and therapeutic agents (antidandruff) are added to distilled water held at 65–74°C. This mixture is agitated for 15 min. The solution is then cooled to 49°C, and the other ingredients, such as preservative, perfume, or antidandruff agents, are added. The final mixture is then cooled to 38°C and agitated at high shear for 2 min. Addition of silicone (the conditioning agent) can cause problems. It should be added in the form of an emulsion. The process for preparing such emulsions is described in one of the Unilever patents (12).

> **Comment**
> As in the case of fabric softeners, the production line should be completely free of bacterial contamination. The machinery, the plant environment, and the raw materials (particularly colorants and water) should all satisfy this requirement.

Manufacture of All-Purpose Cleaners

The process is simple; the different ingredients in the formulations given in Chapter 7 are mixed on a liquids production line such as the one described in Figure 12.4.

Manufacture of Shower Gels and Bath Foams

This process is more or less similar to that described for shampoos.

Manufacture of Soap

Raw Material Preparation

The fats/oils can be bleached and deodorized before or after mixing. The second option is preferred. Prior to bleaching and deodorizing, contaminants from fats (carotene, blood, sap, or chlorophyll) and impurities from the environment (water, rust, or dust) are removed. The bleaching line (Fig. 12.6) includes

- a mixer [1]
- provisions for heating/cooling of the fat,

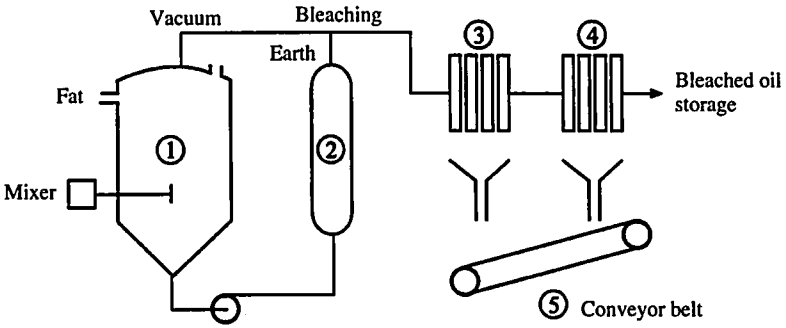

Fig. 12.6. Fat bleaching line.

- bleaching earth [2],
- a main filter [3], and
- a finishing filter [4].

The spent filter cakes are used to make animal feed.

Manufacture of Soap by Direct Saponification of Fats

Three examples of this process are given.

Traditional Process. This process (batchwise, in kettles) can be used to manufacture many metric tons of soap at the same time. A mixture of fat and a caustic soda solution (47%) is boiled in open vats. The main problem with this process is the difficulty in obtaining a homogeneous mix; as soon as part of the fat reacts with the caustic solution, soap is formed and thickens the mixture. Steam is injected into the mixture to help the reaction, but the problem is mastering the process so that the vat does not boil over!

The Jet System (Continuous). This is the most widely used process, consisting of heating fat and caustic solution and pumping them into a "jet," which is a juncture of four pipes, the first carrying fat, the second caustic soda, the third steam (to help the reaction and to clean), and the fourth to remove the reaction mixture (see Fig. 12.7).

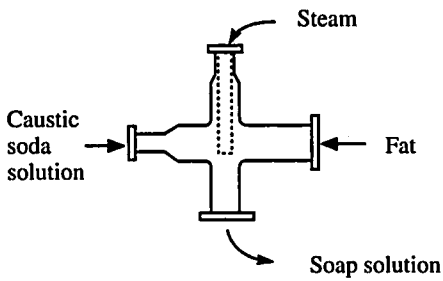

Fig. 12.7. The jet system.

The mixture is kept liquid by addition of a diluent. The diluent could be water. However, additional water not only lowers the soap concentration but also that of glycerine. Glycerine recovery is thus made more difficult and more costly because of the additional water that must be evaporated. For this reason, part of the glycerine solution recovered later in the process is used. The mixture, including soap, glycerine, excess caustic soda, salt (from the diluent), and water is subjected to cascade dilution as shown in Figure 12.8.

The Alfa Laval Process. This is a continuous process which employs a reaction column (~3 m × 0.75 m) with an external circulating loop. Fat is introduced at the bottom of the column using a proportioning pump. Caustic soda solution is introduced into the loop through a similar pump. The rate of the saponification reaction is increased by high pressure (4 atm, T = 140°). The soap from the reactor is pumped into a second similar column (without loop), in which the reaction is completed (Fig. 12.9).

Before transferring to the second reactor, cold diluting liquid is introduced to reduce temperature and fluidize the mixture. Reaction time is ~15 min in both columns. At present, there is a more modern version of this process without the circulating loop. In this version, the caustic soda/fats mixture reacts in the bottom of the reactor with agitation under high shear.

Washing. The next step separates the glycerine from the soap produced in one of the processes described above. Separation is based on the principle that glycerol is soluble in brine, and soap is not. Washing also helps to remove a large part of any colored impurities.

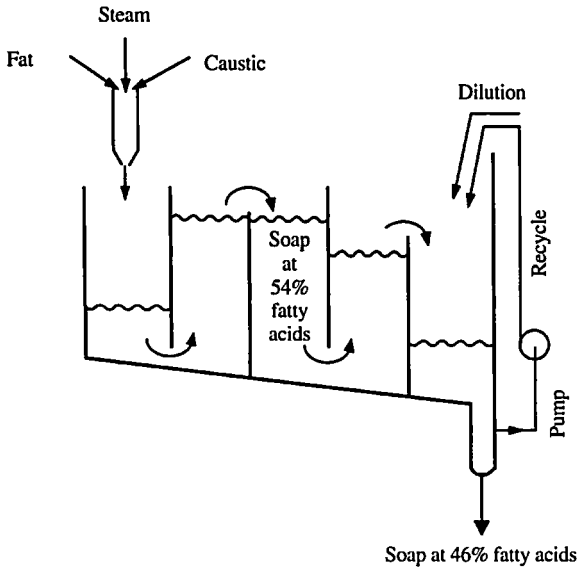

Fig. 12.8. Cascade dilution.

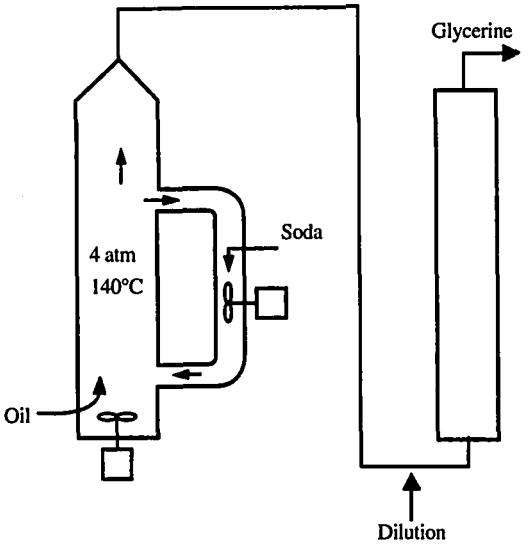

Fig. 12.9. The Alfa Laval process.

Kettle process. Washing is effected by mixing soap with a given amount of brine, using steam jets for agitation. After a few hours at rest, the soap rises to the top of the kettle while the glycerine and brine mixture drops to the bottom. This operation is repeated ~3 times using cold brine to remove all of the glycerine from the soap.

Countercurrent process. This system involves a series of tanks in a cascade arrangement in which soap is pumped (or flows) from one tank to the next, while the brine is pumped from one tank to the next but in the other direction, as shown in Figure 12.10. In each tank, soap and brine mix with each other, and with the brine in the lower layer. At the end of the process, the glycerine content in the brine is much higher than in the kettle process (~12–20% vs. ~5–10%).

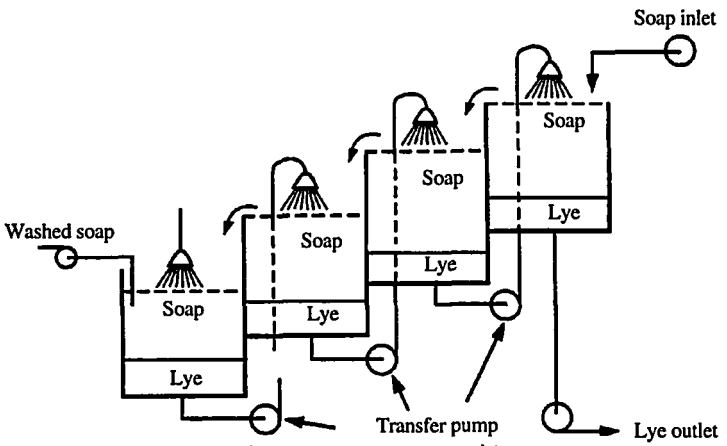

Fig. 12.10. The countercurrent washing process.

Dilution. The solution of brine + glycerine is sent for evaporation to recover the glycerine for sale, and the salt for reuse. The rest is recycled as diluent in the process.

Fitting. At this stage, the soap still contains a lot of salt that would harm its performance if left untreated. The fitting process reduces the amount of salt, removes residual colored impurities, and concentrates the soap solution. It consists of vigorously mixing the soap solution with a calculated amount of dilute caustic soda. Depending on the amount of NaOH, this gives a top layer of neat soap (63% fatty acids) and below, either a mixture of water, salt, caustic soda, and impurities (without soap) or a niger containing up to 25–30% soap, caustic soda, and impurities. In continuous processes, fitting is accomplished by injecting dilute caustic soda into the pipes that carry the washed soap to the centrifuge, whose speed separates neat soap.

> **Comment**
> In the modern integrated soap manufacturing plant, the fitting step is no longer needed.

Manufacture of Soap by Neutralization of Fatty Acids

As already discussed, this method is less common than the one described above. Its disadvantages are the costs (stainless steel equipment) and the fact that it produces large quantities of fatty acids, which only large manufacturers can handle. It also has considerable advantages. It is simple (see Fig. 8.4); there is no need for the washing and fitting steps; and it is flexible, particularly because the fat charges can be changed quickly. This process takes place in three steps, i.e., preparation, distillation, and neutralization of fatty acids.

Preparation. Water is pumped in at the top of a separator column and fat is introduced at the bottom. In the lower part of the column, the lower-density fatty matter rises, meeting the water/glycerine mixture near the top of the column. Conversely, in the upper part, the higher-density water drops through the rising fats (see Fig. 12.11). This process requires very high pressure (50 atm) and a temperature of ~250°C, so that the water does not boil while the fat hydrolyzes into fatty acids and glycerine. Steam is injected at different levels to maintain the temperature and to disperse the fat in the water. The fatty acids are then subjected to reduced pressure, the water they still contain boils off and thus separates easily from the 15% of glycerine (glycerol recovery).

Distillation. Fatty acids are distilled in two steps as follows: (i) a predistillation removes volatiles and odorants (<5%); and (ii) the main distillation eliminates unsaponified fatty matter, as well as degraded or polymerized fatty acids or polymers (≥5%).

Neutralization. This is generally done in a loop. First, a high shear mixer is filled with a mixture of distilled fatty acids at 100°C, followed by concentrated

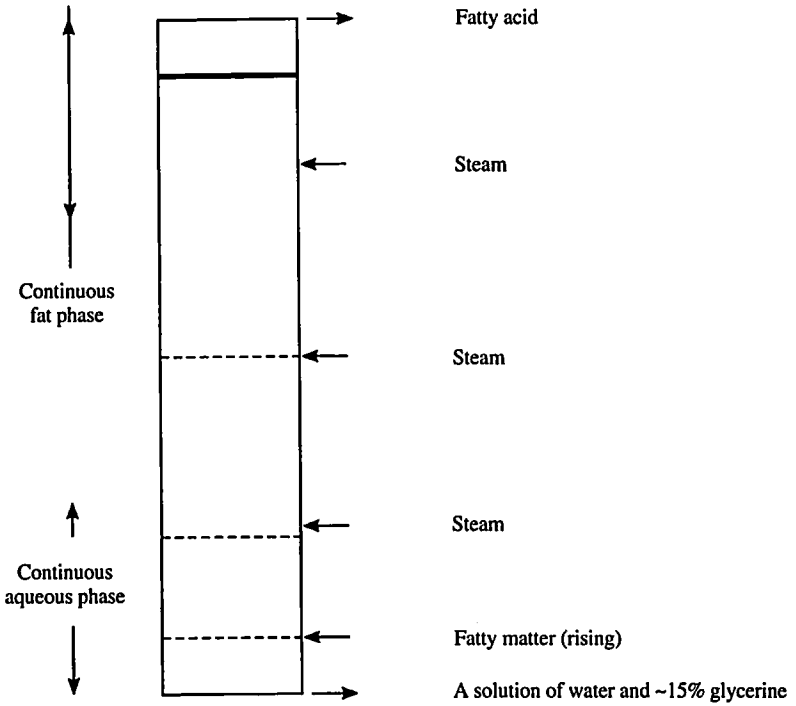

Fig. 12.11. Preparation of fatty acids.

caustic soda in solution at 90°C, and water containing salt, glycerine, and preservatives. This mixture is pumped into the loop under pressure (~5 atm) at ~140°C. The soap/water mixture thus obtained (~76/24) is then dried.

Drying of Soap Paste

The paste produced by one or another of the processes described above is dried under vacuum in an evaporator (Mazzoni and others), to give a dry soap containing 12–14% water (see Chapter 8).

Soap Finishing

Dried soap, whether in noodles or flakes, can be packed directly in large containers to be sold to other companies. This gives a financial advantage to companies that use soap flakes directly because, as we have seen, the manufacture of soap base is expensive and requires substantial investment. These companies can then "personalize" their soap by different attributes, such as color, perfume, or shape.

Returning to the manufacture of soap tablets after drying, the flakes are usually stored in silos that feed continuous packing lines. A weighing hopper is filled with 200–300 kg of flakes mixed with colorants and perfume in a first extruder, and then

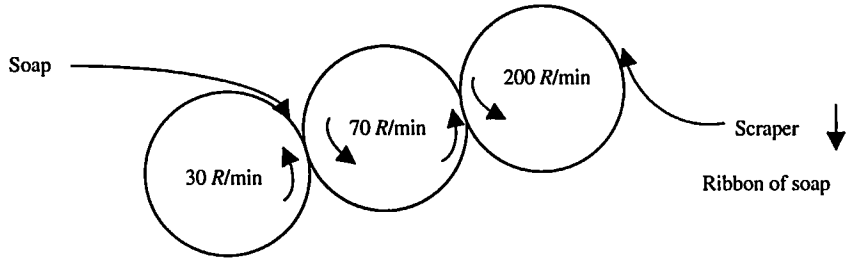

Fig. 12.12. Soap flake homogenization mills. Abbreviation: *R*, rotations.

sent to a series of three-roll mills which rotate at different speeds and in opposite directions (see Fig. 12.12), to obtain a fine ribbon and to remove all soap particles that may be too hard. These mills are cooled with refrigerated water because this operation increases the temperature of the soap.

A second extruder (refiner) further homogenizes the mix, and is generally coupled with a vacuum plodder (which removes any air bubbles). The plodder ends in a cone fitted with a perforated plate in the center through which emerges a continuous log of soap, ready for cutting and stamping (Fig. 12.13). The bar is then cut into cakes of a given length (billets), which are then stamped in a die press. To prevent the soap from sticking, the dies are refrigerated (Fig. 12.14).

The dye presses generate a certain amount of soap scrap, which is returned to the start of the process for reworking. The speed of the line is between 200 and 300 soap tablets per minute. The soap is then packed, first in a piece of cardboard to protect the product during transport and handling, then in a printed wrapper. The wrapped soap is then put into cases. Figure 12.15 shows the entire soap finishing operation.

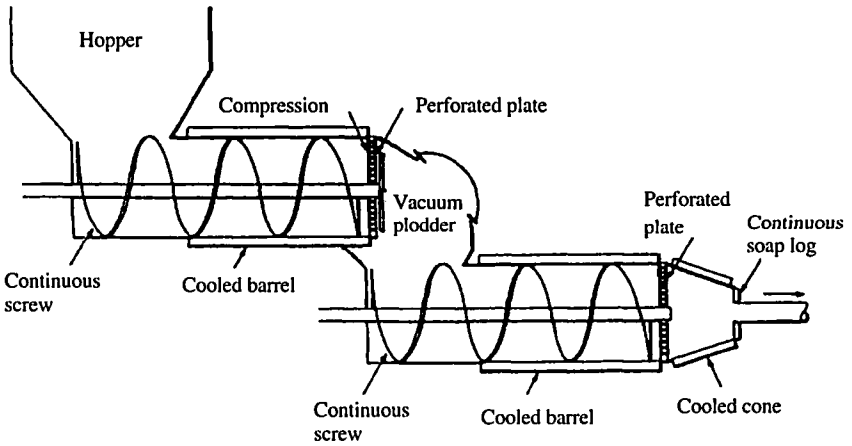

Fig. 12.13. Plodder.

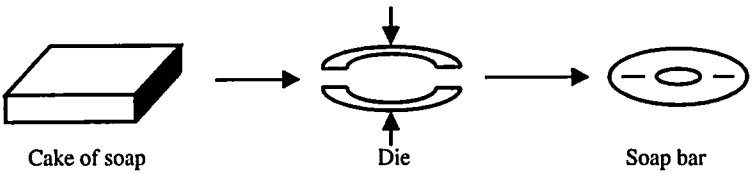

Fig. 12.14. Soap die.

Manufacture of Detergent Bars

Hard soaps and syndets are both made using the same extrusion technique. For syndets, a premixer neutralizes sulfonic acid with sodium carbonate. Thereafter all of the other ingredients are added. After going through a mill, the mixture is sent *via* a belt to an extruder from which it emerges in bar shape to be cut into cakes for stamping (sometimes using refrigerated dies). The process for manufacturing bar syndets and cream bars (e.g., Dove™) is very similar to the toilet soap finishing process (see Fig. 12.15).

Manufacture of Detergent Pastes

The process is the same as that for detergent and dishwashing pastes. All of the ingredients are mixed in the presence of heat. The semisolid paste is then stored in a tank before entering the packing lines (see Fig. 12.4).

Manufacture of Toothpastes

Processes differ by manufacturer. Generally, the variations are not very significant, and as we have said, manufacturers of mixers supply their customers with advice on the use of their machines. We give here an example of toothpaste manufacture

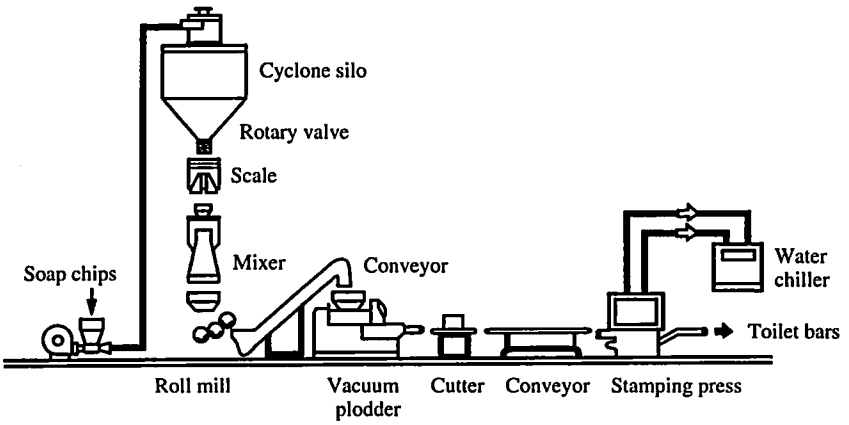

Fig. 12.15. Toilet soap finishing line.

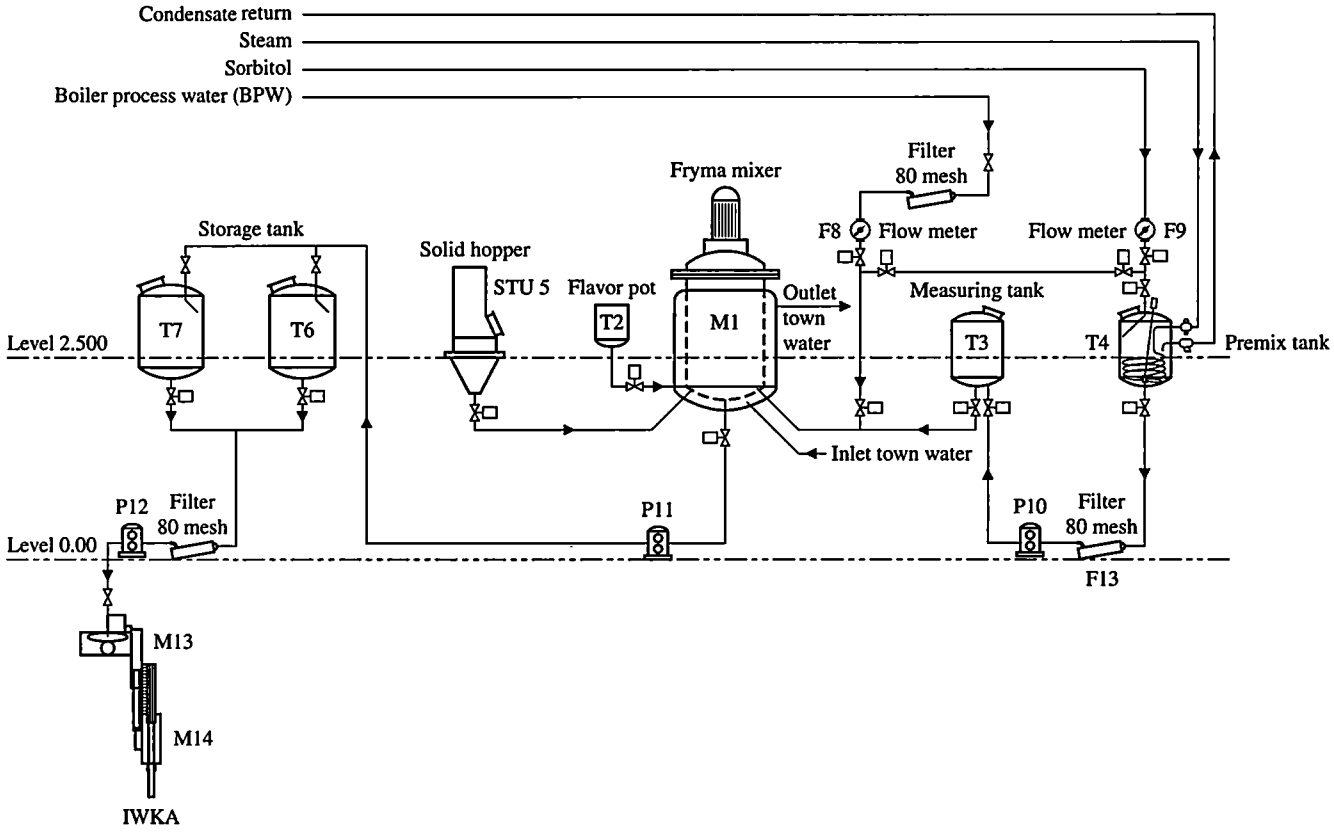

Fig. 12.16. Toothpaste manufacturing line.

to make a product with two anticaries agents, as described in one of the Goupil patents (13). This process involves a main mixer and secondary tanks with premixes. A dispersing mixer is used, for instance, to make 1500 kg. A premix is prepared as follows:

1. In one 200-L tank, the fluorides are dissolved in 30 L purified water. This mix is then pumped to another stainless steel tank, and constitutes Solution A.
2. In a second 200-L tank, sodium saccharinate and sodium benzoate are dissolved in 100 L of purified water with agitation.
3. In the mixer (e.g., Fryma type), the remaining purified water, sorbitol, xylitol, phosphates, titanium oxide, and precipitated silica are added.
4. The mixer is started and operates for the time needed to obtain a homogeneous mixture.
5. Solution B is pumped in *via* a filter.
6. Sodium lauryl sulfate is added, and a few minutes thereafter, the sodium carrageenate, solution A, and finally the flavor, in which methyl p-hydroxybenzoate will previously have been dissolved with agitation.
7. The mixer runs for 30 min to obtain a perfectly homogeneous mixture.
8. Air is removed under a vacuum for 15 min.
9. The paste is then filtered, homogenized, and stored in a tank.

Figure 12.16 (p. 312) gives an example of a toothpaste manufacturing line.

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CHAPTER 13

Perfume in Detergent and Personal Care Products

Introduction

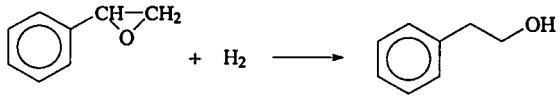
Strictly speaking, perfume is not a single raw material. Rather, it is a very sophisticated mixture of aroma chemicals specifically developed for each product. Each perfume has its own specific characteristics. In this respect, perfume is clearly different from other raw materials. With very minor exceptions, perfume is part of the composition of all products discussed in this book. The creation of a perfume is a combination of art and science. "We live in a world of odors, in the same way as we live in a world of light and of sounds" (Hendrick Zwaardemaker). A wash load is judged, not necessarily in this order by sight, by touch, and by smell. Smell is very much part of the final result.

Except for special cases, such as deodorant and antibacterial perfumes, perfume does not contribute directly to product performance. However, it has the capacity to attract consumers, to reinforce a product image, and to subjectively reinforce product performance. It is a determining factor in the purchase and repurchase of a product. In this chapter, we will explain the nature of perfume used in consumer products by describing its main characteristics, how it is developed, and what properties it should have when used in a functional product.

What is a Perfume?

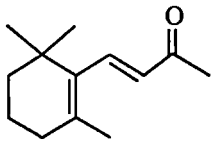
The Raw Materials

A perfume is a harmonious mixture of fragrant materials. Some materials are natural; others are synthetic with molecules that attempt to copy nature. For example, phenylethyl alcohol, which is characteristic of the rose, can be prepared by hydrogenation of styrene oxide using the following reaction:

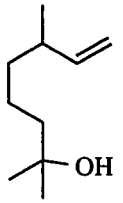


The perfumer also uses substances called bases; these are premixes of natural and synthetic products that have been developed by perfumers for direct use in perfumes. Other molecules are the result of laboratory research and do not exist in any natural form. Several hundred molecules have to be prepared to obtain a product with interesting odor characteristics. Perfumes are made from these different

sources, and part of the richness of perfumery is the multiplicity of available products. Synthetic raw materials bring contrast, whereas essential oils soften the notes. For example, the following molecules are widely used in perfumery:



β-Ionone



Dihydromyrcenol

Characteristics of the Raw Materials. Perfumery products have some common characteristics. They are all volatile because they act on the nose and have olfactory properties. Volatility is defined by vapor pressure, which is different for every product. Each raw material also has a threshold of perception and has an odor different from all others. The quality of the fragrance is the most important parameter in the acceptance of a new raw material; however, the threshold value and the "odor value" that define the olfactory power of the material are also taken into account.

Vapor pressure. Vapor pressure is the concentration of the raw material in question in its gaseous phase when it is in equilibrium with its liquid or solid state. This is generally expressed in units of pressure (mm Hg); in the case of perfumes, vapor pressure is also expressed in μg/L. The measure uses the head space technique and chromatography to quantify the gaseous phase of a material at the point at which equilibrium is reached. This number gives the tendency of a product to become volatile when in its pure state, and for raw materials used in perfumery, it ranges from 0.05 to 50,000 μg/L (1).

The limit of perception. This is a threshold value which is that concentration at which a person will no longer perceive the odor of a given product. It will be characteristic of both the molecule and the individual concerned. To obtain a representative score for the material in the whole population, one conducts consumer tests on a panel of ~20 people. The threshold value is measured on an olfactometer in which the concentration of a perfume can be adjusted with precision in a gaseous flow. The perfumed flow is directed toward one of three possible channels, chosen at random by the machine, and the evaluator identifies the channel from which the flow is coming. Each concentration is tested three times, and the evaluator is allowed to make one error. If the conditions are met, the concentration of perfume is reduced by half and the evaluation starts again. When the evaluator makes two mistakes at a given concentration, the limit at which the product can be perceived is considered to have been reached. The range of measures is from 0.002 to 2000 μg/L (1).

Odor value. Perceived intensity is often determined by smell, comparing the perception of an odor by a panel of individuals with a standard range (2). This is

sometimes difficult to do, particularly when the perfume in question may have dissipated partly during prolonged storage. An objective measure is necessary therefore, and this is known as the "odor value" (OV). Odor value is the ratio of the concentration of an olfactory substance to its limit of perception. The OV is a dimensionless number, which takes the limit of perception for its unit of measure. This limit must be measured very precisely to be able to guarantee the final result. The limit of perception varies from one individual to another. Some molecules may not even be perceived at all by certain individuals. This is known as asnosmia.

Water solubility. To reach detectors in the nose, odor molecules have to cross an aqueous area in which the detectors are located. They must therefore have a certain affinity for water. On the other hand, as we shall see later, the solubility of a molecule in water is linked to a certain number of important properties in the fragrance material, such as substantivity on the wash load, for example. Solubility is generally expressed in parts per million (ppm). Increasingly, this measure is being replaced by a calculated partition coefficient. This quantifies the distribution of a given substance between a polar (water) phase and a nonpolar phase (octanol). It is the ratio of the concentrations of a substance between water and octanol at the moment at which equilibrium is reached. The calculated partition coefficient is the logarithm of these two values. Studies have shown that these values could be obtained by calculation (3). Software also exists for making such calculations starting from the chemical formulations.

Odor. The essential characteristic of a raw material is its odor, which can be defined by objective and subjective criteria (4). The objective criteria, which make up a basic vocabulary used by the profession, are not necessarily directly accessible to the uninitiated. If the odor of green grass is recognized by everyone, the characteristics of "aldehydic" are perhaps less well known. Perfumers also use subjective criteria to describe the atmosphere that an odor evokes, the olfactory quality of the odor under consideration, and the functional criteria by which the perfume will be judged. For instance, a perfume to be used in a detergent should reinforce the objective criterion of cleanliness. Table 13.1 lists the descriptions that are widely used (5).

Creating a Perfume

The selection of raw materials to make up a perfume will vary according to the type of product to be perfumed and the function of the perfume in the usage of the product. The perfume for a dishwashing liquid is intended to make the task more agreeable, but under no circumstances should the odor stay on the dishes. Perfumes for dishwashing are therefore made up mainly of volatile raw materials that are released on contact with hot water. This requirement considerably restricts the palette of raw materials which can be combined to produce a perfume.

Perfumes used in laundry detergents should not only perfume the product but also deposit on the wash to give it a pleasant odor. The perfumer's palette now expands to include molecules with higher vapor pressure and lower solubility. The

TABLE 13.1
Widely Used Descriptive Terms for Various Odors

Term	Description
Aldehydic	Odor of fatty long-chain aldehydes (fatty odor, ironed clothes, the sea)
Animal	Musky odor, civet, ambergris
Balsamic	Heavy odor, soft like vanilla or cocoa
Camphoric	Odor reminiscent of camphor
Citrus	Fresh odor, stimulating like oranges and lemons
Earthy	Odor of humus, reminiscent of wet earth
Floral	Generic term to describe the odor of flowers
Fruity	Generic term to describe the odor of fruits
Green	Odor of cut grass
Medicinal	Odor reminiscent of disinfectant (phenol, methyl salicylate)
Metallic	Odor that can be detected on metal surfaces
Mentholated	Odor of mint
Moss	Odor of the forest
Powdery	Odor associated with powders such as talcum
Spicy	Generic term to describe the smell of spices
Waxy	Odor close to that of candles
Woody	Generic term for the odor of wood (sandalwood, cedar)

structure of a perfume to be used in laundering is represented by the diagram in Figure 13.1.

The top notes give the product its odor. They consist of volatile raw materials such as limonene, dihydromyrcenol, linalool, or phenylethyl alcohol. These products have relatively high vapor pressure. Because of their volatility, they disappear quickly during the wash and successive rinses and do not stay on the clothes. The

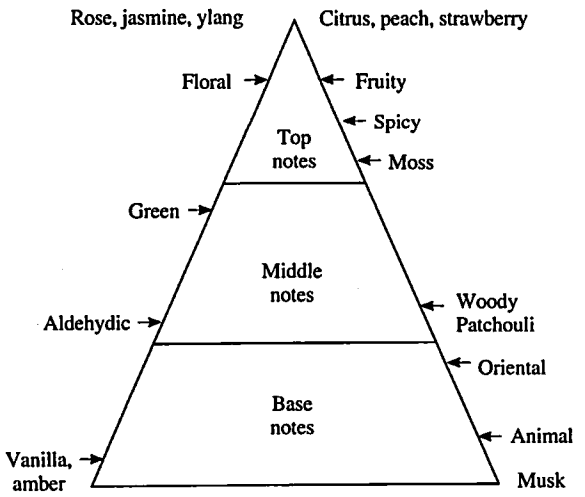


Fig. 13.1. The different notes of a perfume.

middle notes are molecules of intermediate volatility. The parts that are less soluble in water remain on the clothes, but at low concentrations. The base notes are made up of raw materials with very low vapor pressure and solubility. This gives them a strong affinity for the wash and an odor that will last for several days. Typical raw materials include galaxolide and fixolide, which are polycyclic musks, and other materials such as hexylcinnamic aldehyde.

The perfumer must ensure that the perfume keeps its character throughout the stages of its usage: in the product, after it is deposited on wet laundry, and on dry laundry. The transition from top to middle to base notes should proceed harmoniously.

Everyone senses the general characteristics of an odor, e.g., lemon, orange, or lilac, in very much the same way. This is not true of all raw materials, some of which may not be sensed at all by some individuals; this is the anosmic phenomenon referred to earlier. The perfumer must take this into account in creating the perfume, often using several musks to make up the base. It is worth noting that anosmia is more common with large molecules, such as musks, than with small ones.

Perfume Development

Perfume Stability. Perfumes developed for functional uses must meet a number of technical criteria; in particular, they must be olfactorily stable in the product, which is the subject of long debates between perfumers and their clients. Often the client will come to see the perfume supplier with a study showing that certain parts of the perfume disappear during storage, to which the perfumer may reply that chemical and olfactory stability are not the same thing and that confidence in the odor is the key issue. There is no standard answer to this dilemma, each case being judged on its merits.

First, the perfumer is conscious of the risks inherent in using certain materials that may not be perfectly stable, but to exclude them may greatly reduce the options available. One difficulty often arises from the fact that products used in consumer tests are not usually subjected to the same treatment as products going through the normal distribution process, particularly in terms of storage. If the long-term stability of a perfume is a problem, the perfumer can subsequently adjust the formulation to improve it. While 1-yr stability testing is not practical, at least a 1-mo accelerated storage test vs. market controls is usually the minimum before fielding a large-scale consumer test.

In most cases, the disappearance of a particular part of the perfume is related to the appearance of new substances, which change the odor of the product slightly. This is understood by the perfumer and it is perfectly acceptable. Typical reactions are the isomerization or hydrolysis of esters such as linalyl acetate. This does not change the perfume characteristics fundamentally; nevertheless, the perfumer will prefer to use the acetate. There are other very unusual situations in which perfumed products change, losing their perfume or becoming functionally or olfactorily different. Such problems must be addressed with the perfume supplier.

Perfume stability tests. The client approaches the perfumer with an overall description of the desired "message" which the perfume is to convey to the ultimate consumer. This description is called a brief. The perfumer has a number of tools available to reply to such a perfume brief. The first decision is what palette of raw materials to use. To do this, each potential raw material is dosed into the base product under study and then stored under different storage conditions, as required by the client. These tests take time because storage can last for several months. Often the perfumer will rely on experience in choosing the materials but the correctness of that choice will not be confirmed until after the storage trials. These trials give some indication of the behavior of a given raw material in a product, but since they are tested at a concentration much higher than that in the finished product, only olfactory evaluation of the final composition will confirm those choices.

Accelerated tests. In the case of detergent powders, the choice of raw materials for a perfume is made more difficult by the fact that some powders react more strongly to perfumes than others. To overcome this, rapid tests have been designed to classify detergents into families according to their behavior. The process is as follows: Detergent powders can be divided into families according to their propensity to degrade perfumery raw materials. Over the years, perfumers have learned how their products will behave in the different detergent families. Thus, when a new powder has to be perfumed, the main issue will be to establish which family the product belongs to and then choose the right raw materials accordingly.

To determine the family, perfumers use a mixture of raw materials that react with two key properties of the powder: alkalinity and oxidizing power. These two reactions are the main cause of perfume loss by chemical degradation; unfortunately, simple knowledge of the powder composition or its pH in aqueous solution is not enough to predict the interaction with a perfume. The stability test consists of introducing an equal mixture of the chosen molecules into the unknown powder and measuring their disappearance after storage under typical conditions. The behavior of the molecules will give the identity of the powder family and will determine the available palette of raw materials. The point of accelerated tests is that they give reliable results quickly. However, it should be noted that this method is based on chemical analysis and thus does not give any information on olfactory stability.

The Behavior of Perfumes in Detergent Products. Perfumes behave differently in detergents depending on the physical state of the product (liquid or solid) and depending on its chemical makeup.

Detergent powders. When a powder is blown, perfume is usually added by spraying into the base powder, before other postdosed ingredients are added (e.g., bleaching agents or enzymes). When the powder is dry-mixed, perfume is sprayed onto the finished product. It may seem that dosage of the perfume into the base powder would be better because some of the perfume components are degraded by oxidizing agents. In fact, this is not the case, because the perfume diffuses very quickly once it has been sprayed onto the detergent; equilibrium is reached after a few

days, which is not significant in relation to the life of a powder. It is as though there were a liquid phase on the surface of the powder granules, into which the perfume is dissolved. The composition of this phase depends on the powder formulation, but it contains water, nonionics, and various ions, including the oxidizing perhydroxyl ion. The rate of degradation of the perfume, and probably that of the other fragile elements of the formula, such as enzymes, perborate, or tetraacetylethylenediamine (TAED), is closely linked to the concentration of free water in this liquid phase.

Some ingredients in powders tend to retain certain molecules in perfumes because of their adsorbing power. It is well known that zeolite-based powders cannot be perfumed like phosphate powders, because zeolites adsorb perfume.

Liquid detergents. Liquid detergents are generally not aggressive in the chemical sense of the term; however, when they are structured, they tend to retain perfume molecules, which therefore help to reinforce their structure. In this way, perfumes can play an important part in the stability of certain structured liquids. For example, in liquid scourers, the mineral responsible for the scouring properties is held in suspension by surfactants in a lamellar phase within the product. It is at the end of the preparation process that the structure forms, at the moment the perfume is added. The addition of a small amount of perfume causes a large increase in the viscosity of the mix, thereby helping the formation of the structure. The structure of perfumes used in these kinds of liquids usually contains more top notes than those of powder detergents, to compensate for the trapped perfume molecules.

Fabric softeners. Fabric softeners are made of cationics, arranged in lamellar structures. The perfume usually distributes itself between this structure and an isotropic phase made up of a water/isopropanol mixture (Fig. 13.2). In concentrated softeners, the use of large quantities of perfume may create viscosity problems during storage and can even cause the product to gel. The mechanism underlying this phenomenon has not been clearly explained, but it would seem that interactions between the softener and perfume molecules are involved.

Unlike anionic and nonionic surfactants, which tend to reduce the deposition of perfumes, cationic surfactants help deposition because of their affinity for both fabric and the less soluble perfume raw materials.

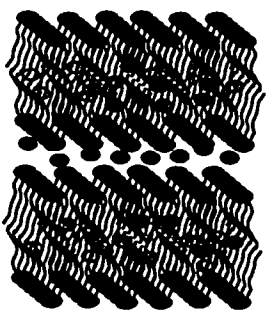


Fig. 13.2. Perfume in lamellar phases.

Product Line Extensions. Interaction of Perfume in the Matrix. Perfumers are frequently confronted with the problem of line extensions, i.e., a perfume developed for a given product is to be used in another type of product. Analysis of the composition of the vapor phase above different product types with identical perfumes shows very different results. Neuner-Jehle and Etzweiler (6) performed this exercise on a scouring cream, a softener, and a detergent powder. Their tests showed that the concentration of a volatile fragrance material above a mixture of fragrance components is practically a linear function of the vapor pressure. When this mixture is added to a product, the matrix effect intervenes, changing the relationship because of the many possible interactions with the matrix, e.g., imprisonment in the lamellar structure, dissolution in water, or adsorption in solids.

To quantify the matrix effect, the authors suggested a matrix coefficient, which they defined as the ratio between the concentration of a given fragrance component above the perfumed product, and the theoretical concentration of this same component, assuming that the perfumed mixture is dissolved and has no molecular interaction with the matrix. They proposed the use of these matrix factors for line extensions.

Example of a Perfume Formula. As already stated, the perfume itself is not a simple raw material but a mixture which usually contains a large number of raw materials. To perfume functional products, the palette of raw materials is already limited because of the various constraints discussed earlier (e.g., stability, irritation, or cost). Despite this, the formula for a perfume in a functional product remains very complicated. To illustrate this complexity, Table 13.2 gives the formulation of a perfume used in a detergent product.

TABLE 13.2
Formulation of a Perfume Used in a Detergent Product

Ingredient	(%)	Ingredient	(%)
Tricyclodecyl acetate	3.3	Eugenol	0.6
Benzyl acetate	2.7	Galaxolide	5.5
Styralyl acetate	0.3	Geraniol	1.1
Agrumex	1.3	Linalyl hexanoate	0.2
Cinnamyl alcohol	0.3	Lilial	9.2
Phenylethyl alcohol	7.8	Limonene	1.1
Hexylcinnamic aldehyde	11.3	Linalool	2.2
Cyclamen aldehyde	0.1	Piperonyl methoxide	0.2
α-Pinene	0.4	Projasmone P	0.3
Benzophenone W	1.6	Verdyl propionate	2.8
β-Pinene	1.2	Amyl salicylate	3.2
Citronellol	1.2	Hexyl salicylate	16.8
Coumarin	0.3	Isoamyl salicylate	3.2
Diethyl phthalate	8.8	Benzyl salicylate	8.0
Dihydroeugenol	0.3	Tonalid	0.3
Dihydromyrcenol	3.6	Solvent	Balance

The Functions of Perfume in Detergent Products

Covering Base Odors

The primary function of the perfume is to cover the base odor, i.e., the bad odor of the raw materials in the product to be perfumed. This bad odor comes from the organic part of the formulation. Alkylbenzenesulfonate does not usually smell very much, but poor quality products can smell of gasoline. Ethoxylated fatty alcohols can have a fatty odor due to the presence of some unethoxylated fatty alcohol. Under certain conditions, these fatty alcohols can oxidize into particularly smelly and persistent aldehydes. Nonaqueous liquid detergents, which are very rich in nonionics, are particularly difficult to perfume because of the high proportion of nonionics deposited on the wash. Cationic surfactants derived from amines are susceptible to producing a fishy amine odor. Fatty acids used in soaps and certain liquid detergents can also contain very smelly impurities. Certain enzymes, particularly lipase, are a nightmare for the perfumer because this enzyme, which hydrolyzes fats, does most of its work during drying. If there are any fatty residues (butter or milk products on a baby's bib, for example) present when the drying stage is reached, the short-chain fatty acids are liberated, generating an odor of vomit. The bleaching activator TAED in detergent powders can give off an acetic acid odor. Polymers, in particular, polyvinylpyrrolidone used in detergent powders to avoid dye transfer, can also be a source of a very disagreeable odor.

These bad odors can appear in the product itself or on the substrates on which the detergent has been used. These substrates can be the wash, hard surfaces, or human skin, in the case of a soap. Covering these off odors generates significant costs, and it is therefore important for the formulator to calculate whether it is cheaper to buy raw materials that have been deodorized. It is also important to establish specifications for raw material odors; if the impurity that causes bad odor can be identified, there should be a specification for a maximum level of this impurity in the raw material. In the more common case in which the origin of the off odor is not known, a quick odor evaluation compared with a reference sample can be enough to refuse acceptance of raw materials that are out of specification.

Substantivity and Tenacity of Perfumes

Perfume performance is closely linked to its ability to deposit on fabrics, giving them a pleasant odor. This is its substantivity. It is also related to the lasting power of the perfume, which defines its tenacity (7). To be substantive, a perfume molecule should deposit on the wash load and have a low perception threshold. To be tenacious, it has to be substantive with a low vapor pressure in order to be released progressively. There is a compromise between optimum vapor pressure and the perception threshold, which means that the perfume compound in question can continue to release a sufficient number of molecules to be perceptible as an odor. If the vapor pressure of a fra-

grance material is too low relative to its perception threshold, its molecules will deposit on the wash load but will not be released in sufficient quantity to be perceptible.

Humidity has a considerable effect on the intensity of a perfume. The presence of water on clothes helps perfume evaporation, and this is why certain perfumes, even when deposited in large quantities on clothes, can be perceived clearly on damp clothes but have no odor on dry clothes.

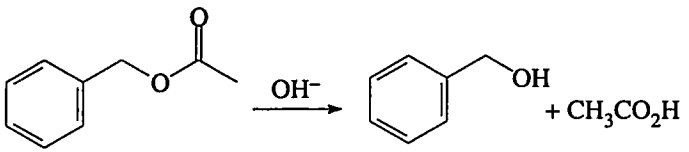
Detergent Powders. The role of the perfume in laundering is to fragrance clothes. Given the low concentration of perfume in the product and the multitude of interactions to which it is subjected, this is a real battle.

Interaction with water. At the concentrations at which perfumes are incorporated, the great majority of the components are in a state of dissolution in the wash liquor. There are certain particularly insoluble musks that can be dissolved only partially. The range of solubility goes from 1 ppm to a few thousand ppm, with a few raw materials that have a solubility >5000 ppm.

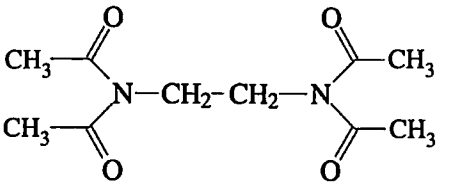
Interaction with surfactants. The role of surfactants is to eliminate oily soils and hold them in suspension, at the same time as the detergent fragrances the laundry by allowing the perfume to deposit; however, the physico-chemical characteristics of perfume are not very different from those of oily soil. One job of the detergent is therefore to exchange an oily soil for the "clean soil," which is the perfume, and herein lies much of the difficulty for the perfumer. The less efficient a product is against oily soils, the more strongly the perfume will deposit, thereby providing a good odor to compensate for the loss of cleaning performance.

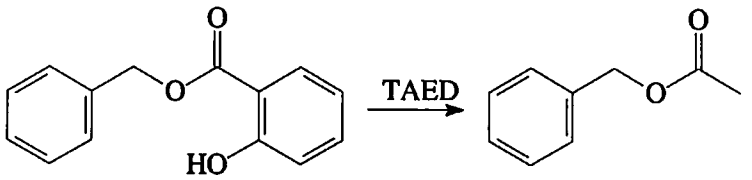
In the presence of surfactants, the perfume partitions itself between a polar phase (water) and a nonpolar phase (the interior of the surfactant micelles). Held in suspension by the surfactants, the perfume will deposit less well on the wash. Fortunately, the proportion of the polar phase is much greater than that of the nonpolar phase, which is why the negative effect of surfactants is quite limited. Observation shows that products that deposit the most are the least soluble; these are also the products that are most affected by surfactants.

Chemical interactions. Laundering is usually carried out in an alkaline environment (pH 9–10.5), and in the presence of bleaching oxidants. Fragile esters, in particular primary alcohol esters, will be partially hydrolyzed. Products degraded by this reaction are classified in decreasing order of stability as follows: dimethylbenzylcarbinyl acetate, terpenyl acetate, methyl benzoate, methyl cinnamate, hexyl acetate, allyl caproate, citronellyl acetate, benzyl acetate, and benzyl salicylate. Benzyl acetate decomposes in an alkaline environment into benzyl alcohol and acetic acid as follows:



Transesterification. This process can sometimes be observed in detergent powders that contain bleach activators such as TAED. Transesterification generates benzyl acetate when benzyl salicylate is present in a powder containing TAED as follows:





Benzyl salicylate Benzyl acetate

Oxidation turns certain fragile aldehydes into carboxylic acids as follows:

$$RCHO \longrightarrow RCOOH$$

Deposition of perfumes on the wash. Figure 13.3 shows the deposition of perfume constituents on the wash in a washing machine. We can see that the top notes tend to be eliminated during successive rinses, the middle notes deposit more strongly on the wash, and the base notes are relatively untouched by the successive rinses, despite being the most affected by surfactants.

Fabric Softeners. Fabric softeners provide a less aggressive environment than do detergent powders. Perfume deposition is helped by the fact that the rinse product added at the end of the wash is not subjected to any further dilution. In addition, the cationics used in softeners help perfume to deposit on the washload. In softeners, even the most water-soluble ingredients of a perfume deposit in good quantity because when the washload is taken out of the machine, it is not dry, and the residual water contains dissolved perfume. The graph in Figure 13.4 shows the deposition of perfumes during a machine rinse with softener.

Figure 13.5 shows a comparison between deposition of a perfume in washes with and without a softener. It shows clearly that perfume deposition is much greater when a softener is used in the rinse. When a wash is followed by a rinse with a conditioner, interference between the two perfumes is possible; however, in most cases, the softener perfume predominates.

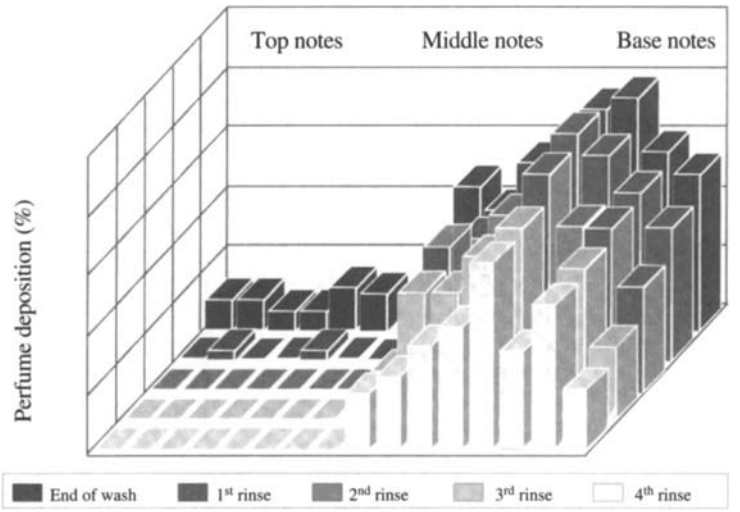


Fig. 13.3. Deposition of perfume on the wash.

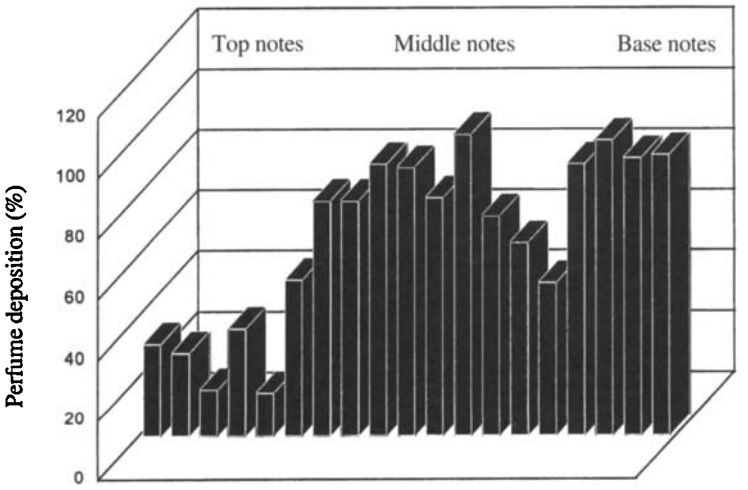


Fig. 13.4. Perfume deposition by a fabric softener.

Performance Improvement in Detergent Powder Perfumes

Controlled Release of Perfume

Since the 1980s, much work has been done to improve perfume performance in detergent products. Various techniques have been patented either to avoid perfume loss during product storage or to improve deposition. More recently, certain fabric softeners have appeared on the market with precursors of perfume molecules,

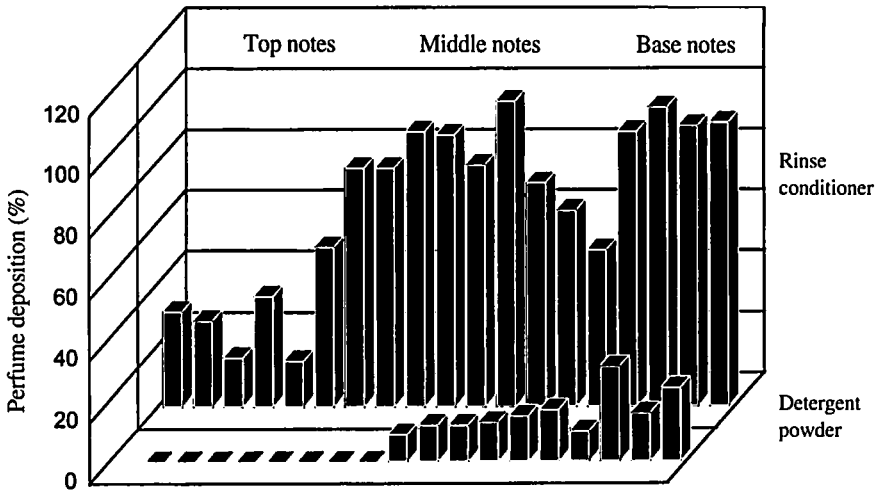


Fig. 13.5. Perfume deposition with and without a fabric softener.

which help the deposition of perfume raw materials. These new technologies are aimed at correcting imperfections in the behavior of perfumes (stability, loss of materials during use). The great difficulty comes from the fact that perfume is not a simple raw material but a mixture created by the perfumer. The arrival of a new technology should not change the creation, something that is difficult to avoid.

Stability of Perfumes in Powder Detergents

A significant part of the perfume in detergent powders is lost through evaporation even before the products go on sale. This loss is between a few percent and 50% depending on storage conditions, temperature, humidity, package size, and type of packaging. Even when the loss is relatively small, it occurs mainly in the top notes, which bring freshness to the perfume; in extreme cases, these top notes can disappear completely. Perfect protection of the perfume would result in a product without odor, and thus is not desirable. Different techniques have been patented to limit perfume loss.

Adsorption on Porous Particles

Some patents claim to improve the performance of perfumes through adsorption on minerals such as zeolite (8), silicate (9), or clay. Others recommend the use of organic polymers (usually cross-linked polymethacrylates), which are insoluble in water. Such adsorbents are available and are incorporated by mixing the perfume with the adsorbent.

Adsorption on a Material with External Protection

External protection is added in certain cases to prevent the perfume from diffusing in the powder during storage. This technique (10) involves a system in which the

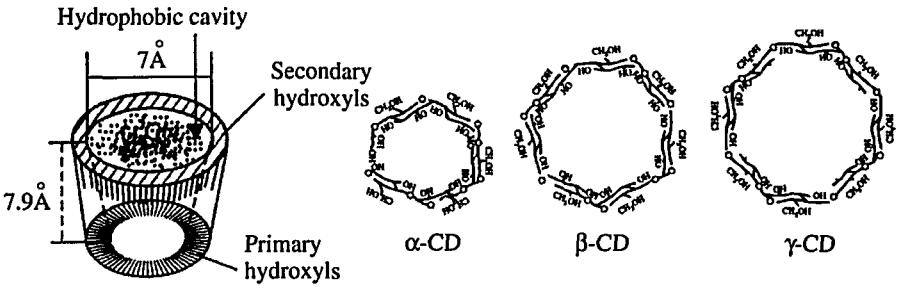


Fig. 13.6. The action of cyclodextrins.

protection is supplied by hydroxylated products such as sucrose, glucose, and the maltodextrins.

Inclusion in a Water-Soluble Matrix

The perfume is dispersed in a water-soluble matrix, and the particle is then formed either by elimination of the water, or by extrusion.

Cyclodextrins. Cyclodextrins (CDs) are cyclic polyglucoses consisting of 6(α-CD)-, 7(β-CD)-, and 8(γ-CD)-glucose units (Fig. 13.6). They have a cage-like structure, which forms complexes with perfume molecules. The interior of the cage is hydrophobic, whereas the outside is hydrophilic because of the presence of numerous hydroxyl groups in the structure. These complexes are displaced from aqueous solution in the presence of surfactants and, in particular, nonionics (11).

The β-CD is by far the most widely used. It has been patented for the limitation of perfume loss in detergents (12). It is also used to stabilize perfumes during clothes drying in machines. The perfume CD complex is incorporated into a dryer softener formulation (13). This technique is used in Bounce (Procter & Gamble) in the United States. CDs also have deodorant properties and have been used recently for the deodorization of the wash (14). In this case, substituted β-CD are used to increase their solubility in water and the solution is sprayed directly onto the wash to "freshen" the laundry with a pleasant scent and prevent odors caused by bacteria.

Microencapsulation. Microencapsulation creates perfume particles in which the perfume is protected by a barrier made of polymer (Fig. 13.7). This type of protection is obtained by coacervation or by interfacial polymerization processes.

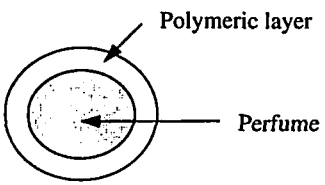


Fig. 13.7. Perfume microcapsules.

Coacervation involves dispersing the hydrophobe phase to be encapsulated in an aqueous solution of gelatin and an anionic polymer heated to ~60°C. A coacervate is formed when the pH is adjusted to ~4. At this pH, gelatin has cationic properties and can react with the anionic polymer. This coacervate deposits on the surface of the droplets of perfume, which are kept in suspension by agitation. The temperature is then lowered, and the protective barrier is hardened by the addition of a cross-linking agent, such as formaldehyde or glutaraldehyde. Interfacial polymerization keeps the perfume in suspension in the aqueous solution by a surfactant. The polymerization reactants are to be found in the aqueous phase. Addition of a polymerization initiator starts the reaction, which takes place on the surface of the droplets. The protection offered by these techniques is extremely effective. More significantly, the particles thus formed can contain up to 85% perfume. Application of this technology to detergents is made difficult by the need for mechanical action to free the perfume. The technology has been patented for softeners and detergent powders (15).

Perfume Precursors. A very interesting innovation which has appeared recently in some fabric softeners is that of perfume precursors. Many patents have been published in this area. The invention consists of combining a perfumery material with an odorless molecule to obtain a molecule with sufficiently low volatility and solubility to make it substantive. It decomposes while the wash is being dried, liberating the perfume molecule. This technique is used mainly for softeners. Procter & Gamble (16) suggest the use of geraniol and nerol esters, which hydrolyze slowly and release the perfume with long-lasting effects. When the rinse is preceded by a wash with a detergent containing lipases, perfume release is improved (17). As mentioned earlier, lipases hydrolyze fatty acid esters and are active principally during drying (18), sometimes causing bad odors. The idea of precursors is to minimize the negative action of lipases and help release pleasant odors.

Perfume Analysis

Chemical analysis helps perfumers to control the quality of their products, to track competitive progress, to understand the reactions between perfumes and products, and to simulate odors found in nature.

Quality Control

Perfume is a complex mixture in which some ingredients are included at very low levels (<0.1%). Quality control tries to ensure that all products sent to customers are within specification. The most important evaluation is done by specialists using their noses. Other measures include color, the refractive index, and density. The latter two measures are straightforward, becoming increasingly automated, and can quickly identify any major production error. However, the information is not usually

very exact and more sensitive measurements are required to detect smaller variations. This is done using gas–liquid chromatography (GLC).

Analysis of Competitive Products

The first stage is to extract the perfume from the product, using various techniques. Perfume extraction can be performed with the Soxhlet, a device for the extraction of solids. The product is placed in a filter for extraction, which takes place overnight. Because of its low boiling point, pentane is generally used as the solvent. Since pentane also extracts nonionic surfactants, an additional step of steam distillation is needed to isolate the perfume. The Likens Nickerson apparatus, another extraction technique, makes possible simultaneous steam distillation and extraction with pentane. The test product is diluted with water and the solution is brought to a boil. Pentane is allowed to boil to extract the perfume definitively into the U-tube (Fig. 13.8).

By its principle, this method cannot extract materials with high water solubility. It is better either to pre-separate these or to neutralize any products that might destroy fragile perfumery molecules. In the case of detergents, the environment should be buffered around neutral, and catalase should be added to destroy hydrogen peroxide formed upon dissolution of perborate or percarbonate.

Extraction in the supercritical state. Above its critical temperature, a fluid is not in equilibrium with its vapor but is in a special transition condition called the critical state. In this condition, fluids have very interesting properties for extraction. Compared with liquid solvents, supercritical fluids diffuse more quickly; their volume mass is smaller and their viscosity is much lower. These properties allow

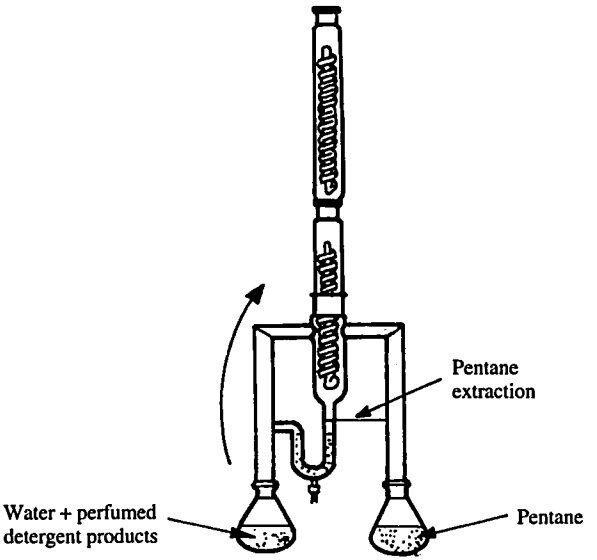


Fig. 13.8. Extraction of perfume (Likens Nickerson).

supercritical fluids to penetrate much more quickly into solid matrices and speed up extraction considerably (Fig. 13.9).

Extraction in the supercritical state has the advantage of not destroying fragile molecules, while simultaneously allowing the quantitative extraction of highly water-soluble products. Whatever the method used, the resulting extract always contains impurities from the detergent base, mainly from the surfactants as follows:

1. Alkylbenzenesulfonate always contains a small part of unsulfonated alkylbenzene, which is sparsely soluble in water, but which can be driven out by steam; this is why it is not possible to separate it from the perfume during extraction.
2. The second source of impurities comprises nonionics and sulfated alcohols, which usually contain considerable quantities of fatty alcohols. These fatty alcohols are detected during the analysis, but they interfere with olfactory evaluation because they have a bad odor.
3. In softeners and shampoo bases, methyl and/or isopropyl esters of fatty acids are found, arising from synthesis or the reaction with solvents present in the raw material (such as cationics dissolved in isopropyl alcohol).

Extraction is followed by the analytical phase during which the extracts are examined in detail by chromatography, with or without the use of mass spectrometry (MS). Chromatographic separation is done on two different types of columns to help identification. The retention times are thus determined on both types of column and are used to confirm the MS identification and to determine the proportion of the different constituents of the perfume. Retention indices are relative indices calculated in comparison to paraffins (Kovats indices) or fatty acid methyl esters. These help to explain variations that may occur between one column and the other, and between one chromatograph and another.

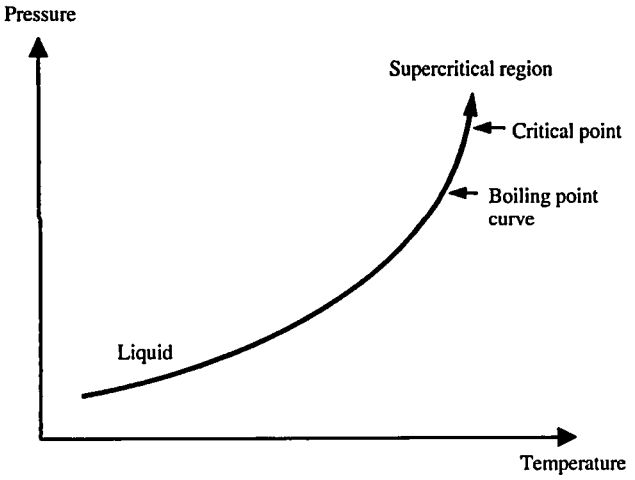


Fig. 13.9. Extraction of perfume in the supercritical state.

These techniques allow most of the constituents of a perfume compound to be identified. However, some of the constituents are dosed at very low levels because of their cost and thus cannot be detected by conventional techniques. An additional procedure is none other than a chromatograph with a system that helps to detect odors after separation.

Sometimes perfumes contain very volatile ingredients that can be lost during extraction or that are not separated from the solvent during the chromatographic analysis. These ingredients can be identified using the Solid Phase M Extraction (SPME) technique. An adsorbent is placed on a wire that runs through the inside of a syringe needle. When the syringe piston is depressed, the adsorbent is in contact with the atmosphere, adsorbing the molecules in the open air. Once the sample has been obtained, the syringe is pulled and an injection made into the chromatograph. This analytical technique of head space analysis does not quantify the identified products; that is the task of the perfumer using his nose. Once all of the elements of the chemical analysis are in place, the formulation is weighed, re-analyzed by gas chromatography, and adjusted by the perfumer, at which point the formulation is established.

Head Space Analysis. Head space analysis consists of taking a sample of gases above an emitter of volatile products. This "emitter" can be a flower whose scents are being studied, or a perfumed product, whether solid or liquid.

The so-called static head space analysis consists of injecting the vapor phase found above the given subject directly into a chromatograph. This technique does not require a concentration step and is used for small volumes of liquid or solid samples, whose emanations are important. Dynamic head space analysis includes a concentration phase and is used to work on products without much odor. The product under study is put into a closed space that is linked to the outside by an entry tube and exit tubes (Fig. 13.10). A pump draws air through the recipient. The incoming air is purified by using an active carbon trap. The molecules emitted by the product are collected in the trap.

The analysis consists of passing a given volume of air over the product to determine the quantity of differently smelling substances collected. The trapped components are flushed out with a given volume of solvent. The solution is then ana-

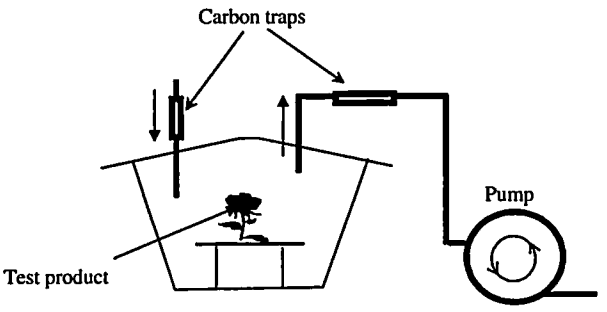


Fig. 13.10. Head space analysis.

lyzed by GLC together with MS. This method can be used to study the diffusion of a perfume through powder boxes or soap wrappers and to compare different types of packaging.

The Electronic Nose. The electronic nose concept is based on the mechanisms of odor formation and detection. Odors are detected in the nose by detectors made of complex proteins located on the surface of the nasal mucous membrane. It is generally accepted that receptors in the nose are specific to each molecule. However, recent studies have shown that in fact there are only a few hundred receptors, and that each can detect not just one single molecule, but many. The odor of a given substance seems to be the result of signals sent by these different receptors. Different intensities arise from a more or less exact fit between the key (the molecule with odor) and the lock (the receptors). The specificity is such that two optical isomers, which are difficult to separate, could indeed have completely different olfactory characteristics. Essentially, this translates into very wide differences of detection limits, while the nature of the odor remains unchanged. This is the method used by chemists to try, as best they can, to synthesize the strongest smelling optical derivatives.

The odor of a perfume is the result of a multitude of interactions between the odoriforous molecules and receptors. These interactions are managed by the equilibrium constants between these molecules and the receptors. This complexity explains why each perfume has its own odor.

In the electronic nose, the receptors consist of probes in the form of different metallic oxides which react differently to volatile gaseous products they are in contact with. As a result, their electrical resistance decreases. The decrease is recorded for each of the detectors, and all of the measures together constitute a characteristic of the perfume equivalent to a fingerprint.

The world of fragrances is totally subjective. Industrial users of perfumes are not always perfumery experts. Thus they prefer to use both sensory and objective measures. The ideal area in which to use the electronic nose is in quality control, because it can deliver specific and objective information on the product tested. To obtain objective measures in perfumery is always delicate and requires significant resources. Much time has to be spent on reconstituting an odor if the odor itself is not sufficient to characterize it. The electronic nose brings an imperfect answer in that it cannot perfectly describe an odor, but it is adequate in many circumstances, e.g., in its role in quality control.

Base odors that make it difficult to perfume detergent products come from the raw materials, as we have seen. It is very difficult to identify the molecule that causes a bad odor, but when we do identify it, we can then specify its maximum acceptable level. In certain cases in which the quantitative relationship between the signal given by the electronic nose and the intensity of odor of a raw material can be obtained, it becomes possible to specify an acceptable odor in a quantitative manner. In detergents, this can be used to check that products have been correctly perfumed, without excessive fragrance loss.

Challenges for the Future

Biodegradable Perfumes That Will Not Affect Living Organisms. The detergent industry uses more perfume than any other industry in the world. Procter & Gamble use 25,000 t of perfume every year in their worldwide production (19). The effect on the environment is a constant concern, raising the question of the use of certain materials. Nitro musks were banned by the large detergent manufacturers because of their lack of biodegradability and their ability to accumulate in fats. Musk xylene was rejected for its carcinogenic properties, and musk ambrette for its neurotoxic properties.

Today, polycyclic musks are being questioned strongly with regard to their lack of biodegradability and poor solubility, even though it has not been established that they are toxic to living organisms. Replacements for these important fragrance constituents, which provide lasting perfume on fabrics, are being studied by the perfumery industry and represent a major challenge for perfumers. The study of the environmental impact of perfumery products is far from over and is sure to lead to further dramatic changes in the future.

Produce Efficient Perfumes. Several routes are open to improve perfume efficacy. These include the search for cheaper methods of raw material preparation, the search for more effective perfumery ingredients, and the use of other technologies to offer better perfume utilization. Some of these technologies are already commercially available, including perfume precursors and certain encapsulation methods. These methods have yet to be integrated into the perfume creation process to bring real efficiency. The perfumer of the future will need to imagine what these different techniques could bring to the creation of perfume and ways in which to use them better.

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CHAPTER 14

Packaging

Introduction

Having discussed the detergents themselves, it is now time to look at the way they are presented to consumers on the shelves of stores and supermarkets. To manufacture detergents or shampoos is one thing; protecting the products from external damage and making them attractive to the consumer are quite different matters. These are two different jobs, and yet they are extremely complementary. It is difficult to imagine the typical consumer at the corner store asking the storekeeper for 200 g of detergent X for high temperature wash, the one with blue bits in it, or, perhaps, 50 mL of softener, the pink one with the strawberry smell.

In addition to its protective function, packaging today must fight for the consumer's attention and must be as functional as possible, not forgetting environmental considerations, which require that packaging material not be excessive, and that it should be recyclable or safely disposable.

The Functions of Packaging (1)

If we follow our detergent from the factory gates we will be able to define the different functions of its packaging in the following terms. The individual packed product is grouped, usually into outer cases of one kind or another, making it easier to transport the product to warehouses and into stores. This outer packaging is important because it provides a first barrier against externally caused damage, including mishandling, severe variations in temperature, and exposure to light and humidity. Once the outer cases reach the retailer, it is the "primary" packaging that takes over and that must protect the product in the store, possibly for some weeks. This is one of the reasons why all large manufacturers regularly check their own products at the point of sale.

In addition to its protective function, packaging on the shelf should reflect the personality of the brand, its logo and colors, which are the signs of recognition for the consumer. Indeed, the consumer will buy the package before buying the product inside (even the best product in the world will not sell if its packaging is ugly!). Packaging must therefore communicate and provide a source of information to the buyer, including the answers to the following questions: What type of product is it? Where can I use it? How should I use it? In what quantity? What is it made of? What precautions must I take? Where do I obtain additional information? Are there safety "rules"? What do I do if I have a problem?

Packaging information also includes an array of "legal" information on the weight or volume, the manufacturer, the composition, and so on. Once the consumer is satisfied by all of the aesthetic and functional aspects as well as the

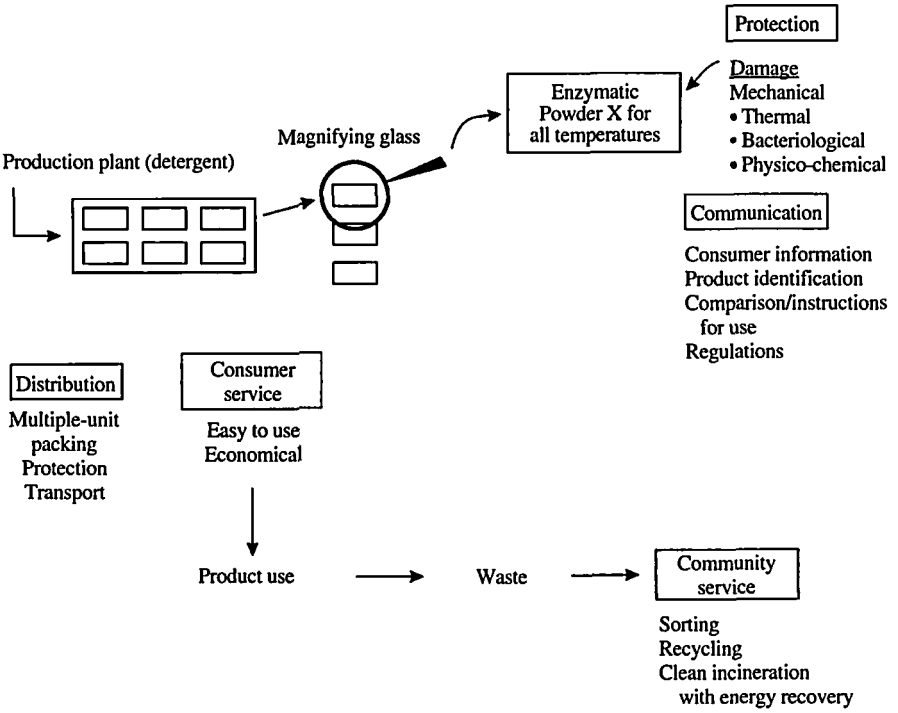


Fig. 14.1. The different packaging functions.

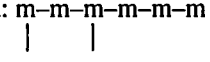
price, the purchase decision can be made. The diagram in Figure 14.1 summarizes all of these functions.

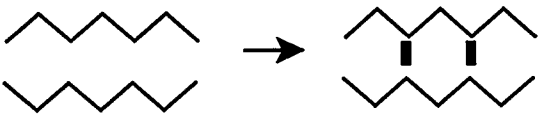
Packaging Used for Detergents

The rather simplistic idea of packing solid products in cardboard boxes and liquid products in plastic is now out of date. In recent times, we have seen solid products such as machine dishwashing products packed in plastic, economy refills for detergent powders packed in flexible plastic, and conversely, liquid products such as laundry detergents packed in cardboard-based composites. Domestic cleaning products are sold in a wide variety of packaging, including hard and soft plastics [e.g., *polyvinyl* chloride (PVC), high-density polyethylene (HDPE), polyethylene terephthalate (PET)], cardboard, paper (toilet soaps), and composites such as paper/plastic combinations. Such a wide choice is a good opportunity for the marketing teams of large manufacturers to keep their product up to date by introducing new variants, running promotions with packages of different sizes, or selling two different products together. For these reasons, most large companies no longer make their own packaging as they might have done some years ago. More often, they approach specialized manufacturers who are flexible and quick to meet their requirements.

Plastic Packaging (2)

Different Types of Plastic. Plastic is made of polymers (resin) and additives. The polymers are macromolecules obtained by repeating a basic design (sometimes as many as 100,000 times). The number of repetitions of the basic design determines the properties of the plastic. Thus PVC is obtained by repeating the design (–CH_2–CHCl–) *n* times. This design is the monomer, in this case, vinyl chloride. Polymers include the following:

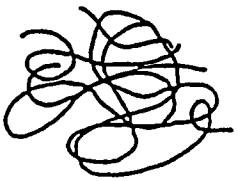
1. Homopolymers, with monomers (m) of the same kind. These may be
   (i) linear: –m–m–m–m
   (ii) branched:
   
   or (iii) cross-linked:



An example of this class is HDPE or low-density polyethylene (LDPE).

2. Copolymers are obtained from different monomers of which there are different types as follows:
   (i) random copolymers:
   m_1–m_1–m_1–m_1–m_2–m_2–m_1–m_1–m_1–m_1–m_2–m_2–m_1–m_1–m_1–m_1
   (ii) alternating copolymers:
   m_1–m_2–m_1–m_2–m_1–m_2–m_1–m_2
   (iii) block copolymers:
   m_1–m_1–m_1–m_1–m_2–m_2–m_2–m_2–m_2–m_2–m_2–m_2–m_1–m_1–m_1–m_1

The molecules of these amorphous polymers are presented in Figure 14.2.



A. Tangling of nonoriented amorphous polymer chains

B. Oriented amorphous polymer chains

Fig. 14.2. Representation of amorphous polymers.

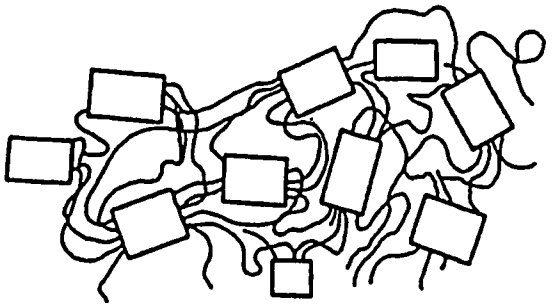
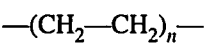


Fig. 14.3. Semicrystalline polymers.

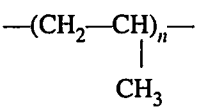
There is a distinction between amorphous polymers and semicrystalline polymers (Fig. 14.3); the latter comprise a disorganized conformation of chains (tangled), but this morphology can be changed to obtain an oriented amorphous polymer. The crystalline zones are dispersed in an amorphous matrix.

Main Plastic Raw Materials Used in Detergents Packaging. These include the following:

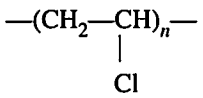
1. Polyethylene (PE) (low and high density) with the formula:



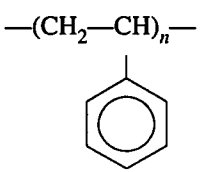
2. Polypropylene (PP)



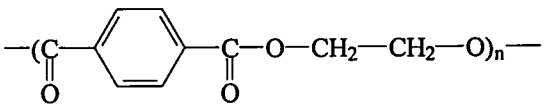
3. Polyvinyl chloride (PVC)



4. Polystyrene (PS)



5. Polyethylene terephthalate (PET)



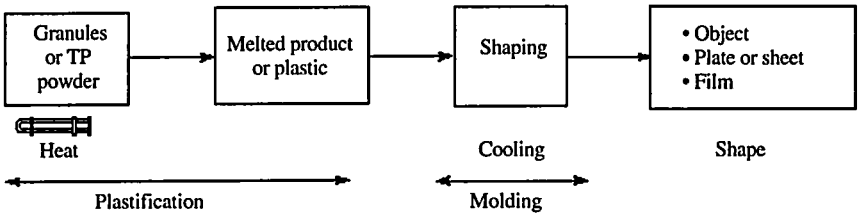


Fig. 14.4. Manufacture of plastic.

Manufacture of Plastic Packaging. Plastics used in the detergent industry are of the thermoplastic type. The initial granules or powder are heated to obtain a plastic product which is subsequently molded to make film, bottles, and so on. The different stages in the manufacture of plastic are shown in Figure 14.4. The two main processes used are extrusion/molding and injection/blowing.

Extrusion. This process is shown schematically in Figure 14.5. For example, in the manufacture of a tubular product in PVC, the melted polymer is extruded through a draw plate and cylindrical die. The extruded material is drawn out, formed, cooled, and cut into the length required (or reeled). PE or PVC bottles can be manufactured by extrusion and blowing.

Injection and blowing (PE or PVC bottles). The main steps in the process are as follows: injection/preforming, holding at temperature, blowing, and ejection of the bottle. The main advantages and disadvantages of plastics used in the detergent industry are summarized in Table 14.1.

Additives. Numerous ingredients are used in the manufacture of plastics, either as processing aids, or to improve some of their properties. These additives include antistatic agents, which limit the accumulation of surface electrical charges and thus minimize the adherence of dust, lubricants, plasticizers (to reduce viscosity), and emulsifiers. Mechanical properties are improved by antioxidants, ultraviolet (UV) absorbers, and fungicides. Aesthetic improvements include colorants and agents that improve the transmission of light.

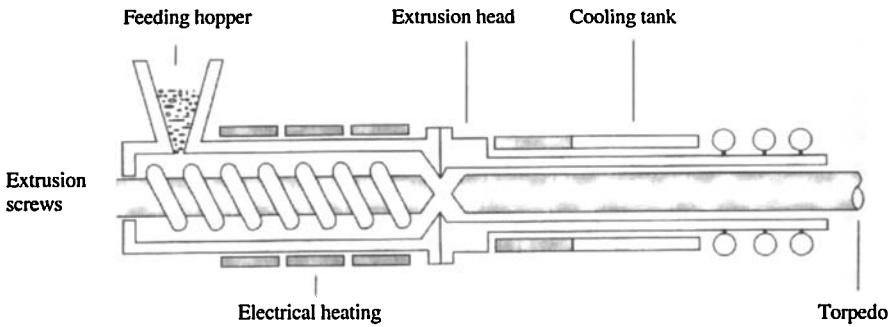


Fig. 14.5. Plastic extrusion.

TABLE 14.1
Advantages and Disadvantages of Using Plastics in the Detergent Industry

Material and Use	Advantages	Disadvantages
Polyethylene (PE)		
Film (bags, overwrap)	Easy to make	Easily permeated by gases
Bottles	Light, supple	Photodegradable (sensitive to UV)
Composites (on cardboard, aluminum, paper)	Nontoxic (food quality)	Easily flammable
	Chemically inert	Average heat resistance
Stoppers	Shockproof	
Capsules	Easy to mold (~100°C)	
	Cost	
Polypropylene (PP)		
Films	Light	Easily permeated by gases
Bottles	Good mechanical properties (rigidity, bending)	Photodegradation
Complexes (on cardboard, aluminum, paper)		Difficult to thermoform
	Do not scratch	Easily flammable
Stoppers	Shine	
	Food quality	
	Heat stable	
	Chemically inert	
	Cost	
Polyvinyl chloride (PVC)		
Supple and semirigid film	Easy to make	Gives off hydrochloric acid when burned = toxic
Retractable sleeves	Good mechanical strength	
Bottles	Do not scratch	Not resistant to heat (70°C)
Flasks	Shine	Highly gas permeable
Composites	Food quality	
	Chemically inert	
	Supple when used with plasticizers	
	Cost	
Polystyrene (PS)		
Stoppers	Light	Not very resistant to chemicals (solvents, oils, hydrocarbons)
Bottles	Transparent	
Boxes	Food quality	
Tubular packaging	Supple	Standard PS does not like shocks
Pots	Dimensional stability	Low use temperature (~60°C)
Polyethylene terephthalate (PET)		
Supple/semirigid films	Light	Average resistance to temperature, acids, strong bases
	Scratch-resistant	
Flasks	Food quality	Limited thermomechanical resistance
	Quite impermeable to gas	
	Shine	
	Good shock resistance	Less easy to use (has to be dried before shaping + formation of acetaldehyde)
	Good for oils and greases	

Paper, Cardboard, and Composites (3,4)

Manufacture of Cardboard and Paper. Technically, both paper and cardboard are made from wood fibers. The difference lies in the weight per square meter, which is defined as <225 g/m^2 for paper and >225 g/m^2 for cardboard (Fig. 14.6).

Composition. Vegetable fibers used to make paper and cardboard are made mainly of pure cellulose (40–50%), hemicellulose (20–30%), which is quite similar to cellulose, combined with cellulose and lignin. Lignin, representing 20–30% of the fibers, is also a polymer. The rest of the composition comprises small quantities of minerals, ~2%, depending on the type (e.g., calcium, sodium, magnesium, or potassium), rubbers and organic compounds, and rosin (organic acids).

Manufacture. The manufacture of paper and cardboard can be divided into two successive stages, i.e., preparation of pulp and manufacture of the sheet of paper itself. Pulp is obtained from wood either by mechanical or chemical processes. The pulp is then passed through presses and drying drums that dry it progressively, reducing the water content from an initial 85% to ~5–10% in a sheet of paper. Flatboard manufacturing is identical, either from sheets of paper glued together, or from pulp, possibly containing other substances. Flatboard is a mixed material consisting of three surfaces: front, back, and inside.

Specific treatments. Many papers contain additives introduced with the pulp; these are intended to improve opacity, printability, or dimensional stability. They are mainly minerals (kaolin, titanium oxide, calcium carbonate), fluorescent whitening agents, starch (for whiteness and improved cohesion of the sheet), and sizing agents to make the paper hydrophobic. Mechanical treatments improve the brightness of paper and include friction with a heated cylinder, calendering or supercalendering in the case of greaseproof papers. Examples of chemical treatments include the following:

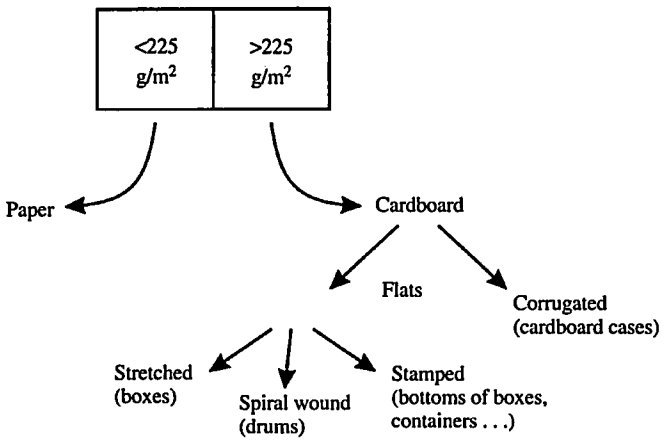


Fig. 14.6. Paper and cardboard.

Fig. 14.7. Corrugated cardboard.

1. Sulfurization, by soaking in sulfuric acid which makes the paper impermeable to fats and gives it nonstick properties. Sulfurization solubilizes the surface of the cellulose fibers, which then become cemented together. Sulfurization is followed by washing in clean water.
2. Waxing by coating or impregnation, a process used extensively in food industries.
3. Other treatments are based on proteins, melamine, or phenolic resins to confer wet-strength on paper.

> **Comment**
> Packaging made of fiberboard is often covered with a film of low-density polyethylene or polypropylene, to ensure effective protection against humidity and permit heat sealing.

Corrugated cardboard is a composite material made of several sheets of paper (2–7), with one or several fluted sheets (Fig. 14.7). The covers are made of unbleached paper board; the corrugation, which increases the strength and resistance, is obtained by passing the board through two cylinders at 180°C, in the presence of moisture. Corrugated cardboard is used to manufacture such items as outer cases.

Aluminum Packaging (3–5)

In the detergent and personal product industries, aluminum is used especially to make toothpaste tubes and aerosol containers, as well as certain composites. Aluminum is used as such ("nonalloyed") 99.5% pure, or more often, "alloyed" with ~3% of other elements, which improve its resistance to fatigue, corrosion, or to solder, for example.

Aluminum is an interesting material because it can be used to make very thin packaging, which is unbreakable (thus easy to transport); it is resistant to temperature change, and its barrier properties make it very popular for use with food in particular. Moreover, aluminum is impervious to dust, light, gases and liquids, and microorganisms. Aluminum resists corrosion because oxidation forms a protective layer of alumina on the surface. On the other hand, aluminum is attacked by highly acidic or alkaline products, and also by chloride and organic acids. For this reason, aluminum used in toothpaste packaging is generally coated with a resin film to avoid any chemical interaction.

Composites

In the packaging industry, composites are made of materials of different origin that are used in multilayers to combine the benefits of each of the individual layers. With up to 13 different layers, some very complex composites exist! Composites:

(i) protect the product from outside influences, acting as a barrier against light, humidity, and oxygen;
(ii) allow the product inside to keep its characteristics, e.g., flavor or color;
(iii) are easy to use on production lines (e.g., heat sealing); and
(iv) can be flexible or semirigid.

Raw materials for composites include sheets or films of plastic, paper, cardboard, and aluminum. The methods of manufacture include the following:

1. Lamination, the most widely used technique, is to dry-glue the films and laminate them between two cylinders.
2. Extrusion and layering, in which an amorphous polyolefin (e.g., low-density PE) is extruded directly onto a base film at high temperature (~300°C).
3. Extrusion and lamination (composites based on sheet aluminum). Low density PE is extruded directly between two films, where it serves as an adhesive and waterproofs the resulting composite.
4. Coextrusion, in which polymers of the same family with different characteristics can be made into composites, (e.g., low-density PE + high-density PE).
5. Metallization, in which aluminum vapor is condensed in a vacuum onto the surface of a plastic. The metallized films are impermeable to gases and water. These are expensive and have to be protected by varnishes, or by gluing to another plastic film.
6. Coating, which consists of protecting one or both of the faces of the film.

Packaging and Legislation (4)

A visit to the supermarket will demonstrate that most products are large users of packaging. In 1993, France produced 20 million tons of household waste, or almost 1 kg/day/person. The cost is enormous! The cost of collecting and treating domestic garbage is estimated at ~$100/t/year, or ~10 billion dollars to be paid for out of the budgets of local governments. Each person in France throws away a yearly average of 180 kg of packaging, which may not be a large amount compared with the Americans at 250 kg/year, but it is still too much compared with the European average of 116 kg/year.

Five years later, in 1998, France was still the biggest producer of household waste at 120 kg/capita/day, to the point that legislation has now been passed reflecting public concern and giving high priority to reduction of the problem both in France and in other European countries.

French Legislation

The decree of April 1, 1992, applied the law of July 15, 1975, on removal and destruction of waste and was implemented as of January 1, 1993. The intention of the decree

was to involve producers, packagers, and importers in recycling and elimination of waste packaging from the products they sell. The scope of the text applies to all packaging used to protect or present to the public products for use by the ultimate consumer. The application creates two options: direct responsibility and responsibility delegated to an intermediary. Direct responsibility implies that the manufacturer must recycle packaging waste in two possible ways. In packaging on consignment, the package directions permit consumers to return used packaging and receive a refund of their deposits. Alternatively, manufacturers can place collection bins where consumers can deposit their used packaging. An agreed-upon control system was confirmed by the ministerial authorities for measuring the effectiveness of the system. In fact, such systems are rarely or never used.

Using an Intermediary. The manufacturer may elect to contract with an organization specializing in this area to handle package recycling and reuse of packaging waste, subject to agreement by the ministerial authorities. This agreement is valid for 6 years and contains the terms of reference to be observed by both the organization and its customers. In practice, the industries got together and decided to appoint one central organization, a new limited liability company called Eco-Emballages, which is responsible for collecting all domestic packaging (e.g., softener bottles, detergent boxes, milk, and water bottles). The manufacturer is charged for this service and for the subsequent distribution of the revenues to local communities to help them set up collection and disposal units. The fees paid by the manufacturers are based on the volume of space taken up by rigid packages, and on weight for flexible packaging. These fees are applied to every unit the consumer buys and then throws away. To help recognition of the packages by Eco-Emballages, manufacturers put a special logo on these packages.

Comment
These regulations are specific to France.

Directive of the European Parliament Concerning Packaging and Packaging Waste

In terms of legislation, the European directive 94/62/CE is the most important. The management of waste includes many approaches: source of reduction, sorting, and recovery of value. Source reduction is obviously the best solution, based on the principle that prevention is preferable to cure.

A Community Obligation. European directive 94/62/CE, concerning packaging and packaging waste, "targets as a first priority the reduction of packaging waste at [the] source; then the reuse of packaging; recycling; and other ways of [creating value], and finally the reduction and elimination of the waste itself." The main demands of this directive concern the following:

1. The manufacture and composition of packaging:
   - To limit the volume and weight of packaging to the minimum compatible with the required level of safety, hygiene, and acceptability for the product itself and for the consumer.
   - To aim at making design, manufacture, and marketing of the package reusable, or to give it value by recycling, and to reduce to a minimum its effect on the environment after its use.
   - To reduce to a minimum any materials in packaging that are dangerous or a nuisance.
2. The reusable nature of packages.
3. The end value of the package. This can be recovered through recycling (value of the materials), energy recovery (energy value), or composting and biodegradability.

The European Definition of Prevention. A first, official definition of prevention is given in the same directive as follows: "the reduction in the extent of damage to the environment:

- Of raw materials and substances used in packaging and packaging waste, of packaging and packaging waste at production, sale, distribution, use and disposal, particularly by developing products and techniques that do not pollute."

This definition shows that source reduction is considered from two aspects, i.e., quantitative, in terms of metric tons saved, and qualitative, in terms of the reduction in harm to the environment. It states that the prevention of packaging waste concerns all aspects of the life cycle of a product and its packaging.

Scope. The consumer may know only one or two levels in the use of packaging, but experts can identify many more.

1. The consumer package itself can be in two parts, the consumer unit (the package itself) and the consumer sales unit; the latter is often confused with the consumer unit, but it also includes the additional packaging material required to combine several consumer units. The consumer unit is identified by a bar code.
2. The outer packaging, generally a handling unit, which one person can carry (a case), or a transport unit (a pallet), intended to optimize storage and handling.

This packaging system is necessary to transport the product and to keep it in good condition from manufacture to consumption. European directive 94/62CE gives the official definition of packaging and its scope. Packaging is defined as "any product of any nature whatsoever, which is intended to contain or protect a given product, from raw materials to finished products, to allow them to be handled and transported from the producer to the consumer or user, and to present the product. All 'throw away' articles which are part of this system are considered to

be packaging," (see below for the definition of primary, secondary, and tertiary packaging). This directive is therefore very important for the development of household products because it includes the package in the development of the product (package + product are one and the same), whether from the point of view of quantities of materials used and then thrown away by the consumer, or from that of harmfulness to the environment (manufacturing processes, transport, materials discharged into the atmosphere).

Code of Good Environmental Practice

The role of major manufacturers, and in particular the detergent manufacturers and their association, the AISE, was vital in the creation and start-up of Eco-Emballages and in avoiding even more constraining and costly legislation (such as the D.S.D. system in Germany). The AISE (European Soap Manufacturers Association) code of good environmental conduct was launched on July 23, 1998, in Brussels, strongly supported by the European Commission. Among other things, it plans to reduce the amount of packaging used by 10% over 5 years. The text of this code along with its Appendix is reproduced below.

> AISE has been committed for a long time to protect the consumer and the environment; its members have in fact contributed significantly to the establishment, publication, and application of environmental policies. To maintain and give a new dimension to this commitment to reducing the effect of detergents on the environment, the AISE has established this new code of conduct. Support for this Code is proof of an unequivocal and explicit commitment to consumer safety and protection of the environment, and also to durable environmental development. There are manufacturers who commit themselves to pursue innovation in environmental matters, together with consumers and all other parties concerned who might have an influence on the environmental effects of household detergents. AISE commits itself to review this code at least every five years and to report at least every two years on progress achieved. This voluntary program is open to all businesses, hereunder designated as "the manufacturer" who produce and/or sell household detergents, whether or not they are members of their National Associations, or themselves members of AISE.

In this Code, the term "products" today covers household detergents used to wash clothes. To observe this Code, the manufacturer must make the following commitments:

1. The manufacturer must think about the composition and the packaging of its products, taking into account their main effects on the environment in accordance with recognized scientific criteria.
2. The manufacturer must supply the consumer with information about how to use the product correctly. This information will be based on facts from analysis of the life cycle of the category of products concerned.
3. Product safety evaluation for the consumer and the environment should observe the principles of the "Guide on the Evaluation of Risk" established by the European Commission in the context of Rule EU 1488/94, which describes the criteria relative to the consumer and

the environment to reassure them as well as possible regarding safety matters. All actions useful to this evaluation will be undertaken.

4. All products sold by the manufacturer should follow in all particulars legislation relative to protection of the consumer and the environment, and especially the European Union directives on surfactant biodegradability (EU 73/404, 82/242, 82/243), on classification and labeling under the Directive for Dangerous Preparations (EU 88/379), and on the limitations for sale of certain dangerous substances and preparations 5EU 94/62). In addition to safety labeling, the list of all ingredients should be included on the packaging, in accordance with the Recommendation of the European Union on labeling components (EU 89/542), and, when appropriate, dosage instructions relative to soil, the load, and water hardness.
5. Manufacturer's environmental advertising claims for their products must be authentic, based on real facts, and intended to inform the consumer. They must meet the demands of the specific codes of the International Chamber of Commerce on environmental advertising claims or those of the equivalent national codes, which specify recommendations of acceptable advertising claims and how they may be communicated.
6. Manufacturers who commit to observe this Code of good practice and its appendix must supply a written declaration signed by their legal representative that they will conform without reserve to all the principles laid out in the present Code and commit themselves to continue the work on "the life cycle and risk evaluation techniques" in order to identify and collect all additional useful facts that can contribute to further reduction in harmful environmental effects.

Appendix

Any business producing and/or selling household detergents (hereinafter called the manufacturer), whether or not it is a National Association member of AISE, which adheres to the present AISE Code of good environmental practice, commits to making all efforts to reach the objectives set out below. These objectives are valid for the EEA (European Economic Area) which took effect January 1, 1997. They can be adapted to each national market taking into consideration progress on environmental matters, washing habits, and consumer choice. They are agreed to for a period of five years.

Energy savings (kwh per wash cycle): Objective: 5% reduction in energy used in the washing process.

Product consumption: Objective: 10% reduction in the consumption of detergent per inhabitant.

Packaging consumption (including primary and secondary packaging): Objective: 10% reduction in the consumption of packaging per inhabitant.

Biodegradability (measured by recognized biodegradability tests): Objective: 10% less consumption per inhabitant of the organic ingredients in household laundry detergents that are not naturally biodegradable.

1. Manufacturers who make these commitments also commit themselves to supplying the necessary basic facts about their businesses (base 1996) for each of the environmental objectives defined, to measure progress, and to account to the AISE.

2. The AISE promises to collect and manage these facts and to publish a report by country and at the European level, at least every 2 years.

Example of Packaging Economies (6–8, 9–10)

The Product/Packaging Cycle. Imagine the development of a "miracle detergent," its launch, its use by the consumers, everything through to the final destruction or disposal of its package. The packaging cycle and packaging waste processes are illustrated in Figure 14.8.

1. Product concept
2. Packaging concept
3. Manufacture of packaging
4. Product manufacture
5. Packing
6. Product use by the consumer
7. Destruction or recycling of the package

At each stage, both the quantitative aspects (the amount of packaging material saved) and the qualitative aspects (with minimal or zero environmental effect) will be studied. For the product concept, an obvious example is that of concentrated products (compact powders, fabric softeners with 3–10 times concentration), which greatly reduce the amount of packaging. For the packaging concept, in order to optimize the waste problem, the ideal is to "reduce at source"; this means that each element of packaging, whether primary, secondary, or tertiary will be minimized. This involves not only the physical packaging and the waste it generates, but also the nonuse of energy. In this context, the term packaging includes the following:

(i) the primary package or the packaging that is sold to the consumer at the point of sale;

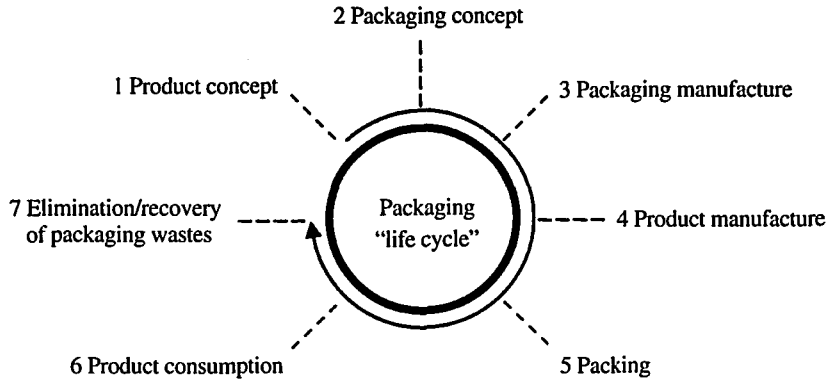


Fig. 14.8. Life cycle of packaging.

(ii) the secondary package, which groups primary packages for presentation at the point of sale, whether or not the product is sold "grouped" (secondary packaging can be removed without changing the characteristics of the product in any way);
(iii) the tertiary packaging, which is to protect a number of primary or secondary packages during transport and to make them easier to handle.

Prevention is the key word throughout the process, from concept to final destruction. From the beginning, all aspects have to be taken into account, and an overall balance sheet drawn up. For example, there would be no point in reducing a bottle weight by a few grams if this resulted in the need for a stronger outer case that had to be sourced from many miles away. Figure 14.9 illustrates the packaging sources, i.e., primary packaging (the detergent), secondary packaging (e.g., outer case), and tertiary packaging, including binding, plastic film, and pallet.

Industrial Involvement. In 1996, the Ministry of the Environment in France issued a "Catalogue for the Prevention of Packaging Waste" highlighting the efforts made by industry to reduce waste. To reinforce this situation and to work together on a prevention policy, the National Council for Packaging was formed in France on May 20, 1997. It unites many fields of expertise with its members working cooperatively in eight sections. Its mission is in line with national policy; it works with government, industry, European organizations, and many associations. It is the indispensable link for discussion and agreement among the interested parties. Some examples from the detergents and personal products industries are given below. The examples for personal care products were supplied by Elida Gibbs Fabergé.

Shampoo. Development of a new bottle for Sunsilk with a 36% saving in plastic was achieved by the following measures: (i) reduction in thickness of the bottle; and

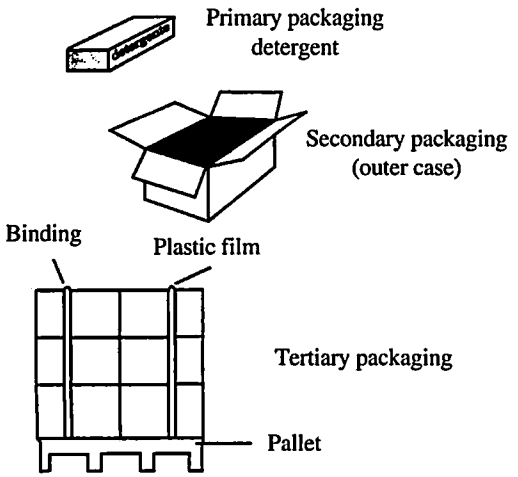


Fig. 14.9. Packaging sources.

TABLE 14.2
Packaging Economies by Lever France in 1993

Product	Packaging	Savings	Gains in the year 1993 (metric tons not wasted)
Various liquids and dishwashing powders	Plastic	15–25%	610
Concentrated powders	Cardboard	45%	1650

(ii) lighter design using two labels instead of a shrinkwrap sleeve. These changes required the use of a heavier polyethylene cap. Because the distributor wanted shampoos delivered in units of 12 instead of 20, cardboard consumption increased. The manufacturer nevertheless managed to maintain the level of consumption by reusing the cases used to deliver bottles to the factory. The net results were as follows: polyethylene, –47 t; polypropylene, +6.6 t; cardboard, 0. This yielded a total annual reduction of 40.4 t. The reduction in packaging reduced the volume for transport by 25%, or the equivalent of 400 pallets or 15 truckloads per year.

High-density PE bottles for bath foams and shower gels. The optimization of Dove bottles for bath foams and shower gels was accomplished by a computer-aided program. The outcome was a saving of 20% in high-density PE at equal bottle strength. The outer cases were replaced by "display trays," which were lighter and could be used to display the product at the point of sale; the number of units per pallet was also increased. These various changes brought cardboard savings of 51% for the shower gel and 76% for the bath foam. The results are summarized as follows: HDPE packaging, –20 t; outer cartons, –45 t; total annual reduction, –65 t.

Packaging for detergent powders. This is certainly one of the areas in which source reduction was first applied. It should not be forgotten that the "phosphate war" had already taken place and the large manufacturers were already acutely aware of ecological considerations and their effect on manufactured products. The economies achieved by Lever France in 1993 in consumption of cardboard are summarized in Table 14.2.

Reuse–Recycling–Recovery (1)

These are the three ways of reducing the effect of waste on the environment. We will examine them in turn.

Reuse

Reuse of primary household packaging is possible in certain industries, for example, glass water bottles, but not in others. If we include industrial packaging, household detergent manufacturers can reuse the following packaging: (i) pallets; (ii) intermediate "transfer" cases; (iii) reusable boxes for use with refill packages; and (iv) refill packages that do not include a plastic dosing mechanism, i.e., consumers reuse the one they have.

Recycling

To recycle matter requires first obtaining it. Slowly, collecting systems are being set up to recycle packaging and to sort it at specialized centers. This is a complex and costly infrastructure which is gradually being put into place. It is now possible to recycle used cardboard and plastic and return them to the packaging industry for recycling, saving both money and new materials.

Cardboard. For many years, industry has had systems to recycle paper and cardboard. About 80% of all cardboard used by the detergents industry is recycled.

Plastic. HDPE. Unfortunately, the performance is not as good for plastics, with only 8–10% comprised of recycled material. The main area of interest is HDPE, for which recycling involves a sensitive operation and a complex chain. HDPE is the main plastic retrieved for recycling, with the exclusion of packages that contain motor oil, pesticides, solvents, and similar products. Once collected, HDPE is separated from other plastic containers such as PVC, PET, or PP. The HDPE is then washed and recycled in a machine that removes all solids, residual products, and paper. After washing and drying, the clean material is chopped into small pieces and extruded through an 80-m filter before granulation.

To achieve 25% recycled HDPE in every bottle, a multilayer coextrusion process is used. An internal layer of virgin plastic resin protects the product from the recycled plastic. To maintain the appearance of the bottle, particularly when it is white, the outer layer is also coated with virgin resin. Regenerated HDPE is therefore used between these inner and outer layers of new plastic. Every bottle contains about 25% recycled HDPE, and numerous tests have shown that this percentage could be increased without affecting the look or the quality of the packaging, if there were a greater supply of used material (i.e., when recycling and treatment have become standard procedure). Figure 14.10 illustrates the 25% recycled bottle with the external layer of new plastic, the middle layer, and the internal layer of virgin plastic. This sandwich process completely isolates the product from the recycled material.

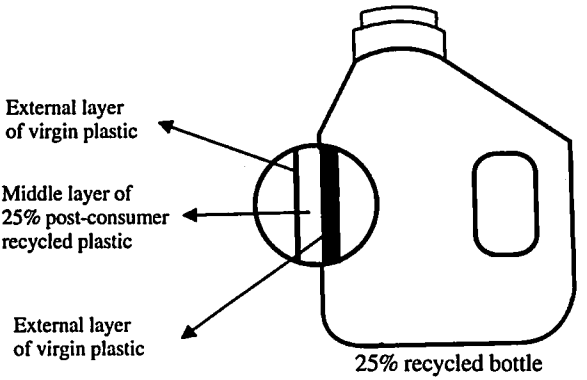


Fig. 14.10. Use of recycled plastic.

Recycling of plastics other than polyethylene. The following examples show that PE is not the only plastic that can be recycled (although today it is virtually the only product that is used in detergent packages).

1. PVC. Almost all impurities can be removed from PVC by the following operations:
   (i) pneumatic separation of all particles with hardness different from that of PVC;
   (ii) washing;
   (iii) brushing (washing in strong agitation);
   (iv) decanting; and
   (v) drying.

   (This operation is quite energy efficient, with a yield of ~80% and ~1% impurities.) The material can be used in tubes and public works (e.g., road surfaces, tiling).
2. PET. Recycling involves sorting and recovering noncolored products; brushing, washing, and separating of other materials by flotation; and granulation of the flakes. The material can be used in blister packs.
3. Mixtures. Studies are presently in progress for the use of mixed plastic raw materials. The limiting factors are similar to those for polyethylene, i.e., sources, which should be plentiful and of good quality, and costs (the cost of a recycled plastic can be higher than that of virgin materials).

Chemical Recovery

Laboratory techniques can decompose polymer molecules into usable raw materials for the chemical and petrochemical industries. These include vacuum pyrolysis, which can be used on all plastic raw materials, hydrocracking (hydrogen and heat treatment), gasification at 1600°C to produce a synthesis gas which in turn can produce methanol or ammonia, and chemolysis (decomposition to obtain monomers, e.g., by hydrolysis).

Biodegradation

Some microorganisms are capable of degrading polymers, and this technique seems to be attracting some interest. There are already applications, such as McDonald's in Austria, which uses corn-based polymer knives and forks that biodegrade in a few months; thus all the other refuse (hamburgers or paper) can be composted *without* any sorting. Yogurt containers based on polylactic acid (APL) are used in Germany. APL is obtained by fermentation of dextrose (beetroot or corn) into lactic acid, which is then polymerized. The problem is cost, which is twice that of polystyrene. Very powerful groups are taking a close interest in biodegradable plastic; some are working on polymer molecular chains, which have weak points that bacteria can easily break. The cost today of tomorrow's materials is still very high (between 2 and 10 times more expensive), but it is a good bet that in a few years such materials will be readily found in our supermarkets.

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CHAPTER 15

Storage Tests

Accelerated Tests

Finalizing a new detergent composition is not simply a matter of going through a certain number of necessary stages in the laboratory, in pilot plants, or in the factory, while controlling quality at each stage. A final requirement must be satisfied once everything else has been successfully completed. How do we ensure that the product that left the factory in 100% satisfactory condition arrives in the same condition in the user's home, having been through a number of intermediate stages? These stages include:

- storage in warehouses prior to shipment (these can be very hot in summer and equally cold in winter);
- passage through distribution channels (which may be fast or slow);
- storage in wholesalers' warehouses;
- storage (which can be long), in stores and on shelves; and finally
- storage in the home (which can be more or less long), often under harsh conditions, e.g., in a damp atmosphere underneath a kitchen sink.

All of these parameters will tend to affect the quality of the product and its performance in a negative manner. But as we have already said, the pressure of *time* is one factor that is always present in the formulator's life; there is simply not enough time to do tests under real conditions for periods of up to 6 mo. Thus, the passage of time has to be accelerated. This is done in huge cabinets in which formulations under study are stored.

These cabinets can be adjusted for temperature and humidity and can operate in freeze/thaw cycles every 24 or 48 h. This is very effective for liquids because, if the product is unstable, this will become apparent (in the form of a phase separation in which a sediment will appear) after just a few days. This kind of storage can therefore reveal stability problems quickly. For control purposes, identical tests are carried out in parallel, but in real conditions of temperature and humidity. Examples of the types of studies are given below.

Powder Detergents

The main criterion is related to the absorption of moisture, which results in an unpleasant feel to the product, difficulty in pouring due to lumps, and even in complete solidification! The presence of additional water will also affect the way in which the product flows from the dispenser, i.e., dispensability, and the speed with which it goes into solution. In addition to physical changes, the absorbed moisture will reduce (sometimes strongly) the activity of certain sensitive ingredients in the

formulation, the most important of which are enzymes, tetraacetylethylenediamine (TAED), and the perborate, but it will also affect the stability of the foam depressants. There are other more subjective criteria that can change during storage, including the color of the powder (e.g., turning yellow) or the perfume, which can degrade.

Liquid Detergents

Bottles and carton boxes, for example, may not always pose the same problems. The crucial point for liquids is physical stability because formulations can separate into two liquids or a sediment can appear in structured products. In either case, the outcome is disastrous for performance.

> **Comment**
> It should be noted that few manufacturers ask users to shake bottles before use because this can create the impression of a second-rate product.

Other parameters influenced by storage conditions are more similar to those of powders, including:

- medium-term tests, for example, are generally conducted at temperatures a little below 40°C with a relative humidity of 80–90%, and at temperatures ~20°C with the humidity at ~60%; and
- rapid freeze/thaw cycling is conducted in other equipment that can give rapid increases and decreases in temperature. These require daily visual control, while products undergoing medium-term tests for 1, 2, or 3 months can be checked every 8 or 15 days or even once every 1, 2, or 3 months.

At the end of the storage period, the formulator has all the facts, both objective and subjective, and is in a position to judge whether the new product behaves correctly under the conditions described above and meets the objectives set down at the beginning of the study.

Properties to Be Checked

The detergent compositions are checked after storage for 4, 8, or 12 weeks under severe conditions for the following parameters, which can vary from one manufacturer to another.

Physical Parameters

Flow Properties. In a simple method, the pack is opened and the product poured out slowly. Flow properties are classified from perfect flow, to the presence of lumps, to no flow at all in extreme cases.

Lumps. The proportion of powder that has become lumpy is evaluated, for example, as a percentage of the total, as is the "quality" of the agglomerates.

Feel. When humidity is present, the feel of the powder changes from granular to "rubbery." This can be evaluated on a simple 5-point scale.

Control in the Washing Machine. A powder that has been stored under different conditions, often simulating "real life", will behave differently from a product that is taken straight off the production line. Two criteria must be checked in the washing machine: how the product flows from the dispenser and, because foam depressants suffer during storage, the quality of the foam.

Dispensing. In general, normal machines that are representative of the market (different detergent dispensing systems) are used. It is important to control the following four parameters:

- water pressure when it reaches the dispenser;
- the amount of water used;
- the time it takes; and
- the temperature of the water, which should be adjustable and controllable.

To compare a fresh product with one that has been stored, the powder remaining in the dispenser is weighed dry after removal of moisture.

Foam. Foam control is conducted in a washing machine that has been modified to permit measurement of foam level. During the wash, the foam level is recorded on a computer and is compared with the foam profile of a powder that has not been stored. The evaluator has a number of parameters to consider depending on the specific requirements of the study, including water hardness, the wash load (textile types, weight of laundry), and the presence or absence of soil (household or artificial), product dosage, and wash cycle (duration and temperature).

To control the foam level in a front loading machine, the sensors are linked to a computer that records the foam level and prints a report at the end of the wash (Fig. 15.1). By

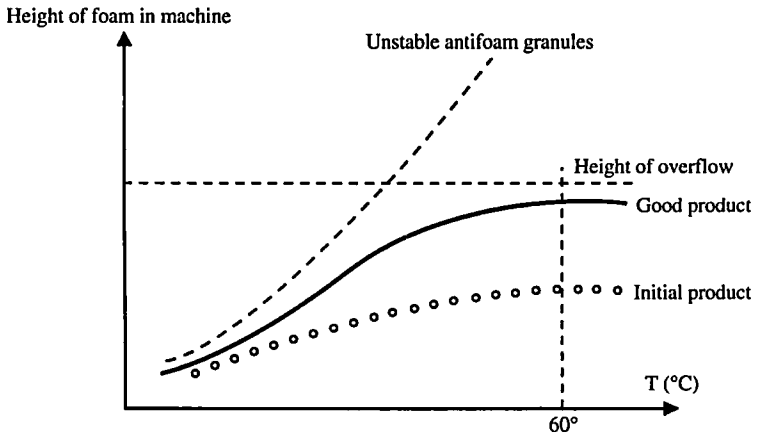

Fig. 15.1. Stability of foam depressant granules.

comparing the three curves, the evaluator knows immediately whether the suds depressant system is still sufficiently active.

Chemical Parameters

Sometimes the evaluator may wish to study the effects of storage more completely, in which case performance evaluation tests will also be conducted in the laboratory or in the machine. Usually, an analysis of the main chemical criteria will give a good idea of product stability. The main chemical controls are the activity for each of the enzyme varieties and the decomposition of the perborate/TAED system. Over several weeks of storage, the curves are compared with one or several reference products. Each prototype is thus positioned on a series of graphs and the choice between the different options is made much easier. If results are unsatisfactory, other prototypes will have to be examined, or the stability of the existing ones improved, possibly by encapsulation.

Other Parameters

Two other criteria are also checked during storage tests, namely, color and perfume.

Color. For a rapid test, a small panel of ~10 people will be enough if the color differences are sufficiently distinct. Prototypes that have been stored for x weeks under given conditions are compared with reference products that have been stored under the same conditions and also with products stored in the dark in a refrigerator. The observation is done in artificial daylight, and an order established (see Chapter 17, point 1, concerning statistical tests used for detergents). If greater precision is required in the results, a reflectance or tristimulus measure can be used.

Perfume. A panel can distinguish even small differences. This panel can consist of 10 specially trained experts, or at least 25 untrained people (see Chapter 17, point 1, dealing with statistical methods). In certain cases this can be pushed further to include chemical analysis.

Packaging. The compatibility between the product and its package is also tested, e.g., in terms of nonionics bleeding through the package, or a loss of printing quality.

Liquid Detergents

Storage of liquids can affect three physical parameters, sometimes significantly: separation, sedimentation, and viscosity.

- Separation occurs when two liquids that have been thoroughly mixed at time $t = 0$ separate into two phases.
- Sedimentation can occur, for example, in the case of structured liquids; if the structure weakens during storage, the solid ingredients will sink to the bottom of

the bottles. These two phenomena are generally assessed by the naked eye. The extent of the problem is measured at regular, sometimes very close intervals. Rapid freeze/thaw cycles (cold/hot every 24 h) are highly discriminating and a 2-week period is sufficient to reach conclusions.

- The third criterion is the viscosity of a liquid detergent. Under difficult conditions, this can tend either toward insufficient viscosity (like water) or toward a gelled product. In both cases, the effect on dosing of the detergent is obvious, without mentioning the user reaction.

As in the case of detergent powders, tests may also be required in washing machines to evaluate performance, foam, and dispensing.

Chemical Parameters. Here again, the most sensitive ingredients can be closely tracked over time (in particular the enzymes) and compared with reference products.

Other Parameters. Color and perfume are checked either by panel evaluation or by objective analysis. The plastic bottle must be compatible with the liquid product it contains (no interaction).

Shipping Tests

In tandem with the above tests, it is also necessary to do shipping tests on the product and its packaging. Random samples of the product in its final packaging are taken from the production line during final commercial tests and are subjected to transport tests under severe conditions. The products are loaded onto trailers, particularly in the areas in which vibrations are strongest (above the wheel base) or in which temperatures change the most (summer and winter). The products are then transported over hundreds or even thousands of kilometers, in three or four trips, with samples being taken for laboratory checking after each trip.

Physical Checks. For powders, these include settling, solidifying, flow properties, and density. For liquids, sedimentation, appearance of crystals, and appearance of the liquid (clear or cloudy) are significant.

Chemical Checks. These are particularly important for powders, e.g., to determine whether the foam depressant granules, enzymes, speckles, perborate, or sulfate have segregated during transport. These ingredients are analyzed in samples taken from different levels of the box.

Packaging Checks. Here the important inspections concern staining of bottle labels or of printing on boxes, crushing, or leaks (for both liquids and powders).

CHAPTER 16

Analytical Methods

Introduction

Before looking at the main analytical methods of detergent manufacturers, let us first consider what has to be analyzed. The four main areas to be examined are:

1. Quality control of raw materials and finished products. Although a detergent manufacturer may produce a certain number of raw materials on site, most will be purchased from third-party suppliers. For surfactants such as linear alkylbenzenesulfonate (LAS), primary alcohol sulfate (PAS), and lauryl ether sulfate (LES), or semifinished materials, such as foam depressant granules or tetraacetylethylenediamine (TAED) granules, which can be made on site, analyses will be conducted regularly during production.

   For purchased raw materials such as phosphates, zeolites, perborate, and enzymes, the supplier discharges his responsibility by issuing a quality certificate with each delivery, spelling out the terms that have been agreed upon contractually with the manufacturer. These include the number and type of quality control checks conducted, methods, and the limits of acceptability. This is accepted as adequate proof of quality by the detergent manufacturer, who will simply conduct spot checks on a regular basis.

   For finished products, analytical checks will be conducted to ensure that the detergent, toothpaste, or shampoo leaving the factory has been manufactured correctly and that it conforms to the formulation established for the product.

2. New products under development. Unlike "routine" analysis, new product development requires many types of analysis if problems are to be avoided. For example, why does a liquid separate into two phases under certain temperature conditions? To understand what is happening, each of the phases will require analysis to determine what it contains. If crystallization occurs, the crystals need to be analyzed to identify their origin and to make the necessary changes to the formulation.

   Analytical methods are also very useful for evaluating the stability of new ingredients. For instance, in the case of a new perfume showing signs of instability, we must determine which ingredient in the perfume is unstable, and possibly with which other ingredient it might be reacting. Similarly, storage of foam depressant ingredients will help in identifying the cause and in finding a solution, whether this be changing the formula, the process, or the ingredient itself.

3. Competitive products. The formulator is curious by definition. One's own products are very well known, but it is always important to know the competition. Analyses of competitive products are essential for two clear reasons:

(i) They help in understanding the general formulation policy of the competitors, some of whom may be working on environmental issues; others may concentrate on specific segments such as low temperature washing; and still others may give priority to innovation in whatever form; and

(ii) Analysis will "translate" competitive technological progress into formulations and processes.

Thus, if new granules appear in a competitive product, detailed analysis will reveal their composition and their manufacturing process. All competitive products are analyzed regularly to track formulation changes from year to year and to estimate product costs. These may be only estimates because both sampling and the analysis itself can be sources of error. Also, some ingredients such as perfume are very difficult to quantify and for this reason they are not usually included in a cost estimate. For comparison purposes, the reference formula that manufacturer A uses for a comparison with a formulation by manufacturer B poses the same problem of errors in sampling and analysis. If a competitive formula with equivalent performance costs 20 or 30% less than one's own product, a definite challenge lies ahead!

4. Pollution analysis. Every factory needs to know exactly how much air and water pollution it is generating. This requires special probes for taking samples from the air and rivers, and also specific equipment to quantify the problem, e.g., how much SO_2 is present in the smoke, what quantities of alkylbenzenesulfonate (ABS), sodium tripolyphosphate (STPP), and other substances are discharged in waste water or from accidents and are being sent into rivers. Legislation and established norms are becoming increasingly strict; manufacturers must be able to supply information to various authorities on request (see Chapter 18).

From the above, we can see that there is a constant need for analysis over a wide range of areas.

Standard methods for the analysis of raw materials or finished products are published and updated regularly by organizations such as the American Oil Chemists' Society (AOCS), the Association Française de Normalisation (AFNOR), the International Standards Organization (ISO), and the American Society for Testing and Materials (ASTM). They cover both the physical properties and chemical analysis. In addition, manufacturers will have their own in-house methods. Raw material specifications are agreed upon between the supplier and the detergent manufacturer based on standard methods, except for cases in which different methods are used that may be internal and specific to either party. In either case, the description and method are accepted by both parties. Standard methods have the advantage of being known to all suppliers and manufacturers and thus permit easy comparisons between the products of two potential suppliers. However, it is not enough to have ultrasophisticated methods if sampling is not representative. We will therefore look in more detail at sampling and the different stages in the analysis of an unknown finished product.

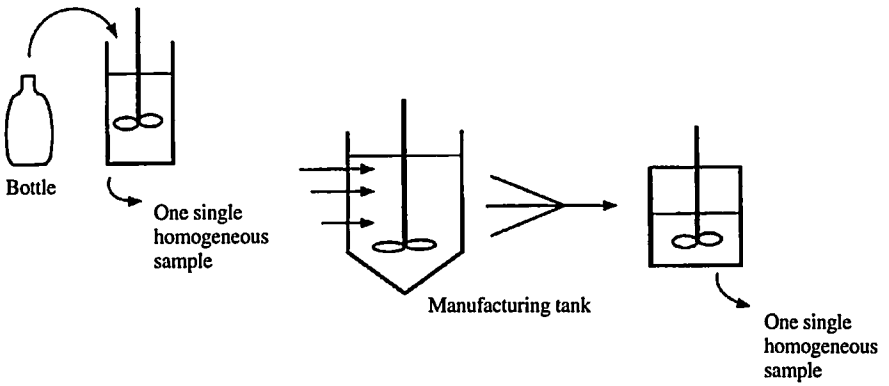

Fig. 16.1. Sampling of liquid products.

Sampling

Liquids

For liquids, the problem is simple. The bottle should be shaken before taking the production sample. If the sample is from a tank, several samples should be taken from different levels and then combined to make one sample (Fig. 16.1).

Powders

For powders, the problem is more complex; it is not possible to obtain a representative result when the analysis is conducted on only a few grams of product taken from a single package; thus, there is a high risk of error. For a competitive product, one method which reduces error is as follows:

(i) Purchase x packs from a similar production batch using the production code to identify the same day but different hours. This will eliminate variables due to possible changes in the product over time;

(ii) Buy x packs from different production dates, thereby taking into account possible variances over time. By mixing the two, we can obtain a relatively representative overall sample.

Next, we must ensure that the sample taken from many kilograms of a competitive product is also representative. Special sampling equipment is available for this purpose. The example in Figure 16.2 (an HD 22 sampler) shows a sieve supplied with powder from a hopper through a flap that feeds ~10 distributors to yield a well-mixed sample.

Thus, if we need x g of powder from a 5-kg pack, we need to repeat the operation a sufficient number of times to obtain the required amount of powder (Fig. 16.3). The apparatus shown is very simple; there are automatic versions that can deliver several samples of a given weight in one operation.

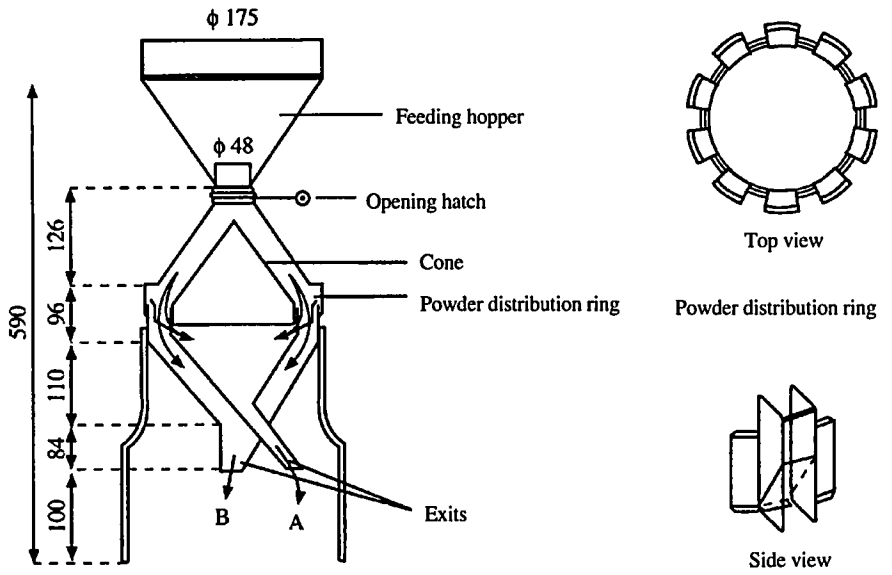

Fig. 16.2. An HD 22 sampler. Dimensions are in mm.

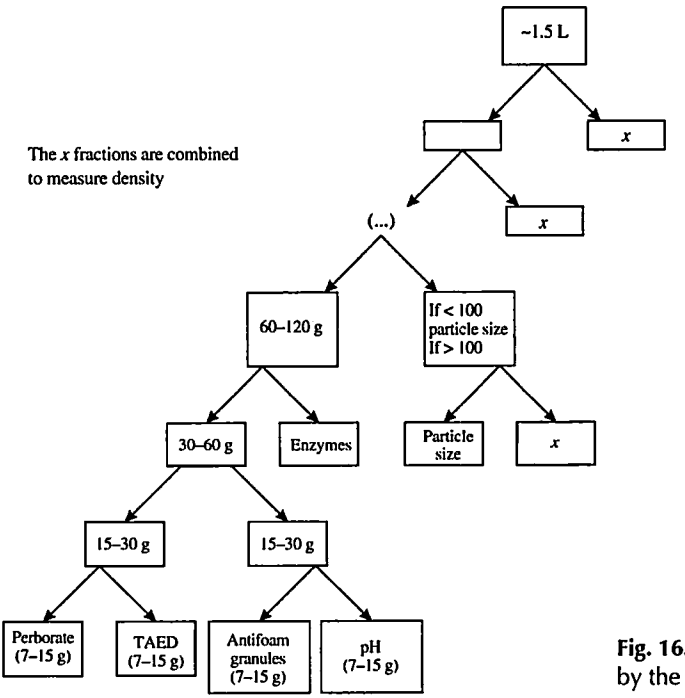

Fig. 16.3. Sample division by the HD 22.

The Different Steps in Analyzing an Unknown Finished Product

This is the most complex problem of all; it arises, for example, when we wish to analyze a competitive product. The approach is as follows:

(i) Start with visual observation. A trained technician will be able to gather some information by simply looking for certain raw materials or semifinished products, e.g., enzyme granules or foam depressant agents, and by smelling the product.

(ii) Identify the physical characteristics, i.e., for a liquid, measure the density, viscosity, etc. For a powder, measure density, the granulometric quality, and the flow properties. In addition, more detailed observationwould be obtained with a scanning electron microscope.

(iii) A binocular magnifying glass or an optical microscope will make it possible to sort specific particles for subsequent analysis to identify a raw or semifinished material of interest to the formulator.

(iv) Make an aqueous solution to help identify ingredients such as anionics, TAED, and inorganic salts (e.g., STPP, silicate, perborate, or carbonate); use solvents (or any other method of separation) to extract and subsequently identify the surfactants and the structure of other molecules.

The whole scheme is shown in Figure 16.4.

Examples of Instrumental Analytical Methods

The research laboratories of manufacturers are often as well equipped as the most modern universities [e.g., nuclear magnetic resonance (NMR), mass spectrometry, or high-performance liquid chromatography (HPLC)].

In the following, we will outline only a few examples of analytical methods that are quicker than classical chemical analysis and, in particular, three techniques that are often used in the laboratories of the larger production units: analysis by autoanalyzer, analysis by HPLC, and absorption or emission spectrometry.

The Autoanalyzer

This instrument can be used to perform a wide range of analyses, including the following:

(i) enzymes, including protease, lipase, amylase, cellulase;

(ii) certain inorganic salts, including the percentage of total phosphates and their species (STPP, ortho, or pyro); and

(iii) soluble silicates or carbonates.

The most widely used instruments are made by Technicon and Skala. These companies supply technical assistance on analytical methods along with their equipment.

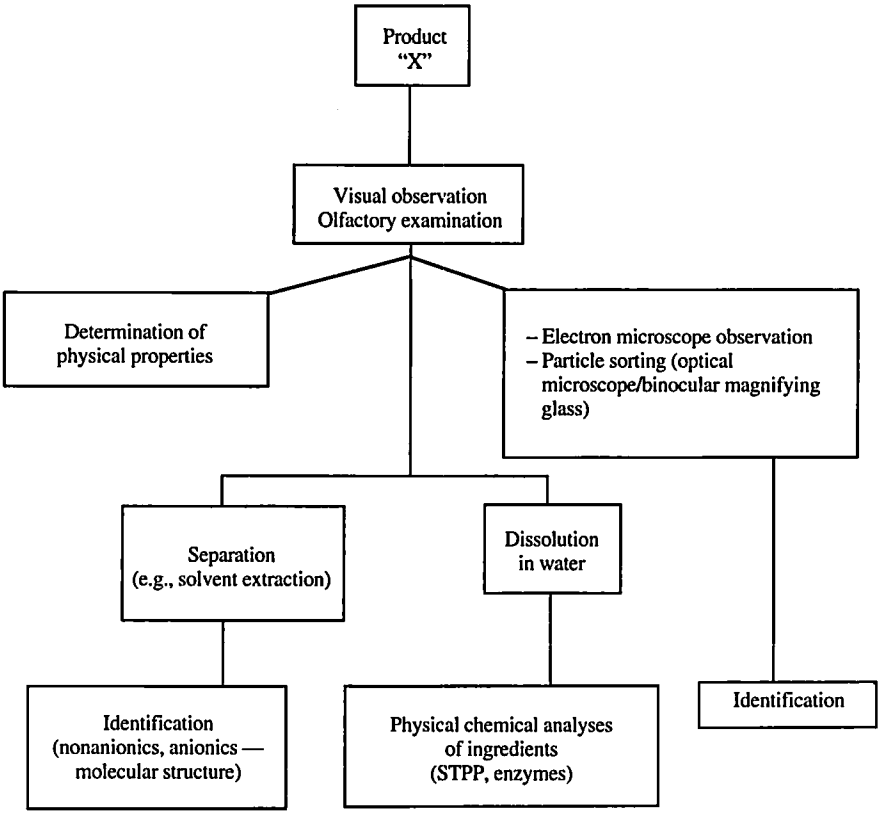

Fig. 16.4. The different stages in analyzing an unknown product.

Skala, for example, will sell modules that allow the user to meet precise needs. As examples, we describe two systems for the analysis of enzymes and phosphates, respectively.

Analysis of Enzymes. An example of the setup is given in Figure 16.5. It includes the following: a sampler, a pumping system, a bath (at 50°C), a colorimeter, a recorder, and a timing system.

This arrangement, which is one of many, is capable of analyzing enzyme activity on delivery from the supplier, controlling the presence of enzymes in a finished product either before shipment, or after a period of storage to assess stability, and measuring the amount of enzymes in the atmosphere of a workplace.

Analysis of protease: the 2,4,6-trinitrobenzenesulfonic acid (TNBSA) method. Enzymatic activity is measured at constant pH. The principle is as follows: The detergent composition is dissolved and then mixed with buffered acetylated casein, the TNBSA solution, and sodium sulfite solution (to prevent interference by sodium perborate in powders with a bleaching system). At 50°C, casein degrades, and its

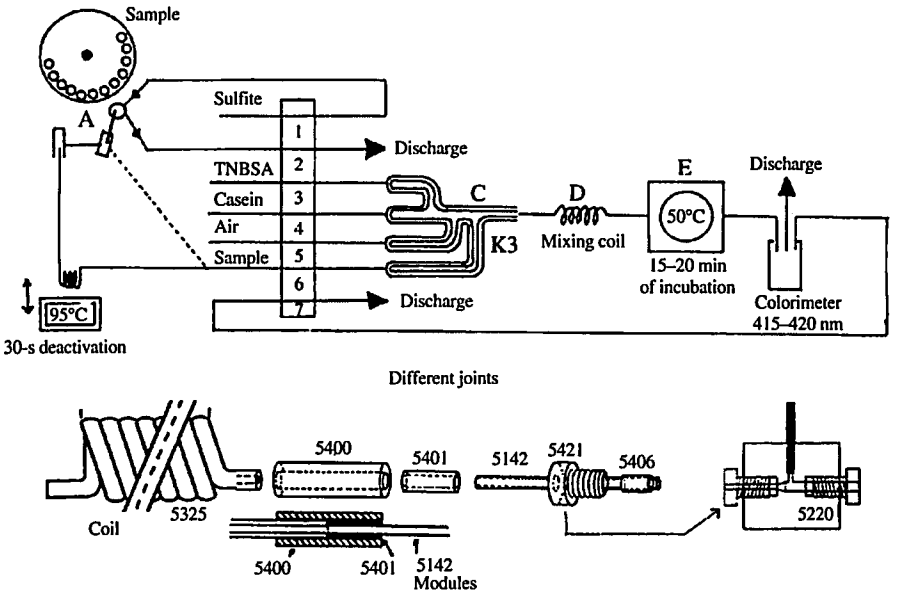

Fig. 16.5. Diagram of an autoanalyzer for analyzing protease.

degradation products produce a colored reaction product with the TNBSA solution. The intensity of this color is measured in the range of 415–420 nm. Enzyme activity is calculated automatically relative to a corresponding standard reference curve.

Analysis of amylase. The method is based on the action of α-amylase on 2-chloro-4-nitrophenyl-β-D-maltoheptaoside, which breaks the maltose chain into smaller units. These are converted into 2-chloro-4-nitrophenylglucoside by the action of α-glycosidase. Further reaction with β-glucosidase forms glucose and 2-chloro-4-nitrophenol, which has a yellow color. The reaction is followed closely and the change in absorbance at 405 nm per unit of time is measured. Amylolytic activity is calculated automatically by reference to a corresponding standard curve.

Analysis of lipase. One method is based on the esterase activity of lipase on *p*-nitrophenyl valerate, which produces yellow-colored *p*-nitrophenol. The reaction is tracked *in situ* and the change in absorbance at 405 nm per unit of time is again calculated automatically relative to the standard curve.

Analysis of total phosphates and chemical species (STPP, pyrophosphate, orthophosphate). A diagram of the apparatus is given in Figure 16.6. The principle is as follows:

The detergent powder is dissolved and fed into an autoanalyzer. Its path takes it

(i) through a system of tubes and coils in which it is diluted with water and mixed with dilute sulfuric acid, a solution of ammonium molybdate, and a solution of ascorbic acid; and

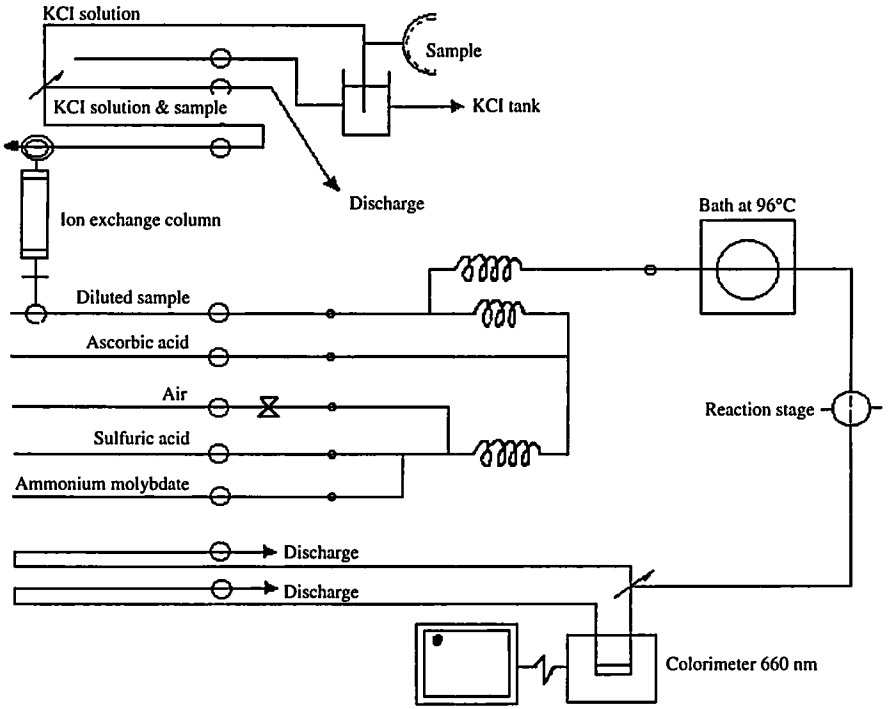

Fig. 16.6. Diagram of phosphate analysis and its chemical species.

(ii) through a bath at 96°C to hydrolyze condensed phosphate into orthophosphates.

Simultaneously, orthophosphate reacts with ammonium molybdate and ascorbic acid (as a reducing agent) to form a blue-colored complex. The intensity of color is measured by colorimetry. The peaks obtained are compared to reference curves and calculated as a percentage of P_2O_5 present in the original sample. To determine the chemical species, an ion-exchange resin is inserted into the reaction chain, the various peaks are integrated, and the percentage of pyrophosphate, orthophosphate, and

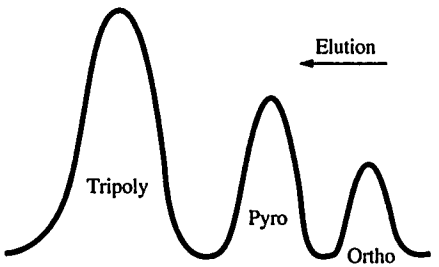

Fig. 16.7. Chemical species in sodium tripolyphosphate (STPP).

STPP is determined. The graph in Figure 16.7 shows an analysis of the chemical species in STPP.

High-Performance Liquid Chromatography (HPLC)

What is liquid chromatography? It is a method that can separate complicated mixtures in solution into their components. In principle, a mobile phase is run through a tube or column packed with porous granules. At time t, the mixture to be separated, which is dissolved in the mobile phase, is injected onto the column. The different components of the mixture then elute at different speeds and leave the column one after another together with the mobile phase. Individual components may be characterized by the length of time they reside on the column (retention time).

At the column exit the eluate passes through a suitable detector to determine the presence of different components. The type and sensitivity of the detector will allow the integration of the chromatographic peaks and calculation of the concentration of the individual components.

Classification. The various types of chromatographic analyses include liquid-solid chromatography (LSC), liquid-liquid chromatography (LLC), and gel permeation chromatography (GPC).

The most widely used types are the following:

(i) liquid-solid chromatography (LSC), in which separation is based on the differences in adsorption of the molecules in the mixture on the stationary phase;

(ii) liquid-liquid chromatography (LLC), in which separation is based on differences in solubility among different molecules, and the differences in their interaction with molecules bonded on the stationary phase; and

(iii) gel permeation chromatography (stationary phase: resins).

Separation characteristics. A good separation implies that the various parts retained in the column have an affinity for the stationary phase and that there are well-separated peaks. A diagram of a high-performance liquid chromatograph is given in Figure 16.8. Specifics of the various parts of the chromatographic apparatus are as follows:

1. Solvent reservoir. The volume is 1 L or a suitable volume for the analysis of a batch of samples. Mobile phases may be single solvents, e.g., toluene, or more complex mixtures of miscible solvents. The use of a closed vessel prevents evaporation and the dissolution of water vapor or soluble gasses.
2. Pump system. Pumps function at pressures up to 1000 psi (70 bar). There are two types of pumps, pneumatic and electric. The advantages of this setup include an unlimited volume of solvent, a very limited chamber volume, and the fact that flow can be regulated by changing piston speed and the volume of the chamber. A further advantage of a small pump volume is that it provides pulseless flow.

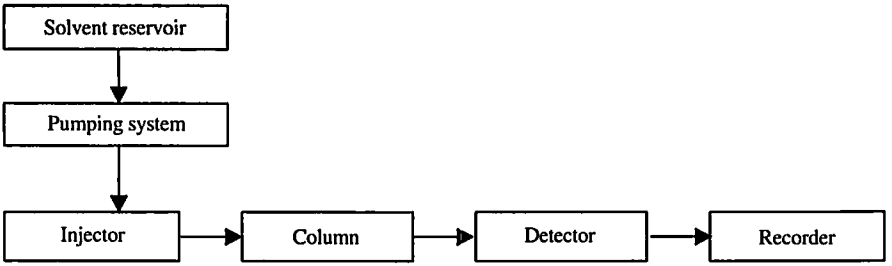

Fig. 16.8. Diagram of high-performance liquid chromatography.

3. Injector. Different sized loops allow the in-line injection of sample with minimal dilution before application onto the column.
4. Separation. A wide range of columns with different packing materials is available and can be chosen to optimize separation.
5. Detector. The possibilities include the visible ultraviolet (UV-vis) spectrophotometer, spectrofluorometers, refractometers, and electrochemical detectors. All allow continuous measurement of the eluate from the chromatographic column. The differential refractometer has universal application and may be considered essential in HPLC, whereas other detectors may be limited in their application. However, all detectors may be limited by their response to the components in solution and the mobile phases being used.

Most detectors used in HPLC are of the differential type; they measure variations in intensity, proportional to the concentration of specific components in the eluate. The peak areas obtained ultimately are linked to the quantity of the ingredient in the solution that has passed the detector. The equation is expressed as $M_i = K_i \cdot A_i$, where M_i is the mass of substance i that has passed the detector, A_i is the area of the corresponding peak, and K_i is a proportionality factor or the response coefficient. Calculation is based on the relationship between the peak of the analyzed sample and that of the standard.

Examples. HPLC analysis permits rapid analyses of a large number of components. For example, it is possible to analyze for flourescent whitening agents, alkyl chains in LAS or nonionics, the perfume content in a finished product, TAED, silicones, and nondetergent other materials (NDOM). Some sample chromatograms are given in Figure 16.9.

Spectrometry: Trace Metal Analysis

Principle. This method can help determine traces of elements, e.g., the detection in raw materials of trace metals that could adversely affect the product and/or the environment once they are discharged. The method is based on the absorption of light by the atoms in a sample and/or emitted by these same atoms.

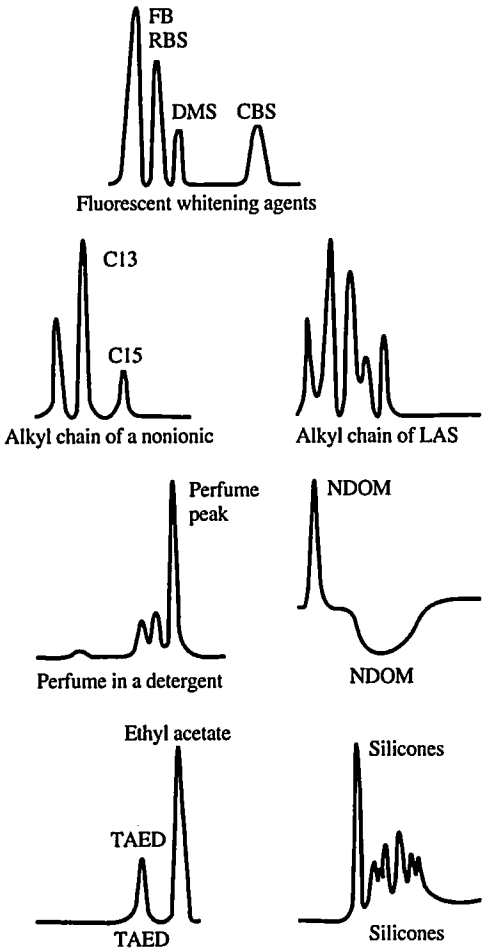

Fig. 16.9. Chromatograms of different compounds.

The Bohr theory states that when energy is absorbed by an atom, an electron passes to a higher orbital level (the highest energy level). The atom may also drop back to a lower energy level by emitting a photon (hv) (Fig. 16.10).

An atom in an excited state is less stable than in its initial state; it therefore returns to a lower energy level by losing energy by, for example, colliding with

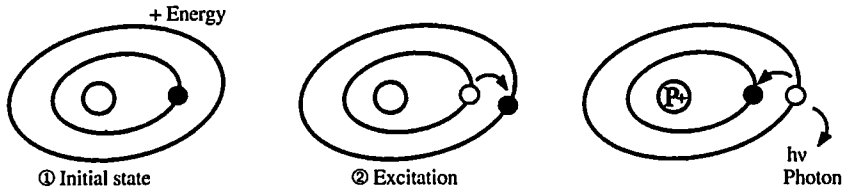

Fig. 16.10. The Bohr theory.

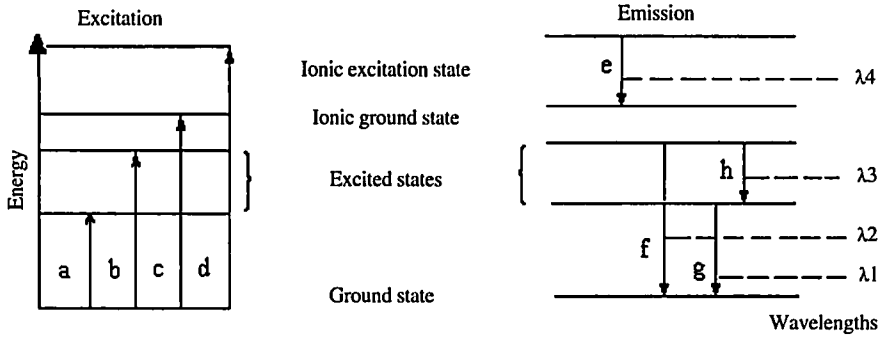

Fig. 16.11. Conditions of atoms and ions. a-b, excitation; c, ionization; d, ionization/excitation; e, ionic emission; f-g-h, atomic emission.

another particle or by releasing an electromagnetic radiation photon. If the energy absorbed by the atom is sufficient, an electron can disassociate itself from the atom to leave a positive ion. The energy necessary for this process (called ionization) is called the ionization potential, and it is different for each element. Ions, too, have ground and excited states, i.e., they can also absorb and emit energy by the same processes as atoms (Fig. 16.11). As energy increases, wavelength diminishes. Every element has its own energy level characteristics and thus its own specific wavelength. This property is the basis of atomic spectrometry. The three main systems are discussed below.

Comments

There are three sources of atomization and excitation, i.e., a flame, an oven, and an electrical discharge. Plasma corresponds to any form of matter that contains an appreciable (>1%) fraction of electrons and positive ions in almost equal numbers in the presence of a larger number of neutral atoms and molecules. For spectrometry, the plasmas used are high-energy ionized gases. An example of a plasma spectrometer is given in Figure 16.12.

Atomic Absorption Spectrometry. Light of a wavelength characteristic of an element is projected across its atomic vapor (flame). The atoms of the element to be analyzed absorb some of the light; the quantity of light absorbed by these atoms is measured, and the concentration of the element in the sample is determined relative to a standard (Fig. 16.13).

Atomic Emission Spectrometry. The sample is subjected to high temperatures, which cause dissociation of the atoms (ionization) and also excitation as a result of atomic collisions. Once excited, the atoms or ions drop to a lower energy level while emitting thermal or radiant transition energies. The intensity of light emitted at given wavelengths is measured and used to determine the concentrations of elements relative to standard samples (Fig. 16.14).

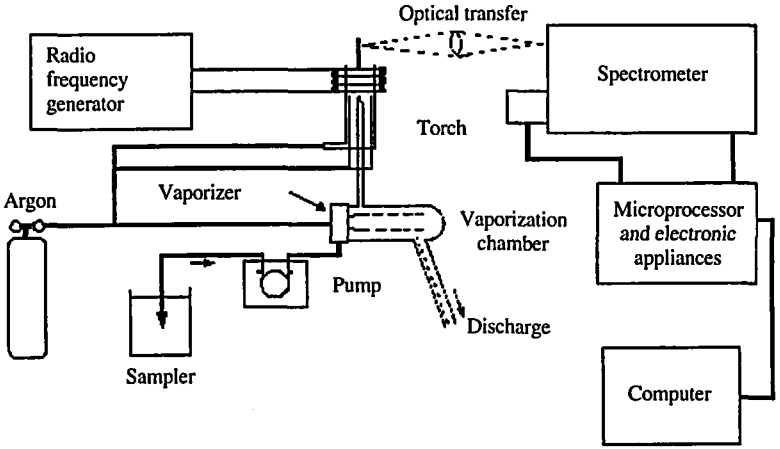

Fig. 16.12. Plasma spectrometer.

Atomic Fluorescence Spectrometry. As in the absorption method, a source of light is used to excite only the atoms of the element to be analyzed for. When these excited atoms return to lower energy levels, their light emission is measured to determine their concentrations. This method is different from the absorption method because emission rather than absorption is measured (Fig. 16.15).

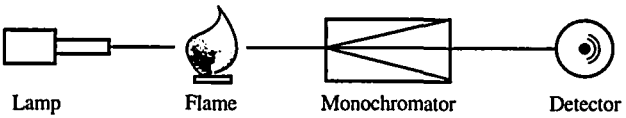

Fig. 16.13. Atomic absorption spectrometry.

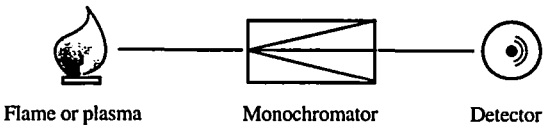

Fig. 16.14. Atomic emission spectrometry.

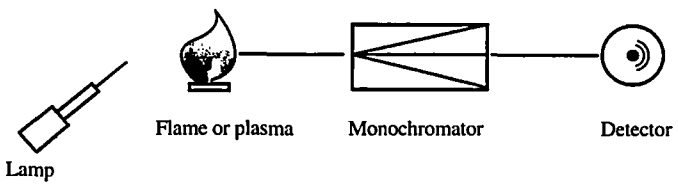

Fig. 16.15. Atomic fluorescence spectrometry.

Application Examples. Zeolite levels. In a packed powder, introduce x g of crushed powder into a 1-L flask. Add y mL distilled water and z mL hydrochloric acid. Stir for a specified time. Fill to 1 L, stir again, and filter. In the plasma analysis for aluminum, with the empirical formula of zeolite as $Na_{12}(AlO_2)_{12}(SiO_2) \cdot 27H_2O$ and x as the quantity (in ppm) of aluminum in the solution, the calculation is as follows:

$$\% \text{ zeolite} = x \text{ ppm} \cdot (1000/PE) \cdot (10^2/10^6) \cdot (2190/324) \cdot (1704/2190)$$

where PE is the weight of the sample.

Phosphorus levels by plasma emission. Prepare a stock solution of x g/L. 1 mg of phosphorus corresponds to a solution containing 4.390 g/L of KH_2PO_4. Dilute the stock solution to obtain a standard at y ppm. For example, in a powder solution at 5 g/L containing x ppm phosphorus in the solution, the percentage of P in the powder is obtained by the following calculation:

$$\% \text{ P} = x \cdot (1000/5) \cdot (10^2/10^6) = 0.02x$$

Recent Trends

A more recent development is the use of solid phase HPLC (on a column with grafted silica). All of the surfactants are adsorbed and are then eluted with a solvent.

In the laboratories of the major manufacturers, the universal ^{13}C NMR techniques and mass spectrometry can very quickly determine the nature of different molecules and their concentrations.

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CHAPTER 17

Consumer Testing

Introduction

Once the formulator has finished laboratory development of a new prototype, and pilot plant tests and full-scale production tests have been completed, there remains a final stage, namely, product evaluation by consumers. No laboratory method can reproduce real use conditions or the immense range of different conditions under which the product will be used. The launch or relaunch of a product generally involves heavy investment. It is therefore essential to check consumer reaction to the new product under real use conditions. Manufacturers employ a battery of tests to measure the risks and probability of success before launching or relaunching a product. Even perfumers, who manufacture only a small part of the total mix in a detergent formulation, use similar techniques. The tests in question are well known and differ little from one organization to another.

Consumer evaluation can include sensory evaluation, e.g., reactions to and comparisons between products with different perfumes, appraisal of the degree of softness provided by a fabric softener, or other general household product evaluations. Consumers are asked to evaluate products in a number of ways including the following:

(i) panel tests organized by the manufacturer;

(ii) consumer tests organized by specialist market research companies; and

(iii) test markets that involve both the manufacturer and specialist organizations.

Before examining these tests in more detail, it is worth looking briefly at the main statistical methods used to calculate the results.

Reminder of Some Statistical Methods

The methods described in this section provide an overview of the most common techniques used by the Consumer Research Institute. For more detailed information, the reader should consult a statistics textbook.

Some Definitions

All of the replies given by consumers will be analyzed using the notion of probability. The probability of something happening is expressed by a number between 0 and 1. Zero represents absolute impossibility, and one represents absolute certainty. For example, we are all mortal: probability of dying = 1; a coin will come down heads or tails: probability = 0.5; a die will fall on a given value at the first throw (1/6): probability = 0.1666; a man will swim across the Atlantic: probability = 0. These statistical methods allow us to conclude from a given result in a panel test, for example, the probability that one product will be preferred to another.

Binomial Law. This law is normally used when the population can be divided into two categories: good or bad, white or black, answers of "yes" or "no." It allows us to estimate the proportion of defective products in a given quantity and, more exactly, the limits between which this proportion might vary. The confidence interval at $x\%$ allows us to say that the proportion found in the sample can vary between a lower limit and a higher limit, given by calculation.

The Normal Curve (Laplace-Gaussian Distribution). This concerns a continuous random variable x that can take on values between $(-\infty, +\infty)$. The curve showing this distribution is the famous bell curve, which is symmetrical about the value $x = m$ (Fig. 17.1).

Some useful definitions include the following:

(i) mode is the specific value of the variable that occurs most often (highest point in the graph);

(ii) median is the value of the variable with 50% of the population on either side; and

(iii) arithmetic mean is the total of all of the values known for the variable divided by the number of values ($\bar{x}$).

Other important definitions are as follows:

1. Amplitude or range: Symbol W. This is the difference between the largest and smallest variable.
2. Quartiles: All of the values are classified by increasing value, i.e., the first quartile is the value of the corresponding variable at a cumulative frequency of 25%; the second quartile has a cumulative frequency of 50%; and the third quartile has a cumulative frequency of 75%.
3. Deciles: These have the same definition as quartiles but use cumulative frequencies at 10% intervals.
4. Standard deviation: This is the square root of the variance, S or σ.

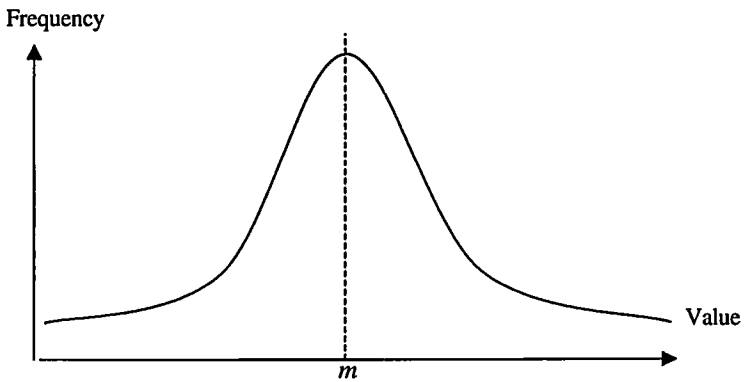


Fig. 17.1. Gaussian curve.

5. Variance: This is a quantity equal to the square of the standard deviation, calculated as follows:

$$S^2 \text{ or } \sigma^2 = \frac{\Sigma(x_i - \bar{x})^2}{\Sigma n_i}$$

6. Coefficient of variation: This is the relationship between the standard deviation and the mean, calculated as follows:

$$CV = \omega = S/\bar{x} \text{ or } \sigma/\bar{x}$$

Some characteristics of the normal curve include the following:

$m \pm 0.66\sigma$ covers 50% of the population;

$m \pm 1\sigma$ covers 68% of the population;

$m \pm 1.25\sigma$ covers 80% of the population;

$m \pm 2\sigma$ covers 95% of the population;

$m \pm 3\sigma$ covers 99.8% of the population;

m and σ permit us to calculate the probability of finding lower or higher values than a given value x_i, or than contained between two values x_i and x_j.

Examples of Statistical Methods Applied to Consumer Tests

Comparison Between Two Means and Two Standard Deviations. A choice has to be made between two products, A and B. From each sample, we obtain the number of measurements (n_a, n_b), the means ($\bar{x}_a$, $\bar{x}_b$), and the standard deviations (σ_a, σ_b). In fact, A has an mean of $\bar{a}$ and a standard deviation of σ_a, and B has an mean of $\bar{b}$ and a standard deviation of σ_b.

In principle, we start with the assumption that the difference between the two products is zero ("the null hypothesis"). We ask ourselves whether the difference in the averages $\bar{x}_a - \bar{x}_b$ is compatible with the hypothesis $\bar{a} - \bar{b} = 0$. If the probability is low (e.g., 0.1%), the hypothesis should be rejected; it can be said that there is a highly significant difference between the products. Table 17.1 shows the relationships among the different parameters.

Sign Test. A panelist is asked classify two objects that have received some treatment which is difficult to measure instrumentally (e.g., softness to the touch).

TABLE 17.1
Methods Based on the Null Hypothesis

If the null hypothesis has a probability of happening of less than	We consider that this hypothesis is	We say that the difference is
10%	Low	Slightly significant
5%	Doubtful	Significant
1%	Suspect	Very significant
0.1%	Almost impossible	Extremely significant

The pairs are put in order, counted, and signs are given (–) or (+) to one of the two components of the pair. Calculations will determine whether the results are different (at a level of significance) by counting the number of (–) and (+) signs. For example, in 16 tests with A and B, there were 13 (+) for A and 3 (+) for B. The calculation shows that A > B ($\alpha = 0.05$); the risk of making a mistake is 5 in 100.

Wilcoxon Test. An application example is as follows:

In an analysis of the scores given to two test products by users (e.g., product efficacy or stain removal), the Wilcoxon test can be used to compare two samples of any size by simply noting the ranking of observations (no assumptions about normality).

Paired Comparison Tests. An example would be a sensory analysis such as for perfume: Which sample has the strongest perfume? Which one do you prefer? The researcher does not know the answer. For example, from 20 panelists, 17 prefer product A; the calculation will indicate a preference with a 99% degree of probability.

Monadic test. In this kind of test, the approach might be as follows: Working with 30 panelists, the researcher knows that A has a stronger perfume than B.

First question: Yes: 24	Is there a difference between the two samples?
No: 6	Very significant difference; probability 99.9%
Second question: Yes: 22	Is sample A more strongly perfumed than B?
No: 8	Very significant difference; probability 99%
Third question: Yes: 23	Do you prefer A to B?
No: 7	Very significant difference; probability 99%

If the answers to the third question had been reversed, the formulator would have known that the product was perfumed too strongly!

Rank-Order Test. This test asks panelists to rank-order products from the least perfumed to the most highly perfumed, or from finest particle size to largest, or from softest to harshest, and so on. Results are interpreted by the sum of the rankings. Table 17.2 gives an example of the ranking of seven cloths (T_1–T_7) by five people, from softest (= 1) to harshest (= 7).

The total score by one panelist is $1 + 2 + 3 + \cdots + 7 = 28$; the total score for the panel is $28 \times 5 = 140$; the average score for each panelist is 140/7 = 20. Calculations of concordance coefficients and significance (Snedecor tables) indicate whether a degree of agreement exists among the panelists and if the ranking order is significant. It is then possible to decide whether the differences among the products are significant or not. In this case, the calculation would yield the following: $T_6 > T_4$, T_5, T_7 and $T_1 > T_4$, T_5, T_7 or T_6, $T_1 > T_4$, T_5, T_7 ($\alpha = 0.05$).

TABLE 17.2
Results of Rank-Ordering of Cloths by Five People

	T_1	T_2	T_3	T_4	T_5	T_6	T_7
Judge 1	2	4	3	7	5	1	6
Judge 2	1	2	5	6	4	3	7
Judge 3	1	3	4	6	7	2	5
Judge 4	2	5	4	3	6	1	7
Judge 5	3	2	4	5	7	1	6
Total (sum of ranking)	9	16	20	27	29	8	31

Round-Robin Test. This type of test is generally used for consumer testing. Even though such a paired comparison is simpler, it is difficult for a consumer to give an opinion on two products used at 15-day intervals. In addition, the researcher must usually test more than two products (sometimes as many as four or five), and must reach a general conclusion about the overall performance or specific performance aspects of different products.

For reasons of accuracy, time, and money, it is not possible to ask each panelist to use n products. In this situation, one conducts a round-robin test, in which each panelist is asked to state a preference for one of the two products he or she has received; all preferences are recorded for all products.

For example, three detergent powders, P_1, P_2, and P_3 are to be tested among 540 people. The objective is to learn whether the stain removal properties differ among the three powders. Each user receives two boxes of powder (the order of use is rotated) and replies to the following question after use: Which of the two products do you prefer?

There are three possible answers: the first, the second, and no difference. Because there are three powders in total, there are three possible pairs, P_1 and P_2, P_1 and P_3, and P_2 and P_3; there are therefore three subpanels of 180 people, and we obtain the type of results shown in Table 17.3.

These results are analyzed by calculating the percentage of "no difference" (is there a difference among the three subgroups?) and finding any net preferences. Net preference (NP) between two products, P_1 and P_2, is the difference between

TABLE 17.3
Preference Results

		Prefer					
	Pair	P_1	P_2	P_3	Indifferent	Total	% Indifferent
1st subgroup	P_1 and P_2	78	50	—	52	180	29
2nd subgroup	P_1 and P_3	95	—	31	54	180	30
3rd subgroup	P_2 and P_3	—	95	36	49	180	27
					155	540	29

TABLE 17.4
Example of the Calculation of Net Preference for the First Subgroup

	n	*n'*	%	Calculation
Prefer P_1	78	78	61	= (78/128)
Prefer P_2	50	50	39	= (50/128)
No preference	52	—	—	
Total	180	128		

the "percentage" preferences expressed for each of the products without taking into account the "no difference" score. The net preference calculation for the first subgroup is shown in Table 17.4.

In this case, the net preference is 61% for P_1 and 39% for P_2; $P_1 - P_2 = 61 - 39 = 22\%$. In the current case, there would be three subgroups, and the direct comparison results would appear as in Table 17.5.

The comparison between "for" and "against" by pair of products, expressed as NP, are calculated as follows: (i) for P_1 – for $P_1 = 22 - 22 = 0$; for P_2 – for $P_1 = 39 - 61 = -22$; for P_2 – for $P_3 = 75 - 27 = 46$; for P_1 – for $P_3 = 75 - 25 = 50$; and so on. The results are summarized in Table 17.6.

By using these results, we obtain a better NP estimate than by direct comparison.

$P_1 - P_2 = 24 - (+8) = +16\%$ (instead of 22 by direct comparison)

$P_1 - P_3 = 24 - (-32) = +56\%$ (instead of 50 by direct comparison)

$P_2 - P_3 = 8 - (-32) = +40\%$ (instead of 46 by direct comparison)

TABLE 17.5
Net Preference of the Three Subpanels

		Prefer				% Preferences			Net preference
	Pair	P_1	P_2	P_3	Total	P_1	P_2	P_3	(NP)
Subgroup 1	P_1 and P_2	78	50	—	128	61	39	—	22
Subgroup 2	P_1 and P_3	95	—	31	126	75	—	25	50
Subgroup 3	P_2 and P_3	—	95	36	131	—	75	27	46

TABLE 17.6
Net Preference per Product

For↓ / Against→	P_1	P_2	P_3	Total	NP per product (divide by *n*)
P_1	0	+22	+50	+72	72/3 = +24
P_2	–22	0	+46	+24	24/3 = +8
P_3	–50	–46	0	–96	–96/3 = –32

This gives the following order: P_1, +56% NP; P_2, +40% NP; and P_3, 0. The significance of the differences in NP is then calculated as follows:

$$\begin{array}{ccc} P_1 & > & P_2 \quad >> P_3 \\ (\alpha = 0.005) & & (\alpha = 0.001) \end{array}$$

Panel Tests

For the development of a new product, the following sequence is quite typical:

(i) objective laboratory performance tests (the starting point);
(ii) internal tests using employees;
(iii) panel tests;
(iv) consumer tests; and
(v) the test market.

All of this takes place before entering a product into the national and international markets. Panel tests are a first step in the process in which consumers are asked to use a prototype and to give an opinion on the product. Such tests are usually organized by the manufacturer, who usually has regular volunteers.

Panelist Database

There are many advantages to running an internal testing service. Factors to be taken into account include the following:

1. Ideally, the panelists should be distributed geographically across the country.
2. The family profile in terms of numbers and age, i.e., the larger the family, the more washes there will be. Age is also important because types of soil will be quite different for young children than, for example, a retired couple.
3. All appliances are listed, including the brand and model of washer, dryer, and dishwasher, along with their dates of purchase.
4. Other information includes the different household surfaces to be cleaned, e.g., baths, faucets, floor coverings, tiles, sinks, or modern surfaces.
5. The panelists' habits are recorded, e.g., those who systematically use a softener, those who never prewash or who use only certain detergents, and how many washes they do in a week.

We mentioned above the geographical distribution of panelists; this is important because habits vary from region to region and also because water hardness varies widely and has a strong effect on the wash results. Water hardness is known to the researchers because each new panelist must submit water samples for analysis. Of course, the presence of a water softener must be recorded. This list is far from exhaustive and can even include details, such as the date vacations are normally taken, to avoid sending samples on those dates.

To demonstrate how this information is used, in the following example, a manufacturer needs to test a product quickly (e.g., there may be concerns about the quality of a product manufactured during a particular shift). Thus, a test in washing machines must be organized promptly, using the following criteria:

(i) it must take place from August 15 to September 15;
(ii) it requires 20 washes per panelist;
(iii) panelists' machines must be <2 y old;
(iv) panelists must be representative of the whole market;
(v) they must be regular users of concentrated powders; and
(vi) they must live in areas of water hardness between 150 and 300 ppm $CaCO_3$.

To meet these requirements, the researcher must know that the panelist will be at home during the required period, that the panelist washes at least five loads per week, that the database is up-to-date, the nature of the market for which the product is destined (one of the criteria being the distribution of front- and top-loading machines), the panelists' laundering habits, and the water hardness for each new recruit.

Organization of a Panel Test

There are two types of panel tests, i.e., one-time-only/short-term tests, usually lasting 3–4 weeks, and longer tests, for example, to establish the longer-term effects of a new product on redeposition or mineral incrustation in the case of laundry, or on the damage to decoration in the case of dishwashing products. In both cases, the process for the formulator/researcher is the same:

1. Before all else, check that the test products present no danger for the panelists (on safety, see Chapter 19).
2. Do a complete test of the physico-chemical characteristics of the product before sending it out; there would be no point in testing the enzyme efficacy of a powder that contains only half the theoretical quantity of enzymes. If time permits, the product can also be tested in the laboratory to ensure that performance is up to standard.
3. The various prototypes, which can include products from the trade or competitive products, are packed in "blind" packaging (usually white) with just a reference code; a minimum of instructions on how to use the product, along with safety precautions would be included.
4. Panelists are selected by computer on the basis of a supplied list of criteria.
5. The required written materials are prepared. These include a letter telling the chosen panelists the date the test will start and the type of test; a "diary" in which the user will note the usual use conditions for the product, for example, in a washing machine test; which cycles were used or how much product dosed; and one or several questionnaires to be completed on product performance. These are similar to questionnaires used in consumer testing (see p. 382).

Advantages of a Panel

A panel provides the manufacturer with a number of advantages. A panel can be modified according to specific needs (e.g., choice of geographical areas and water hardness). A panel can be used for testing products on all kinds of hard surfaces (e.g., tiles, enamel, or plastic) and in different specific machines. Tests can be very specific, e.g., in front-loading machines among consumers who do not use a fabric softener and with children under 3 years of age. Test cloths can be added to every wash by the panelist, and certain articles can also be put into a dishwasher. These are then returned to the formulator for visual observation and objective measurement (see Chapter 11). This is valuable information because it comes from hundreds of homes under real washing conditions. An exact predetermined dose can be given to the panelist, if such is required as part of the test. It can be very useful to have several thousand homes available if quick answers to a given problem are required.

For example, if there are several hundred metric tons of product with a particular problem (e.g., particle size out of specification or a product insufficiently perfumed), the possible consequences of putting it on the market can be measured quickly before making a decision.

Most of the communication between panelists and the formulator takes place by mail. However, it is also possible to use special researchers who visit the panelists to help with complicated studies. Further, panelists may be asked to visit the manufacturer, who will have a special area for such a purpose (mini-hair salons, special rooms). For perfume evaluation, in particular, it is vital that the test take place somewhere that is free of odors, properly lit, and equipped with computer terminals.

Disadvantages of Panels

Managing a panel is a major task. The database must be kept up-to-date, including changes in machines, changes of address, purchases of a water softener, and so on. A natural attrition of the panel that must also be considered. Some panelists leave and have to be replaced, and it is also advisable to change panelists after a few years because they lose their ability to react spontaneously. Therefore, continuous recruitment is needed. Of course, the main problem is cost; a whole department of people is required, and postage of sometimes heavy samples (e.g., 5-kg boxes) is a major expense.

Consumer Tests

Because they are complicated, consumer tests are usually organized by specialized consumer research agencies. The principle is to go farther than panel tests because, at this stage, the marketing aspect of the product has become at least as important as the technical aspects. Recruitment is done by telephone, according to preestablished criteria, to obtain a sample population representative of the required universe, e.g., sociodemographic criteria or users of a particular brand, or any of the other criteria mentioned under panels. Groups of 100–150 people are often used to test one product under one set of conditions. Products can be "blind" or branded.

When the criterion being tested is fundamental to the brand, the sample is usually divided between regular users of the brand and nonusers of the brand. This helps to determine whether regular users like the change and will continue to buy the product and whether nonusers would be sufficiently attracted to the new product with its proposed modification to switch from their usual (competitive) brand.

In general, the developers and marketing teams agree on the objectives to be achieved beforehand, e.g., the prototype should be at least equal to the reference product for certain criteria, and better for others. If the objectives are not reached, the prototype should be improved.

The consumer fills out a series of questionnaires after the use of each product. The following indicates the type of information that is sought:

1. Overall judgment, e.g., on a 7-point scale in which 7 is excellent, 6 is very good, 5 is good, 4 is average, 3 is not bad, 2 is bad, and 1 is very bad.
2. Particular aspects of the product such as its general efficacy, its performance on stains (coffee, oily stains, fruit), on whites, on colored items (keeps colors looking like new; colors do not fade), its usage at all temperatures, its physical properties (how it looks, how easily it dispenses) and its physico-chemical characteristics (does not foam too much, does not leave clothes sticky). For each of these criteria a scale from 1 to 4 can be used; 1 = totally disagree; 4 = totally agree.
3. Purchase intent. A 5-point scale can be used to answer the following question: Which of the following phrases best describes your buying intentions if the product were on sale in your store at an acceptable price? The choices are: I would certainly not buy it; I would probably not buy it; I don't know if I would buy it; I would probably buy it or not; or I would certainly buy it.

Opinions can also be collected on the package (convenience). The results can then be studied using the same statistical methods outlined at the beginning of this chapter. For instance, Figure 17.2 shows the average score for overall judgment of four test products, based on the 7-point scale. A statistical calculation may conclude, for example:

$$P_1, P_3 > P_2\ (\alpha = 0.05) \text{ and } P_1, P_3 >> P_4\ (\alpha = 0.01)$$

It is also possible to compare the results for a prototype with a standard product used in the test; results could be presented as in Figure 17.3. The 0 bar represents the

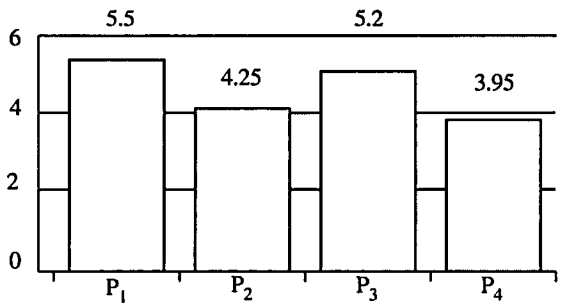


Fig. 17.2. Scores for four consumer-tested products.

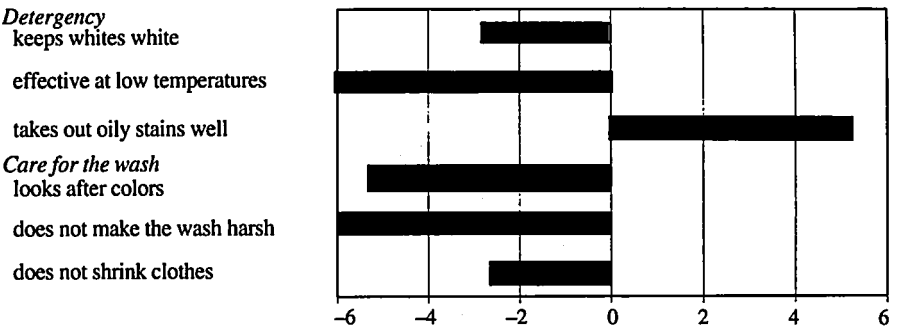


Fig. 17.3. Comparison between prototypes and a standard product.

scores of the standard product. For this particular prototype, it can be concluded that it is better than the reference product in removing oily stains but performs less well on the other parameters.

On a scale from 1 to 4, it is also possible to compare two products, P_1 and P_2, as shown in Figure 17.4.

The Particular Case of Perfume Tests

A marketing team may wish to change a perfume, which is a very important parameter for the consumer. Changing the perfume of a product that is selling well is always risky, but it could also be the key to increasing its market share. In such a case, consumer tests are used in the classical manner described above, e.g., the test may include two or three prototypes with identical formulations but with different perfumes from

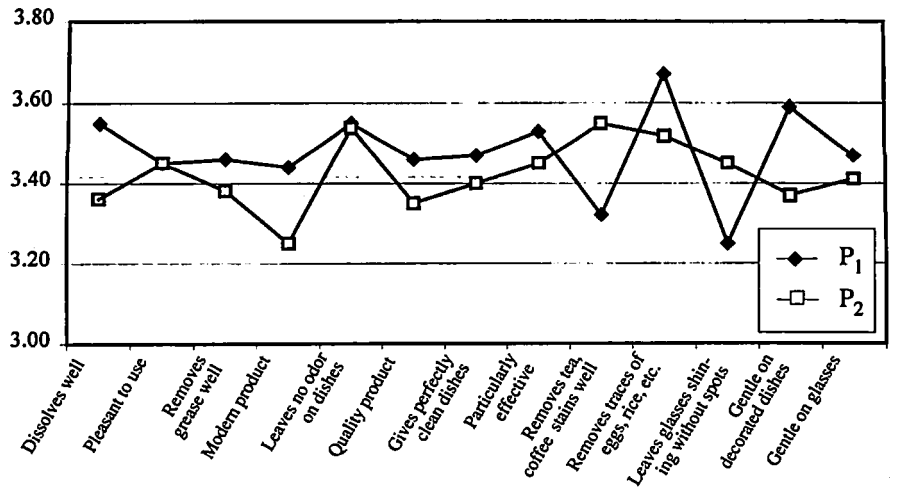


Fig. 17.4. Comparison between two products P_1 and P_2.

different suppliers, along with a reference product with the current perfume and those of one or two competitors.

Questions concerning product performance and its physical properties are included, and are as numerous as in a formal comparison test to avoid introducing a bias by asking questions only about the perfume. Thus, little by little, consumers are led to the questions on perfume, not only in the product itself but also in use, during dosing in the dispenser, washing, rinsing, drying, ironing, and putting away washed articles. Substantivity or capacity to stay on the clothes is also measured.

Answers to these types of tests are sometimes surprising. It is not unusual to see a good perfume produce better product efficacy scores than one that is not as good, even if the formula itself is identical. In this kind of test, particular care should be taken to balance the results between users of the brand, who should not be let down, and nonusers, who should be attracted.

Test Markets

In a test market, the new product is put on the shelves in a given geographical area to determine consumer reaction. In the test area, the new product will be treated exactly as though it were being launched nationally with media advertising, including press, radio, local TV, and in-store activities, direct mailing, sampling, and so on. Over several months, millions of consumers may be involved.

The Main Advantages of Test Markets

A test market helps improve knowledge of the product itself, e.g., how it behaves physically and chemically after transport, storage in warehouses, and on store shelves. Product purchases are made regularly and returned to the laboratory for analysis of all aspects. A consumer inquiry service can pick up feedback very quickly from people who want help or have a complaint; this gives a good indication of the advantages and disadvantages of the product in use.

Another means of obtaining feedback on consumer opinions includes placing prepaid reply cards into the packages.

The test market is particularly useful in determining whether the chosen product concept is supported in terms of packaging, the product, the perfume, and the price. Often it is not the first purchase that is the most important, but the repurchase rate that indicates whether customers are happy. At the end of the test market period, the decision will be made to launch nationally or not, generally depending on the market share achieved in the test area.

The Main Problems of Test Marketing

Apart from the cost, the main problem of a test market is that it allows competitors to prepare their defenses. For a major new product or technical innovation, the test market is not the best way to take the opposition by surprise. Manufacturers know that being first and surprising the competition is a good way to gain market share.

CHAPTER 18

Quality Assurance

Quality Aspects

To make a good household detergent takes more than simply a good product; it would be incorrect to think that anybody who wanted to could make such a product, even with detailed information about the formulation in hand.

Quality is a constant preoccupation of all major manufacturers, and it concerns all aspects of the life of the product, from raw materials to point of sale and beyond. Quality is essential if the end-user is to remain loyal to a brand. After all, what is easier for the consumer than to change a brand of detergent, shampoo, or toothpaste, given the large number of advertising promotions? This is a fact of life in the consumer goods industry. Therefore, some of the important criteria that define quality control are discussed here.

Detergent Powders

The parameters include the physical characteristics which the user sees and feels when using a powder, and also the chemical properties responsible for the efficacy of the product.

Physical Properties. The whiteness of the powder is essential because it symbolizes the purity of the laundry once clean. What could be worse than a dull grey or yellowish-colored powder! The powder should be free of all foreign bodies, e.g., black specks from raw materials or the manufacturing process. The powder should remain free flowing, without lumps, and should not become sticky throughout the life span of the product. Of course, this depends to some extent on the user's good sense, e.g., knowing not to leave the product uncovered in a humid environment. Manufacturers advise consumers on the care of their products; customer service departments also deal with user problems. Once the product has been fed into the machine either by dispenser or by a dosing mechanism such as a ball, it should dissolve easily and quickly in the water. It should not stick or disappear too slowly, particularly during rinsing.

Chemical Properties. Chemical properties have a direct effect on results; if the amount of enzymes, perborate, or surfactants is insufficient, detergency will be unsatisfactory, the laundry will be grey and poorly washed, and stains will not be removed. Quality control must ensure that all of the ingredients have been included at the correct levels and that they are stable over time. Here again, the user has a role to play by not storing the powder in a hot or humid environment. Perfume is a specific case. It has no direct effect on wash performance, but incorrect dosage (whether too little or too much) will be quickly noticed by the user.

Liquids, Gels, and Pastes

Physical Properties. For these products, the important physical properties which must be controlled include:

Stability. Temperature changes (freeze-thaw cycles) can cause phase separation, which the user may not see through an opaque bottle, but which will quickly become apparent through loss of efficacy and a change in viscosity.

Product appearance. Notably in translucent bottles, the problem will be apparent immediately.

Appearance of crystals. In dishwashing liquids, sodium sulfate crystals can deposit. Their formation is the result of the presence of excess sulfuric acid in linear alkylbenzenesulfonate (LAS). This is another example of the importance of controlling raw material quality. Even worse is the phenomenon of gelation. A gelled product will not come out of the bottle. Gelation is preceded by a change in viscosity as a result of which a thin liquid product becomes thick or *vice versa*, a thick liquid becomes too thin. This affects dosage and hence performance. If the bottle must be squeezed to deliver the product, this is immediately perceptible to users.

Chemical Properties. Chemical properties include:

(i) the correct quantities of ingredients such as enzymes and fluorescent whitening agents that have a visible effect on the result;

(ii) ingredients that affect stability in storage, e.g., the level of hydrotopes in a dishwashing liquid; and

(iii) the biological aspect, an additional problem presented by liquids, gels, and pastes relative to powders. An inadequately protected product (insufficient alcohol or preservatives, or a bacterial contamination on the production line) can produce microorganisms, leading to mold formation.

Soaps

There are other specific controls for soaps, apart from those mentioned above. Soap has a tendency to crack when the surface dries. Cracks are unpleasant to the eye and can act as collectors of dirt (Fig. 18.1). The tendency to "mush" is also controlled for each production. The test method simulates this condition by allowing soap to be in contact with water in a soap dish. Contact with water ultimately leads to the formation of a gel phase.

The use-up rate of a piece of soap is also checked regularly. At equal cost, the consumer will prefer a soap that lasts longer.

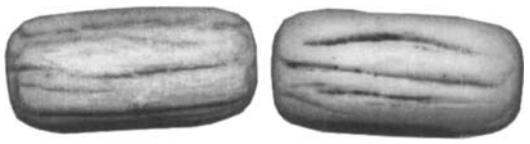


Fig. 18.1. Soap with cracks.

Fig. 18.2. Soap with hard specks from reworked soap.

Hand washing tests under real use conditions are conducted to identify any hard particles in the soap, which can be very unpleasant. They can come from poorly reworked soap (Fig. 18.2).

The presence of perfume is evaluated. Perfume must be present until the soap is completely used up.

Storage tests are conducted to check the behavior of the soap with respect to perfume retention and biological contamination which eventually might lead to mold growth.

Toothpaste

Quality evaluation includes points already discussed for other products, i.e., black spots, presence and stability of the flavor, absence of large particles, which are disagreeable, bacteria, and of course the presence and stability of the fluorides.

Two criteria are particularly important in quality control:

1. Stability. The product must be in satisfactory condition on leaving the factory, and it should remain so during storage and normal use conditions.
2. Consistent quality. Not only should each product have the right characteristics, but similar products produced at different times should also retain the same characteristics. There are two reasons for this. The first is to avoid disappointing the user from one purchase to the next. The second is the legal aspect. The weight of a product must be shown on the package. This means that weight has to be constantly controlled during manufacture to ensure that at the point of use, the product has the stated weight. An easy solution of adding 10% more product to the package, for example, to avoid any risk of "underweighting" would cost a fortune and is not practical. The solution is found in the use of very precise machinery and constant and rigorous control on the production line.

Review of Statistical Methods Used in Quality Control

Some of the methods are identical to those used for consumer product testing described in Chapter 17.

Random Sampling

As an example, a production line will be running for 3 h, producing packages of a product of which x samples are required for control. When should the samples be taken? It is essential to take samples on a random basis to avoid wrong conclusions

TABLE 18.1
Random Values Table

	5	10	15	20	25	30	35	40	45	50
	13407	62899	78937	90525	25033	56358	78902	47008	72488	57949
	50230	63237	94083	93634	71652	02656	57532	60307	91619	48916
	84980	62458	09703	78397	66179	46982	67619	39254	90763	74056
	22116	33646	17545	31321	65772	86506	09811	82848	92211	51178
5	66645	15068	56898	87021	40115	27524	42221	88293	67592	06430
	26518	39122	96561	56004	50260	68648	85598	83979	09041	62350
	36493	41666	27871	71329	69212	57932	65281	57233	07732	58439
	77402	12994	59892	85581	70823	53338	34405	67080	16568	00854
	83679	97154	40341	84741	08967	73287	94952	59008	95774	44927
10	71802	39356	02981	89107	79788	51330	37129	31898	34011	43304
	57494	72484	22676	44311	15356	05348	03582	66183	68392	86844
	73364	38416	93128	10297	11419	82937	84389	88273	96010	09843
	14499	83965	75403	18002	45068	54257	18085	92625	60911	39137
	40747	03084	07734	88940	88722	85717	73810	79866	84853	68647
15	42237	59122	92855	62097	81276	06318	81607	00565	56626	77422
	32934	80227	58707	44858	36081	79981	01291	68707	45427	82145
	05764	14284	73069	80830	17231	42936	48472	18782	51646	37546
	32706	94879	93188	66049	25988	46656	35365	13800	83745	40141
	92190	27559	95668	53261	21676	98943	43618	42110	93402	93997
20	81616	15641	94921	95970	63506	22007	29966	38144	62556	07864
	26099	65801	69370	84446	58248	21282	56938	54729	67757	68412
	71874	61692	80001	21430	02305	59741	34262	15157	27545	14522
	08774	29689	42245	51903	69179	96682	91819	60812	47631	50609
	37294	92028	56850	83380	05912	29830	37612	15593	73198	99287
25	33912	37996	78967	57201	66916	73998	54289	07147	84313	51938
	63610	61475	26980	23804	54972	72068	19403	53756	04281	98022
	01570	41701	30282	54647	06077	29354	95704	75928	21811	88274
	24159	77787	38973	82178	46802	90245	01805	23906	96559	06785
	92834	52941	88301	22127	23459	40229	74678	21859	98645	72388
30	16178	60063	59284	16279	48003	44634	08623	32752	40472	05470
	81808	32980	80660	98391	62243	19678	39551	18398	36918	43543
	28628	82072	04854	52809	86608	68017	11120	28638	72850	03650
	62249	65757	12273	91261	96983	15082	83851	77682	81128	52157
	84541	99891	01585	96711	29712	02877	70955	59693	26838	96011
35	89052	39061	99811	69831	47234	93263	47386	17462	18874	74210

when a recurring problem is present (for instance, when a machine malfunctions for 30 s every 10 min). If a sample is taken every 10 min, the conclusion could be that all of the product is bad. For this reason, there are tables of random numbers created in a random manner (see Table 18.1).

To use these tables, a selection key is determined (a group of numbers), which depends on the size of the population to be studied. For example, for a population

of 500 units, the selection key will have three numbers, and for a population of 50, there will be two numbers. A spot is chosen at random in the table and the numbers read either horizontally or vertically using the selection key. Example: Production begins at 5:00 and ends at 8:00; five random samples over a period of 3 h are required. Table 18.1 can be used, starting with the three last figures in the fourth column and working downward; the first sample is taken at 5:25 in agreement with the starting number (525), 6:34, 6:47, 7:11, and 7:41 (741). The selection key in this case is three numbers.

Average, Standard Deviation, Variance, Coefficient of Variation

Definition. The arithmetical average is the total of all of the values taken for a given measure (e.g., the weight of soaps during production) divided by the number of values taken, i.e., $\bar{x} = (x_1 + x_2 + x_3 + x_4 + x_n)/n = \Sigma x_i/n$.

Range or amplitude (W) is the difference between the highest and lowest measure.

Variance is the average of the squares of the difference between the various values of the variable and the average value of this variable, i.e., $\sigma^2 = [\Sigma(x_i - \bar{x})^2]/\Sigma n_i$.

The standard deviation (SD) is the square root of the variance σ.

The coefficient of variance (CV) is the relationship between the standard deviation and the average, i.e., $CV = \omega = \sigma/\bar{x}\%$.

The median (m) is that value of the variable such that 50% of the population is on either side of it.

Information Given by m *and* σ. These two parameters make it possible to calculate the probability (P) of finding higher or lower values than value x, or contained within two specific values x_i and x_j. To do this, x is set equal to $(x_i - \bar{x})/\sigma$. This is the distance of x_i relative to the average for the population as expressed in the SD.

If $u > 0$. For example, $x_i = 15.5$, $\bar{x} = 12$, and $\sigma = 2$ yield $u = (15.5 - 12)/2 = 1.77$. In examining standard statistical tables, $P[f(u)] = 0.9599$ for $u = 1.77$. The probability of finding a value $< x_i = 15.5$, for example, is 0.9599 (95.99% or 96%). Alternatively, the probability of finding that a value $> x_i$ is $1 - 0.9599 = 0.0401$ (4%) (Fig. 18.3).

If $u < 0$. For example, $x_i = 10$, $\bar{x} = 12$, and $\sigma = 2$ yield $u = -1$; looking in the tables, we find $P[f(u)]$ for $u = -1$, $f(u) = 0.8413$. There is a probability of 0.8413

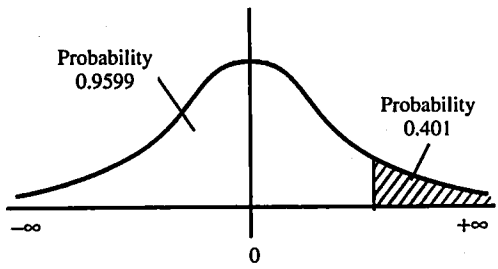


Fig. 18.3. Probability of finding values higher or lower than x, where $u > 0$.

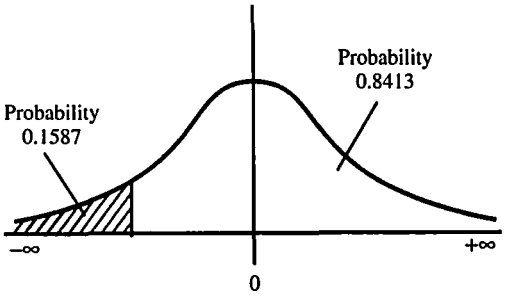


Fig. 18.4. Probability of finding values higher or lower than x, where $u < 0$.

(84%) of finding a value $> x_i = 10$ and a probability of 0.1587 (16%), that a value could be $x_i < 10$ (Fig. 18.4).

The confidence intervals for the normal distribution are shown in the diagram in Figure 18.5. For 2 SD, the total of the frequencies is 68%; for 4 SD, it is 95%; and for 6 SD, 99.7%. This means that $m \pm \sigma$ includes 68% of the population, $m \pm 2\sigma$ includes 95% of the population, and $m \pm 3\sigma$ includes 99.7% of the population.

Example of the Search for Sources of Variability. The question of how to take samples to obtain a representative quantity in the context of powders was discussed above. The sources of variability can be studied by looking at ingredients, particularly those that are used in small quantities, for example, enzymes. For enzymes, variability can be high, and we look here to determine the causes. We can then change certain parameters to reduce the variations between one package and another sold to the consumer in order to guarantee consistent quality over time. Below is a theoretical example of how such a study could be performed. To analyze a 5-kg package, a rotating sampler, and an HD 22 sampler are required to take a sample of ~50 g.

Variation due to the analytical method. The 50 g sample is dissolved completely in 5 L of water. The enzyme level is measured on an autoanalyzer and 10 analyses are done on the same solution. The results are as follows: $\bar{x} = 5.15$ GU/mg (glycine units/mg); $\sigma = 0.0411$; and CV = $\omega = 0.82\%$. This is the variation due to the operation of the autoanalyzer.

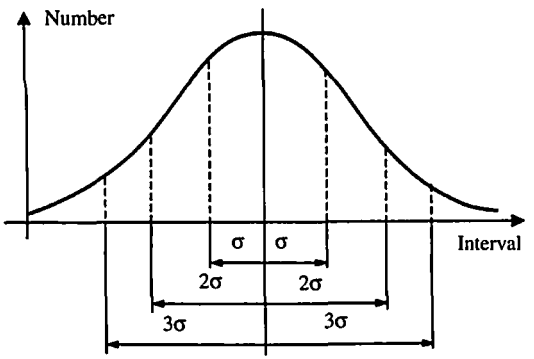


Fig. 18.5. Confidence intervals for the normal distribution, representative curves.

Variability found on a sample of enzymes (raw materials). The sample of enzymes incorporated into the powder is divided into 10 parts. The 10 samples yield the following results: $\bar{x} = 744$ GU/mg; $\sigma = 11.25$; CV = $\omega = 1.51\%$. This is the variation due to the differences in one lot of enzyme granules.

Variability between different samples coming from an HD 22 sampler. To find the variation due to the HD 22 sampler, the process is as follows: An 800-g package is divided into 16 samples of 50 g by the HD 22. Analysis of the samples yields the following results: $\bar{x} = 3.4225$; $\sigma = 0.1157$; CV = $\omega = 3.38\%$.

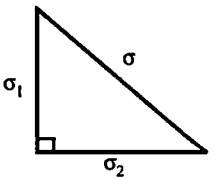
Variability of samples divided by the rotating sampler. To find the variation due to the rotating sampler, one 5-kg pack is divided into 50-g samples. All of the samples are analyzed and yield the following results: $\bar{x} = 3.4225$ GU/mg; $\sigma = 0.21$; CV = $\omega = 5.75\%$.

Variability between different lots of raw materials (enzymes). This study covered 259 measurements spread over 12 wk with the following results: $\bar{x} = 773.86$ GU/mg; $\sigma = 36.30$; CV = $\omega = 4.69\%$.

Variability between different production runs of finished powder. In this case, 115 analyses were conducted over a period of 4 wk on finished products leaving a factory. Results were as follows: $\bar{x} = 3.70$ GU/mg; $\sigma = 0.39$; CV = $\omega = 10.54\%$.

Statistical Analysis of the Results. If σ_1 is the estimated SD of the analytical reproducibility for a given solution and σ is the estimated SD for enzyme content (raw material), including the influence of analytical reproducibility, then σ_2, the estimated standard variation for enzymes (raw material) excluding analytical reproducibility can be calculated by the following:

$$\sigma_2 = \sigma_1^2 + \sigma_2^2$$



In the same way, it is possible to calculate the different coefficients of variation (CV) supposing that σ is proportional to the average value, which can be represented as in Figure 18.6. This model shows how each parameter (autoanalyzer, HD 22, and others) contributes to the variability in enzyme activity among different packages of detergent leaving a factory.

In this example, it appears that the CV of enzymes in the product leaving the factory is 10.54%, which is too high. From here, the various parameters can be examined and the decision may be made to improve mixing efficacy during manufacture (CV = 7.64%) and/or the enzyme supplier could be asked to reduce the variability of enzyme activity among the different lots (CV = 4.69%).

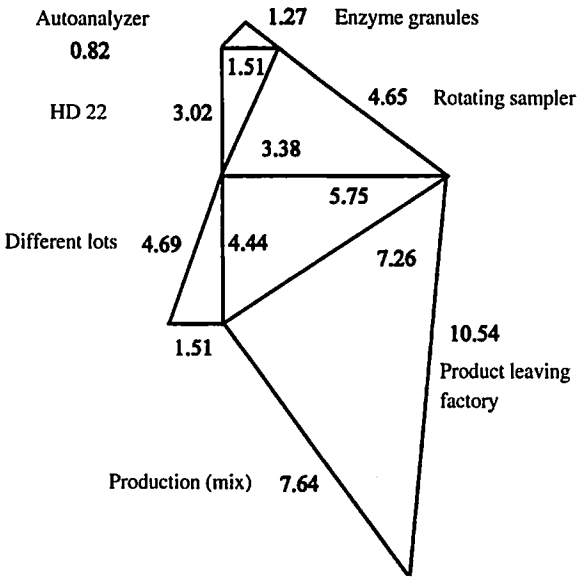


Fig. 18.6. Identification of the sources of variability (CV) of enzymes in a detergent powder.

Examples of Some Simple Methods for Controlling Physical Properties

Volume Mass

Although many factories have automatic equipment today, in many others, measurements are still taken "by hand." Volume mass depends on the flow properties of the powder, and therefore on temperature and humidity; it cannot be measured on a continuous basis at any random point in production. The aim is to automate the manual method by taking several successive measurements (e.g., 5) at short intervals, thus removing the influence of inevitable variability from measuring errors, sampling, and so on. The average obtained is the figure that is retained; it will reveal whether the system is going wrong, for instance, relative to previous data.

The manual method involves a funnel, closed at the bottom, with powder in the cone. When the funnel is opened, the powder falls from a given height into a calibrated receiver. The powder is then weighed with a suitable electronic weighing balance. Excess powder is recovered and recycled. This method is included in the Association Française de Normalisation (AFNOR) norms.

Flow Test

Several methods have been developed to evaluate powder flow. Poor flow results from granules sticking together and makes life unpleasant for the user. In one method, a given volume of powder in a glass tube is passed through a calibrated orifice and the time taken for passage is measured. Very accurate sensors can measure the time with

precision. Given time t and volume V, the flow coefficient in mL/s can be calculated. An average of three measurements is generally used.

Granulometric Quality

The granulometric quality of a powder is important in two areas:

(i) for the user, who is concerned about general appearance, flow properties, absence of dust, and presence of large particles; and

(ii) for the washing machine, where performance can be affected by poor dispersion (slow dissolution of the powder, for example) or excessive decomposition of phosphates.

The method consists of filtering a given quantity of powder through 6–10 sieves with meshes ranging in size from large to very fine; the quantity of powder left in each sieve is weighed and translated into a cumulative percentage per level. The AFNOR norm can be used for this measurement. There are different ways of expressing an average diameter. For example, in the Rosin-Rammler method, the average diameter is defined as the size that retains 36.8% cumulatively.

Quality Assurance

Quality should be present throughout the production process (from raw materials to packaging, through to the finished product as it leaves the factory) and then to the home for the rest of the product's life. Controls are needed at each stage.

Raw Material Quality

Suppliers. Before agreeing to buy a raw material, the detergent manufacturer conducts a number of tests in the laboratory, pilot plant, and production unit to be sure that the product tested meets expectations. In parallel, a number of tests should be conducted to develop a thorough understanding of the raw material and how it might change over time or between two deliveries. The results obtained are compared with the specifications agreed upon with the supplier, including both the physical properties and the chemical and biological analyses. The methods used to establish this specification are often normalized (AFNOR, ISO), but sometimes internal methods are settled on by the two parties. After agreement is reached, the supplier is responsible for the quality of the product and a certificate of quality accompanies each delivery. The quality control manager of the detergent factory will make occasional random checks to be sure that the products meet specifications.

"In-House" Raw Materials. Raw materials manufactured on site such as primary alcohol sulfate (PAS), lauryl ether sulfate (LES), and also semifinished products such as tetraacetylethylenediamine (TAED) granules are usually the subject of exact specifications. Controls are more regular and more systematic, e.g., 3–4 times per shift. An example of a specification for LES is given in Table 18.2.

TABLE 18.2
Specification for LES

Raw material specification		Date: ————
Chemical name for the substance, e.g., sodium lauryl ether sulfate 70%		Number of the raw material: ——
Commercial name:	A (manufacturer X) B (manufacturer Y)	

Type of control	Limits, examples	Method used
Surfactant	70% minimum	m_1
Anionic		
Unsulfated matter	4% maximum	m_2, m_3
100% active mineral salts	3.7% maximum	m_4
pH (solution at 5% at 25°C)	7.5 ± 1.0	m_5
Color (solution at 5% at 25°C)		
Klett colorimeter; cell, 4 cm	50 maximum	m_6
Filter number 42		
Trace metals		
Fe	2 maximum	Plasma
Cr	1 maximum	Plasma
Ni	1 maximum	Plasma
Co	1 maximum	Plasma
1,4-Dioxane at 100%		
(100% active) ppm	50 maximum	m_7 Gas (chromatography, GC)
Chain length distribution	Minimum 99% C_{12}–C_{15}	m_8
Density (25°C)	1.05 g/mL	m_9
Preservatives	0.2% Formol	m_{10}
Bacteriology	No contamination at delivery	m_{11}

Packaging Controls

Packaging, like chemical raw materials, should be subject to specifications agreed upon in the same way between the supplier and the manufacturer, and a quality assurance certificate should come with each delivery. If there is a problem during production, e.g., packages that cannot be glued properly, the manufacturer will contact the supplier to discuss the reasons and find solutions.

Finished Product Quality Control in the Plant

The control specifications are settled between the formulator/developer and the plant manager. They should be realistic and take into account constraints in the plant, such as types of machinery. In a plant, the main controls are the following:

(i) physical properties checked continuously on the production line, i.e., volumetric mass, flow properties, and granulometric quality for powders and viscosity for liquids; and

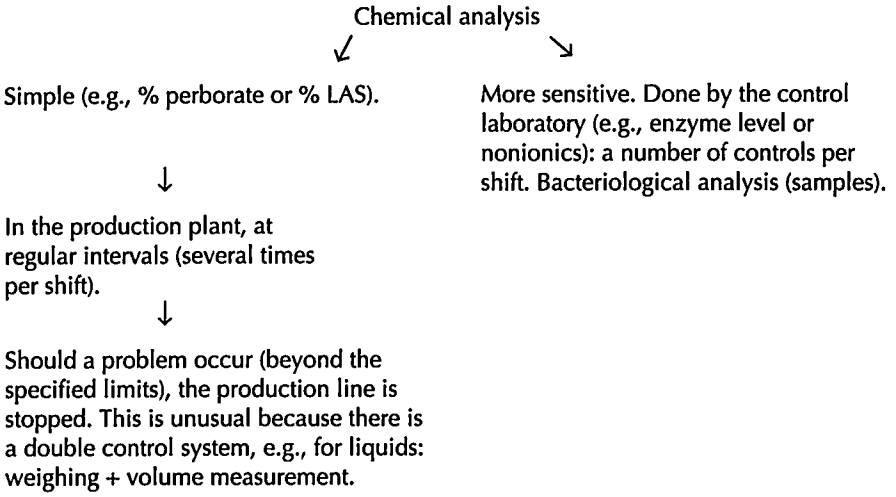


Fig. 18.7. Chemical control of finished products.

(ii) chemical properties (Fig. 18.7). Some analyses cannot be done quickly. To avoid any risks, the finished product is stored in a warehouse until the laboratory gives its approval for release.

Control at the Point of Sale

Every 2 or 3 mo, products are purchased at the point of sale to examine what has happened to them since they left the plant. Purchases are made in different regions in several stores and supermarkets in the area. Competitive products are also bought to make comparisons. The controls are similar to those carried out when the finished product leaves the plant, including physical, chemical, and biological characteristics. The packaging is also thoroughly inspected for signs of crushing, staining, or marking, tearing, or loss of functionality, and so on. In addition, ease of opening, presence of the dosing device (if relevant), weight of product, and tightness of caps on bottles can all be checked. The conclusions that follow from such studies can be important:

- In the first place, they provide precise information on the condition in which consumers find products when they buy them (physical and chemical).
- If there are gross variations between the product in the store vs. when it left the plant, this should be investigated and explained immediately. An extreme example: if perborate has been incorporated at a level of 15% and one finds 10% in the distribution channels, the cause must be established (unstable raw material).
- In parallel, the examination of competitive products is a source of valuable information. It allows manufacturer A to take a position relative to manufacturer B in terms of quality, and also to track any changes in the competitive products.

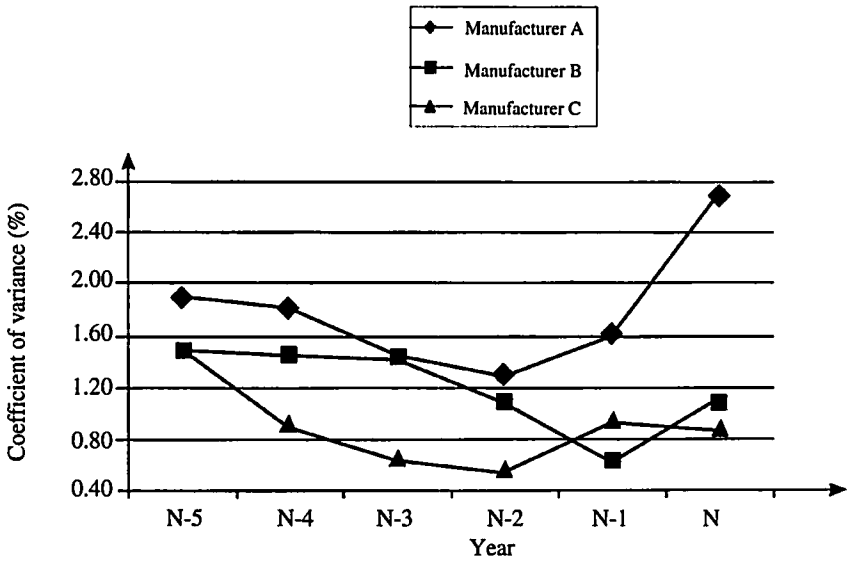


Fig. 18.8. Variation of surfactant levels in hand dishwashing products.

The information collected is given to development teams and to the marketing department.

- Analysis can be pushed further, not only in terms of immediate results (e.g., Product × from Producer A contains 10% of ABS while its competition contains only 8%) at a moment in time, but also in terms of the variance of the results.

To achieve this last goal, the coefficient of variance (CV) is a very useful tool. Comparison of CVs from one control to another, or from one year to the next, can give a very good indication of process improvements (see the enzyme example given above).

An example of tracking quality in dishwashing liquids is given in Figure 18.8.

It is clear that the search for quality must be an ongoing process at all stages of the manufacture and life of a product. At the same time, as the formulator develops a new product, the quality norms that are to be implemented must be established and the means by which the objectives will be achieved must be described. To conclude this chapter, we can say that the major manufacturers do not simply sell dishwashing liquids, shampoos, or toothpastes; they sell quality above all else.

CHAPTER 19

Toxicology and Ecotoxicology

Introduction

The role of formulators and developers is not simply to develop products that meet consumer needs for efficacy and quality. In addition, the formulator must first be satisfied that these products are neither dangerous to manufacture or to use, and that they will in no way have a detrimental impact on the user's health; second, that they will not accumulate in the environment and harm the ecological balance. To satisfy these requirements, the products must meet certain criteria for their degradation. All manufacturers have the same concerns about the safety and health of their workers and consumers and the preservation of the environment. These are major priorities on which their reputations depend and that lead them to take very significant precautions.

Toxicity

Before a new raw material is used, it must be studied in its totality from a toxicological point of view. The major manufacturers have central laboratories capable of conducting the long and rigorous studies that are necessary to check the following:

(i) local effects, e.g., skin irritation and allergic reactions, penetration under the skin;

(ii) systemic effects that can be either acute or chronic; and

(iii) potential risks, such as mutagenesis, embryotoxicity, or carcinogenesis.

These risks concern workers exposed to raw materials and also consumers using products. There are three types of exposure:

1. Contact with eyes or skin (in a workplace or during product use, or even from residues on clothing).
2. Ingestion (usually by accident, and particularly by children).
3. Inhalation (in the workplace or during use).

For a new substance, the complete study can take between several months and several years! For a formulation in which only known ingredients are used, the study may take a few weeks or months. In general, consumer testing cannot even begin until the toxicology teams have given their approval.

Product Toxicity

We indicate below the toxicity for workers and consumers of the main ingredients used, either alone or in combination.

Surfactants. Interaction can take place between surfactant molecules and biological structures such as proteins, enzymes, and cellular membranes.

- Proteins form adsorption complexes with both cationics and anionics, and these complexes denature proteins. Enzymes can suffer a reduction or even loss of catalytic activity, and then a change in metabolism.
- With nonionics, the complexes do not denature proteins, but simply cause a certain solubilization at high concentrations. Cationics and anionics barely penetrate the skin; nonionics are a little more aggressive. In general, however, the risks are very slight (1–3).

  The film of protective liquids on skin is emulsified by surfactants and the barrier is removed; skin thus becomes permeable and drier.
- *Ingestion* of anionic and nonionic surfactants is not serious because these surfactants metabolize very rapidly. Cationic surfactants metabolize a little more slowly. However, there is no accumulation of any of these surfactants in the organism.
- *Prolonged exposure* could lead to more significant problems.
- For eyes, which are more sensitive than skin, normally a serious problem would arise only from long exposure to a high concentration of surfactant without an immediate copious washing of the exposed eye with water (4).
- Acute *oral toxicity* in surfactants is low.
- Numerous chronic toxicity tests have shown total safety (5). No carcinogenic activity has been shown, either through ingestion over the long term, or from continuous exposure to the skin (6).

> **Comment**
> To reduce the negative drying effect or irritation caused by anionics on skin, amphoteric surfactants or zwitterionics can be added to liquid products (e.g., shampoos or dishwashing products). These carry a positive charge and mix easily with anionics, thus preventing their absorption into skin.

Builders. The main builders used are phosphates, zeolite 4A, and nitrilotriacetate (NTA).

Sodium tripolyphosphate (STPP) is nontoxic, but ingestion of large amounts can cause problems as a result of the high pH level in concentrated solutions (7).

Very intense toxicology studies have been done on zeolite 4A. Ingestion does not cause any problems of acute toxicity, nor is it carcinogenic. Eye contact poses no problem greater than that found with any other foreign body such as dust. Inhalation does not cause illnesses such as silicosis. It can therefore be said that zeolite does not present toxicity problems for either consumers or workers (8).

NTA has a minimal effect on skin, which is frequently exposed to the product, but it can be said that it is nonsensitizing. Inhalation and ingestion cause weak acute toxicity. Elsewhere, it is possible that the use of NTA could result in traces of this

compound being present in drinking water because of its solubility. However, the concentration is so small that it does not present health risk (9).

Enzymes. Enzymes used in detergents present no toxicological problems. But like all proteins, allergic reactions are possible in some people, either through direct contact or by inhalation.

The consumer. Any risk from inhalation of enzymes by the consumer can be discounted because enzymes are incorporated into detergents in the form of strong granules. The only risk of allergy would arise from prolonged contact between skin and a detergent solution containing enzymes. However, the risk is small because no correlation has been found to date between an increase in allergic reactions and the use of an enzyme detergent. It can therefore be concluded that enzymes will not cause skin irritation, nor will they aggravate allergic reactions (10).

Workers. Prolonged contact or inhalation of large amounts of enzyme dust can cause asthmatic reactions, in addition to the irritation and allergies mentioned above. This appears when workers handle enzymes daily in the workplace, which is why manufacturers generally institute special precautions to protect their workers' health.

As was explained in Chapter 2, enzymes are compressed into granule form to reduce handling risks to a minimum. In Chapter 12, we outlined the precautions to be taken in post-dosing enzymes; below, we give further information as examples.

Handling of enzymes, and detergents that contain them, needs to conform to strict procedures. Systems exist to avoid releasing dust into the work environment. The recommended procedures are outlined below:

1. On receipt of the raw material (drums or large bags). Quality control visually checks that the containers are in good condition, and searches are made for any leaks or exterior contamination. Samples are taken to check the levels of dust and enzyme activity.
2. Unloading of containers. Containers must be unloaded in a special area in which the air is filtered. Vacuum cleaning systems with special filters should be used for cleaning this area. Only trained workers who are responsible and trained in this type of handling should have access to this area, which is completely isolated from the rest of the factory. Drums are destroyed according to precise instructions to avoid any risk of reuse. Operators wear protective clothing, which is sealed in special air-proof bags before washing. They wear gloves and special masks for breathing. Workers are required to shower at the end of each shift.
3. Dosing of encapsulated enzymes into powders. Ventilation systems must be used; these are linked to filters and isolated from the rest of the workplace. Should an accidental spill occur, it should be cleaned up using a mobile vacuum system with special filters.
4. Packing enzyme powders. The possible sources of dust in a packing workplace are near the filling heads. These areas must be enclosed and correctly ventilated.

Any spillage must be treated as outlined above. Workers making lengthy repairs on the filling heads should wear special masks.

5. Treatment of damaged packages. Damaged boxes rejected by the system cannot be recycled. They must be handled in a closed and ventilated workplace. The contents are poured into bags for rework. If there is any risk of exposure to the product, special masks must be worn.
6. Treatment of accidental spillages. For cleaning up spills, mobile vacuum units with two-stage filters are used. No enzyme dust must be allowed to re-enter the work environment. For deactivation/decontamination, the following two methods are used on clothes or in equipment:
   (i) hot water (80°C for 30 min), and
   (ii) hypochlorite solution.
7. Cleaning and maintaining filters. Filters can be highly contaminated by enzyme dust. Changing or cleaning them must therefore be considered a high-risk task which requires protective clothing, gloves, and a mask. The filters can be cleaned by vacuum and the refuse sealed in plastic bags; suitable warning must be given to anyone handling used filters.
8. Work permits. All employees and workers involved in enzyme handling should be specially trained and have their responsibilities explained to them. They must have a special permit allowing them to enter sensitive zones. This permit means that they are aware of the risks and the precautions to be taken to avoid any danger.

System to control the presence of enzyme dust in the air. Dust filters are installed in sensitive zones. These can be simple systems that suck in ambient air through paper filters. The amount of air and the differential pressure are measured. The apparatus works for a given period and then the enzyme activity in the trapped dust is measured and converted to activity per m^3 of air. For each measuring point, maximum tolerances are defined and an alarm system is available should the norms be exceeded. Control points should be located permanently near the filling heads and near the unit that handles encapsulated enzymes (raw material). Occasionally, they should be placed near the enzyme dosing unit and in the "rework" areas (including trade returns).

The procedure for control is established. According to norms established by the manufacturers' toxicology laboratories, a value V_1 is fixed. If $V < V_1$, there is no problem.

If V is higher than the limit V_1, the cause of the problem needs to be identified. If V is more than twice the limit of V_1, a second control needs to be conducted after 2 hours. If the second control confirms the high value, the production line must be stopped and the personnel evacuated, until such time as the problem has been completely resolved. Table 19.1 shows an example of a normal control sheet for enzyme presence.

Other Ingredients. Perborate. A concentrated solution of perborate can irritate skin after prolonged contact, not because of the product, but because of the high pH. Through perhydrolysis or hydrolysis, perborate will be converted to borates and boric acid. The latter will be absorbed by the organism only if it penetrates

TABLE 19.1
Example of Enzyme Control[a]

	Packing workshop (heads)	Encapsulated enzyme receiving area	Other areas in which powder is handled
Dust (g/m^3)	V_1	$<V_1$	$<2 \times V_1$
Protease (GU/m^3)	$<P_1$	$<P_1$	$<P_1$
Amylase (MU/m^3)	$<A_1$	$<A_1$	$<A_1$
Lipase (LU/m^3)	$<L_1$	$<L_1$	$<L_1$

[a]Abbreviations: GU, glycine unit; MU, maltose unit; LU, lipase unit.

through membranes, mucus, or damaged skin. It can be said, however, that only the slightest risk of acute toxicity exists because a very high level is required for a lethal dose (18–20 g) (11). The latest studies in Germany have concluded that boron has no adverse effects on algae, reeds, and trout under present usage conditions of perborated powders. The World Health Organization has recommended that there be no more than 0.3 g/L of boron in water. The European Soap Manufacturers Association (AISE) toxicology working group concluded after their studies that 1 mg/L in drinking water is acceptable with no risk to health; this coincides with the Organization for Economic Cooperation and Development (OECD) recommendation (12).

Fluorescent whitening agents. Numerous studies have shown that these present no health risk and do not cause skin irritation. In fact, flourescent whitening agents are highly substantive both on cotton and the outside keratin layer of skin, which prevents their absorption into the organism. It can be concluded that flourescent whitening agents commonly used in the detergents industry present no health risk (13).

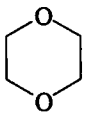
Hypochlorite. Hypochlorite-based products have been present in households for >120 years, yet very few accidents can be attributed to such products. Studies completed in the United States and in France concluded that most cases of exposure to hypochlorite are not serious. When a health effect does occur after ingestion or breathing the fumes, it is limited, and recovery is rapid and without aftereffects (14).

Perfumes. As we saw in Chapter 13, perfumes are complex compositions with dozens of different ingredients. Although used in very small quantities in detergents and personal care products, these ingredients can cause skin irritation, particularly because one of the main qualities of a perfume is its substantivity. Major manufacturers ask their perfume suppliers to avoid using ingredients that could cause skin irritation, and a perfume cannot be used until the toxicology unit has given its approval. This approval is not arbitrary, but is based either on toxicology tests or on experience with the ingredients in the perfume, which are revealed confidentially to the manufacturer's toxicology unit by the supplier. Particular care is taken in the case of shampoos for babies or other hypoallergenic products.

Combinations of Ingredients (Complete Formulations). If the ingredients singly are not toxic, or only mildly so, their combination could become toxic either by a cumulative effect or by chemical reactions, yielding toxic by-products. In fact,

everyday consumer products present only very low acute toxicity. Accidental ingestion usually causes nausea, vomiting, diarrhea, or irritation of the mucous membranes of the intestines. These are not serious health risks, even in children. The only weak risk is skin irritation from long contact with concentrated solutions, particularly if the pH is high. However, if consumers follow usage instructions, it can be concluded that the risks are minimal.

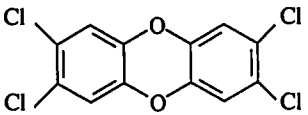
Potentially Toxic Products. We would like to draw the reader's attention to some products that can cause toxicity problems. These are either impurities in raw materials or compounds that can produce toxic products through chemical reactions. One example is 1,4-dioxane with the following chemical formulation:



This product is formed in ethoxylation of fatty alcohol, which is conducted in an acid environment and at a very high temperature. It can therefore be present in ether sulfates (e.g., lauryl ether sulfate, LES) used in dishwashing liquids and shampoos. It is suspected of being potentially carcinogenic. It is therefore important to set very strict specifications regarding the maximum allowable presence of dioxane in LES coming from suppliers.

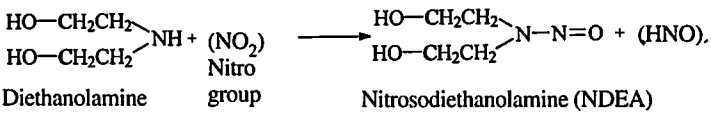
Comment

Dioxane should not be confused with dioxin, which is very toxic. This is the 2,3,6,7-tetrachlorodibenzodioxin with the following chemical formula:

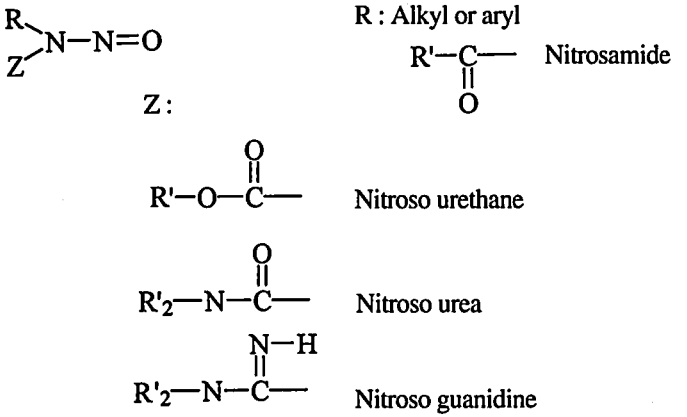


It is a trichlorophenol impurity (in Europe, everyone remembers the Seveso tragedy in Italy). Dioxin and products used in the detergent industries have nothing in common. Free ethylene oxide, which is present in ethoxylated fatty alcohols (nonionics), is toxic. The risk is practically nil if a very strict limit is set on the level of free ethylene oxide in the specification for ethoxylated fatty alcohol.

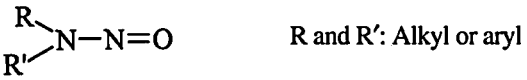
Some products have nitrogen groupings that can contain impurities. These can react with secondary amines to form nitrosodiethanolamine (NDEA) based on the following:



NDEA is potentially carcinogenic. Today, maximum levels of impurities present in substances containing a group that has undergone nitrosation and that could react with secondary amines to produce NDEA are established in shampoos and liquid detergent formulations. This brings us to the problem of nitrosamines, which can be produced by the reaction between impurities in products that have undergone nitrosation and substances in the formulation. Nitrosamines and nitroamides make up the N-nitroso compound (15). These two categories differ in their chemical stability and their toxic mechanisms. Nitrosamides can be hydrolyzed and generate malignant tumors on application, as in the following:



Nitrosamines, on the other hand, are very stable once they have been formed and become toxic only when they have been subjected to a chemical change through an enzyme reaction:



Ecotoxicology (The Environment)

Manufacturers' Environmental Policy

As responsible industrialists, manufacturers owe it to themselves to protect their public image. Their environmental policy cannot limit itself simply to ensuring that safe products are put on the market which do not accumulate in the natural environment. It applies as well to the production of raw materials for which systematic research toward cleaner and more energy-efficient processes needs to be mounted. The manufacture of finished products also needs to be subject to strict controls, i.e., clean energy and limits on what can be released into the atmosphere, the water, or the ground. The use of recycled and recyclable materials should be encouraged. Research needs to identify new

products that require less energy in use (e.g., by reducing wash temperatures with the use of bleaching activators). In the following, the procedures and tools are discussed.

Ingredient Selection. Ingredients have a two-fold impact on the environment, i.e., they can adversely affect nature, and they can require high energy consumption during manufacture.

The four key factors in choosing an ingredient are:

(i) rapid and complete degradation;
(ii) low toxicity;
(iii) lowest possible use of water and energy in their manufacture;
(iv) highest efficacy at the lowest use level.

The Tools. Two tools can help the formulator to take into consideration the environment in an optimal manner: environmental risk assessment and life-cycle analysis (LCA).

The first is shown schematically in Figure 19.1. To be complete, the situation in the natural environment must also be included.

A number of factors that have a direct influence on the estimate of predicted environmental concentration (PEC) (16):

1. The amount of product to be sold on the market. In the case of a new product, it is difficult to predict the market share that it might attain. In this case, we take the worst-case scenario and assume that the ingredient will be included in all of the products of the category concerned.
2. Direct discharge without effluent treatment. In some areas (in Europe and elsewhere), used water is discharged directly into rivers or the sea. At the point of discharge, concentrations are inevitably higher and can reach levels that are noxious to aquatic life.
3. Mathematical modeling. Mathematical models can be used, but if they are to be useful and reliable, they need to be based on an excellent understanding of modeling theory and must be validated by observation in the field.
4. Dilution and mixing with the receiving water. In certain extreme cases, such as wide rivers with little turbulence, mixing of effluent with the river water may not be complete for many miles downstream. To be realistic in calculating the PEC in this case, it is reasonable to assume that there will be some dilution, but care should be taken in estimating the most appropriate predicted no effect concentration (PNEC).

Factors that influence PNEC include the following:

1. Application factors. Although toxicity scores obtained in laboratories on fish, daphnia, or algae are based on rather sensitive organisms under extreme conditions of exposure to the ingredient in question, it is necessary to divide the

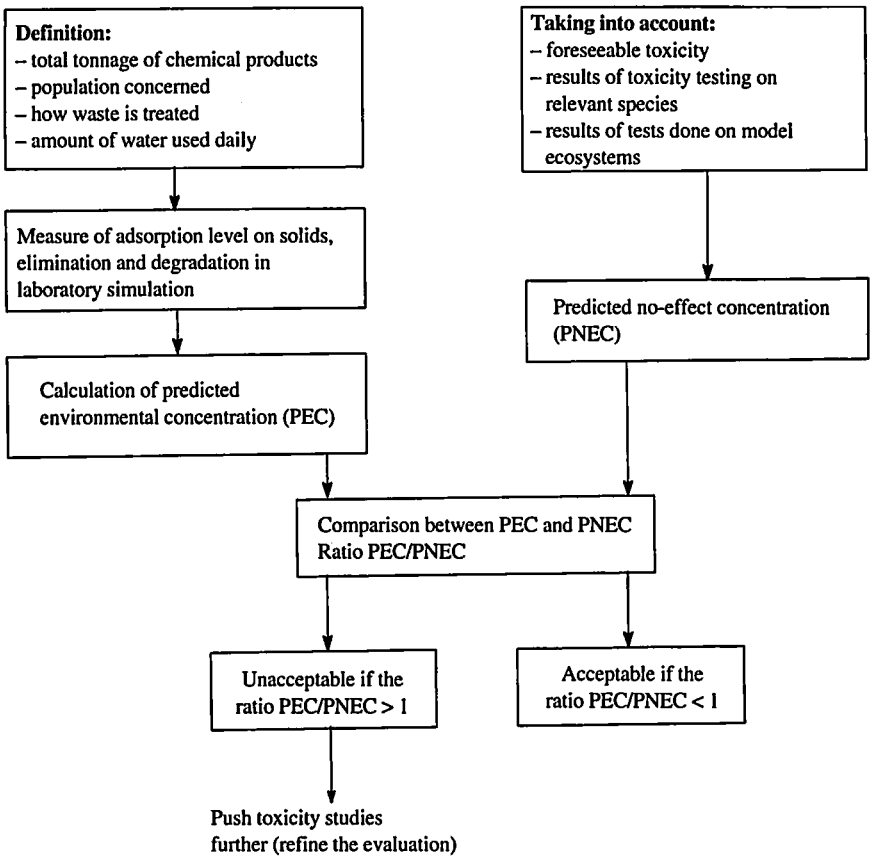


Fig. 19.1. Steps in environmental risk assessment.

lowest of these scores by quite a large safety factor in estimating a PNEC that will protect all species under all conditions of possible exposure.

2. Physico-chemical properties. Some ingredients can adsorb onto solid objects or form complexes with other ingredients, thus reducing their availability in the aquatic environment. In such a case, it is better during the research phase to perform the toxicity studies on the test organisms with the test ingredient in the form in which it will be under real conditions.
3. Environmental risk analysis. This can be complicated by the presence of isomeric by-products in the ingredient under study. These may possess biodegradation and adsorption properties that differ from the pure ingredient.
4. Presence of other toxic products. In the laboratory, the PNEC is estimated in toxicity studies in which the ingredient is present by itself. This is rarely the case under real conditions. The use of river water in these studies is therefore more realistic.

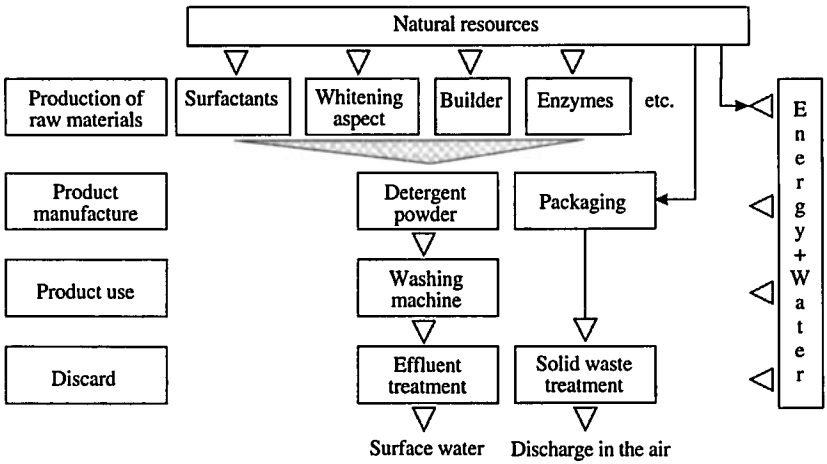


Fig. 19.2. Example of a life-cycle analysis of a detergent.

Life-Cycle Analysis (LCA). An example of the life-cycle analysis of a detergent is given in Figure 19.2. Life-cycle analysis makes it possible to calculate the impact of a product on the environment at each stage in its life.

It would seem that the most important impact lies with the consumer as illustrated in Table 19.2.

Raw materials. Are they obtained from renewable sources? What energy is used to extract, manufacture, or transform them? What are the consequences of their manufacture for the environment (e.g., air, water, and ground pollution or transport)? Each question needs to be answered with accurate figures so that an informed choice can be made.

Manufacture of the product. The same estimates must be made for energy consumption and waste. All sources with an impact on the environment have to be studied in the greatest detail. For example, is it better to use cardboard or recycled plastic for large detergent package handles?

All transport used, including that for packaging and finished product, needs to be taken into account.

TABLE 19.2
Example of a Life-Cycle Analysis for a Detergent

	Raw material production	Product manufacture	Distribution	Use and disposal
Use of resources	++			
Energy consumption	++	+	+	+++
Discharge into the atmosphere	++	+	+	+++
Discharge into the ground				+
Discharge into water	+	+		+++
Amount of solid waste generated	++	+		+

Product usage. Product life cycle must take into account energy used by consumers (hence the interest in bleach activators, for example, to lower wash temperatures), and specific performance properties of the product (e.g., a detergent that foams too much would score poorly because of the amount of water required to rinse it away properly).

Discharge of unused products into the environment. The amount of product thrown away should be minimal (hence the interest in concentrated products); these discards must not be toxic.

Biodegradation

Biodegradation is the phenomenon by which any organic molecule is degraded in the natural environment. The vast majority of detergent ingredients end up in the sewage system where they are usually treated before being sent to the rivers and waterways that make up our environment. It is therefore essential to ensure that products, once used, do not have an adverse impact. The main concern here is laundering since it involves the largest quantity of cleaning products and hence carries the greatest responsibility *vis-à-vis* the environment.

Sources of Pollution. Figure 19.3 illustrates the main sources of pollution. The waste from household detergents represents between 10 and 15% of all effluent; for this reason, such waste has attracted particular interest for many years. Surfactants and phosphates are the subject of special legislation in most developed countries because of their extensive use and impact on the ecosystem. In the following, we will look in more detail at the problems of these two ingredients.

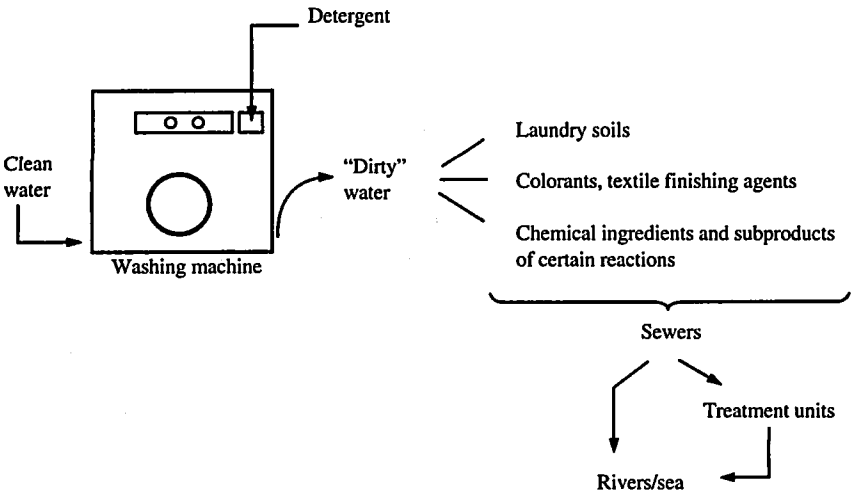


Fig. 19.3. Pollution sources.

Surfactants. The case of alkylbenzenesulfonate. In the 1950s and 1960s, the extensive use of synthetic anionic surfactants in replacing soap in laundry products caused huge problems of foam in sewage plants and, subsequently, even in rivers and lakes. The reason was the poor biodegradability of tetrapropylenebenzenesulfonate (TPBS, branched ABS), traces of which were found on surface waters, in deeper waters, and even in drinking water, fortunately at very low concentrations. Although nontoxic to humans, the taste at 1 mg/L was not very pleasant. Research discovered that replacing the tetrapropylene-branched alkyl chain by its linear isomer resulted in a highly biodegradable product. The best example is LAS (linear alkylbenzenesulfonate), a very effective and widely used anionic that biodegrades ~40–50 times more quickly than TPBS under the same conditions. Even when effluent is poured untreated into rivers, LAS degrades as soon as the polluting effect has disappeared (when the dissolved oxygen level is restored). The aquatic toxicity of LAS is a little higher than that of TPBS, but this disadvantage never manifests itself in the environment, even after direct discharge.

Some definitions. The following terminology is used in discussing biodegradation:

1. Primary biodegradability. The change in chemical structure of a substance, resulting from a biological action that causes the loss of the specific properties of the substance (i.e., surface activity, in the case of surfactants).
2. Ultimate biodegradability under aerobic conditions (in the presence of oxygen). The level of degradation at which all of a test substance has been consumed by bioorganisms to produce carbon dioxide, water, mineral salts, and new constituents of microbe cells (biomass).
3. Ready biodegradability. This is an arbitrary classification for chemical products that respond positively to immediate biodegradability tests. The severity of the test (biodegradation and acclimation time) indicates that we can be sure that such compounds will degrade quickly and completely in an aquatic environment under aerobic conditions.
4. Intrinsic biodegradability. This is the classification of chemicals which undergo primary or ultimate biodegradation without ambiguity during any biodegradability test.

Methods used to determine biodegradability. Various tests have been developed to measure the rate of biodegradation. They are based on the quantity of oxygen consumed, the disappearance of dissolved organic carbon (DOC), and the quantity of carbon dioxide given off. ISO and Association Française de Normalisation (AFNOR) have laid down procedures to determine biodegradability. A number of methods are included in the OECD guidelines to classify chemicals as a function of their ease of biodegradation in an aerobic aqueous environment. These methods include the following:

(i) 301 A, tests the disappearance of DOC;
(ii) 301 B, measures CO_2 evolution (modified Sturm test);

(iii) 301 C, modified MITI test (Ministry of International Trade and Industry, Japan);

(iv) 301 D, closed (shake) flask test; and

(v) 301 E, modified OECD "screening" test.

As examples, we present some of the tests used to measure immediate and intrinsic biodegradability.

Immediate biodegradability testing is designed as a severe test in which acclimatization time is limited. A chemical that gives a positive result in this type of test will biodegrade quickly in the environment and can be classified as "readily biodegradable."

Experts consider that the following "threshold levels" provide a good indication of immediate biodegradability after 28 days: CO_2, 60%; DOC, 70%. A number of methods are proposed, including the modified Sturm test described below. The extent of biodegradation is calculated by expressing the concentration of DOC that has disappeared (corrected from the observed value in a control containing inoculum) as a percentage of the original concentration. Primary biodegradation can also be calculated from chemical analysis of the test substance at the beginning and at the end of incubation, or from the amount of CO_2 given off.

The principles of the modified Sturm test are shown in Figure 19.4. A measured volume of a cultured inorganic environment, containing a known quantity of substance to be tested (10–20 mg/L of DOC) as the only nominal source of organic carbon, is aerated in darkness or under diffused light, by the passage of air without carbon dioxide at a controlled rate. Degradation is tracked by analysis of the carbon dioxide produced during a period of 28 d. The CO_2 is trapped by barium or sodium hydroxide and its amount is determined by titration of the excess hydroxide or as inorganic carbon. The quantity of carbon dioxide produced by the test substance (corrected by the value obtained from the control containing inoculum) is expressed as a percentage of theoretical CO_2 (Fig. 19.5).

The tests of intrinsic biodegradability allow long exposure of the test compound to microorganisms under conditions that are favorable to biodegradation. A product that gives positive results in this test can be described as "intrinsically biodegradable," but because of the favorable conditions used, it is not possible to be certain that its biodegradability will be ready and certain in the environment. Because intrinsic biodegradability can be considered as a specific property of a compound, it is not nec-

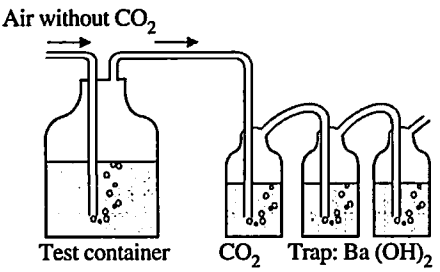


Fig. 19.4. Modified Sturm test.

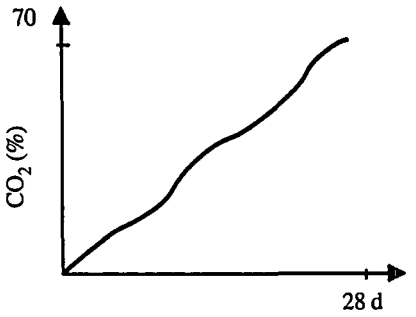


Fig. 19.5. Percentage of CO_2 as a function of time.

essary at this stage of testing to define the limits in terms of duration of the test or the extent of biodegradation. Biodegradation >20% is a sign of primary intrinsic biodegradability. A mineralization level of 70% can be considered as a sign of ultimate biodegradation.

One of the methods used to measure intrinsic biodegradability is the semicontinuous activated sludge (SCAS) method.

The principle of the SCAS method is as follows. Activated sludge from a water treatment plant is placed in an aeration unit. The compound is added along with decanted domestic sewage water. The mixture is aerated for 24 hours. When aeration stops, the sludge is allowed to settle, and the supernatant liquid is removed. The sludge remaining in the aeration unit is then mixed with a new quantity of the test substance and decanted sewage water.

Biodegradation is measured by the level of dissolved organic carbon (DOC) in the supernatant liquid. This result is compared with the one from a flask containing a control solution composed only of decanted sewage water. As biodegradation progresses, the values recorded in the two test units should approach those of the control units. When the difference between the two values remains constant after degree successive measurements, three additional measurements are taken and the degree of biodegradation of the substance is calculated (Fig. 19.6).

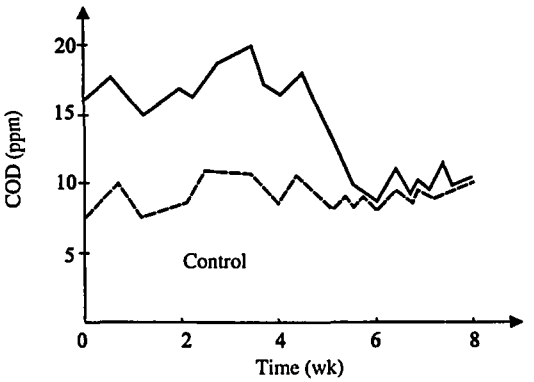


Fig. 19.6. Semicontinuous activated sludge (SCAS) test: Dissolved organic carbon (DOC) in the effluent.

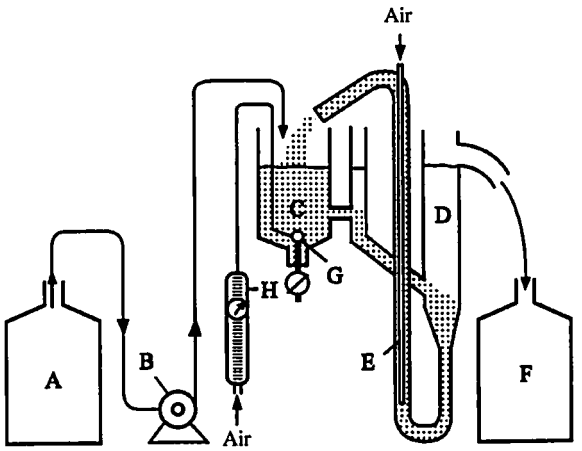


Fig. 19.7. OECD simulation test. (A) storage container; (B) dosing pump; (C) activated sludge vessel (3 L); (D) separators; (E) air lifting pump; (F) collector; (G) aeration unit; and (H) air flow meter.

The OECD simulation test (303 A) is representative of tests that give an idea of the extent of biodegradation under clearly determined environmental conditions. Tests of this kind can be subdivided according to the type of environment that they are simulating, such as biological treatment (aerobic or anaerobic), river, lake, estuary, sea, or land. The principle of the method is based on the use of an activated sludge installation as shown in Figure 19.7.

Receiving vessels (A) and (F) are made of glass or an appropriate plastic, and they should hold at least 24 L. Pump (B) carries a constant flow of synethic sewage water to the aeration unit; during normal operation, this unit (C) should contain 3 L of liquid mixture. The quantity of air blown in through the aerator is controlled with a flow meter. Other parts include a carbon analyzer, a membrane filtration unit, and the usual glassware for preparing samples. For the test, synthetic sewage water is prepared. Into 1 L of tap water, dissolve 160 mg peptone, 110 mg meat extract, 30 mg urea, 7 mg $NaCl_2$, 4 mg $CaCl_2 \cdot 2H_2O$ and 2 mg $MgSO_4 \cdot 7\,H_2O$.

The large manufacturers will often have pilot-scale water treatment plants next to their laboratories and close to a town from which they can collect real sewage water and study biodegradation under conditions that are close to reality.

Phosphates. The question of phosphates is complex; leaving aside the views of the media on this topic, we will examine the subject objectively, looking at all terms of the equation. Unlike most products that have been attacked in the name of environmental protection, phosphates are a particular problem because they are not toxic in themselves. These salts, derived from phosphorus, are indispensable to human, animal, and vegetable life. This is why they are used in food products and as fertilizers.

Phosphate pollution has been attacked on the following grounds: When released into water, phosphates help to nourish aquatic plants, particularly algae, which multiply quickly and excessively in relatively static water in lakes and certain slow-running

rivers. Because these algae use much oxygen, they "asphyxiate" their environment; this is known as "eutrophication."

Comment

The position of the experts is far from unanimous:

1. Eutrophication exists. However, it takes place under conditions that must be clearly defined, and include temperature, the amount of water and its flow, its aeration, the presence of other elements, and geochemical or geophysical considerations.
2. Experts wonder how to respond. They know that it is possible to remove phosphates in water treatment plants, as has been done in Sweden and other countries that followed suit. They also think it should be possible to replace phosphates in detergents, but with alternatives that are really less polluting.

Detergents are not the only product responsible for phosphates in the system. There are lively debates on the percentage of total phosphates contributed by different sources, e.g., for detergents, some say 10%, others 30%; for agriculture the figures are between 30 and 50% if we include animal excrement; and 30% from human sources.

The subject must be addressed in a calm manner if we are to avoid impulsive reactions. As we have already stated in Chapter 2, phosphates in detergents are difficult to replace for the simple reason that they fulfill many functions, including the following:

(i) they remove calcium by complexation which enables them, among others, to soften water and to break the link between soil and the wash, making the detergent action more effective;

(ii) they keep soil in suspension in the solution; and

(iii) they bring alkalinity to the wash.

Replacement products do not fulfill all of these functions; thus, a variety of substitutes is required.

Consider zeolite, which has been used as a replacement for STPP for ~15 years. We can now look quite rigorously at its advantages and disadvantages. From a performance perspective, zeolite cannot eliminate the Mg^{2+} ions present in hard water (17); gives average results at low temperature, in short wash cycles, and when the wash is dirty (18); and requires alkaline agents, polymers or cobuilders, either to eliminate the Mg^{2+} or as dispersing agents.

On the positive side, zeolite absorbs (can carry) a larger quantity of liquid surfactants and is less sensitive to "underbuilt" conditions.

From the environmental perspective, debate continues on the replacement of phosphates by a zeolite/polymer system. In certain states in the United States, such as Virginia, and in some towns in Florida, the phosphate ban for detergent has strongly reduced the amount of phosphates in the water (19). In other states, the removal of phosphates from detergents has not brought any improvement (20). In the state of Illinois (Lake Michigan), the improvement in water quality has been

reported to be unrelated to the phosphate ban (21). Studies by the Environmental Protection Agency (EPA) covering 493 lakes in the United States have concluded that phosphate bans result in only a slight improvement in water quality (22).

The fact that the removal of phosphates has a negligible impact is supported by the following considerations:

The primary source of phosphate is that which is absorbed in the ground by geochemical mechanisms. This phosphate is "released" by sediments into rivers, which completely overshadows the already minimal contribution by phosphate-containing detergents. Thus, even after large plants have been constructed to eliminate phosphates in water treatment plants, supported by well-known techniques, the level of phosphate in environmental waters has remained unchanged over the 20 years from 1970 to 1990 (23).

In Europe, some studies have shown that the removal of phosphates from detergents has resulted in a clear improvement in water quality (24,25). But according to other studies, the removal of phosphates has not brought the hoped-for benefits. Impact on water quality in Switzerland, for example, has been minimal (26,27). Studies conducted in the United Kingdom (28,29) and in Italy (30) also have shown that the primary sources of phosphates are geophysical and geochemical, as mentioned above.

Some authors even believe that zeolite increases the quantity of sludge in water treatment plants, reducing its heating value for combustion (31). For others, the reuse of sludge can increase the concentration of soluble aluminum as a result of reaction between zeolite and acids in rain or soil (32).

In a life-cycle analysis, Landbank compared detergents with phosphates and detergents with a zeolite/polycarboxylate builder system. An environmental impact score (negative) is attributed to each ingredient. For 1 kg of "builder," tripolyphosphate had a score of 107, compared with 110 for zeolite (33). According to Landbank, the means of eliminating phosphates are known (removal in treatment plant and recycling), while knowledge about recycling zeolite is not (34).

What solutions can be brought to these problems of phosphate and its substitutes (particularly the zeolite/polymer system, widely used today)? We do not pretend to know all the answers, but we present our point of view below in four points:

1. The phosphate question involves four contributing factors, i.e., detergents cannot take all the blame for eutrophication. The relevant factors are detergents, fertilizers, and animal and human waste. The best solution therefore is to remove phosphate from water before it is released for further use.
2. It is useful to limit phosphate levels, even if detergents containing them are responsible for only a very small part of the problem with consequences that cannot be measured—small improvements are better than nothing. This was the view taken by the major manufacturers even before the agreement was signed with the French Ministry of the Environment. Products that used to contain almost 40% of phosphates 15 years ago now contain 25% (since 1991).

3. The free choice of consumers must be respected by supplying products with and without phosphates.
4. The use of concentrated products is also a part of the solution, because fewer chemicals are discharged into the environment.

In sum, research must continue to find still better substitute products, i.e., soluble builders and biodegradable polymers.

Packaging. This subject was dealt with extensively in Chapter 14.

Legislation

In most industrialized countries, governments have legislated to limit the impact of chemical substances on the environment. The concerns are similar from country to country. The European Community countries, for example, are subject to certain directives on the biodegradability of surfactants; the methods are defined and the substances must satisfy a minimum biodegradability score of 90%. The manufacturers associations are active in developing programs to reduce pollutants in the atmosphere. In the United States, for example, work is being done on phosphates, heavy metals, borax, and volatile organic compounds (VOC). As we have seen, some states have banned phosphates. Other countries have introduced programs reducing the amounts of phosphates used in household detergents.

In France, for example, there is an agreement between the government and the Soap and Detergents Industry Association (AISD), whose objectives are as follows:

- To draw the consumer's attention to detergent dosage, keeping in mind water hardness as follows: soft is <200 ppm $CaCO_3$, medium is from 200 to 350 ppm $CaCO_3$, and very hard is >350 ppm $CaCO_3$.

  Consumers are given convenient methods to determine water hardness, and programs to complete the information are in progress.
- To communicate to consumers the composition of the product formulations (names of the principal ingredients and their levels), e.g., <5%, 5 to <15%; 15 to <30%; and ≥30%.
- To put in place a committee charged with pursuing a research program to study the long-term impact of the different ingredients used in detergent formulations.

The companies concerned regularly supply the French government with consumption figures of the components. The Convention signed in 1989 is updated regularly. For example, in 1991 the maximum incorporation levels for phosphate were agreed upon (in grams of phosphorus per liter of wash solution). They are shown in Table 19.3.

Further, the use of EDTA was first limited, then progressively reduced, and finally eliminated completely. All major manufacturers belong to the association, and all have committed to introducing a nonphosphate detergent into the market. The Code of Good Environmental Practice was signed in July 1998 by the AISE (see Chapter 14), committing European manufacturers to reduce by 10%/inhabitant both

TABLE 19.3
Maximum Concentration of Phosphorus in the Wash Solution

Water (°F)	All-purpose products (g phosphorus/L)	Fine wash detergents
<20	0.85	0.70
20–35	1	0.80
>35	1.15	0.95

detergent consumption and the consumption of nonbiodegradable organic ingredients in household laundry detergents. The manufacturers committed to this program will supply the relevant basic facts concerning their businesses (based on 1996 data) for each of the agreed-upon environmental objectives, to measure progress made and to report to the European Union. The association will collect and manage all of the data and will publish a report every two years in each European country and for the whole of Europe.

Of interest is the decision by the European Union dated July 25, 1995, establishing the ecological criteria for the use of an Eco Label (35). The following criteria have to be met to justify the use of this label:

(i) total weight of primary packaging (total + new material);
(ii) total weight of the chemical ingredients;
(iii) critical volume of dilution-toxicity (VCD);
(iv) the presence of phosphates;
(v) the level of insoluble inorganic compounds;
(vi) the level of soluble organic materials;
(vii) the level of aerobically nonbiodegradable organic compounds;
(viii) the level of anaerobically nonbiodegradable organic compounds; and
(ix) biological oxygen demand (BOD).

These parameters are calculated and expressed in g/wash cycle or in L/wash cycle. A score is given to each of the criteria, and if the total meets the requirements, the use of the Eco Label is authorized. The method of calculation is quite complex and explains in part a certain reserve on the part of the industrial community. For this reason, a revision of the criteria is in progress to make compliance with the Eco Label criteria attractive to manufacturers.

Comment
The surfactant biodegradability label on packages should not be confused with the Eco Label.

Plant Controls

Manufacturers must be concerned not only with the impact of their products on the environment, but also with their own manufacturing sites. In addition to normal

controls to be found in all factories, detergent manufacturers in particular have to control waste discharge into water from their plants, e.g., the presence of phosphates and surfactants, oxidizable materials, and suspended matter.

Phosphates and Surfactants. Measurements of P_2O_5 and LAS are made very frequently. A system for continuous measurement is being planned. Limits can be set and corrective action decided upon, such as stopping production if the maximum acceptable level is exceeded.

Oxidizable Materials in Waste Water. Oxidizable materials (OM) are expressed as a weighted average of the chemical oxygen demand (COD) and the biological oxygen demand (BOD). BOD is the amount of oxygen consumed by microorganisms when they metabolize a test substance (the quantity is expressed in milligrams O_2 consumed per milligram test substance). COD is the amount of oxygen consumed during oxidation of a test substance. COD gives a measure of the amount of oxygen present and is expressed in milligrams O_2 consumed per milligram test substance.

Suspended Matter. The amount of suspended matter in a given amount of water is determined by filtering through a glass fiber filter and then weighing the residue. In France, different types of waste are controlled by the regional Bureaus of Industrial Research and the Environment (DRIRE). As far as possible, manufacturers have installed systems to re-use water in a closed system, and significant precautions are being taken in high-risk areas (e.g., a recovery tank around each decanting zone or near tanks containing pollutants).

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CHAPTER 20

Recent Trends

Introduction

Throughout this book, we have highlighted new molecules, new product types, and the different trends that indicate possible progress. It would seem useful now to summarize these trends for the year 2000 and beyond so that the reader can have a clearer idea of what to expect. Before tackling that subject, it is important to remember that the technological evolution in the product categories discussed in this book is slow, despite the huge resources deployed by the major manufacturers. Products are not developed and launched overnight; some developments even stretch into years!

In the future, manufacturers of detergent and personal care products will need to deal with constraints and pressures in numerous areas, including:

(i) innovations in household appliances, textiles, and surfaces;

(ii) environmental regulations and consumer safety issues;

(iii) changes in the marketplace; and

(iv) changes in consumer needs.

The industry must be capable of developing products that not only meet these requirements, but anticipate them and perhaps go even farther.

In this chapter, we will examine the different trends, constraints, and pressures on the industry, the challenge we have been given, and our profession. I beg the reader's patience if I express some personal ideas based on my experience and a keen interest in technological developments reported in the published literature. We must be modest because mistakes are often made. Sometimes the market does not follow "scientific" logic, proving this is not the only factor in success. As has often been said, "It is difficult to plan, particularly for the future."

Let us consider two examples. In Europe, when liquid detergents for laundry or machine dishwashing were first put on the market, most manufacturers believed they would take large market shares within a few years because of the advantages of liquids over powders (e.g., rapid dissolution, exact dosage, practical). In the same way, concentrated powders were going to be a decisive step forward in laundering because they would bring to an end large, cumbersome, and impractical detergent packages, replaced by pleasant, light, and practical small boxes.

In reality, however, the outcomes were often quite different. With more detailed analysis, and the advantage of hindsight, we can understand the factors that have guided the consumer's decisions.

Liquids. Even if consumers readily accepted the concept of a liquid as a product, they were disappointed in the actual performance and the price. For dishwashers, it was difficult to equal the performance of the powders because these were simple

and effective formulations, based on chlorine, metasilicate, and phosphates, at the time that the liquids were first launched.

In textile laundering, it was not possible to add bleaching agents such as perborate/tetraacetylethylenediamine (TAED) to aqueous liquids. Stains normally removed by these ingredients were not properly removed by liquids. Therefore no real equivalence could be found between powder and liquid—and the consumer was not satisfied.

Concentrated powder. Consumer acceptance has varied among countries and even continents. If the reasons were clear in some cases, other cases proved that consumer acceptance of change was not always easy to explain. In Japan, the success of concentrated powders could be explained by a lack of space in homes (an important factor in some countries). In countries such as Germany and Holland, it was more the ecological aspects that carried the day because concentrated powders required less packaging material and generated less chemical waste. In the United States, the ecological factors were not as clear-cut as in the example above, and space was not a problem, so it is more difficult to explain the success of concentrated powders.

In France and, more generally, in Europe, standard, normal density products remain more important in the market than the concentrated versions. The probable explanation is the force of tradition. In Europe, consumers are used to their own way of dosing, and they adapt with difficulty to dosing in smaller quantities. They tend to underdose normal powders and overdose concentrated powders, and incur a much higher cost per wash.

Future Developments

Household Appliances

For textile washing machines, there are three types of markets, i.e., affluent countries in which all homes have machines and purchases are generally replacements (99% in France), Southern and Eastern Europe in which the detergent market is still growing, and the Third World, in which machine ownership may be as low as a few percent of households: 20% in China (but 90% in Shanghai!), 20% in Thailand, and 2–3% in Vietnam.

For dishwashers, the market is almost nonexistent in many countries. Even in countries with a high standard of living, ownership is much lower than for textile washing machines, and the pace of market penetration is slower.

Developments in Washing Machines. Washing machine manufacturers are trying to attract new consumers, not only with aesthetic improvements or by reducing cost to a minimum (by examining the value of everything in their machines), but more importantly, with real technological innovation and improvements, often related to electronics and informatics. We are beginning to see "intelligent" machines coming onto the market. For example, some washing machines can weigh the wash and adapt the amount of water and the duration of the cycle accordingly, or program an extra rinse cycle if there are residual traces of detergent at the end of the wash. There are also environmental factors, such as a reduction in the amount of water or electricity used, with energy labels appearing in some countries.

In Europe, the volume of water consumed per wash is 70 L, and ~2% of total electricity consumption is used for laundering. Machine manufacturers are therefore trying to reduce both the amount of water utilized and electricity consumed by their machines. In addition to trying to reduce the amount of water used (from 70 to 30 L in Europe, and 160 to 90 L in the United States), the idea of using a recycling system or a sprinkling system is in active development by certain manufacturers.

In Europe, manufacturers have committed themselves to reducing electricity requirements. Cooperation between the European Commission and the European Committee of Domestic Machine Manufacturers has led to an agreement to reduce the amount of electricity consumed by 20% by year 2000 relative to 1994 levels. Energy labels have been agreed upon between the European Commission and machine manufacturers; they are already appearing in a number of countries. In addition, manufacturers are required to provide information on washing efficacy, water consumption, and rinse speeds for each of their machines.

In the United States, where machines are large and consume a great deal of water, there will probably be a move toward less "greedy" machines, even if the move to replace vertical axis machines with horizontal axis machines is far from complete because of the enormous investment involved for the manufacturers. Manufacturers have been required to indicate the average amount of energy used by their machines per year.

The policy of machine manufacturers is now to inform their users and to recommend:

(i) filling the machine to the maximum;

(ii) using low temperature cycles;

(iii) using optimal rinse speeds; and

(iv) dosing the right amount of detergent.

In summary, we can say that the trend is to shorten the cycles, to reduce the amount of water used, to improve the machines generally, and to increase rinse speeds. Of course, constant efforts are being made to improve materials and reduce costs.

Substrates. Fabric types, dishes, kitchen appliances, and other surfaces are all changing very quickly.

Fabrics. In the past we have seen cotton being replaced by synthetic fibers, but for some years now there has been a return to natural fibers, in particular to cotton. In countries such as Japan, cotton now represents almost 90% of textiles sold! In the U.S., however, synthetics and microfibers have recently experienced renewed popularity in women's fashions in particular. However, somewhat fragile colored articles continue to make up the majority of our wardrobes, with almost 4000 different colorants available.

Dishes and other hard surfaces. In this area as well, there are positive developments for our industry. Most luxury porcelain manufacturers are now selling products that are machine washable. Less expensive crystal that can be washed in

machines is growing in market share. Other hard surfaces are becoming tougher, particularly floor coverings.

Consumer Needs. In Europe, three situations exist.

In Northern Europe, the market is practically saturated. The launch of a new laundry product, for example, will serve only to replace an existing product. Consumption is between 8 and 12 kg per inhabitant per year.

In Southern Europe, there are still good opportunities for growth because the markets are still developing. Eastern Europe is gradually opening up, but consumption remains at <3 kg per inhabitant per year.

In the Americas, large differences exist between North and Latin America, with the United States consuming 9.8 kg of detergent per person per year, compared with only 3.8 kg in Latin America, suggesting that good development potential exists.

In Asia, we also have to distinguish between the richer and developing countries, with consumption varying from a factor of 1 to 2 or 2.5, and even 4.5 for shampoos. The quantities of shampoo, toothpaste, and detergent consumed in Southeast Asia and Japan, expressed in kg/person/y are 0.33 vs. 1.55, 0.2 vs. 0.4, and 2 vs. 4.5, respectively.

These figures represent immediate implications for manufacturers. In less developed countries, in which the formulations are more basic and correspond to consumer needs, i.e., the main objective is to increase volume and to enable as many people as possible to achieve at least minimal hygiene standards.

We saw in Chapter 9 that the occurrence of caries in the Third World used to be lower than that in industrialized countries, which consume more sugar. The situation is now reversed because of improved oral hygiene (regular and frequent use of fluoride toothpastes) in the Western world.

In developed countries, consumers are more demanding in a number of ways:

1. Product costs. In times of prosperity, the consumer is interested in more than simply the price of an article and may be prepared to pay a little more for a specific benefit. When times are harder, however, price becomes a major criterion of choice. In developed countries, prices have increased less than inflation, and in some cases, have even dropped in absolute terms. Thus, the share of detergents in total consumer spending falls year after year.
2. Performance. The habits of a lifetime change very slowly, whether in terms of products or of the washing process. People wash clothes more frequently, but the laundry is less dirty than some years ago, dosage has dropped, wash cycle temperatures are falling, and what may be enough to "freshen up" clothes is not enough to thoroughly clean some tenacious stains. Where dosage is concerned, consumers in Japan have reduced consumption from 25 to 20 g and then to 15 g in 1996, and in Europe dosage has been halved, falling from 150 to 100 g and then to 75 g. The consequences of these developments are felt

directly in price and performance, i.e., the problem of residual stains has led to the various pretreatment solutions; for some years now, low temperature washing has led to the need for more effective products, in terms of both detergency and stain removal. In Japan, clothes are washed in cold water in short wash cycles, demanding not only effective products but also good solubility.

3. Quality. The consumer judges both the quality of the package (e.g., its practicality, the legibility of the instructions, or ease of storage) and the product itself. Efficacy remains the first criterion, in particular stain removal, followed by care of articles washed (colors, looking like new for a long time). The physical properties of the product are also important (easy pouring, no lumps). For household cleaners, shining surfaces are a requirement in addition to efficacy.
4. Pleasure in use. The perfume must be pleasant. Consumers are spending more time at home and want to be surrounded by pleasant ador, including those on their clothes and other surfaces (floors and so on). For hand washing products, the consumer wants milder products and good foam levels.
5. Safety. Increasingly, consumers want products that are neither harsh nor toxic. Consumers are better educated in environmental matters and are more aware of these aspects. They know which products present risks, and they pay attention to the chemical ingredients shown on the package. In terms of practicality, the product should be easy to use (easy opening, dosage). New product forms such as tablets will please certain consumers. For example, in Japan where space is at a premium, compact products are very successful. Nevertheless, a certain contradiction exists between the desire to simplify household tasks as manifested, for example, in multifunctional products (e.g., detergents with softeners, or 2-in-1 shampoos) and the need for perfect results. In developed countries, this has led to a multiplicity of specialized products for floors, windows, and chrome faucets, not to mention fabric softeners and specific products for each type of hard surface, while in the Third World, one product often does everything!
6. Hygiene. We know that some bacteria can become resistant to antibiotics. There have been cases of food poisoning because dishes have not been washed properly. Conscious of these problems, consumers are increasingly demanding antibacterial products for both low temperature washing and hard surface cleaning.

Environmental and Regulatory Constraints

The Environmental Factor

Problems related to the environment have changed considerably the way in which new product development or the adoption of new raw materials is approached. Indeed, detergent manufacturers have often led the field in this area. Respect for the environment can be summarized by the following phrase from the Bruntland Commission report in 1987: "The objective is to satisfy present needs without sacrificing those of future generations." The need for change is accepted by all, because there still is real

waste. However, people in developed countries are not ready to change their lifestyles and reduce their comfort. At the same time, people in poorer countries aspire to an improved quality of life. As responsible industrialists, it is our duty to contribute to respect for the environment in the following areas:

1. Water. This is a major problem area, one that could limit socioeconomic progress. In developed countries, we can consume as much water as we like, while most of the world's population does not have enough water for domestic use and sometimes does not even have clean drinking water. It is essential for us to do everything we can to save water in our production plants (e.g., by using recycled water) and through the products that we develop so that washing and cleaning require less water.
2. Energy. We must consider energy reduction in different ways, i.e., by launching products for low temperature washing and by promoting and developing production processes that use less energy.
3. Natural resources. We should consume fewer raw materials and packaging materials, as discussed in Chapter 19 in the context of the AISE agreement with the European Commission. The use of renewable raw materials should be encouraged.
4. Pollution. We must beware of pollution by both factories and consumers in terms of air quality and waste poured into rivers or the soil.

Life-cycle analysis will be essential and systematic for all changes.

Regulations and Associations

In Europe. The classification of dangerous products in the 1988 directive means that all products must be evaluated. If they are dangerous, they should be placed in the appropriate category (e.g., very toxic, toxic, irritant, corrosive, or inflammable), and their packaging should carry the necessary warnings. Obviously, detergent manufacturers would prefer to avoid having to write "hazardous to health" on their packages.

In the future, it is unlikely that legislative bodies will be solely responsible for the control of environmental problems. Increasingly, there will be agreements between governments and businesses, *via* their associations, resulting in the reduction or complete removal of nonbiodegradable products over the short-to-medium term (e.g., The AISE Code of Good Environmental Practice).

Whatever happens, the debate should be scientific and not emotional. Only willingness to be open and transparent, by both government and industry, will yield reliable and exact facts, supported by experts where necessary, that will be beyond question by certain pressure groups. Acting in this manner could have avoided the unfortunate conflict in Denmark with regard to restrictions on the use of linear alkylbenzenesulfonate (LAS). Under pressure from farmers who use sludge from water treatment plants, the government arbitrarily fixed the authorized level of LAS (decree no. 832) without consulting the detergent industry or considering any scientific evidence.

In the Americas. In North America, as in Latin America, the steps being taken are quite similar. The industries responsible have tried to find solutions to environmental problems for many years, while at the same time avoiding the easy solution provided by "green marketing," which consists of simply putting seductive slogans on their packages, such as "recycled" or "biodegradable." The solutions lie in areas such as concentration, reductions in packaging, and reusable and recyclable packages.

In Latin America, legislation is sometimes severe, to the point that in Argentina, factories have been closed and directors put in prison for disregarding toxic waste legislation. In general, the trends are similar to those seen in Europe. Environmental issues are everyone's concern. It is the responsibility of large companies to communicate widely and factually based on techniques such as life-cycle analysis. It is necessary to establish consensus among governments, industries, and other environmental groups.

In Asia. In Japan, many laws are already in place regarding the production, use, and disposal of products. Development is sometimes fast, such as the move from alkylbenzenesulfonate (ABS) to LAS and other more biodegradable surfactants in the period of only a few years.

In many other countries, environmental concern is often considerably less developed than in the regions discussed above. Sometimes legislation is minimal, covering water, air, and dangerous substances, and these countries are looking to Japanese and Western industries for help.

Summarizing this section, we can say without fear of contradiction, that the major manufacturers have the following desires:

(i) *to maintain a dialogue* with the authorities and intermediary groups, such as associations, e.g., AISD in France, AISE in Europe, or the SDA in the United States;

(ii) *to operate transparently* by giving the relevant authorities open access to all of the required and relevant scientific facts at their disposal;

(iii) *to communicate* their know-how and knowledge of the environment, and to explain their environmental policy;

(iv) *to educate* consumers in better ways to use their products; and

(v) *to eschew "eco-marketing,"* which would damage the image of the entire industry.

The Challenge for Manufacturers

Research and Development

To meet the various constraints and keep up with developments, consumer needs, and innovation, manufacturers must dedicate the necessary resources to research and development. Each step is a challenge, e.g., the need to find new molecules,

the need to introduce products into the market before the competition, the need to meet new consumer needs in packaging and products quickly, and the need to adjust to the ever-increasing constraints of legislation.

We have already shown that product development is a long process. Today, however, evolution is so fast that innovation has to move just as quickly, and the "winner" is often the first onto the market! Innovation must therefore move even faster.

Fundamental Research. In addition to research for new usable molecules in the areas outlined above, researchers need to study how synthetic molecules function and learn to optimize their efficacy. Very sophisticated research in the area of genetic engineering, in particular, will result in enzymes targeted at specific stains. Such research will be lengthy, however, even with the use of computer modeling to accelerate the pace.

Process. Very frequently, replacement of one raw material by another gives rise to production problems. For example, high levels of primary alcohol sulfate (PAS) and/or nonionics, or the presence of zeolite and silicate in the same formulation, can cause certain difficulties in the spray tower.

New products sometimes require new processes and a completely new plant. Examples include:

(i) structured liquids;
(ii) nontower route (NTR) powders, dry-mixed and agglomerated in several stages without going through a spray tower; or
(iii) tablets or other forms of concentrated products.

Intermediate semifinished products also require specific technologies, which must be studied before industrial application (e.g., granulation or encapsulation) can occur.

Continuous Studies of Consumer Needs and Washing Habits. Consumers are tracked very closely at all times to ensure that any new trends or expectations are picked up quickly and transferred to the research teams; this helps them organize their research based on precise criteria, with the least possible delays.

Technology Transfer

This huge infrastructure requires considerable investment, and the costs are impressive! A large multinational business in the consumer goods business spent more than U.S. $800 million on research and development in 1995. It is not unusual for such companies to spend between 3 and 8% of their sales revenues on research and development.

It is worth noting that 90% of all research and development funds are expended in five countries (United States, Japan, Germany, France, and Great Britain), even though these countries represent only 10% of the world's markets! In my opinion, this is understandable for the following reasons:

1. In industrialized countries, products are much more sophisticated than in developing countries; therefore, there are more research and development facilities.
2. The results of this research can be transferred very quickly and easily, at least by multinational companies, from one country to another.

   I would like to relatee a personal experience here. With knowledge acquired during 25 years with Lever France, I was able, in a very short period of time, to develop an entire range of products from the simplest to the most sophisticated to meet the needs of local consumers. Today, products identical to those sold in Europe or the United States are available in Saigon or Hanoi. Of course, cheaper products with optimized formulations also exist to meet the needs of other consumers.

   This is just one example among many of technology transfer; the list includes: telecommunications and the cellular telephone, television, and satellite dishes, which can transmit dozens of channels. Only a few years ago, basic telephones and televisions were available to only an elite few. This leads us to address briefly the question of "globalization, regionalization, and localization."

Globalization, Regionalization, and Localization. Globalization. The general policy of multinational businesses is to concentrate on their core businesses and to sell any nonessential businesses in order to invest in more important markets (e.g., China, India, or Latin America). In such cases, the transfer of technology as described above is relatively easy, but it is often detrimental to local businesses.

Regionalization. Some regional companies are sufficiently strong in research and development so that they do not suffer from the effects of globalization; they are able to survive and prosper in their own area. This is the case, for instance, for the Japanese companies.

Localization. With their relatively limited resources, local companies cannot afford significant expenditures in research and development. They are limited to relying on unpatented conventional technology, which over time can be a disadvantage. However, such companies do have at least one source of help, namely, the raw material suppliers, who have large research resources and who can be the source of valuable information.

I believe it is very important to change one's mind-set concerning patents that are in the public interest, particularly those concerned with the environment (biodegradability, pollution-related problems, and everything to do with economical use of water, energy, and natural resources). In particular, I believe that licensing should be made more flexible.

Partnerships

With Official Bodies and Various Associations. We discussed above the relationships between the detergent industry and the various official organizations. These require honesty, open-mindedness, and confidence based on scientific facts.

With Manufacturers of Laundry Appliances and Textiles. We have discussed the changes taking place in washing machines. These changes can come about only if there is close cooperation between machine and detergent manufacturers. The ideal situation would be for the latter to be involved in washing machine design in order to avoid any risk of incompatibility between machine and product. For example, if a manufacturer decides to reduce the size of the detergent dispenser from 100 to 50 mL, it is obvious that there will be performance consequences. On the other hand, machine manufacturers should also make prototypes of their machines available to detergent manufacturers as early as possible. Conversely, a detergent manufacturer who decides to introduce a new product form into the market should ensure that it does not pose a problem for the machines. Similarly, detergent manufacturers must keep themselves informed of developments in all other industries relevant to their business, e.g., textiles, dishware, and hard surfaces. One method is cooperation between manufacturers in testing products and prototypes in order to optimize the product/substrate equation.

With Raw Material Suppliers. Until recently, manufacturers relied on their own basic laboratories for the discovery of new molecules and development of processes for their synthesis. Once the new molecules had been discovered (and patented), the detergent manufacturers would approach suppliers to negotiate production and costs for the new materials.

At the same time, raw material manufacturers also work to discover new compounds which they try to sell to their customers. Each party safeguards its research programs, as well as initial results, right up to the final stages.

This policy was relevant at a certain period in time. Today, however, in order to accelerate innovation and to avoid wasting resources, a different mentality is required, one that involves closer collaboration and partnership contracts. This new trend would seem more logical and more efficient. The development of new molecules is becoming more complex than in the past and also more expensive. Moreover, all companies are trying to reduce their overhead expenses, which has significant consequences for research and development. It is no longer possible for each party to work in isolation. The best compromise must be found which allows each party to obtain maximum benefit, both financially and in terms of scientific know-how.

Today, companies increasingly concentrate on their areas of core expertise. Unilever, for example, has recently sold its chemical subsidiaries (Quest, Crosfield, National Starch, Unichema), while Rhône-Poulenc has created one subsidiary for pharmaceutical products and another for its chemical products (Rhodia).

Some projects can also be pursued in collaboration with university laboratories or with third parties who have the necessary equipment (e.g., catalysis, polymers, or surfactants). We dare to hope that this new approach in terms of partnerships will be the key to innovation in the 21st century.

Technology Trends

My estimate of future research areas, in decreasing order of priority, is: surfactants, bleaching agents, enzymes, builders, polymers, and processing, always bearing in mind performance, cost, quality, and respect for the environment. We will summarize below the various technical aspects already mentioned in the course of this book.

Raw Materials. Surfactants. These must increasingly meet criteria of biodegradability and come from renewable raw materials. LAS (which has not yet completely replaced ABS) will certainly be used for many years to come. PAS (biodegradable and renewable) is slowly gaining ground. In certain coconut-rich countries, it has already overtaken LAS. In the Philippines, for example, manufacturers are obliged by law to use 60% PAS in their active systems. PAS will certainly be the surfactant that will gradually replace LAS. The most widely used *nonionics* are still ethoxylated fatty alcohols. In time, fatty alcohols will come from renewable (vegetable) sources, and ethoxylated alcohols with a narrower ethylene oxide distribution will be used.

The *new molecules* discussed in Chapter 1, such as alkyl polyglucosides, *N*-methyl glucosamide, or methyl ester sulfonates, are easily synthesized, biodegradable, renewable, and perform well, but are still more expensive than LAS or PAS. They are certainly molecules of the near future, as their prices drop with increased volumes.

In *cationics*, quaternary esters are already being used and will be still more widely used in the near future; the pathway of their degradation by hydrolysis is known, and their efficacy has been proven. Other molecules under development will soon be available in the fabric softener area; in Chapter 1, we mentioned tertiary amido amines, quaternary dialkylamidoamines, and dialkyl imidazolinester. Raw materials containing one or several nitrogen atoms will be used less frequently because of the potential problem posed by the formation of nitrosamines.

Builders. Phosphates. In developed countries, the use of phosphates has decreased steadily, and will now remain stable for some time until an ideal builder has been found. They have been replaced by ecologically more acceptable zeolites, which require the presence of a polycarboxylate cobuilder. In developing countries, phosphates will be used for several decades to come because of their multifunctional performance and their cost; this will also be true in countries in which water is soft and there are no eutrophication problems.

Zeolites. A period of stability or even reduction in consumption is likely. There has been time for reflection, and some experts are beginning to question this raw material as a phosphate substitute. Our hypothesis is also based on the fact that suppliers and manufacturers are working hard to find an ideal builder that performs well, is biodegradable, and not expensive.

Layered silicates. We have discussed soluble builders, including layered silicates. These are already being used in some products and will develop significantly in years ahead. We hope that others will become available in the near future.

Heavy metal complexants. In the area of complexants, new, more biodegradable molecules will take over from products such as the rapidly disappearing EDTA. We gave examples of biodegradable complexants in Chapter 1, e.g., methylglycine diacetate (MGDA) and ethylenediamine mono- and disuccinate (EDMS and EDDS).

Bleaching agents. The perborate/TAED combination still has a good future as the basic system for laundry powders and for automatic dishwashing detergents. However, pressures may build up against the levels of boron in drinking water, in which case the use of percarbonate could develop strongly.

The trend toward lower wash temperatures will continue in the decades ahead, requiring more effective ingredients such as biodegradable activators; these would be catalysts for dishwashing and/or laundering, provided the new molecules do not damage the wash, as well as other peracids (e.g., PAP) whose stability and biodegradability mechanisms are beginning to be understood. New molecules are therefore expected in this area.

Polymers. Polymers used as cobuilders will reduce the levels of builder or complexing agent used in formulations. Their use will grow, but their biodegradability will need to be a subject of further research. As we have seen, research is promising, and we believe that products will be on the market in the near future. In Chapter 2, we pointed out two promising copolymers, i.e., polyacetals and poly-L-aspartic acid. Other polymers will also be developed with soil release, dye transfer inhibition, and antiredeposition functionality. These will help in formulating concentrated liquids (detergents and softeners) and in the deposition of softening agents and perfumes. While these new molecules are being developed, the current use of polycarboxylates and acrylic/maleic acid copolymers will continue.

Enzymes. As discussed in Chapter 2 on enzymes, these are the real ingredients of the future, for the following reasons:

(i) they are effective at low incorporation levels, which is very significant for concentrated products;

(ii) they are the ideal raw material in relation to the environment;

(iii) with proper precautions, they can be handled without risk;

(iii) biotechnology research and genetic engineering will make it possible to "manufacture" enzyme types with the precise performance features required, such as enzymes effective in specific stains (e.g., oxidizable stains that are currently removed by bleaching). They include oxidase, hydrolase, peroxidase, and pectinase, as well as enzymes that work under difficult conditions of low temperatures, high or low pH, shorter action times, or lower surfactant levels.

Fluorescent whitening agents. Given the consumer demand for whiteness and brightness, it will be difficult to do without flourescent whitening agents, but new molecules will need to be biodegradable.

Perfumes. In this subjective area, the need will remain for perfumes that are pleasant, and signal cleanness and efficacy. Sophistication, which is already quite

apparent, will increase in the years ahead with a move toward luxury perfumery notes. Developments will also take place in terms of safety and respect for the environment, with the example already given in the removal of musk xylene. Levels of other nonbiodegradable molecules will have to be reduced by 10% in line with the AISE agreements.

Other ingredients. In general, research and development will be oriented toward multifunctional raw materials such as percarbonate or layered silicates. Solvents that are unsafe or that present a risk to the environment no longer will be used, and less noxious solvents, such as short alkyl chain amphiphilic molecules or essential oils, will be adopted. Finally, it should be noted that animal testing already reduced considerably, could be eliminated if *in vitro* testing can be validated as a realistic replacement.

Products. In the short-to-medium term, two main areas of development for laundry detergents will be *greater concentration* and *"complete"* liquids. We will examine these in turn.

Greater concentration is recommended as consumers learn to manage the cost/performance aspects. We have already mentioned that concentrates have not met with the anticipated level of success. Their market shares seem to be stagnating or even falling, which shows how much will have to be done to encourage their use. The return to conventional powders is not simply a French phenomenon, but is also apparent in the rest of Europe. If this trend continues, it would be a step backward, and solutions such as the following would have to be found:

1. Use the concentration concept in other forms. Tablets are making their appearance for laundering. In Europe this is perhaps one of the solutions for the future, if tablets will meet with the same level of success as they have in machine dishwashing (>50% of the market). According to recent statistics, laundry tablets reached an 8% share in July 1998 and should reach 20% by the year 2000. It is hoped that researchers will find other forms of concentration that are more acceptable than current concentrated powders.
2. To find a compromise between the existing concentrated and conventional powders. One such compromise (which is purely the author's opinion) would be to remove everything from the formulation that is not functional, particularly water and sodium sulfate, which sometimes account for as much as 15–20% of the formulation. To avoid the problems of overdosing, density should not be pushed too far; if density is too high, consumers tend to overdose for fear of not obtaining a good result. In this case, a conventional powder weighing 4 kg could replace one weighing 5 kg (recently reduced to 4.5 kg after the agreement between AISE and the EC), thereby reducing cost without affecting performance.

Complete liquids, with bleaching systems, should totally satisfy the segment of loyal users who like the convenience and ease of dosing liquids.

In the machine dishwashing area, predosed products will continue to progress. New developments will move toward greater simplification (the use of three products to wash, rinse, and soften water is a nuisance for many consumers). In personal care,

product form probably will not change significantly (unlike packaging), but the products will become more sophisticated and provide better skin care. Hard surface cleaning will not be revolutionized, but there may be greater specialization by type of surface to be cleaned.

Our Profession

In writing this book, I wanted to give interested readers an idea of the different aspects of the detergent industry in its broadest sense. Some parts are probably a little dry because of their content, and it is difficult to write about molecules and process while using the language of Balzac—the reader's forgiveness is requested. I use this conclusion to remind the reader once again of some of the principles that are the basis of our skill. I use the word "skill" in the noblest sense of the word, a job well done, with the image in our minds of the master soapmakers who, only a few years ago, were still judging the quality of their product by appearance—and by taste!

Our job, therefore, is not simply to produce household detergents. The first priority is to satisfy consumer needs, to meet these needs with quality products, which are efficient, safe to use, and without danger to our environment. Our mission is also to enable as many people as possible to have access to a decent level of hygiene, and it is clear that we, the detergent manufacturers, have a role to play in the public health of underdeveloped countries.

To conclude, I would like to borrow some sentences from Ned Rival's chapter in *L'Histoire Anecdotique de la Propreté* (*Anecdotal History of Cleanliness*), in which he states:

> If the progress made in laundering and personal care since the end of the 19th century is not the only factor in the improvement of living standards, it has certainly made a significant contribution. Medical and surgical progress, biology, the organization of health services, better education, more varied and balanced diets, and so many other aspects of our civilization that we tend to underestimate, have played a determining role. In *Cleanliness and the Health Revolution* (New York, 1983), Dr. V.W. Greene, professor of environmental health and microbiology at the University of Minnesota, cited a study conducted in more than 120 countries which clearly showed a direct relationship between soap and detergent consumption in a country and its rate of infant mortality. In Afghanistan, . . . the population consumed 0.6 kg of soap per inhabitant in 1978, and the rate of infant mortality was 18%. By comparison, we should emphasize that the rate of infant mortality in developed countries is <2%, and the consumption of soaps and detergents is generally >10 or even 20 kg per inhabitant per year.

"Health and hygiene: a silent victory" was the last sentence of Ned Rival's chapter—to which I would like to add, "So, what could be a more satisfying job?"

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