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Fabric Softeners

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I. INTRODUCTION

Fabric softness refers to a pleasant feel when using garments, which is maintained by regularly treating the laundry with appropriate products. Fabric softeners, however, deliver much more than a soft, fluffy, luxurious feel to most fabrics. They reduce the static cling and electric shock generated by static electricity buildup. They decrease fabric wrinkling and make ironing easier and drying time shorter. They reduce fiber damage. Moreover, due to their fragrance, they impart a pleasant smell to the washed fabric. They may also deliver various actives such as soil release agents, whitening agents, and antiwrinkle agents to the fabric.

After considering the justification for fabric softeners, the origins of the need and benefits delivered, this chapter reviews the technology of these products — chemistry and process — and the physical chemistry of fabric softening.

II. HISTORY

A. Origin of the Need for Fabric Softening

Textiles in contact with the skin must have a pleasant feel. Since natural fibers are harsh, textile manufacturers coat them with a finish. Before World War II, natural oils and fats were used as fiber finishes. Garments were essentially washed by hand and dried outdoors. Domestic washing was carried out with laundry soap, which, in hard water, forms insoluble lime soap that deposits on and softens fabrics.

The revolution in laundering started in the late 1940s. Because of the raw material shortage, many sulfonated oil substitutes were developed during World War II and the subsequent growth of the petrochemical industry made them available at a reasonable price. They were more compatible with acidity and with water hardness than soap; they were also more efficient in removing fatty soils. Hence, from the early 1950s soap was gradually replaced by the much more efficient but aggressive alkaline built detergents. These synthetic detergents were based on alkylbenzenesulfonates and builders such as phosphates, carbonates, or citrates to prevent the deposition of the insoluble alkaline earth salts of surfactants.

At the same time, fabrics were no longer hand-washed, but laundered in washing machines, undergoing hot washing and strong mechanical agitation. These new conditions were so efficient that they gradually washed out the finish and all natural lubricants from the surface of the fibers without leaving any beneficial residues.

Moreover, the strong mechanical stress degrades the individual fibers and makes them less flexible. Because of the higher washing temperatures, fabrics shrink and become more wrinkled.

The situation was not as bad in the U.S., where washers were much larger and wash cycles shorter. Loads, however, contained more and more synthetic fibers that

must have the same feel as natural ones. Also, electrical tumble dryers were — and still are — more popular. They impart a perceivable softness to garments, but at the end of tumble drying the items cling together because of the static electricity generated in the dryer. Hence a need arose for static control.

Coating the fibers with a greasy material counteracts the damage generated by the more aggressive washing conditions. The coating may be applied to the garments during the rinse, during the drying, or now even during the wash. Best softness results are obtained by introducing the softener during the last rinse. Since the product then undergoes a huge dilution, the actives must exhibit a large affinity for the substrate (the affinity is defined as the partition coefficient between fabric and liquor). Therefore most fabric softeners were based on cationic surfactants, which exhibit an outstanding affinity for fabrics. Moreover they are extremely efficient in neutralizing static electricity.

B. Pioneering Companies and Products

Cationic surfactants appeared on the market in 1933. They were originally used as dye leveling agents in the textile industry, to improve the water fastness of direct and acid dyes on cellulose [1–3]. Some of the first cationic actives were synthesized by Ciba (Switzerland) and commercialized as Sapamines [1]. Very quickly, the soft feel delivered by long-chain derivatives was noticed and exploited to restore the fabric finish.

In the late 1940s cationic surfactants were widely used as finishing agents in commercial laundries. The multifarious benefits they delivered — improvement in feel, pleasant scent, and static control — attracted much interest for developing a new line of household products. The first cationic-based liquid rinse products for domestic use appeared in local markets in the U.S. in 1955, and were nationally launched in 1957 [4].

The first European product was launched in Germany in 1963 [2,4], which quickly became the largest market outside the U.S. [1].

From the beginning, the history of fabric softeners has been driven by innovation, by the producers' voluntary commitment to propose more efficient or convenient products delivering additional benefits, by technical changes in the production processes and appliance technologies, and also by legal constraints.

The first products were made of 4 to 6% active, a fragrance, and a viscosity modifier [5]. The dispersions of cationic actives indeed remain easily pourable as far as their concentration does not exceed 7% by weight; since the softening efficacy levels off at concentrations above 6%, this was not a concern. In the mid-1970s improved softening systems made of two actives appeared on the market. They were still based on the same quaternaries, but synergistically combined with other fatty materials called “co-softeners” to enhance their performance/cost ratio.

A new era started for brand relaunches, which had been until then limited to claiming new perfumes [6]. The development of products based on these double-active systems led to true product improvements and opened the door to the formulation of concentrated products. The first concentrates were introduced in the German market in 1979. Five years later, they were available in most other European countries and in North America. They contained about three times the usual level of softening actives and were usually positioned as extensions of the traditional brands.

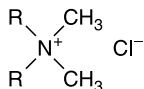
The incentive to the launch of concentrates was threefold: convenience, cost, and subsequently environmental profile [7,8]. Being less bulky, they are indeed much more easily handled than the large bottles in which regular softeners are usually sold. They also enable a greater plant throughput with existing equipment and require less shelf space in each stage between production and retail outlet and in the washing area — a true advantage in the home. They lead to a reduction in shipping costs since less water is transported. Finally, they contribute to the reduction of plastic bottle waste in the environment. A serious drawback is that they are more difficult to dose correctly. Because of consumers' sensitivity to cost per unit volume of fabric softeners, they never became very popular in many countries such as those of southern Europe.

The 1980s were rich in innovation. As cationic actives precipitate in the presence of anionic surfactants, thereby losing most of their efficacy, the anionic surfactant concentration in the liquor must be kept as low as possible. Therefore, the fabric softener had to be introduced in the last rinse of the wash cycle, when the detergent carryover is at a minimum. That represented a true constraint if the washer did not contain a dispenser for softener. The user had to stay near the washer to introduce the product at the beginning of the last rinse or had to run an extra rinse at the end of the laundering.

Many efforts have been devoted to overcome the technical difficulties, leading to several alternative systems: dryer cycle fabric softeners, which appeared on the shelves in the 1970s [9], wash cycle fabric softeners, and finally detergents containing the fabric softener or "softergents." Effective fabric softening in the wash cycle, however, supposes using alternative cleaning and/or softening actives. Each system presents advantages and shortcomings over the others; they are discussed below.

The next milestone in fabric softener history was the reconsideration of the use of di-hard tallow dimethylammonium chloride (DHTDMAC) as one of the most prominent softening ingredients. A dialogue took place between Dutch and German authorities with the industry. This dialogue focused on the existence of environmental data on DHTDMAC, covering the information available on aquatic toxicity and biodegradability. These contacts allowed identification of the much more cleavable esterquat that the industry selected to rebuild its softener compositions. By 1993, DHTDMAC consumption in Europe fell by 70%. In the U.S.,

where its environmental profile had not been questioned, the reduction was only 20% [5,6,10].



Di-hard tallow dimethylammonium chloride (DHTDMAC), where R is a hydrogenated tallow alkyl (C₁₆/C₁₈ chain).

The replacement of DHTDMAC by esterquat in fabric softening compositions represented a turning point. Before then, only two actives accounted for 95% of the cationic softeners in use. Since then, every manufacturer has had its own active ingredient [11,12].

Innovation in the fabric softener business not only focused on compositions, but also on packaging. As an alternative to plastic bottles, heat-sealed flexible polyethylene pouches were introduced to the market in the early 1980s [7], followed by several other containers: free-standing flexible pouches with a solid base, different “bag in a box” rigid units, and refill cartons coated with chemically resistant polymers. These novelties led to a 40% reduction in plastic bottle consumption, the use of more biodegradable, renewable, easily recycled material, and a decrease in the packaging and distribution cost. New bottles made of 100% “post consumer recycled” plastic sandwiched between two layers of virgin resin also became available [7].

Short Historical Survey of Companies and Brands

In the late 1940s Hagge and Quaedvlieg patented DHTDMAC for imparting a soft feel and increased durability to cotton (DP902610 cited in [13]). The claim relied on fabric abrasion measurements. Ten years later, Harshaw Chemical, a raw material supplier, launched the first household fabric softener [1]; the company needed several years to invest in handling hot raw materials and succeed in getting satisfactory dispersions. Later, it sold the formulation to the Corn Products Company [1], which launched the product nationally under the trade name Nu-Soft in 1957 [4]. Afterwards, A.E. Staley introduced Sta-Puf and Procter & Gamble Downy. Eventually, the major detergent companies dominated the market. Within six years, domestic fabric conditioners represented a \$30 million market, and \$300 million market six years later [1].

In the 1960s brands such as Comfort (Lever), Soupline (Colgate-Palmolive), Lenor (Procter & Gamble), Silan (Henkel), and Orincil (Nobel Bozel) were launched in Europe, and Humming (Kao) in Japan [7]. All these systems were 3 to 8 wt% aqueous dispersions of cationic softener active. They mainly differed

in the level of active and in their presentation (color, perfume, etc.). They delivered from 1.0 to 2.5 g of softener solids per kg of dry fabric [3].

In 1972 S.C. Johnson & Son, Inc. launched Rain Barrel in the U.S. [1]. This quaternary-based wash cycle fabric softener was intended for use with the consumer's choice of detergent. Because of their poor performance/cost ratio, this type of product never became very popular.

In the early 1980s two-in-one detergent softener compositions such as Bold 3, Axion 2, and Dynamo 2 were on sale on the European market. Fab Total, the latest generation, was still available in Latin America a few years ago.

The first dryer-added system appeared on the market in 1976 [14]. Brands such as Cling Free, Bounce, Snuggle, Sta-Puf, and Toss'nSoft sheets quickly represented 40% of the U.S. fabric softener market [7].

Among liquid products sold in polyethylene pouches, Add-Soft (Colgate-Palmolive) quickly gained 50% market share in Australia and Minidou (Lesieur-Cotelle) 65% in France [7].

C. Consumer and Producer Needs and Expectations

Defining consumer needs is not an easy task. Developing compositions that meet their expectations while fulfilling the safety and environmental requirements is even more challenging!

Fabric softeners are the most cosmetic of the household products. For consumers, their benefits are functional and emotional. Both types of attributes justify their use.

The softener performance perceived by consumers is the balance between the absolute efficacy determined in the laboratory and the product aesthetics. In other words, the consumer perception of the product performance is heavily influenced by aesthetic attributes such as fragrance and viscosity. Consumer tests indeed show that perfume, and more precisely perfume substantivity* on fabrics, is the main reason for preferring one product among several delivering the same softness. Consumers appreciate both the odor of the product itself, which generates the appeal and causes the purchase intent, and the smell of the laundered fabrics, which settles the repurchase intent.

Among the aesthetic attributes, viscosity also deserves special mention. The final viscosity of a rinse cycle fabric softener is indeed critical for the perception of product performance. Thick usually means rich in the consumer's mind. Thickness also affects the performance. Too thick a product is indeed not easily poured from the bottle and may disperse badly in the rinse, leaving residues in the dispenser of

*The substantivity may be defined as the tendency to adsorb onto the surface of various materials; it is measured by the proportion of product introduced in the rinse that is still present on the laundry after drying.

the washer; its efficacy will be altered. If, in contrast, the product does not exhibit enough consistency, it is also difficult to handle and to dose; it will be perceived as a poor performer and not economical to use. Cook [15] even considers the product appearance as the most attractive characteristics to consumers; afterward comes the feel and the touch, and eventually the absence of unpleasant odor.

Consumer expectations vary over time. In 1973 it was admitted that fabric softeners must fulfill the following functional requirements [15]:

1. They must keep white fabrics bright and should not cause dulling, yellowing, or graying.
2. They must not alter the shade of colored fabrics.
3. They should not impair the fabric affinity for water.
4. They should not induce corrosion of metal equipment.
5. They should not induce rash or dermatitis when in contact with human skin.

Nowadays, consumers ask for highly convenient products with the best price/performance ratio. Major functional benefits of fabric softeners are [10,16]:

1. To deliver a pleasant feel (softness) and smell.
2. To control the static electricity that impairs the comfort of handling and wearing clothes when ambient humidity is low.
3. To exhibit strong fabric care properties (fiber protection, looks new longer).
4. To make ironing easier.

Besides varying over time, the relative importance of the various functional benefits also varies with geographical location. They are not the same everywhere in the world, depending on washing habits and procedures. They are also linked to cultural, psychological, climatic, and lifestyle-related factors. For instance, laundering is fully automated in developed countries while washing by hand is still very popular in emerging markets; tumble drying is frequent in North America, while line drying is more common in the rest of the world.

It is admitted everywhere that the most important roles of fabric softeners are delivering softness and perfume. However, the next most important expectation varies from region to region: ease of ironing in Europe and Latin America, antistatic properties in North America and Asia.

The care aspects, fiber care and color care (and stain guard in Latin America), are much the same everywhere. Other benefits, closer to personal care attributes, are more specific to regions: long-lasting freshness and deodorization in Europe and North America, clean freshness in Asia and antibacterial activity in Latin America; skin mildness in Europe and Asia, luxury/comfort in Europe, and antimildew in Asia [16].

The major emotional benefits are pleasure, sense of task accomplishment, and caring for loved ones. These emotional attributes are generally reinforced through the product aesthetics, the package labels, and the advertising.

As expected, the relative importance of emotional benefits also varies from one region to another. Environmental considerations are essential in Europe (and increasingly in the rest of the world), and ease of use and price/performance ratio prevail in the U.S. The attitude is functional and technology-driven in Asia and emotional in Latin America. In all regions, using a fabric softener means to display personal commitment to laundering because of the importance of personal hygiene and the social image of clean, fresh-smelling clothes [16]. This is why the right choice of color, fragrance, and even texture to fit the product concept is so important and may markedly vary from region to region. The acceptability of a possible candidate must consequently be confirmed through different consumer tests in the countries of launch.

Fabric softener manufacturers also have specific needs:

1. Active molecules must be polyvalent because of the great variety of fibers and use conditions.
2. The fulfillment of the various requirements.
3. The availability of the technologies.

To be selected, a softening active must consequently fulfill the following conditions [5,17–19]:

1. It must be effective, delivering a pleasant touch to textiles without imparting a greasy feel or impairing their rewetting properties. It cannot alter the fabric color and must exhibit an antistatic efficacy. It should also deliver new consumer-perceivable benefits, if possible.
2. It must allow the formulation of stable, regular or concentrate finished products, with easy viscosity control. The finished products must be readily dispersible in water and deposit immediately when in contact with the washed fabrics, to get a uniform deposition within the short rinse cycle duration.
3. It must be chemically stable to avoid loss of performance on storage and any generation of undesirable odor or color.
4. It must be industrially available at the right quantity and quality, with an acceptable ecological and toxicological profile. In Europe, a valuable candidate must also satisfy the directives of the European Union (formerly European Community, EC).
5. It must exhibit a better cost/performance ratio than existing actives; manufacturers are indeed facing severe cost constraints.

No active offers all the characteristics of an ideal ingredient.

III. BENEFITS AND DRAWBACKS

The importance of softeners in fiber treatment has long been recognized. They were routinely used in the textile industry for the lubricity and flexibility they

impart to yarns, protecting them from damage during textile processing. They also impart a pleasant touch that enhances the consumer desire for a textile item.

From a consumer standpoint, fabric softeners deliver multifarious benefits. They may also present some side effects.

A. Benefits

1. Basic Benefits

(a) *Softness.* Softness has been defined by Mallinson (quoted by Datyner [20]) as an alteration in feel making the item more pleasant to the hand. In other words, it is a pleasant feel perceived when the fabric is in contact with the skin. Fabric softeners prevent textile stiffening, usually observed after a wash with a detergent in a washer, and keep the garments in the state wanted by the user.

The improvement of the fabric feel and comfort is particularly noticeable on cotton items, but softeners' beneficial effects are also perceived on other fabrics such as wool, viscose, acetate, polyamide, and polyester.

(b) *Antistatic.* Cellulosic fibers such as cotton and viscose do not develop static charges under normal relative humidity. The situation is quite different for synthetic fibers at low ambient relative humidity such as that encountered in winter months or when an automatic tumble dryer has been used. The well-known static cling takes place upon tumble drying and an electric shock may even occur when removing the items from the dryer. In areas with a dry climate, friction can also generate electricity upon wearing garments, causing synthetic fibers to stick to the skin and to attract charged dirt present in the air.

These effects were very unpleasant to consumers, and the problem became more acute as synthetic fibers became more popular. Much more serious are the fire and explosion hazards created by static charge if clothes produce electric sparks in an atmosphere of a flammable solvent.

These inconveniences are overcome using a fabric softener.

(c) *Perfume.* It is commonly believed among softener manufacturers that many users purchase the product only for its fragrance. Whether this is true or not, the product scent is certainly one of its key characteristics since a pleasant fragrance is the first signal of the softener efficacy. It differentiates fabric softeners from one another and sustains the claims for new products (e.g., effectiveness, freshness, more softness, new and improved). Perfume suppliers even claim that the differentiation resulting from the incorporation of a higher quality — hence more expensive — fragrance is enough to provide larger market shares [21]!

Considerable time, effort, and money are devoted to the development of a softener fragrance. Fabric softeners must be nicely perfumed in the bottle, and impart a typical and pleasant smell to the laundry that is immediately and repeatedly perceived by the user at various stages of the laundering process. These include when pouring the softener into the washing machine, when removing wet

laundry from the washing machine, when removing dry laundry from the line or from the dryer, when folding or ironing the clothes, and when using them. That is achieved by carefully designing the perfume composition.

2. Additional Benefits

(a) *Smoothness and Easier Ironing.* Hot ironing is usually necessary to remove the wrinkles from pure cotton garments. Fabric softeners improve the ease and efficiency of the ironing process. Their actives work as lubricants and favor fiber slipperiness. As a result, the garments are less wrinkled and the friction between the fabrics and the iron is reduced, thereby facilitating gliding of the iron. A 10 to 20% reduction of the time necessary for ironing may be achieved [13,22], which is especially meaningful in industrial laundries.

Benefits such as ease of ironing and wrinkle reduction are, however, less easily perceived by consumers.

Recently a new family of fabric care products appeared on the market. Called fabric conditioners, they are actually fabric softeners with enhanced antiwrinkle properties. By facilitating the ease of ironing, they address the basic consumer need of spending less time in one of the most tedious household chores. One of these products moreover exhibits completely different aesthetics from traditional fabric softeners, drawing attention to its specificity.

Compared to usual fabric softeners, the improvement delivered by fabric conditioners is not clearly consumer-perceivable. Consumers want more: no ironing at all. As a result, their market share remains low.

(b) *Drying Time.* Because of the hydrophobicity of their actives, softeners make fibers to bind less water; moreover, softened fabrics retain water less firmly. The extent of the effect varies. Bräuer *et al.* report about 10% less water linked to the fibers [23]; the spinning time is consequently reduced by 40% [22]. Lang and Berenbold report a 7 to 15% [24] or even a 15 to 20% [13] decrease of residual humidity after final spinning of the fabric. The drying time in tumble dryers is also decreased [11,18,24–26]. Barth *et al.* find that the effect remains marginal [4] while Berenbold reports an about 14% cut of the drying time [11], leading to a 12% reduction of the energy consumption [24].

Paradoxically, softener-treated cotton also exhibits an improved permeability to water vapor, leading to an improved comfort in wear.

(c) *Fiber Protection.* In the washer and dryer, and during wear, fabrics undergo severe mechanical and chemical constraints that can damage the fibers. Fabric softeners replace the finish removed by the detergent and lubricate the fibers, reducing the interfiber friction. This results in a reduction of the fiber damage [3,11]. Although the protection only takes place when the garments are dried and worn, not in the wash, fabric softeners increase their life span. Clothes look better and newer after repeated launderings [27]. Fiber damage reduction is illustrated in Figure 12.1.

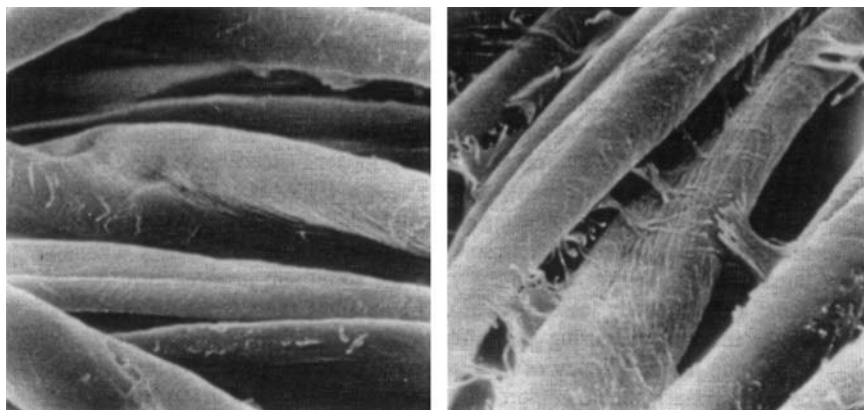


FIG. 12.1 Fiber damage reduction by fabric softeners. These electron micrographs are of cotton bath towels after 12 cumulative wash cycles with fabric softener (left) and without fabric softener (right).

(d) *Antibacterial Activity.* Because of the trend for lower washing temperatures, the microbial threat becomes increasingly probable. Bacteria and fungi are detrimental since they degrade textiles, produce malodors, and generate skin irritation or infection [20].

Domagk [28] first reported the bacteriostatic activity of cationic surfactants in 1935. As most fabric softener compositions are based on cationic actives, it sounds logical to expect some biological protection from these products. Not all authors, however, agree on their exact efficacy. According to Martins *et al.* [29] and White [30], they are antibacterial agents. Laughlin speaks about a germicidal effect [26] and Milwidsky considers them as moderately good bacteriostats [18]. Chalmers stresses the fatty chain length effect: a bactericidal activity is observed for a C_{12}/C_{14} chain length, longer chains exhibiting bacteriostatic properties only [1]. In contrast, Barth *et al.* report that cationic surfactants used as fabric softeners do not exhibit any antibacterial activity [4].

These differences are possibly due to variations in the experimental conditions of the various studies (e.g., ionic strength). Nevertheless, the antibacterial efficacy of softener actives under normal use conditions remains questionable.

B. Damage

Fabric softeners are safe for all washable fabrics. Some side effects are, however, possible in the case of misuse. For instance, pouring the softener directly onto garments may cause fabric staining while strongly overdosing the product may lead to a greasy feel and reduced affinity for water and/or to color alteration [15,31].

1. Color Alteration

By color alteration is meant graying or yellowing of whites, and hue alteration or color fading of dyed items. These problems have their origin in various phenomena:

1. Cationic actives interact with anionic fluorescent brighteners and reduce their whitening efficacy [2,26]. Whether this is visually perceptible or not varies among reports. Crutcher *et al.* [32] and Wilson [33] conclude that, after a larger number of cumulative launderings, the loss is visually perceptible. On the contrary, Baumert and Cox Crews report that the decrease of whiteness index is significant, but not visually perceptible [34].
2. Cationic surfactants cause deposition of detergent residues loaded with soil, which are present in the liquor because of incomplete rinsing [1]. Some alteration of the fabric appearance may occur even in the absence of softener. Some soil redeposition on clothes may indeed take place in the wash, resulting in lightly soiled whites turning gray or yellowish and colors to become dull [35].
3. Colored impurities such as iron, nickel, cobalt, or copper salts are present in the rinse liquor [1].

The whiteness index of softened fabrics depends on the fabric softener treatment, on the number of launderings, and on the fabric type. Dryer softeners significantly improve the whiteness index of cotton [34].

2. Hydrophobicity

(a) *Wettability.* The intrinsic affinity of fibers for water depends on their chemical nature. The absorption capacity of a given amount of hydrophilic fibers such as cotton is much larger than that of the same amount of hydrophobic fibers such as polyester. Adsorbing chemicals such as surfactants may modify that characteristic. For instance, softeners make hydrophilic fibers more hydrophobic. Hence, it is not surprising that they reduce the wettability upon use. The effect is stronger with mixed fabrics than with plain cotton [24]. This characteristic is important, as softened textiles must absorb the humidity of the skin with which they are in contact. That is a true drawback in the case of terry towels that may exhibit less wiping efficacy. In fact, it is the water absorption rate that is impaired by the presence of softener at the fiber surface, with the absorption capacity remaining unaffected [1,36].

This problem can be avoided by limiting the amount of softener in the rinse. Because of the softener buildup with time, an increase of the cationic concentration at the fiber surface is nevertheless unavoidable. At the levels used under practical conditions, no difference exists between treated and nontreated garments.

As already mentioned, softener-treated cotton items exhibit enhanced permeability to water vapor. That paradoxical effect is due to the reduction of the water

content inside the fibers. Since they swell less, the fabric is more permeable to vapor [13]. This effect decreases as the amount of softener on the fibers increases.

(b) *Greasy Feel.* Since fabric softeners are made of greasy material, it is not surprising that fabrics treated with an excess of fabric softener exhibit a greasy touch.

3. Compatibility with Anionic Surfactants and Dyes

Cationic surfactants are incompatible with anionic surfactants. They are precipitated by various ingredients that can be present in a wash or rinse liquor, such as bentonite, TiO_2 , starch, and phosphates.

4. Flameproof Treatment

It is often said that cationic softeners should not to be used on baby clothes. This is because of a possible negative effect on the flameproof treatment.

IV. FABRIC SOFTENER MARKET

The most important markets for fabric softeners are Europe, the U.S., and Japan. In all three the in-home penetration is high ($>60\%$) and also the consumption (17 l/household/year) [16]. In 1997 the worldwide fabric softener market accounted for \$3.5 billion (\$1.1 billion in the U.S.).

Many authors (e.g., [14]) explain the growth of the softener market by the evolution of the type of fabrics in laundering. Natural fibers must be softened and static electricity must be countered on synthetic fibers. On top of these criteria, the evolution of consumer needs and expectations discussed above has had major consequences for the evolution of the softener market. Effective cleaning is a must, fabric softening a pleasure.

The factors influencing the appearance of new products have changed over time [7] and with region:

1. Prior to the 1980s, the prevalent parameters were the identification of the need, of a population with a discretionary income, and of a cost-effective distribution and sale.
2. From 1984, the development driver has been improved consumer convenience. It led to the appearance of concentrates.
3. From 1988, environmental considerations have taken precedence, causing the reformulation of European fabric softeners.
4. Today, building profitable market shares faces low penetration/low net income in high-growth markets and severe competition in developed markets. The major trend is a growth in low-cost packaging, with low-cost bottles and refills in developed markets and low-cost bottles and unit dose sachets in high-growth markets [16].

Several examples illustrate the key role of some parameters on the success of products exhibiting objective advantages. In the early 1980s Germany was the leading fabric softener market in Europe. Consumption reached a maximum in 1983. From 1985, the public debate on the relative benefit delivered by rinse cycle fabric softeners relative to the water pollution that they allegedly caused led to a steady fall in consumption. From 1988, stagnation was also observed in other “green” European countries such as The Netherlands, Denmark, Austria, and Switzerland [11].

Concentrated products lead to a reduction of plastic waste and distribution costs. They enable space savings on the shelves at the point of sale and at home. Their success, however, varies strongly from country to country: introduced in Germany in 1980 [14], they represented 95% of the German rinse cycle fabric softener market in 1994 and only 10% of the Spanish and Italian ones [21]. In France and the U.K. they are at parity with regular products [5]. Likewise, they appeared on the Japanese market in 1988 and represented 50% of sales six years after [5]. On the contrary, in emerging countries, regular products still remain the most popular, as consumers feel they get more for their money.

Of course, differences of penetration are also linked to objective parameters. For instance, electrical tumble dryers have always been more common in North America than anywhere else in the world. In 1983, 65% of U.S. households owned a dryer, the proportion being only 10% in Europe [14]. In 1994 the figures were 75% in the U.S. and 20% in Germany [11]. Today, the proportions are 70 to 80% in the U.S., 21% in Western Europe, only about 15% in Japan, and still less in other parts of the world [3].

Because of the static electricity imparted to synthetic fabrics by tumble drying, and the increasing proportion of synthetic fabrics in the U.S., the sales of dryer-sheet fabric softener rose much more in the U.S. than in the rest of the world. By 1983, these products accounted for 40% of all household fabric softener sales. Today, tumble dryer sheets and liquid softener sales are of the same order of magnitude [5,6,16]. In contrast, rinse-added softeners had a much larger impact in Europe, where 100% cotton items have always been dominant and line drying is still standard practice; hence, the softener effect is more noticeable to consumers.

V. COMPOSITIONS

Fabric softener compositions have been regularly modified, as a result of variations in the performance needs, in the expected secondary benefits, and in regulations. They have always been fascinating and challenging products, as they must be stable in the bottle and destabilize upon dilution to deposit onto fabrics during the rinse. This is achieved by carefully choosing the ingredients.

A. Softening Ingredients

Fabric softener actives can be classified into three groups: organic, inorganic, and silicones. To the organic class belong cationic surfactants, lime soaps, and oils. Cationic surfactants are by far the most frequently used. They are found in wash, rinse, and dryer softeners. Montmorillonite clay is the main inorganic softener and is essentially used in softergents. Silicones are much less common and are generally used as a minor component in combination with organic softeners.

To be worth considering, a fabric softener candidate must fulfill several requirements, which have been reviewed above.

1. Organic Actives

(a) *Cationic Surfactants.* For 40 years most rinse cycle fabric softeners have been built from cationic surfactants, because of their high degree of substantivity and high exhaustion rates from dilute solution. Thousands of patents exist, covering hundreds of different molecules and of mixture compositions. Only a few of them have been of practical importance.

The characteristics of each active result from the details of the molecule structure. This includes the number and length of the alkyl chain(s), degree of saturation, and presence of oxygen atoms. All products have their own strengths and weaknesses; none of the existing actives meets all criteria of quick biodegradability, low toxicity, acceptable cost, good stability, good softening, antistatic efficacy, etc. The most efficient softening molecules are the ones bearing two long alkyl chains. Straight chains are preferred to branched ones and saturated chains to unsaturated ones.

From a softening standpoint, the most efficient alkyl chain length is C₁₈. Industrial raw materials are consequently prepared from natural tallow, in which C₁₆ and C₁₈ chain lengths predominate. Tallow contains 5% C₁₄, 35% C₁₆, and 60% C₁₈ (stearic and oleic). The exact proportion of fatty chain length varies from delivery to delivery, according to the origin (beef, mutton, palm oil), on the season, and on the amount of rain [18]. These molecules are extremely substantive, impart to fabrics outstanding draping properties, and deliver excellent abrasion resistance and static control to synthetic fibers. Once on the fabrics, however, their water absorbency is less than other cationic softeners. They are also more difficult to formulate since they exhibit higher melting points, requiring higher temperatures to handle and disperse, and leading to more viscous aqueous dispersions than shorter-chain derivatives. With unsaturated fatty chains, the softening effect is somewhat reduced but the fabric is still left with a dry and very supple, flexible feel.

The usual counterions are chloride (in Europe and the U.S.) and methylsulfate (in the U.S.).

For 25 years almost all softeners were made of ammonium ion derivatives bearing two straight fatty chains. The ammonium ion makes the molecule water-dispersible, while the alkyl chains account for the tendency of molecules to deposit onto the fabrics and for the softening efficacy. Developed in the 1940s, DHTDMAC was the earliest commercial active, and the most popular one. It is commonly referred to simply as “quat.”

Many authors give details of the synthetic procedures for the manufacture of DHTDMAC [3,37,38]. It is prepared by a rather complicated process, detailed in Figure 12.2.

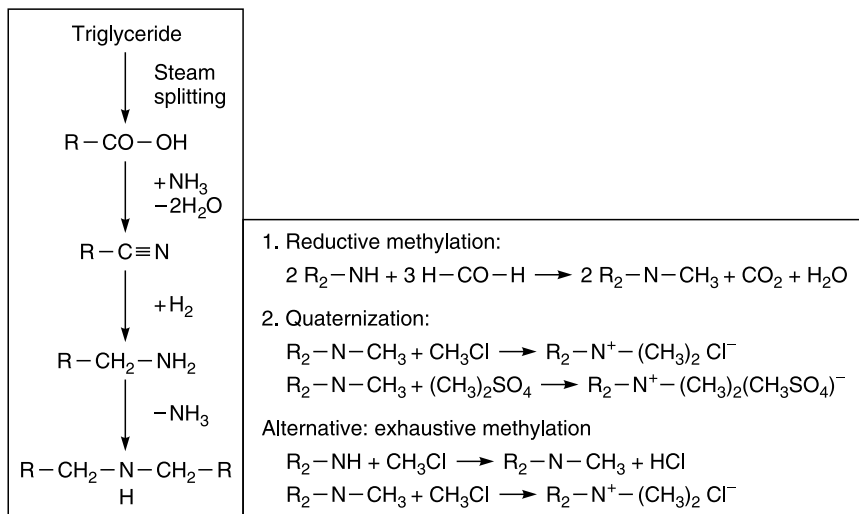
The resulting solid is crystalline. The chains are fully hydrogenated, and they do not bear any functional groups to hinder crystal formation. Pure dioctadecyldimethylammonium chloride (DODMAC) melts and decomposes at 147°C [26]. The melting temperature depends on the level of residual isopropyl alcohol in the raw material. The higher the content, the lower the melting point. This is why the raw material always contains some alcohol, usually isopropanol, sometimes ethanol in the U.S. The amount is critical since the melting point remains too high when the alcohol level is too low, and the active ingredient disperses poorly in water. Organic solvents must be maintained at a low level since, in addition to their unpleasant smell perceptible in the finished product, they interact with the hydrophobic layer of the softener particles, causing the membrane structure to disrupt and the particles to stick together [39]. Hence the active ingredient is generally diluted with 25 wt% of an alcohol–water mixture, corresponding to 15% isopropyl alcohol. As a result, DHTDMAC is commercially available as a waxy solid at room temperature, which becomes fluid at 50°C and can be easily pumped and handled at 60°C.

Although DHTDMAC fully meets all the needs and expectations criteria listed above, its use has dramatically decreased because of changes in European regulations, which led to its replacement by esterquats in the early 1990s to avoid adverse labeling. Moreover, the formulation of DHTDMAC-based concentrated softeners was not possible without the help of cosofteners. With other actives the technical constraints do not exist or are less stringent.

The chemical structure of esterquats is very versatile. The structure may vary by the alkyl chain length and saturation extent, by the mono-, di-, and triester ratio, and by the quaternization degree. It is similar to the DHTDMAC structure in that they essentially bear two hard tallow chains and an ammonium ion. However, in esterquats at least one of the fatty chains is linked to the cationic nitrogen through ester bonds. This linkage is a point of weakness making biological degradation easier and faster [40–44]. Microorganisms in sewage treatments readily cleave the ester bonds, depriving the molecule of its substantivity. As a result, the biodegradability profile is dramatically improved.

The most common esterquats in fabric softener formulation are quaternized di-tallow esters of methyltriethanolamine, dimethyldiethanolamine, or

(a)



(b)

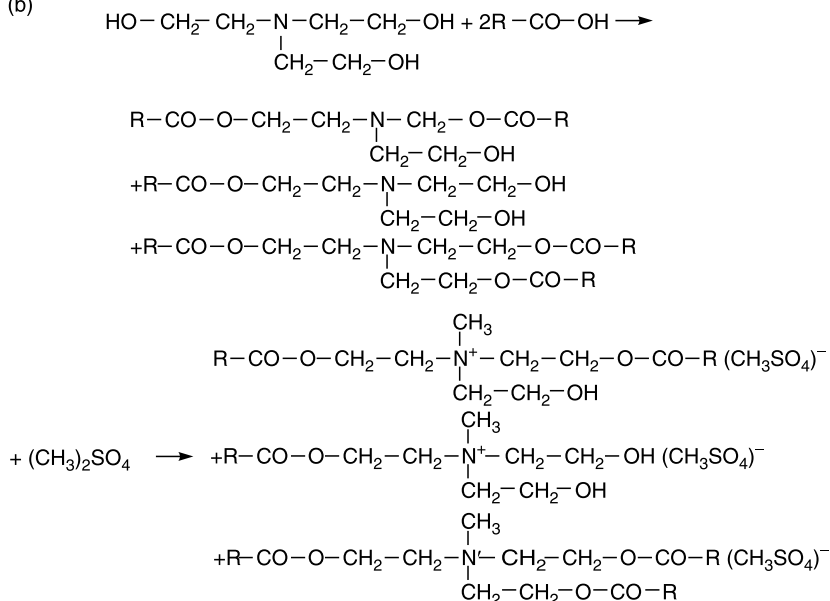
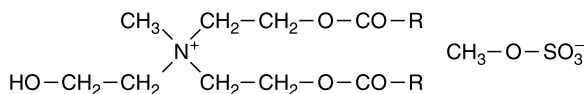
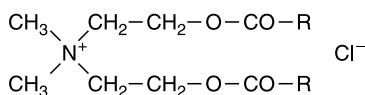


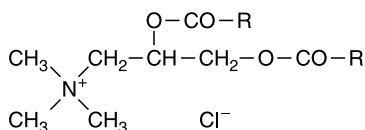
FIG. 12.2 Synthesis of softening active molecules: (a) DHTDMAC; (b) esterquat.



Ditallow ester of methyltriethanolammonium methylsulfate



Ditallow ester of dimethyldiethanolammonium chloride



Ditallow ester of trimethyldihydroxypropylammonium chloride

FIG. 12.3 Structures of the most common esterquats used in fabric softeners.

trimethyldihydroxypropylamine (Figure 12.3). Ester amidoamines are also used, mainly in Japan, and di-tallow imidazoline ester worldwide but to a lesser degree [5,16].

Esterquats molecules are not new. Alkanolamine-based molecules exhibiting a better cost performance were patented much before the environmental controversy. Patents covering esters of methyldiethanolamine were issued around 1970 by BASF and Hoechst while Stepan Company commercialized diethyloxyester dimethylammonium methylsulfate in 1974. The latter molecule exhibits an excellent softening performance but does not readily form stable dispersions. Three years later a patent disclosing the esterquat built on *N,N*-dimethyl-3-aminopropane-1,2-diol [45] was issued. This molecule appeared on the European market because of its excellent biodegradability and aquatic toxicity profiles with no compromise in softening performance [3]. The patent covering the use of triethanolamine-based esterquats as fabric softeners was also issued as early as 1975 [46]. These compounds are prepared by esterifying triethanolamine with fatty acids and quaternizing the resulting esteramines with methyl chloride or dimethylsulfate. The raw material is consequently a mixture of quaternized and nonquaternized mono-, di-, and triesteramines, whose statistical distribution is thermodynamically controlled [3]. The exact composition of the raw material in terms of esterification and quaternization degrees requires the isolation of the individual constituents by solid phase extraction and the elucidation of

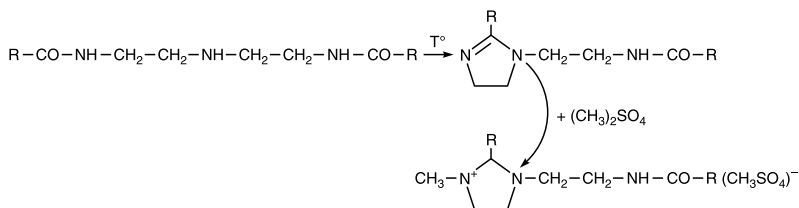
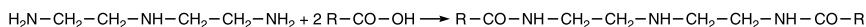


FIG. 12.4 Synthesis of DHTIMS.

their structure by ¹H-NMR [47]. Typical examples of these new molecules are *N*-methyl-*N,N*-di(2-(C₁₆/C₁₈-acyloxy)-ethyl)-*N*-(2-hydroxyethyl)ammonium methylsulfate [48], 2,3-di(C₁₆/C₁₈-acyloxy)propyltrimethylammonium chloride [49], and 2-(C₁₆/C₁₈-alkyl)-3-(C₁₆/C₁₈-acyloxy)ethylimidazoline [50].

Among the many other molecules used for fabric softening, only two have been a commercial success: imidazolinium salts and diamidoquaternary ammonium salts [26]. Imidazolinium methylsulfate (DHTIMS) has been a useful alternative to DHTDMAC in the U.S., and in Europe to a lesser extent. Both actives indeed deliver similar benefits. The counterion here is always methylsulfate.

Imidazolinium salts are also derived from diethylenetriamine. The diamidoamine that results from the esterification of this molecule is dehydrated into an imidazoline, then quaternized with dimethylsulfate, as shown in Figure 12.4 [51]. The resulting molecule is no longer susceptible to hydrolysis. Despite the low price of the material from which they derive, imidazolinium salts are expensive because of their manufacturing cost. This is due to the costly conditions necessary to convert the diamidoamine into imidazoline [3]. Details of the synthesis may be found in Egan [37] or Billenstein and Blaschke [38].

Saturated derivatives are almost as efficient as DHTDMAC for softening, but exhibit the same limitations for formulating concentrated softeners. They are mainly found on dryer-added softening sheets. If the imidazoline is dispersed in water containing enough acid to neutralize the amines, no phase separation occurs after a month of storage at room temperature. Once on the fabric, the ring is hydrolyzed during tumble drying, forming diamidoamine, which delivers more softening [3].

Fatty amides — (R-CO-NH-CH₂-CH₂)₂-N⁺(CH₃)(CH₂-CH₂-O)_{*m*}H — also require low pH (3.5 to 5.0) to be dispersed since they do not bear a permanent charge. They are the third most popular active in North America. Because of the European restrictions on using ethylene oxide derivatives, they are much less used in Europe [7]. They are easily formulated in concentrated products.

effect gets worse upon cumulative treatments. Their antistatic efficacy is usually less than that of other cationic surfactants [52].

Chloride derivatives of the quaternaries have the drawback of causing corrosion of storage tanks, manufacturing vessels, and tumble dryers when dryer cycle fabric softeners are used (see below). Moreover, these chemicals are waxy pastes and must be melted before being dispersed in water. These problems are overcome by using methylsulfate derivatives, which do not corrode stainless steel and are usually liquid at room temperature [1].

The main limitation linked to DHTDMAC is that formulating concentrates with a solid content exceeding 15% is generally not possible without using co-softeners. To exceed this concentration, amidoamine quats or imidazolines must be introduced in the system [6].

Esterquats cause fewer problems for formulating ultras and concentrates [7]. Carefully selecting structural details of the active such as the mono-, di-, and triester ratio, the presence of unsaturation on the alkyl groups and their *cis-trans* configuration, the pH value, and the particle size of the dispersion enables one to get stable, low-viscosity softeners containing 20 to 25% active [6]. Another advantage of esterquats is that they do not stain fabrics [7].

The presence of the ester function in the molecular structure facilitates rapid biodegradation in sewage but also threatens its chemical stability on storage in the bottle and in the rinse, where it has to work at a slightly alkaline pH. At pH 6, for instance, the molecule is completely degraded after four weeks of storage at 50°C [6]. Paradoxically the hydrolytic stability is much enhanced by keeping the pH below 3.5.

Since esterquats were accepted in Europe in the early 1990s because they fulfill European environmental regulations, it was on the European market that the first ultra concentrated products appeared, packaged in plastic pouches or sachets. Subsequently they spread around the world [3].

Imidazolinium salts are said not to impair the wettability of cotton when overdosed in the rinse and to control efficiently static electricity. They are more easily processed than other cationic surfactants, especially in the formulation of concentrates, but they are more expensive, less efficient from a softening standpoint, and possibly cause more yellowing [7,8,22,52,53].

If the amine is used instead of the ammonium derivative, and if the pH is kept low enough to maintain a positive charge on the nitrogen atom, the imidazolinium active becomes more efficient than DHTDMAC for softening, there is less yellowing, and the ability to be concentrated is excellent [7]. Likewise, the oleyl-substituted imidazolinium salt enables an easy formulation of concentrated products, and makes fibers less hydrophobic than its saturated counterpart [8].

Amidoamines exhibit a softening performance close to that of the unsaturated tallow-imidazolinium salts, but are less difficult to formulate in concentrated products exceeding 20% solids without using special additives [3]. They are very mild

to the skin, are more biodegradable than DHTDMAC, and they cause little or no corrosion [7]. The molecule efficacy can be fine-tuned by minor structure modifications. For instance, EO/PO variations affect the ease of formulation, the rate of deposition, the feel of the softened fabric, the static control efficacy, the affinity of treated fibers for water, and the durability of the effects. Some derivatives are expensive.

Various authors have ranked the softening actives [19,34,36,54]. They proposed the following sequence of decreasing efficacy: dialkyldimethylammonium > imidazolinium > diamido alkoxyated ammonium.

(b) Anionic and Nonionic Surfactants. The oldest anionic softeners are soap derivatives. R-SO₃ and R-O-SO₃, sulfosuccinate, and soap have been reported to exhibit some softening efficacy [52]. Their affinity to fabrics remains limited, as their hydrophobicity is moderate and fibers are negatively charged in water. Consequently, they are usually applied by padding [20,52].

Mineral oils, paraffin and other waxes, polyethylene, polyethylene glycol, ethoxylated glycerides, ethoxylated fatty amines, and esters of fatty alcohols and acids have also been used in fabric softening [52], and also nonionic actives such as glycols, sorbitol, and urea, but in combination with a charged active.

Because of their good affinity for water, all these compounds are efficient antistatic agents (especially ethoxylated nonionic actives). They also exhibit a good stability to heat [52]. Polyglycol fatty esters deliver good softness and static control without any drawback [15,55].

Nonionic and even anionic surfactants have also been added in small amounts to DHTDMAC to boost a product's softening efficacy. For example, it was shown in the late 1970s that the performance of a 6% DHTDMAC composition is matched by a mixture of 4.4% DHTDMAC and 0.6% anionic [56]: 1.6% DHTDMAC could then be replaced by 0.6% anionic, which is less expensive. That was quite unexpected, as it was generally accepted that fabric softeners must be introduced in the last rinse of the laundering process to avoid their neutralization by the anionic detergent residues on the fabric, which causes the formation of insoluble species.

Likewise, a dispersion of 3.6% DHTDMAC–0.9% tallow alcohol blend delivers as much softness as a 6% DHTDMAC dispersion [57]. From a performance standpoint, 0.9% fatty alcohol in the mixture is equivalent to 2.4% DHTDMAC, while it contains as many fatty chains as 0.8% DHTDMAC (tallow alcohol: mol wt = 259, 1 chain; DHTDMAC: mol wt = 569, 2 chains). Fatty alcohols alone are not better than DHTDMAC in fabric softening. Due to the insolubility of fatty alcohols in water, this equivalence has been evidenced by spraying alcoholic solutions of actives onto textiles. Actually, the DHTDMAC–cosoftener synergy results from a modification of the DHTDMAC dispersion structure. A dispersion of straight DHTDMAC is made of large multilamellar vesicles while only small

unilamellar vesicles are formed in the presence of cosoftener. It has been shown that the formation of these smaller vesicles is made possible by the insertion of the cosoftener molecules between the ammonium ions at the external surface of the vesicles. The formation of smaller vesicles causes a more even fiber coating, hence a greater softening efficacy.

This synergy has been systematically investigated and exploited to enhance the cost efficiency of fabric softeners, delivering either better performance at equal cost or the same performance at improved cost. It has also opened the door to the formulation of DHTDMAC-based concentrates, which without cosofteners is not possible for viscosity reasons.

The main nonionic cosofteners are fatty alcohols, fatty acid esters, ethoxylated fatty amines, or lanolin derivatives. To the cationic-anionic systems belong ether sulfates, alkyl sulfonates, or fatty acids [5,6,10]. In all the blends, the weight ratio of DHTDMAC to the cosoftener is always greater than unity [10].

2. Inorganic Actives

(a) *Silicones*. Silicones were first used by the textile industry as lubricants [34]. They also improve permanent press finish durability and garment wear life [5,26]. In softeners, they were considered solely for their unique softening properties. The benefit they deliver is, however, much broader, as suggested by the numerous patents that have been filed. They are claimed to reduce fabric wrinkling in the washer, to facilitate ironing by improving the glide of the iron, and to enhance the fabric water absorbency. They also strengthen color protection, shield fibers from staining, and help maintain the shape of garments [27].

Several chemistries have been developed: polydimethyl siloxane polymers (PDMS), amine- or amide-functional polydimethyl siloxanes, and silicone gum-in-cyclic blends. They are usually supplied as emulsions, offering a large choice of candidates to achieve the desired performance and physicochemical properties such as viscosity.

Polydimethyl siloxanes deliver a particular, very well appreciated feel referred to as “silicone-touch.” This is due to the strong reduction of the cotton friction coefficient, which also facilitates gliding of the iron during pressing. These effects are probably due to the flexibility of the siloxane backbone and to the free orientation of the methyl groups at the polymer surface [27].

In esterquat-based and more so in DHTDMAC-based softening compositions, PDMS improves the wettability of the treated cotton at low PDMS/quaternary ratio. This property is surprising, considering the strong hydrophobicity of the material. Since PDMS is not very substantive, it is easily removed in the subsequent wash.

Amine- and amide-functional silicones resist launderings better, as they react with cotton hydroxyl groups through the amine moiety. They are more efficient than conventional nonreactive silicones in boosting the softening efficacy [58,59],

the ease of ironing, and the resistance to wrinkling [60]. They also deliver antistatic benefits [60]. Although they have never been intensively used because of their high cost, amine silicones do bring a consumer-perceptible new dimension to rinse cycle fabric softeners.

Silicone gum-in-cyclic blends are dispersions of very high-molecular-weight silicone polymers in volatile silicone. Cyclomethicone helps the polymer to spread on fibers.

Emulsion characteristics such as the type of emulsion and its particle size are important to determine the nature of the benefit the product will deliver [27]:

- Macroemulsions remain on the external surface of fabrics. They achieve an excellent lubrication through the decrease of the dynamic coefficient of friction (see below). An excellent softness results.
- Microemulsions (<150 nm) can penetrate into the yarn and deposit onto the fibers. They deliver a dry lubrication and feel. They probably reduce the static coefficient of friction.
- Polymer emulsions (150 to 250 nm) deposit on the external surface of fabrics and on fibers. They improve the softness and the ease of ironing since they reduce both static and dynamic coefficients of friction.

The surfactant system of the emulsion can influence silicone deposition. This exceeds 80% when the surfactant is cationic and falls in the 60 to 80% range when the surfactant is nonionic [27]. Anionic emulsifiers are incompatible with cationic fabric softeners.

The silicone level must be adjusted for the final benefit required. More material is needed for ease of ironing than for improving rewettability. The silicone concentration in a regular composition is typically between 0.5 and 1.5%. Silicones usually disperse very well in the composition when introduced at the end of the formulation.

Silicones are expensive materials. Their cost and their very high stability, hence their rather poor biodegradability, have often restricted their use as basic raw materials of fabric softeners. Changing market forces have resulted in silicone removal from most household fabric softener compositions.

(b) Clays. Although some work has been done to develop clay-based rinse cycle fabric softeners, the application of clays as fabric softeners is essentially limited to softergents. These products combine a standard heavy-duty built anionic detergent composition with clay softeners. Commercial products such as the Australian Fab and U.S. Bold were based on this technology.

Clays involved in fabric softening are most often of the montmorillonite type, particularly sodium and calcium montmorillonite. These clays, also referred to as bentonite, are unique in that their particles swell in water, readily forming colloids whose size is between a few hundredths of a micrometer and several micrometers.

Clay particles are actually made of stacks of three to four platelets, each consisting of a sheet of hydrated alumina sandwiched between two sheets of silica. Isomorphous replacement of Si by Al and of Al by Mg imparts negative charges on the surface of the platelets.

Platelets are held together by cations. They impart a positive charge to the edge of the particles. These interlayer cations play a key role in the physicochemical properties of bentonite and in the stability of aqueous dispersions. Normally calcium is predominant and the clay swells to a moderate extent when dispersed in water. When Ca ions are replaced by Na, e.g., by reacting with Na_2CO_3 , the bentonite is said to be “activated.” This activation makes the clay much more swellable.

The swelling of clays is a two-step process. First, hydration of the platelet surface occurs, leading to a slight volume increase. Second, repulsion takes place between the electric double layers, leading to the complete separation of the platelets; this is so-called osmotic swelling.

Sodium montmorillonite quickly and irreversibly deposits onto cellulose at extremely low clay concentrations [61–63]. It exhibits some fiber lubrication properties.

The multilayered swellable clay particles are overall negatively charged, as shown by electrokinetic studies [64,65]. Hence bentonites are quite compatible with anionic-based detergents.

Cheap clays are generally colored by impurities to light brown or gray. This has never been reported to alter fabric color, but mixing powdered clay with the detergent results in an unaesthetic product. For this reason, clay powder is agglomerated into detergent-sized aggregates, which are afterwards added to the detergent without affecting its aesthetics.

An important fiber–fiber friction takes place in the washing machine and, to a lesser extent, afterwards when the clothing is used. Hence, to get the best prevention of damage caused by the wash, the protection must start from the beginning of the laundering process. In that respect, traditional rinse cycle fabric softeners come too late in the process: they protect the laundry only when dried and worn. The situation is completely different with clay-based fabric softeners, which protect the laundry throughout the entire wash, hence preventing the damage caused by the wash (Figure 12.6).

Fiber damage reduction has been demonstrated in the laboratory, according to the yarn-to-yarn abrasion test carried out in the washing liquor. Details of the test procedure may be found in Azoz [66]. Evidence of fabric protection by clay/PDT has also been collected in consumer tests.

In the first washes, the softness obtained with clay, although being perceivable, remains far from that delivered by a rinse cycle fabric softener, despite the high clay levels involved – up to 20% of the product and more. These levels are possible because of the relatively low price of bentonites.

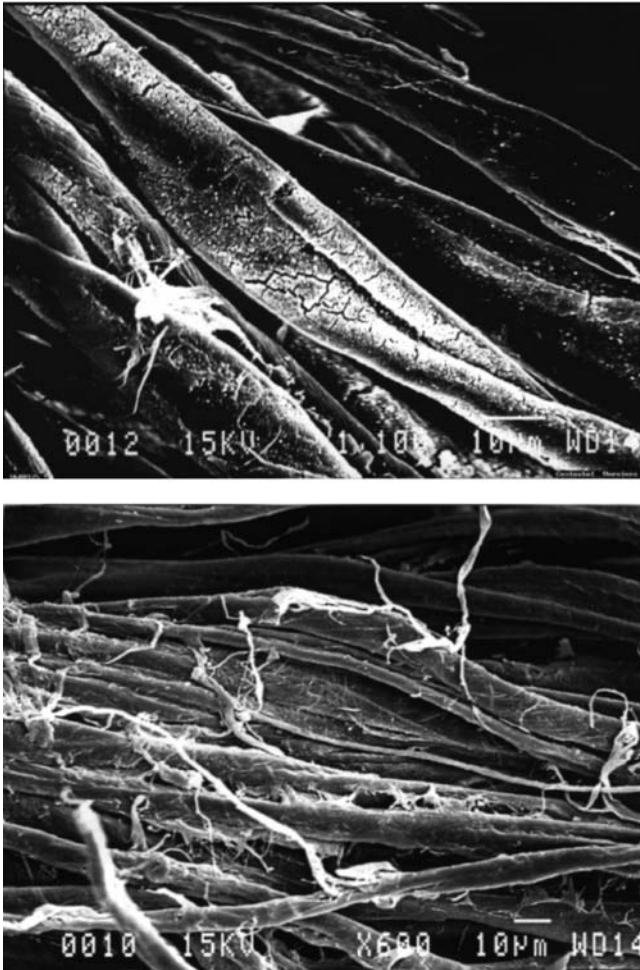


FIG. 12.6 Cotton fiber protection by a clay-based wash cycle fabric softener after 40 washes at 40°C in hard water (European washer). Top: washed with a clay-based softener; bottom: washed with a regular detergent.

Another limitation with clay softeners is that they do not exhibit any antistatic activity. This is a serious drawback in North America, where tumble dryers are very common. Several approaches have been followed to address the problem, such as introducing a neutral amine softener in the composition or encapsulating a cationic softener to avoid its interaction with clay and detergent components [10].

3. Enzymes

The use of cellulases is an alternative way to deliver fabric softness in the wash cycle. They catalyze the hydrolysis of the β -1,4-glycosidic linkages of cellulose. Detergent cellulases are mixtures of endocellulase, which degrades cellulose randomly in the chains, and of exocellulase, which attacks the chains at their ends, releasing glucose and cellobiose, a disaccharide; the latter inhibits the exocellulase activity. Therefore β -glucosidase, which transforms cellobiose into glucose, is also present [67].

Upon use and during successive washes of fabrics, microfibrils, called “pills” when they gather into visible balls, are generated on cotton fibers, which gradually lose their smooth structure. As microfibrils and pills scatter light, whites become grayish and bright colors dull and fuzzy. Microfibrils are also sites where soils are entrapped and CaCO_3 crystallizes from hard water, giving rise to encrustations. By removing the pills and the microfibrils from the surface of cotton fibers, cellulases improve the touch and the appearance of cotton [68,69].

The enzyme performance depends on its concentration. Increasing the enzyme concentration increases the effect, which eventually levels off. It also strongly depends on temperature, which affects the enzyme dissolution rate, activity, and stability in the washing bath. These effects are cumulative and increase considerably with the number of wash cycles carried out [70].

B. Other Ingredients

The aesthetic characteristics of fabric softeners have always attracted much attention from formulators. Each product is personalized by some specific ingredients, which determine its appearance.

An appropriate perfume is usually added to fabric softeners. Neutralizing the base odor and imparting to the product a pleasant smell, which illustrates the benefits delivered by the product, is not the only challenge faced by perfume houses when they develop a fragrance for fabric softeners. The perfume has also to fulfill other important requirements, such as remaining stable in the product — the stability window of many perfume ingredients is rather narrow — and keeping the product rheology and storage stability unchanged. No phase separation, modification of the viscosity, or chemical degradation should occur. Once the fine-tuning is completed and the above conditions fulfilled in a particular composition, the perfume is optimized to receive a positive consumer reaction.

Many fabric softeners are also dyed to cover the yellowish aspect of the product. Traditionally, they were blue, because of the success of Comfort, one of Lever's earliest brands [1]. Nowadays, various dyes are used to adjust the shade and strength of the color desired and any color may be found on supermarket shelves. Suitable dyes, however, must be safe for the composition, for fabrics, and for the

environment. The dyes must be water soluble and biodegradable, and must exhibit nonstaining properties.

Most products are stabilized against biological degradation by preservatives. Despite the antibacterial activity of cationic surfactants, there is some risk of bacterial contamination of fabric softeners.

Most generally, deionized water should be used to formulate fabric softeners. In this way a possible cause of electrolyte variation due to water quality is eliminated. Moreover, it is a way of avoiding the presence of ferric ions, which can cause fabric yellowing. Appropriate treatment of water helps eliminate the initial contamination of the product.

If nondeionized water is used, product viscosity remains low and a thickener must be incorporated. Excellent thickening effects have been obtained with nonionic cellulose derivatives, cationic guar gum, or crosslinked cationic polyacrylates.

Fabric softeners may also contain antistatic agents (anionic or ethoxylated nonionic surfactants) and/or humectants to increase the moisture level at the fabric surface [52].

As stated by Levinson, rinse-added softeners also provide a way of introducing valuable ingredients in the laundering process that may not be compatible with laundry detergents [3]. Several patents have been filed covering the incorporation of polyethylene terephthalate soil release agents, nitrogen-containing polymers or polyvinylpyrrolidone (PVP)-type polymers for dye transfer inhibition and soil release [16], biocidal quaternaries to suppress mildew and odor formation on wet fabrics, and many others [3].

Some ingredients have also been used in some fabric softeners to deliver particular benefits. Among them are the following:

Bleuing agents to counteract the yellowing tendency of cationic actives.

Cosolvents and *hydrotropes* as formulating aids and to make the product easily dosed and dispersed in the rinse liquor without affecting the storage stability [52].

Exhaustion aids to ensure that the best conditions are achieved in the wash bath to get full deposition of the softener. Among these systems are pH controllers [52]. Nonionic surfactants have the reverse effect, as they tend to retain the softening agent in the rinse liquor.

Antifreezing agents. When it thaws after having been frozen, a rinse cycle fabric softener usually undergoes a huge increase of viscosity that remains even after prolonged storage at room temperature. This problem is avoided by introducing an antifreezing agent. The addition of 4 to 7% methanol, ethanol, (poly)ethylene glycol, or glycol ethers protects the product from freezing down to -7°C ; without protection, the product starts freezing at around -2°C . For safety reasons, the amount of antifreezing agent should be kept as low as possible. Methanol,

which is cheaper than ethylene glycol, is registered as a poison in many countries. Imidazolinium softeners are less subject to freeze–thaw instability than DHTDMAC.

Optical brightener. Because of the screening effect of the active, softened fibers may reflect less light and be somewhat less bright. To overcome the problem, manufacturers add an optical brightener to some products. A benefit can indeed be displayed in the laboratory by fluorescence and pair comparison tests; users, who do not perform pair comparisons, hardly detect the difference. The benefit on colored items is more obvious and the consumer usually perceives the color revival. Selecting a candidate requires a preliminary assessment of possible hue changes.

The overall characteristics of the finished product are the result of the presence of the additives (nonionic surfactants, electrolytes, cationic polymers), of the nature and amount of the perfume, and of the manufacturing procedure (temperature, stirring) [5].

C. Types of Products

Cationic actives are usually used at a low level (0.5 to 5.0 g active/kg textile). They may be applied on the fabrics by padding, which is usually reserved for industrial applications. In domestic use, they are rather deposited by exhaustion from liquor or by transfer from a substrate [10].

Household fabric softeners may be applied to fabrics at three different steps of the laundering process: in the main wash, together with the detergent; in the last rinse after the wash; or in the tumble dryer, together with the wet fabrics before drying. The corresponding physicochemical environment of the softener varies greatly and the compositions must be adapted accordingly. DHTDMAC and DHTIMS have been used in formulating all three types of products. The best softness is obtained with DHTDMAC-based rinse cycle fabric softeners.

1. Rinse Cycle Fabric Softeners

The first fabric softeners were used by introducing them in the last rinse of the wash cycle, when most soil and detergent residues have been eliminated. Otherwise part of the active was wasted in forming water-insoluble complexes with anionic materials. These rinse cycle fabric softeners were 225 ml whole-cup “economy” or 115 ml half-cup “premium” products. Today, rinse cycle fabric softeners are still the most popular forms used by consumers. Indeed, they are the fabric softener form that delivers the greatest level of perceived softening efficacy. Markets are moving toward using smaller amounts of more efficient products. Modern washing machines in North America are equipped with fabric softener dispensers holding 115 ml or less. Using 30 to 45 ml of ultra products (see below) is now very well accepted by consumers in many industrialized countries [3].

(a) *Regulars.* These products are intended for direct use, without preliminary dilution. For many years the preferred actives for regular rinse cycle fabric softeners have been DHTDMAC, usually at a level of about 6%, or the tallow derivatives of diamidoalkoxylated ammonium or of imidazolinium [9]. Regular products were usually sold in 4 l bottles. The optimal softener concentration in the rinse depends on several factors such as the nature of the clothes to be treated, the drying conditions, and the level of softness expected by consumers.

The best trade-off between softening and affinity of the treated fabric for water is obtained at 1 g DHTDMAC/kg dry load [13,18,71].

Today, the average content of softening actives in European and in U.S. products varies from 3.3 to 5% solid, on a weight basis. Recommended dosages are usually 1/3 to 1/2 cup (80 to 120 ml) per wash depending on load size (U.S. conditions) [35] and 110 g per wash under European conditions. This represents 1.3 g/kg load under U.S. conditions (80 g product, 3.5% active, 2.2 kg load) and 1.1 g/kg load under European conditions (110 g product, 3.3% active, 3.3 kg load).

The various products present on the market differ from one another by the active ingredient system (structure of the quaternary and level in the composition, type of cosoftener, when present) and by the additives and perfume that fine-tune the performance and aesthetics.

(b) *Concentrates, Ultras, Compacts.* Concentrates and ultra products are up to 10 times concentrated. Usually they correspond to aqueous dispersions of 15 to 30% DHTDMAC, i.e., are 3 to 5 times more efficient than regular products. As already stated, the performance of these formulations is made possible by the synergy developed between softeners and cosofteners, which deliver more softness at the same level of active. In this way the viscosity problems encountered when the DHTDMAC concentration increases are bypassed. Alternatively, the concentration of actives may be raised when saturated chains are partly or totally replaced by unsaturated ones; however, some loss of softening occurs. In this approach, a trade-off must consequently be defined between advantages of concentration and the best softening.

Concentrates are dilute-before-use products. They must be first dispersed in three or four times the amount of tap water and shaken vigorously to regenerate the 5 to 8% concentrate dispersion and avoid clogging the fabric softener dispenser [3,35]. This is not necessary with ultras, which can be added directly in the rinse without preliminary dilution.

The stability of these products is governed not only by their composition but also by mechanical factors. The finished product is shear sensitive. From a formulation standpoint, usual actives do not enable the production of storage-stable concentrated products without incorporating emulsifiers such as fatty esters, ethoxylated fatty amines, or amides, and the viscosity must be further adjusted using inorganic salts. Moreover, the formulation of concentrates requires alcohol-reduced grades

of quaternaries [39], 15% organic solvent in the raw material being then already too much.

(c) *Solid Softeners*. These products are made of a spray-dried powder of DHTDMAC. They may also be made of DHTDMAC sprayed on urea, since they easily form inclusion compounds [8,18]. Usually, some nonionic is incorporated to help dispersion in water.

They are not very popular, since they disperse slowly in water and are not very suitable for washers, which are designed for liquid products.

2. Wash Cycle Fabric Softeners, Softergents

Introducing the fabric softener in the last rinse cycle is a true constraint for users of vertical-axis washers that are not equipped with a fabric softener dispenser. Indeed, the consumer must then either stay in the vicinity of the washer during the wash, to pour in the product at the beginning of the final rinse, or run an extra rinse cycle after laundering completion. This constraint does not exist with horizontal-axis washers, since a compartment for automatically releasing the fabric softener at the last rinse cycle is incorporated in their dispenser.

From the beginning, softener manufacturers sought to eliminate this constraint by introducing the fabric softener in the wash with the detergent rather than in the rinse. The requirements of rinse cycle and wash cycle fabric softening are completely different. In the wash liquor, the cationic softener is neutralized by the anionic surfactants present in most detergents, causing its precipitation. As a result, both the softener efficacy and the detergent cleaning performance are impaired and more active is required to get satisfactory results from a wash cycle fabric softener [26,37]. Hughes *et al.* report that the softening effect of the cationic active neutralized by anionic surfactants is not necessarily completely lost, as the electrically neutral fatty complex may deposit and lubricate the fibers [72]. Milwidsky adds that the corresponding softness is, however, not as good as that obtained with a pure cationic [18]. In contrast, Bräuer *et al.* [73] claim that if the anionic surfactant concentration in the wash exactly corresponds to the DHTDMAC concentration, the deposition of the latter is then more important than in a rinse. This proposal is difficult to reconcile with the common observation that the usual softener deposition is practically complete in the rinse under real use conditions.

Another way to achieve wash cycle fabric softening is to replace cationic actives by amphoteric or zwitterionic actives.

Practically, to avoid excessive cost, the cationic concentration was limited to 9 to 15% [8,9]. At these levels the delivered benefits did not match user expectations. Consumers did not accept the compromise between convenience and efficacy.

Effort was maintained, and a few years later detergents with incorporated softener (softergents) appeared on the market. The two-in-one-product approach is much more acceptable since the formulator has control of both the detergent

and the softener systems, which can and must be adapted to coexist in the same composition.

A first attempt consisted of fully replacing the detergent anionic surfactants by nonionic ones [8]. DHTDMAC or the hard tallow derivatives of imidazolinium or of diamidoalkoxylated ammonium were used in powder softergents, and the corresponding soft tallow or oleyl derivatives in clear liquids. The introduction of high levels of nonionic in a powder remains difficult and this approach has been limited to liquid detergents [18]. Moreover, the amount of DHTDMAC adsorbed on fabrics decreases as the nonionic concentration increases, because of the competition that takes place between these two species to deposit [23]. Other detergent ingredients, except carboxymethylcellulose [14], exhibit only limited interaction with the softener [72]. Hence the softener level had to be increased two or three times to match the performance of a rinse cycle fabric softener [9,14].

A valuable alternative to introducing a softener excess is to prevent or at least to reduce the contact between oppositely charged surfactants by exploiting their characteristic difference of solubility [8]. The effect is maximized by dry-blending the softener with very water-soluble spray-dried particles containing the anionic surfactants [14]. In the washing liquor, the anionic surfactants disperse first and have enough time to remove the soils before the cationic active deposits onto the fabric surfaces [14]. Afterwards, the detergency declines as the anionic and cationic surfactants interact and deposit onto the fabrics.

Alternatively physical separation may be realized by encapsulating the softener in a high-melting matrix such as paraffin wax, high-molecular-weight polyethylene glycol, or fatty acid triglycerides. The softener is released in the liquor as the temperature rises at the end of the wash, when the soil has already been removed.

Another approach is to replace quaternaries by the corresponding tertiary amines. Amines are electrically neutral at alkaline pH; as such, they are entrapped in the textile structure during the wash. In the rinse liquor, the pH is neutral and they bear a positive charge because of a proton binding to the nitrogen atom ($pK_a \approx 9.0$); these compounds withstand the rinse because of their water insolubility [8]. The first product of this type was made by incorporating alkylamide in a detergent composition (U.S. Patent 3,795,611 to Colgate-Palmolive, referenced in Chalmers [1]).

Other systems exist using montmorillonite-type clays as softeners [5]. Clay alone is much less efficient in fabric softening than the usual cationic actives. In their latest version, these softergents match the softening performance of fabric softeners, due to the clay being coated with a large fatty molecule such as a fatty alcohol or pentaerythritol di-tallow [74–76]. In this system the softening is achieved by the organic molecule and the clay works as a carrier.

Clay-based softergents offer the unique advantage of protecting fibers against the mechanical and chemical aggressions from the beginning of the washing cycle at no cleaning penalty. Ethoxylated alcohol surfactants must, however, be avoided in these compositions because of their great efficacy in removing bentonite from cellulose and in preventing its deposition [77].

The first softergents appeared on the market in the early 1970s. They were quite popular in the U.S. between 1981 and 1989 or so, but their popularity declined in the 1990s as a result of the increased softening efficacy of rinse-added softeners and the stronger cleaning efficacy of detergents [10].

Procter & Gamble developed a completely different approach to remedy the lack of fabric softener in washers. They developed a sphere dispenser for ultra fabric softeners designed to be incorporated in the laundry before the wash and to deliver 28 ml of product in the heart of the load at the beginning of the rinse. The Downy Ball has a cap that opens during the spin cycle because of centrifugal force, enabling the softener to flow out [78].

3. Dryer Cycle Fabric Softeners

Electrical tumble dryers are much more popular in the U.S. than in Europe (see [Section IV](#)). Consequently the market penetration of dryer cycle fabric softeners is much more important in North America than anywhere else. They are usually based on the same types of actives as the rinse cycle fabric softeners [35]. Two methods of delivery exist. Nonwoven sheets are impregnated with cationic softener that are incorporated in the wet load at the start of tumble drying or a fabric conditioner is sprayed from an aerosol onto the empty dryer drum before the drying process [16].

(a) *Sheets.* Dryer sheets are nonwoven sheets of synthetic fabrics coated with the softening ingredients. They are added to the damp laundry in the tumble dryer before drying. The nonwoven material simply works as a carrier. The active must have a melting point slightly below the dryer temperature. When the temperature rises and the impregnated sheet is rubbed against the humid load items, the softener is slowly transferred from the sheet to the hot and moist clothes. Afterwards, the softener spreads on the various parts of the fabrics for the same reason. The softener does not diffuse into the fibers but remains on their outer surface. This is the best way to deliver the correct dose of softener [14] — and for a time it was the only successful dryer softener form on the market [8].

Hard tallow ammonium compounds, especially DHTDMAMS, are usually preferred for this application [9]. Methylsulfate derivatives, which do not attack the epoxy resin usually found in U.S. dryers [7], are preferred to chlorides, which are said to corrode the metal parts of dryers during drying [26].

Too quick a release may cause fabric staining [14]. The active is therefore usually mixed with softening and melting point modifiers, polyethylene glycol

esters or fatty amine soap, to optimize its release [7]. Incorporating a small amount of nonionic surfactant improves the spreading of the active onto fabrics; it cannot be too hydrophilic, to remain soluble enough in the base and disperse efficiently. The resulting softening and antistatic effects are stronger, and there is less dusting and fabric staining.

Dryer sheets work by replacing the finish, which is otherwise gradually lost with repeated washing. They are convenient to use and deliver a better static control than rinse cycle products (95% instead of 50 to 80% [14]) with a lower level of active, usually 22 to 45% of the amount delivered by a rinse cycle softener [3]. This is probably linked to the fact that the softener does not penetrate inside the fibers. They are also superior to rinse cycle softeners as regards the soil release effect [34].

From a softening standpoint, dryer sheets are less efficient than rinse-added products but slightly more efficient than wash cycle fabric softeners. Besides the lower amount of solids delivered, the deposition in the dryer is much less uniform than in the rinse [9,34,37].

The dryer sheet market is enhanced by the change from natural to synthetic fibers.

(b) *Sprays*. In 1976 aerosol products became available to be sprayed directly onto the wall of the dryer drum before introducing the wet textiles. The foam substrate allowed the active ingredient to melt and be transferred by mechanical rubbing onto the fabrics [3]. They were efficient and addressed the drawbacks of sheet fabric softeners (staining, dusting, and tackiness) but caused corrosion of the dryer walls. They also carried moisture into the sensing devices of the dryer, causing malfunctions [14].

An alternative is an aerosol foam to be sprayed onto one laundry item in the dryer. This approach is close to that of sheet softeners described above.

VI. REGULATORY ISSUES AND SAFETY

A. Worker Safety

Quaternaries and esterquats contain some alcohol. Their flash point is low (below 37°C, 100°F). The tendency of a liquid to ignite is commonly linked to the existence of a flash point, defined as the lowest temperature at which a liquid generates enough vapor to form an ignitable mixture with air. Here, however, the vapor mixture exhibits a low heat of combustion and releases heat slowly. Hence, fire hazard is limited to the headspace of heated storage tanks and to spillage upon transfer to the formulation tanks. In case of fire, quaternaries tend to self extinguish, as the amount of flammable component is limited. What can also happen is a fire caused by these vapors igniting neighboring flammable material. Naked flames

and high temperatures should therefore be avoided in their vicinity; vapors should rather be exhausted to a safe location by an efficient ventilation system [79].

When formulating, workers may be exposed to flammable vapors. They should wear face shields, respiratory protection, and impervious gloves.

In the case of spillage, absorbent materials are generally not necessary because of the high viscosity of quaternaries at room temperature. Applicable regulations regarding chemicals disposal must be followed.

B. User Safety

Cationic fabric softeners are practically nontoxic by oral or dermal administration [3]. Consumers with sensitive skin may suspect softener-treated fabrics to possibly cause adverse effects. Textiles in contact with the skin can have dermatological effects such as allergic reactions and irritations. Skin irritation, however, depends on many parameters such as textile properties, skin sensitivity, and conditions of exposure (e.g., duration, perspiration, and environmental conditions such as climate) [80].

No problems could be evidenced from visual, instrumental, and self evaluations of intact and damaged skin exposed to treated and untreated fabrics [80,81]. Hence, no adverse effect on human health is associated with the use of DHTDMAC, amidoamine, imidazoline, or ester-based quaternary softeners [3]. In contrast, fabrics repeatedly washed with detergent in hot water become harsh and may cause irritation. Fabric softeners eliminate this problem [1]. Significant differences of stratum corneum, skin barrier integrity, and water holding capacity have been observed after rubbing the skin with softened or nonsoftened fabrics. The differences were always in favor of softened fabrics [81]. Likewise, Tronnier has shown that sensitive baby skin is less irritated when diapers have been treated with fabric softeners that are formulated so as not to sensitize or irritate the skin [80]. This is not surprising, considering the reduction of the skin–fiber friction delivered by the softener.

C. Environmental Safety

Like all other detergent ingredients, fabric softener actives are discharged into sewers and possibly end up in the environment. Their effect on aquatic or terrestrial organisms depends on their concentration and toxicity [6].

Quats are usually less easily biodegraded than anionic or nonionic surfactants, or esterquats, as they are less prone to be attacked by bacteria. Nevertheless softeners are not detrimental to the environment, since, besides their elimination by biological degradation, their concentration in effluents remains very low [15].

The amounts found in the environment depend on several factors, among which the use level, the population density, and the waste treatment process

are the most important [3]. Three mechanisms account for their removal from sewage [8]:

1. They are neutralized by anionic surfactants, whose concentration is much larger.
2. They concentrate at the bottom of surface waters as colloids because of their interaction with minerals.
3. They are eliminated by adsorption onto particulate activated sludge. The adsorbed portion is subsequently further broken down by bacteria if the sludge is incorporated into agricultural land.

A two-step waste treatment process has been shown to reduce softener actives by more than 90% [3]. The rest is diluted in surface waters.

For these reasons surfactants such as DHTDMAC have been safely used worldwide for decades. For instance, despite an annual DHTDMAC consumption of 27,000 tons in 1980 in Germany, there has been no clear evidence of any negative impact on the environment [10].

Nevertheless, as already mentioned, esterquats replaced DHTDMAC in the early 1990s. This move, a voluntary initiative from the industry, allowed the use of materials not classified as dangerous for the environment instead of materials classified as very toxic to aquatic organisms and potentially having long-term effects on the environment.

Microorganisms in sewage treatment readily break down the ester bonds of esterquats, releasing fatty acids and quaternized di- or triethanolamine. The fatty acids ultimately generate carbon dioxide and water [5] while the smaller cationic molecules are not further degraded but are not toxic [5,10]. An example of an environmental study of esterquat biodegradation may be found in Giolando *et al.* [82].

Replacing DHTDMAC by esterquats required a full reformulation of fabric softeners to keep the softening performance and the aesthetic attributes of products. For instance, esterquat hydrolysis may occur upon storage of a product. The reaction is hindered by maintaining the product at slightly acidic pH values (2 to 3.5). Since 1996, the rest of the world has also started to remove DHTDMAC from softening compositions [16]. As a result, DHTDMAC annual consumption has dropped by over 70%.

Packaging reduction has been achieved by simultaneously following several approaches. These include the use of recyclable plastics to reduce the use of virgin plastic and create a market for recycled plastic, introduction of lightweight bottles and refills, which use less plastic than conventional containers, and development of concentrated products. Recycled paper has also been used for cartons made from paper, to reduce the amount of wood fiber used and provide a market for recycled paper [35]. This enabled the launch of concentrated fabric softeners, which were successfully formulated due to product and packaging improvements

(e.g., introduction of self-draining caps to reduce bottle messiness) [6]. These trends have been repeated in the U.S. and Japan [6].

The most striking success in the field of packaging reduction has probably been the sachet developed by Cotelte in France. In 1957 it launched concentrated hypochlorite bleach in a sachet. Twenty-five years later, it used the technology for a fabric softener under the Minidou trade name. The weight of a 250 ml sachet is 10 g, 3.5 times less than a 1 l plastic bottle. Its cost is less than half the price of a rigid polyethylene bottle. From the trade's standpoint, the sachet packaging reduced distribution and warehousing costs.

The product had to be prediluted four times by the consumer, preferably in a 1 l fabric softener bottle. The recommended procedure was to pour the concentrate into a bottle half filled with warm water, then to fill up with warm water and shake vigorously. The bundle was described as a "clever" product that works as well as a bulky and expensive bottle but is more convenient: It is efficient, economical, and easy to carry, store at home, and use. The product was extremely successful and, within a year, it reached the second position on the French market with 22% market share [83].

D. Regulatory

In Europe the environmental safety of detergents is assessed by the PEC-PNEC system. PEC is the predicted environmental concentration of each ingredient of the detergent. PNEC, the predicted no-effect concentration, is the highest concentration at which an ingredient does not affect an organisms exposed to it in relevant environmental situations [5].

PEC and PNEC values are determined experimentally and/or by model calculations. For any ingredient, PEC should not exceed PNEC. Data generated by the European industry under simulated field conditions showed that the concentrations of cationic surfactants found in the environment were significantly below harmful threshold for even the most sensitive organisms [6,11].

Fabric softeners and their ingredients are governed by several directives:

- Existing substances regulation (793/93). Distearyltrimethylammonium has been put on first priority list and a risk assessment for humans has been carried out (CAS 107-64-2).
- The dangerous substances directive (67/548/EEC) and the dangerous preparations directive (1999/45/EC). Their purpose is to classify and label raw materials ("substances") and formulated products ("preparations") on the basis of their intrinsic properties: physical chemical hazards, hazards for humans, and hazards for the environment. Labeling consists of a symbol of danger (black icon on orange background), risk phrases, and safety phrases. Esterquat raw material is not classified as dangerous for the aquatic environment. As a consequence, it does not contribute to the classification

of fabric softeners as potential dangerous preparations from the aquatic environmental perspective.

- The recommendation for labeling detergents (89/542/EEC). The presence of cationic surfactants must be put on the label.

A new detergent regulation is now in preparation. It will cover (and replace some previous directives):

- The labeling (composition).
- The biodegradation of surfactants (surfactants will have to be readily biodegradable).

VII. PRODUCT FORMULATION AND MANUFACTURE

Liquid fabric softeners are formulated by dispersing the melted raw material in well-stirred hot water. Although DHTDMAC aqueous dispersions are not emulsions in the strict sense, chemical and mechanical principles of emulsification apply to control the viscosity and phase stability [10].

In concentrated products, the stability and viscosity depend on other variables such as the type and concentration of solvent in the raw materials, the perfume composition and concentration, and the salt concentration. The order of ingredient addition also influences the product characteristics [3,26].

The product physical and chemical properties consequently depend on many parameters.

A. Principles

1. Chemical Factors

The choice of a softening system relies on several factors [9]:

- Chemical composition of the softening raw material. Since they are synthesized from natural feedstock, which are mixtures of molecules bearing fatty chains of different lengths, the softening raw materials are not pure compounds. Moreover industrial synthesis leads to the formation of mono-, di-, and sometimes tri-chain compounds. Fabric softeners made from these raw materials are more easily formulated than those based on pure double-chain derivatives. Variations in the nature and concentration of the byproducts formed in the synthesis modify the characteristics of the finished product.
- Handling characteristics. These essentially depend on the fatty chain composition. Oleyl derivatives are liquid at room temperature, tallow derivatives are opaque liquids that become clear at 38°C (100°F), and hard tallow derivatives are opaque pastes that become pourable at 50°C (120°F). To get the maximum stability for the dispersion, oleyl derivatives can be

dispersed in water at 21 to 27°C (70 to 80°F) [14], tallow derivatives must be heated at 32 to 49°C (90 to 120°F), and hard tallow derivatives at 49 to 60°C (120 to 140°F) [9].

- **Formulation parameters.** Formulations and processes depend on the level of actives. As a basic rule, formulations are split in two main categories: regular and concentrated. To each category corresponds a well-defined process. The active concentration must exceed 4%, except tallow derivatives, for which 3% is enough [9]. The viscosity of the dispersion increases with the chain length and saturation extent. It is fine-tuned by adding salts such as sodium chloride, sulfate, or acetate.
- **Performance properties.** In the presence of solvents, oleyl derivatives give clear stable dispersions with good freeze–thaw stability [14]. Aqueous dispersions of hard tallow derivatives are milky.
- **Price.** Oleyl derivatives are more expensive than their saturated counterparts.

2. Mechanical Factors

The manufacturing conditions cover both the procedures and the equipment.

A correct dispersion of the quaternary in water requires water heated at 60 to 70°C. The lower the water temperature, the more viscous the product, and below 35°C the dispersion is no longer homogeneous. Above 70°C the final viscosity also increases. The product temperature must be maintained at a minimum to reduce energy usage necessary for heating and to reduce the cooling time at the end of the process.

The particle size distribution of the dispersion depends on the magnitude of the shear and of the flow applied at each step of the formulation. The wrong conditions may induce two kinds of product instability: thickening or clearing upon storage.

Besides their detrimental effect on viscosity, long shears also cause air to be incorporated in the product. The resulting foaming of the product may create problems in the filling step. Foaming can be avoided by reducing the speed or modifying the design of the device. Otherwise, addition of 30 ppm of a silicone antifoam emulsion will solve the problem.

Air incorporation also eventually causes phase separation in the product upon storage. The risk completely disappears when the density of the finished product is close to 0.99. Clearing during aging is considered below, in the discussion on physical stability.

The mixing conditions must consequently be carefully optimized when defining the manufacturing procedure by scale-up experimentation.

B. Process

Fabric softeners are prepared either in a batch or in a continuous process.

1. Batch formulation

Water-insoluble chemicals are premixed in a tank, then pumped into the main tank, where they are dispersed in hot water. The hot product is then cooled.

Since a structured liquid must be obtained, the formulation procedure is stringent. It is a four-step process:

1. Dispersion of water-soluble ingredients (dye, nonionic surfactant, etc.) in hot water (60°C).
2. Dispersion of the hot premix of DHTDMAC or esterquat, cosoftener, fragrance, and other water-insoluble ingredients, if any, in the well-stirred aqueous phase. Overheating should be avoided, as it is detrimental to the product's stability. The stirring is maintained until a homogeneous dispersion is obtained.
3. Cooling step. The final cooling step is the bottleneck of the process. It may be achieved by circulating water at 16°C in the double jacket of the mixers. The cooling speed is slow. During the 3 to 4 hours needed to bring the product back to room temperature, it undergoes a shear that may influence its viscosity profile and may cause the aeration of the product. Using a heat plate exchanger to cool the hot product to room temperature drastically reduces the cooling time (3 to 4 times), hence the shear applied to the product.
4. Addition of minors such as buffer or preservative. Optionally a structuring polymer or some electrolyte can be introduced at the end to adjust the viscosity.

The product is then transferred to the storage tank or to the filling lines.

Another way to enhance the cooling speed is to use the low-energy emulsification (LEE) procedure [84]. Only 25 to 50% of the total amount of water is heated to 60°C. The remaining part is kept at 16°C and slowly added afterwards, when the dispersion of the oil phase is completed. Besides reducing the shear undergone by the product upon cooling, this procedure also leads to a large reduction of energy consumption.

For concentrates enhancing the solid level in the composition only requires an adjustment of the active addition speed to avoid lump formation and the adaptation of the shear applied to the system. Good stability of the product upon aging is observed when the particle size remains below 10 μm . Here, the addition of electrolytes is necessary to reduce the viscosity of the finished product.

Numerous improvements have been gradually incorporated in the basic batch equipment, which have led to fully computer-controlled processes. Large equipment is necessary to reduce the formulation time. The equipment is most often at rest as it operates intermittently. These periods permit changeover and cleaning of the installation between two different compositions.

2. Continuous Formulation

In the continuous process, most mixing operations are achieved with static mixers; only highly viscous or difficult materials are mixed with dynamic mixers.

Raw materials are all stored in separate tanks. Water-insoluble and water-soluble ingredients are mixed in two separate mixers and then mixed together in a third one. The product is then cooled to 25°C in a heat exchanger. The minors and the thickener and/or salt are then incorporated into the product, which is pumped to a storage tank or filling lines.

The amounts are adjusted either by volumetric metering or mass-flow metering [85]. Solid ingredients must first be solubilized, to be metered with a pump (in the batch process, they are directly added into the mixer).

In the volumetric metering approach, the quantities are determined through the pumps used to send them to the mixing lines. Densities of all raw materials must be known under the particular conditions of temperature and formulation, and the accuracy of the pumping rate regularly checked to get the right mass flow rate from the volumetric flow rates.

In the mass-flow metering approach, the control unit adjusts the pump speeds to deliver the right amount of ingredient. These systems are highly accurate and reliable as they measure true mass flows.

In continuous formulation, the temperature constraints are of course the same as in the batch process. The major advantage over the batch process is that the required equipment can be smaller as it operates continuously (mixing pipelines are purged with the subsequent product). Moreover, no aeration can occur in the system, which is closed and pressurized.

C. Aging Studies

The long-term stability of finished products is assessed under accelerated conditions. Stability test protocols vary among laboratories but prototypes are generally aged at 4°C, room temperature, 35°C, and 40 to 43°C for up to 3 months. Freeze-thaw stability is assessed by submitting the samples to three (24 hours frozen, 24 hours thawing) cycles. The physical characteristics that are most usually followed during aging are the product appearance, viscosity, pH, odor, and dispensability. Frequently, the dye and perfume stability to light is also assessed in the sun test.

These methods only give a rough idea of product stability under real conditions.

D. Analytical Evaluations

Several methods exist to determine the level of active matter in raw materials and finished products. Quaternaries can be assayed by standard two-phase titration.

Auerbach's method of quat-methylene blue complex extraction by chloroform is also very popular [86,87].

VIII. PHYSICAL CHEMISTRY OF FABRIC CONDITIONING

Because of their very high affinity for fabrics and relatively low cost, cationic surfactants are the workhorses of fabric softening. Moreover, they are easily formulated. From a softening standpoint, the best results are obtained when the ammonium ion bears two saturated C_{18} alkyl chains. Consequently, fabric softener actives are usually made of hydrogenated ("hardened") tallow acid derivatives.

A. Structure of Liquid Fabric Softeners

Since the chain length of tallow components is essentially between C_{14} and C_{18} , the total number of different structures in the softener active exceeds 15 [26]. The raw material also contains mono- and usually tri-tallow derivatives. Most of those molecules are not water soluble and do not associate into micelles, but form stable colloidal dispersions in water. Maltese crosses can be observed using an optical microscope under polarized light (Figure 12.7), revealing the presence of strongly birefringent particles, typical of liquid crystalline phases [88,89].

The particles are usually composed of lamellar or gel phases [3,90,91]. Electron micrographs (TEM or freeze fracture) show that most DHTDMAC particles exhibit a liposome-like structure called a vesicle (Figure 12.8). In this structure, the surfactant fatty chains form one or several highly organized hydrophobic areas

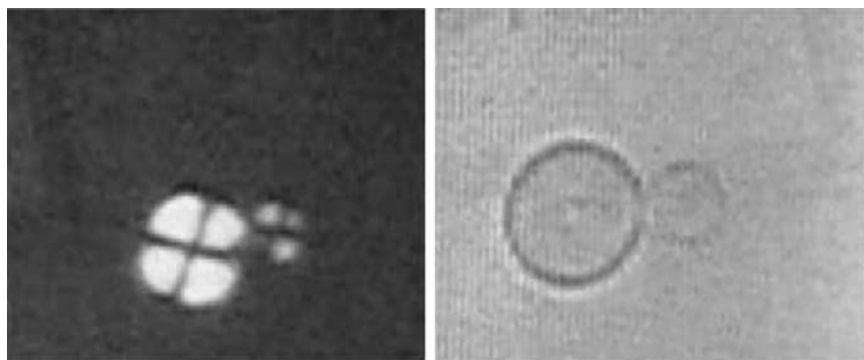


FIG. 12.7 DHTDMAC dispersion viewed with an optical microscope (magnification $\times 800$). Left: under polarized light, Maltese crosses show the presence of multilamellar vesicles. Right: the same under nonpolarized light.



FIG. 12.8 Electron micrograph of a DHTDMAC aqueous dispersion. An intact vesicle is seen on the left, a cross section on the right, in which the lamellar structure is apparent (freeze fracture, magnification $\times 2500$).

called bilayers, entrapping a large amount of water inside. The ammonium ions are at the internal and at the external surfaces of the bilayer, in contact with water [92].

Vesicles can be unilamellar or multilamellar. The exact structure of the aggregates formed in solution by a type of surfactant results from geometric constraints. It is determined by the relative volumes of the hydrophilic head and of the hydrophobic group of the molecule (e.g., see Israelachvili [93]). That is why di- and tri-tallow derivatives adopt a vesicle structure, while mono-tallow ammonium chloride forms micelles [26]. The structure of the dispersions based on other actives such as esterquats is more complicated.

The liquid crystalline phase makes DHTMAC extremely viscous when the concentration exceeds 5%. Because of this inherently high viscosity and the high volume fraction of colloidal particles, the formulation of concentrated products is difficult. In practice, DHTMAC is never used at concentrations above 15%. In contrast, esterquats or other quaternaries bearing unsaturated fatty chains are more suitable for producing concentrated dispersions. As a result of their more disordered fatty chain packing, the particles they form are cubic or isotropic but not lamellar, and the resulting phase viscosity is lower and more stable [3].

In aqueous dispersion DHTMAC spontaneously adopts the vesicle structure. This is uncommon, as vesicle formation not only requires molecular characteristics (double fatty chain molecules, no strong repulsion) but usually also a strong

mechanical energy supply (sonication). No such energy supply is required for DHTDMAC to form vesicles [26].

DHTDMAC vesicles have been characterized by Okumura *et al.* [92]. The width of the bimolecular layer is 50 Å, and the interlamellar spacing is between 100 and 400 Å. Each DHTDMAC molecule is hydrated with 7 water molecules. The particle size distribution, measured by dynamic light scattering and optical microscopy, is very broad, ranging from 0.1 to 10 µm. This may be assigned to the presence of both unilamellar and multilamellar vesicles in the dispersion.

Although a fabric softener is not an emulsion but a suspension of charged particles, it exhibits the same instabilities as an emulsion. The physical stability is twofold: phase separation and viscosity.

1. Phase Stability

Under some conditions, concentrated softeners exhibit a kind of phase separation called clearing. In a product that undergoes clearing, two layers appear on aging, the bottom layer usually being more translucent and clearer than the top one. The viscosity of each layer remains quite stable and low. This phenomenon disappears as soon as the sample is gently moved.

This instability is due to the presence of a bimodal population. The small, sub-micrometer particles remain evenly distributed throughout the dispersion whereas the larger particles move up, because of the difference in density between the dispersed and the continuous phases. If the interactions between the particles are weak, the viscosity remains low and clearing occurs according to Stokes' law [10].

Another mechanism leading to phase separation is coacervation. The symptoms are the same as above but here the destabilization is sensitive to the ionic strength. Coacervation was extensively studied by Bungenberg de Jong and Kruyt and co-workers, among others, in the 1930s (e.g., see [94]).

The phase stability of the DHTDMAC or esterquat dispersions relies on electrostatic repulsion between the particles. The DLVO theory predicts that when the ionic strength increases, the electrical double layer of each particle is compressed and the electrostatic field at any given distance of the particles is reduced. As a result, the electrostatic repulsion between the particles decreases; they may come into closer contact before undergoing the electrostatic repulsion from their neighbors. At the same time, the charged head-counterion interaction is strengthened; as a result, the solubility of the particles decreases. This effect has been quantified by following the equivalent conductivity of DHTDMAC as a function of its concentration. When the particle concentration is enhanced, the increase of ionic strength results from the larger counterion concentration. In DHTDMAC dispersions, particles are too large and the individual quaternary ion concentration is much too low to contribute significantly to the current transportation. Hence the conductivity of the quat dispersion essentially depends on the free counterion

concentration, i.e., on the extent of the vesicle ionization. The ionization extent may be quantified by considering the mobility of chloride ions.

Coming from a fairly high concentration to infinite dilution enhances the proportion of ionized quat from 8 to 27% in a plain quat dispersion, which contains unilamellar and multilamellar vesicles, and from 13 to 47% in quat–fatty alcohol dispersions where only unilamellar vesicles are present. The difference between the two systems results from the larger proportion of quat molecules in contact with the continuous phase.

The particles concentrate at the top or at the bottom of the solution, forming two phases. One of them is rich in colloid, corresponding to a cluster of loosely stacked particles weakly repelling each other and the other is a dilute suspension. Since the repulsion between the particles is much reduced but still present, they do not interact as in a flocculate. Consequently, they are very easily homogenized by gentle shaking, even after long storage periods.

Two phenomena may reinforce the destabilization by coacervation:

1. Ions in solution may affect the particle hydrophilicity according to their position in the lyotropic (Hofmeister) series. As a result, particles are salted-out and aggregate.
2. The decrease of surfactant solubility in solution may also modify the phase equilibria in the system [26].

To improve the uniformity of the dispersions, which must remain constant from batch to batch, an emulsifier such as an ethoxylated fatty alcohol can be incorporated. Emulsifiers form an interfacial film around the dispersed particles and prevent them from interacting with each other, as long as the emulsifier is well located at the interface. Medium-length hydrocarbon chains and long ethoxylated chains usually give the best results. The selection of the right emulsifier can be achieved with Griffin's HLB (hydrophilic/lipophilic balance) system [95]. Jacques and Schramm give an illustration of the method [10]. Once the emulsifier is identified, its concentration, usually in the 0.5 to 1.0% range, must also be fine-tuned to get stable dispersions.

Additional stability improvements can also be obtained by limiting the solvent content in the raw materials and by using hydrophilic polymers, such as polyethylene glycol, which prevent coalescence by steric stabilization.

2. Viscosity

A key attribute of rinse cycle fabric softeners is their viscosity. The control of the finished product viscosity is very delicate, as its value at the end of the formulation depends on several parameters linked to the ingredient composition and the manufacturing procedure. Also, viscosity may vary upon storage.

The effect is particularly critical in concentrated fabric softeners since, according to the particle size distribution, a given composition may lead to a thin liquid or an unpourable gel [10].

Since a large amount of water is trapped in the vesicles, the volume fraction of the dispersed phase is much larger than the volume of lipid and the viscosity strongly depends on the conditions adopted to disperse the active (temperature and stirring speed), i.e., the shear undergone by the product. It also depends on the type of colloidal structure, on the electrolyte content, and on the nature and concentration of other ingredients [91].

Introducing small amounts of salts such as sodium or calcium chloride reduces the viscosity. Bilayers are impermeable to inorganic ions and work as semipermeable membranes, which let only water pass freely. Because of the salt addition, the electrolyte concentration in the inner core of the vesicles is smaller than outside, and water migrates from the interior to the continuous phase to restore the osmotic equilibrium. As a result, the vesicles shrink and the volume of the continuous phase increases. Since more solvent is available to disperse the now smaller particles, the distance between neighboring particles increases and the interparticle interactions (electrostatic repulsion and van der Waals attraction) decrease [39]. These effects reduce the viscosity of the dispersion and hinder phase separation. The strongest effect is obtained by adding the salt at the end of the formulation, so that the electrolyte remains in the continuous phase. Above a critical temperature corresponding to the “melting point” of the fatty chains in the bilayer (30 to 40°C for DHTDMAC), water and electrolyte can pass freely through the hydrophobic layer of the vesicles.

The salt concentration must, however, be maintained at the low side, as levels above 100 ppm induce coacervation in the product. Moreover the particle size reduction effect is limited by the electrostatic repulsion between the head groups in adjacent layers, which increases as the space between the vesicle bilayers decreases [91]. Consequently, the formulator has to identify the electrolyte concentration that decreases the size of the particles as much as possible without affecting the physical stability. Some electrolytes are introduced through water and raw materials, especially the quaternary itself, and their amounts vary from one delivery to the other. Using deionized water eliminates one source of variation.

The temperature effect is considered in Section VII.A.2.

Product viscosity is strongly affected by the shear undergone during the formulation and in the subsequent handling steps (pumping, filling). Because of the larger ionic strength that results from a particle size decrease, smaller particles can come in a closer proximity and interact more strongly with one another than large particles. As a result, a network floc gradually forms and the product viscosity rises.

According to Okumura *et al.*, dispersions whose particle size falls in the micrometer range are less subject to phase separation or viscosity change [92].

They assign the stabilizing effect of micronizing to the formation of the network structure in the dispersion, which counteracts the difference of specific gravity between the dispersed and continuous phases.

This mechanism is contested by Laughlin [26], who stresses that DHTDMAC particles remain independent in solution and do not form a network, as the product structure corresponds to a sol not to a gel [72].

Surfactants also modify product viscosity. At a low level, such as 0.15%, the viscosity increases, becoming hard to stabilize. At higher levels the product is stable and its viscosity decreases. Any excess of surfactant is not detrimental but useless and expensive.

Product consistency is usually adjusted and maintained in a well-defined range of viscosity by post-adding a thickening agent (often a highly charged cationic polymer). When the thickener is dispersed in water, electrostatic repulsion takes place between the charges on the chains. Linear chains unfold and occupy the volume between the particles, imparting a rheological structure to the continuous phase. The best results are obtained with crosslinked chains.

As the fragrance is essentially made of organic compounds, it also interacts with the hydrophobic layer of the softener particles, causing them to stick together [39]. One way of avoiding the fragrance interaction with the particles is to introduce an emulsifying agent in the composition. An alternative, which enables one to avoid the increased cost linked to the introduction of an additional ingredient, is to disperse the fragrance in the melted active prior to its dispersion in water [39].

B. Deposition and Desorption

1. Deposition

The success of cationic surfactants results from their strong efficacy at low concentration, which at least partly results from their huge substantivity on textiles. Once dispersed in the rinse liquor, the softener exists as a very diluted dispersion (250 ppm under European conditions, 100ppm under U.S. conditions; Okumura *et al.* even worked on 33 ppm solutions [92]). The cationic active nevertheless deposits almost quantitatively and coats garments more or less evenly within a few minutes. Some 97% of the DHTDMAC introduced in the liquor is found on cotton at the end of the rinse [96]. This value was confirmed over a wide range of pH and temperature by colorimetric and radiometric evaluations [97]. The homogeneity of the quaternary deposition may be visualized by immersing dry softener-treated fabrics in a 0.01% bromphenol blue solution, followed by rinsing and drying. Softener covered areas appear as blue spots, the dye excess, which is not linked to the cationic active, being released in the rinse.

Substantivity is of course not limited to cationic surfactants. Other surfactants also adsorb onto surfaces — otherwise the detergency would not be possible — but

to a lesser extent and their desorption is practically complete upon the following wash [25,98].

(a) *Mechanism of Fabric Softener Deposition in the Rinse Liquor: Electrostatic Model.* Since the early 1960s the deposition of fabric softeners has been extensively studied to understand the huge substantivity of cationic actives. Among other methods, it has been shown by electrokinetic potential measurements that a cationic surfactant such as dodecylpyridine bromide (DPB) deposits mainly because of electrostatic attraction [99]. Since the softener counterions do not adsorb onto fabrics, Hughes *et al.* conclude that the softener deposition results essentially from an ion exchange mechanism [100]. According to Sexsmith and White, the cation binding proceeds by ion exchange and by adsorption of ion pairs [101]. The binding of soluble cationic surfactants such as cetyltrimethylammonium bromide (CTAB) to cotton proceeds by ion exchange first, at pH values below pK, and by physical adsorption afterwards.

Most work has been done with monoalkyl quaternaries, and the conclusions extended to the dialkyl cationic surfactants. This process is incorrect since the monoalkyl derivatives are much more water soluble than the corresponding dialkyl derivatives and they behave differently. Only a few studies have been carried out on DHTDMAC. They are discussed by Crutzen [102]. A very different approach was that of Kunieda and Shinoda [88] and Laughlin and co-workers [89,103,104] who studied the phase diagram of dioctadecyldimethylammonium chloride as a model for DHTDMAC deposition.

The general picture arising from these studies is that the deposition of cationic actives onto cotton is essentially due to the electrostatic attraction of the positively charged vesicles by the negative charges borne by cotton in water. As a result, the ammonium ions form ion pairs with the carboxyl groups of cotton [25].

The pattern of the curves of quaternary deposition corresponds to a high-affinity adsorption. For many authors, who link the surface affinity for softeners to the ion exchange capacity, such a pattern reinforces the electrostatic attraction mechanism [23,24,30].

(b) *Mechanism of Fabric Softener Deposition in the Rinse Liquor: Hydrophobic Model.* Several experimental evidences refute the electrostatic model:

1. The deposition of a cationic softener onto cotton is always practically quantitative under real conditions, irrespective of the number of carboxylic groups [105].
2. The affinity of cations for the negative charges borne by cellulose increases according to the following sequence: $\text{Na}^+ < \text{CTA}^+ < \text{Ca}^{2+}$ [106]. The affinity of softener actives for fabrics in solution consequently markedly exceeds that arising from pure electrostatic interactions [30].

3. The deposition also occurs onto more neutral fibers [73]. Therefore Laughlin suggested an ion exchange reaction between the counterions of cotton carboxyl groups and the cationic salts, coupled with physical adsorption [26].
4. More recently, it has been shown that electric charges on cellulose are not even necessary for the deposition of DHTDMAC [102]. This was achieved by following the electrokinetic potential of cellulose in the presence of increasing amounts of DHTDMAC, and by evaluating the effect of an organic solvent on the stability of the DHTDMAC–cotton adduct.
5. The deposition of DHTDMAC is favored by water hardness despite the screening of electric charges that reduces the electrostatic interactions.

The reality is consequently more complex than the simple electrostatic model. The adsorption of surfactants onto surfaces is the result of various factors: characteristics of the surfactant and of the surface, lateral interaction between the fatty chains of the adsorbed surfactant molecules, solvation of the surfactant and of the surface, etc. It is not the type of active ingredient–surface interaction that accounts for the deposition onto fabrics.

DHTDMAC is dispersed in water as vesicles, in which fatty chains are sheltered from the solvent. Upon dilution, a modification of the vesicle structure causes the deposition of the DHTDMAC molecules onto the available solid surfaces. Coating cotton by quaternaries leads to the release in the bulk of many water molecules initially interacting with cellulose. As a result, the system entropy increases. This phenomenon is known as hydrophobic interaction. Consequently, the driver of the softener deposition is the hydrophobic ejection out of the aqueous phase and the resulting huge increase of the system entropy.

Once on the fibers, DHTDMAC has little tendency to go back into solution because of its insolubility. Moreover, it interacts with the fabrics through dispersion forces, and electrostatic interactions when charges are present. Among the mechanisms reviewed by Rosen [107], ion exchange and ion pairing (charge neutralization) are more specific of the interactions with cotton, while interactions with synthetics rather involve dispersion forces and hydrophobic bonding, and the polarization of π -electrons to a lesser extent.

Since the deposition of DHTDMAC results from its insolubility in water, it is not surprising that no stoichiometric relationship exists between the charge quantity and the deposition extent. The amount of DHTDMAC on the fabrics depends on the specific surface area of the fibers, and on the softener concentration in the liquor to a lesser extent. As the deposition continues, repulsion gradually takes place between the ammonium ions on the fibers and the oncoming ions. This causes a decrease of affinity and its leveling off.

The neutralization of some ammonium ions by the negative charges enables additional softener molecules to deposit at the same place. This effect accounts for the larger amounts of softener present on charged fabrics (compared to uncharged

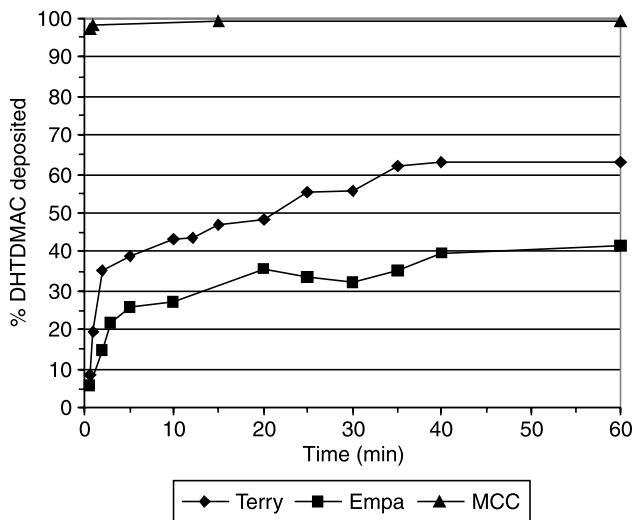


FIG. 12.9 Kinetics of DHTDMAC deposition onto various celluloses as measured by adsorption isotherms. Amounts deposited on the fabrics are expressed as the percentage of DHTDMAC introduced in the liquor (17.3 mg DHTDMAC/g fabric). Terry, bath towels; Empa, short-napped cotton; MCC, microcrystalline cellulose.

fabrics). It also explains why DHTDMAC cannot be completely removed from softened cotton, even by organic solvents such as isopropyl alcohol.

Comparing the adsorption kinetics of DHTDMAC–fatty alcohol on microcrystalline cellulose, terry towel, and short-napped cotton showed evidence that the high substantivity on cotton is due to its very large specific surface area, not to the presence of negative charges. The larger the surface area, the more quickly and completely the DHTDMAC deposits (Figure 12.9). Microcrystalline cellulose is at once saturated, while terry towels adsorb more quickly than short-napped cotton.

The deposition of DHTDMAC onto a charge-free surface with a very large specific area is consequently much larger and quicker than on the same amount of negatively charged cotton with smaller specific area! Previously Sexsmith and White [101] had also found that DHTDMAC adsorbs much more on microcrystalline cellulose than on cotton.

These conclusions are not limited to laboratory experiments. When terry towels are laundered in a washing machine under real conditions (wash with a detergent, rinse with a commercial fabric softener), up to 95% of the DHTDMAC present on the fibers is linked to cotton by hydrophobic interactions [102].

(c) *Parameters Governing Fabric Softener Deposition.* From a number of studies [36,72,92,96,98,108,109], it appears that several parameters influence the rate, extent, and evenness of deposition.

Structure of the active. The most important parameter in the adsorption–desorption characteristics of cationic surfactants is the number of fatty chains linked to the cationic hydrophilic group and the number of carbon atoms of which they are made [25]. It is this bulky part that makes the molecule very hydrophobic and boosts its deposition onto fabrics, independently of the negative charge on the target fibers [16,35].

No consensus exists on the relative speed of deposition of the active. For instance, Linfield *et al.* reports that imidazolinium salts deposit much less quickly than ammonium salts [36], while, according to Hughes *et al.*, they deposit more rapidly at low concentration and at the same rate at higher concentration [54].

The type of counterion, chloride or methylsulfate, has little influence [36]. A more or less extensive ion exchange probably takes place in the rinse liquor with the anionic surfactants coming from the detergent carryover and the anions of water hardness. As a result, it is very likely that no strong difference exists between the two actives once on fabrics [26]. This is not in line with other results showing that anionic counterions of the surfactant are present on the fibers, which suggest an ion pair type adsorption [30]. For instance, iodide is much more substantive than chloride [98].

It should be noted that relative affinities of the different actives for cotton hold in water only. DHTDMAC affinity for cellulose is small in organic solvents such as isopropyl alcohol or chlorinated solvents, which readily dissolve it; higher amounts of active must then be involved to observe a significant deposition [15].

Structure of the dispersion. A good example of the dispersion structure effect may be found in the softener–cosoftener synergy. It is most probably by allowing the formation of small particles, hence improving the uniformity of DHTDMAC deposition, that cosofteners enhance the softener performance (see above).

Type of fibers. The chemical structure of the fabric strongly affects the softener affinity. The following sequence of increasing affinity can be found in the literature [2,4,23,73]: polyacrylonitrile < polyamide < cotton < viscose < wool. Acetate [2,4] and polyester cotton [23,73] are placed between polyamide and cotton. The ranking of the affinity for polyester varies according to the study: less than polyacrylonitrile [23,73], or just larger [2, 4], or even larger than polyamide [99]. These discrepancies may be due to variations of the specific surface area of the materials used in the various studies, as illustrated by the evaluations of the adsorption kinetics of DHTDMAC–fatty alcohol on microcrystalline cellulose, terry towel, and short-napped cotton (Figure 12.9). The experimental conditions, especially the pH of the liquor, should also influence the sequence.

Not surprisingly in the light of these results, softener deposition has been reported to vary with the nature of the fabric finish [34,105]. This aspect has already been discussed [102].

Some authors have also quantified the deposition of DHTDMAC onto various substrates (Table 12.1). Evans [2] reported the deposition leveling off at 1 mg DHTDMAC/g cotton.

TABLE 12.1 Quantification of the Deposition of DHTDMAC onto Various Substrates

Substrate	Fabric saturation (mg quat/g load) [23]	Deposition from a liquor (conc. = 1.5 g quat/kg load) [11]
Polyester	0.6	60%
Polyacrylonitrile	1.1	47%
Polyamide	1.8	
Polyester cotton	4.0	73%
Cotton	7.5	77%
Wool	7.7	100%

pH of the liquor. The deposition extent moderately increases when the pH rises from 2 to 9 [8,26,52,96], and is a maximum at pH 8 [18,97,98]. This may be assigned to the increase of the overall negative charge of the fibers that neutralizes a larger number of ammonium ions on the fabric. More DHTDMAC will consequently adsorb before the electrostatic repulsion prevents any further deposition.

The evenness of common softener deposition (DTDMA and imidazolinium chlorides and methylsulfates) is improved when the exhaustion slows down [1,24,36], i.e., when the pH decreases, and is best at neutral pH [1,8,18].

Temperature. The higher the temperature, the more and quicker the deposition [1,25,36,52,96,98]. The optimal temperature to get almost complete deposition of the softener is 25 to 32°C [97]. The effect has been assigned to a solubilization phenomenon [96]. This proposal is paradoxical, as deposition and solubility are at first glance antagonistic. In contrast, CTAB adsorption onto cotton increases only slightly when the temperature rises [106]. An alternative explanation is that DHTDMAC deposition involves entropy-driven phenomena, such as hydrophobic ejection and hydrophobic interaction.

Duration. The deposition onto the various fibers is almost complete in less than 5 minutes [1,92,97] and reaches a maximum after 10 to 15 minutes [96]. It has also been reported that the deposition of a monolayer over the whole surface of the fiber is usually achieved in 2 minutes, although reaching the equilibrium can take up to an hour [1]. Some sorption also probably takes place inside the fibers [73], which requires time for the fiber to swell.

Water hardness/ionic strength of the liquor. Water hardness favors softener deposition onto fabrics. Increasing the ionic strength can double DHTDMAC deposition onto cotton or polyester [23]. A plateau is reached at a hardness of 300 ppm [100]. The ionic strength of the liquor also influences the rate of deposition [52].

All the effects discussed above are quite consistent with the hydrophobic model. The various observations are explained by the electrical double layer compression.

In the hydrophobic model, quaternaries deposit onto textiles until their concentration on the surface is large enough to develop an electrostatic repulsion that prevents any further softener deposition. The introduction of neutral salts in the medium strengthens the interaction of the ammonium ions with their counterions, decreasing the softener solubility in water and increasing its tendency to deposit. At the same time, the electrical double layers of the particles are compressed, causing the reduction of electric field at any given distance of the particles and decreasing the repulsion by the molecules on the fabric. Consequently, a larger number of softener molecules can deposit per unit area.

Some authors also assign the enhanced deposition at high ionic strength to an increase of the adsorption by ion pair uptake [72,101] at the expense of the ion exchange mechanism [101]. Alternative explanations are a salting-out of the softener [96], or the neutralization of anionic surfactants by bivalent cations, leaving more softener available to deposit.

Finally, an osmotic shock due to the high electrolyte content of hard water has also been suggested as causing a decrease of the softener particle size, thereby enhancing the softening efficacy.

Softener deposition is drastically affected by anionic surfactants such as linear alkylbenzene sulfonate (LAS) or sodium lauryl sulfate (SLS) because of the immediate formation of water-insoluble complexes. For instance, if increasing amounts of SLS are added to a softener dispersion, DHTDMAC deposition is nearly quantitative until both concentrations are equal. The amount of softener on the fabric always corresponds to the concentrations of free softener and of cationic complex. It seems likely that the complex is held on cotton by mechanical entrapment in the cotton fibers [72]. Once the SLS concentration exceeds that of the softener, the complex is increasingly solubilized by the surfactant excess and deposits less and less [72,92,108].

The extent of the anionic surfactant effect depends on the procedure adopted. If the anionic surfactant is added to the rinse liquor after quaternaries, the amount of DHTDMAC present on cotton is reduced to 19% of its initial value. It is reduced to 6% if the anionic and cationic surfactants are mixed in equimolar amounts before their introduction in the rinse liquor and no quaternary deposits if there is an excess of anionic surfactant [100].

Nonionic surfactants such as ethoxylated fatty alcohols also impair softener deposition, presumably because they improve the solubility of the softener particles and compete to deposit onto fabrics [37,73,110].

Surfactants are usually more detrimental in U.S. than in European washing machines. The amount of anionic detergent residues is much lower in European washers, which achieve several rinse cycles before introducing the fabric softener in the liquor.

As regards wash cycle fabric softening, the speed of softening in the wash is not the same as in the rinse. The differences are due to the competition for deposition

that takes place between the various substances present in the liquor. In the beginning, the softening of hydrophilic fibers, cotton and wool, is somewhat quicker in the wash than in the rinse and slower afterwards. In contrast, the softening of synthetic fibers is at least as quick in the rinse as in the wash.

Soils present in the washing liquor decrease the amount of DHTDMAC that deposits onto fibers, since DHTDMAC also adsorbs onto the soil particles, which are negatively charged. As a result, the softening efficacy is impaired. Furthermore, because of quaternary adsorption, the negative charges on the soil particles and on the fabrics disappear, favoring soil redeposition.

These observations have also found application in softergents. The harder the water, the more the cationic softener deposition from an anionic detergent [9], since the compression of electrical double layers leads to a reduction of the anionic–cationic interaction. The deposition from a nonionic detergent may drop from 100% to 50% [9] as the softener, becoming less soluble, tends to interact more strongly with the hardness-insensitive surfactant.

The best softening is observed at a washing temperature of 40 to 45°C [14].

2. Desorption

Once on the fabric, the quaternaries withstand several rinses in plain water [1,97,98]. They are partly removed by anionic surfactants in subsequent washes [6,31], but quat removal is never complete, even after two washes with a detergent [26,96]. The situation is probably different with esterquats because of the hydrolysis that takes place under the alkaline conditions of the wash. In fact, only 25% of the DHTDMAC present on the fibers is removed during a wash with SLS, 75% remaining as a catanionic complex [72]. Molecules with the longest alkyl chain derivatives best resist cumulative rinses [20].

Quaternaries are also not totally extracted from cotton with chloroform [98] or with isopropyl alcohol. The residual amount most probably corresponds to the molecules that form ion pairs with the carboxyl groups at the fiber surface.

Under real conditions, the overall amount of quaternaries on fabrics slowly increases upon cumulative launderings [26,98,100].

C. Softening

1. Mechanism

Fabric softness is the result of the skin–fabric interaction and of the fabric mechanical properties. Fabrics are made of yarns, yarns being assemblies of twisted fibers. Fabric mechanical properties depend on the fabric geometry, on the yarn–yarn friction, and on the yarn mechanical properties. The mechanical properties of the yarn are determined by the fiber rigidity, by the fiber–fiber friction, and by the yarn geometry [26].

During successive launderings and wear, the fabric finish is removed and the fibers are degraded by chemical and mechanical attack. Cotton fibers gradually

unravel and break into microfibrils. In hard water areas, insoluble salts deposit onto the microfibrils during the wash and rinse. The lime scale buildup gives the fibers a “sandpaper-like” structure, making the textiles harsh to the skin. This phenomenon is known as fiber encrustation.

Upon drying, the microfibrils remain up, away from the fiber bundle. Fibers bristled with these microfibrils no longer slip easily over one another and, when garments are dried indoors, sheltered from the wind, no force counteracts the capillarity which brings neighboring fibers into contact. As a result, they interact much more strongly together, losing flexibility and slipperiness [26].

Fabric softeners remedy these degradations and improve the feel by coating the fibers with a protective film of fatty material that reconstitutes the finish, maintains the microfibrils close to the fibers [23], masks fiber alterations, and covers the mineral deposits. Hence, the main mechanism for fabric softening is fiber lubrication.

According to Chalmers [1], the softener forms a film over the entire surface of the fabric, with the fatty chains pointing away from the surface. There is some evidence for the correlation between the soft touch and the reduction of friction, friction between fabric and skin and between the fibers themselves [20]. For instance, Röder and colleagues report an excellent correlation between softening efficacy and the interfiber friction coefficient. The latter was assessed by fixing a piece of treated textile to a metal block and measuring the force applied to move the metal along a fixed piece of the same textile [31]. Once the fiber–fiber friction coefficient decreases, the fibers move more independently of one another [3,27]. The overall result is a 20% decrease of fiber abrasion [13] and fabrics are perceived as more flexible [3]. The friction coefficient, however, increases when the relative humidity rises above 90% [20].

The ability of a film to reduce the friction coefficient depends on two factors: the energy of adhesion of the polar group to the surface and the energy of intermolecular cohesion in the fatty layer [20]. The former must be large to ensure a good film adhesion to the surface; the latter must remain small so that the films are not torn from the surface upon rubbing. To separate adequately the two surfaces, the fatty chains must have at least 16 carbon atoms [20]. A good softener, however, does not always give the lowest friction coefficient. Mooney mentions that unsaturated derivatives better lubricate than their saturated counterparts, as estimated from the friction coefficient. The contradiction is probably due to the lower affinity of unsaturated fatty molecules for fabrics, leading to lower concentrations on fibers [52].

At this point, a distinction must be made between static and dynamic friction coefficients. The force required to overcome the resistance to starting a movement is not the same as the one necessary to maintain an existing movement. The former corresponds to the static friction coefficient, the latter to the dynamic friction coefficient [52]. For instance, silk exhibits high static and low

dynamic friction coefficients. A good softener must reduce both coefficients, but especially the dynamic one [20].

According to Berenbold [13], the presence of softener at the fiber surface also reduces the encrustations due to repeated washes by 35%. The weight increase of terry towels after 25 cumulative washes decreases from 7% (w/w) without softener to 3% (w/w) in the presence of softener [13].

The importance of frictional properties largely exceeds the area of domestic fabric softeners. They are also key in the textile industry, as they condition the slipping of fibers over each other in all mechanical processes [20]. Friction causes breakage of threads and generates static electricity. More generally, softened fabrics are pressed and sewed more easily, as there is less resistance to the metal movement. They also relax more quickly at the dry state since fibers slide over one another more easily. However, it is more difficult to cut fabrics with scissors as the blade slips over the fibers and fewer fibers are torn during cutting [20].

Reducing the friction is not the only way to improve fabric softness. Plasticizing the fibers is another approach. Plasticizing agents can restore the fiber flexibility. To be effective, the molecules of the plasticizing agent must be small enough to penetrate the fibers. The most common plasticizer is water; it is a good softening agent as moist fibers are less harsh than dried ones. Humectants such as urea, potassium acetate, glycerin, and other polyhydric alcohols, which moisten the fibers, can be regarded as possible softening actives [52]. However, because of their very large solubility in water, they are not prone to deposit from the rinse onto the fabrics. This prevents formulators from considering them as ingredients for rinse cycle fabric softening.

2. Evaluation

Some quantitative, instrumental methods exist for assessing fabric softness, but they are not sensitive enough to assess differences between softeners. The evaluation is usually carried out by sensory perception. The feeling of a textile is very subjective as, besides the basic physical properties of the fabrics on which it depends, it is also influenced by many evaluator-linked unquantifiable parameters such as mood and tactile sensitivity [52].

Most commonly, experienced judges are asked to compare the softness of fabrics treated with an experimental softener to that of a reference. The latter may be an untreated sample of the same fabric or a sample treated with the benchmark under the same conditions. The evaluation is conducted in blind pair comparison and in random order.

Pieces of terry towels have been found to be particularly suitable to evidence slight differences. The difference of softness is rated (e.g., 1 = weak, 2 = medium, 3 = strong difference); it is actually an overall estimation of the surface slipperiness, fluffiness, and texture. A statistical treatment gives a significance to the difference and, to some extent, quantifies the softening efficacy of the prototype.

The assessment is sometimes carried out by ranking groups of four to six towels but the evaluation is more difficult and the results less precise.

An interesting but more time consuming alternative is to quantify the softening efficacy of a system by determining the concentration at which it is equivalent to a reference. In another alternative, mentioned by Levinson, towels treated with softeners A and B are compared and ranked against a high standard and an untreated control [3]. A is judged superior to B at the 95% confidence interval if it is preferred by at least 15 out of 20 panelists. Quantification results must be interpreted with care, since the plot of softness magnitude against softener concentration is not linear but an S-shaped curve.

Bücking *et al.* [96] have quantified the effect of alkyl chain length on softening efficacy. They propose the following values (expressed as percentages of the C_{18} softening efficacy): $C_{12} = 0\%$, $C_{14} = 40\%$, $C_{16} = 80\%$, $C_{18} = 100\%$, $C_{20} = 110\%$, $C_{22} = \text{less}$. Williams evaluated the effect of the softener active structure [9]. He proposes the following equivalence: 0.10% DHTDMAC = 0.135% tallow imidazolinium chloride = 0.18% tallow diamidoalkoxylated quat. It is important to note that these results were obtained in the laboratory, on clean loads in the absence of detergent. Differences under actual use conditions should be less because of the presence of soil and detergent residues in the liquor.

Several methods have been developed to quantify the softening efficacy of a system. Most are intended to quantify the various parameters that relate to softness. None is fully satisfactory. For instance, Laughlin mentions the determination of the fiber lubricity, and the determination of the compressibility and of the resistance to folding [26].

Good results are obtained with the Kawabata approach, which measures several different mechanical properties of the fabric at the same time. The Kawabata evaluation system for fabrics uses four devices measuring the tensile and shearing, pure bending, and compressional properties, and surface characteristics of fabrics. Key parameters are the applied force, the rate of deformation, and the tension on the sample. By comparison with subjectively evaluated standards, statistical correlations can be drawn, leading to the objective quantification of fabric softness. The method, however, is too complex for routine work [26]. Some other methods are reviewed by Mooney [52]:

- The Flesher pin method measures the force applied to push several pins into a fabric.
- The Taylor sound meter measures the sound generated by a textile when it is drawn over glass pins.
- The Kakiage method measures the thickness of a fabric as a function of the applied pressure. The pressure of human grip is, according to Mooney, 16 g/cm^2 .

D. Static Control

Static electricity may be generated in different ways [20,111]:

1. When separating two surfaces in contact. The quantity of charge, which is transferred from one surface to the other, depends on their relative affinity for the charge. The phenomenon is very common as different materials always have different affinities.
2. When rubbing surfaces of the same material if their microstructure is different. The large temperature gradient that appears at the interface between rough and smooth surfaces causes particles to move from the hot to the cold side, leading to a transfer of charge if they are charged.
3. When rubbing two identical surfaces of different size. Repeatedly rubbing the surfaces enhances the charge transfer.

The static charge is dissipated in the environment after the separation of the surfaces. The kinetic depends on the surface characteristics. It takes less than one second if the material is a conductor, minutes or even hours if it is an insulator [111]. Static charge occurrence also depends on the ambient relative humidity. The charge on a textile can decrease markedly when the relative humidity rises from 10 to 90%. It decreases by a factor of 7 for every 10% of humidity increase [111].

Dry cotton and wool do not conduct electricity very well, but, at ambient relative humidity above 60%, they adsorb enough moisture to dissipate static charge [20]. The situation is quite different with low-polarity fibers such as synthetic fibers, e.g., polyester (Dacron), polyamide (nylon), polyacrylonitrile (acrylics), and vinyl [4, 10]. Even at 60% relative humidity, they remain poor conductors.

The problems linked to static electricity occur when synthetic fibers are subject to friction under conditions of low relative humidity such as using the garments in a dry climate or drying in an automatic tumble dryer. The static problem is not solved by preventing the formation of charges but by dissipating them as quickly as possible, before the problem appears [111]. In other words, the buildup of static electricity is avoided by creating a layer that conducts electricity on the fibers and enables the charges to leak away. This is achieved by enhancing the surface conductivity and/or the humidity at the fiber surface.

To enhance the surface conductivity, a chemical is deposited that transports the current. Adsorbing a hygroscopic material increases the humidity at the fiber surface [31].

An efficient antistatic agent must consequently exhibit the following properties [23]:

1. High substantivity and homogeneous deposition onto fabrics.
2. Good moisture uptake capacity from ambient air.

3. Ions released on the surface that can move freely in an electric field — polyions that interact more or less strongly with the fabric are less efficient in enhancing the conductivity of the surface [111].

All surfactants develop an antistatic activity. Their efficacy relies both on their ionic character and their capacity to bind water [23]. However, the most efficient antistatic agents are cationic softeners, because of their high affinity for fabrics [20]. Moreover they also reduce the generation of static electricity by lubricating fibers and reducing interfiber friction [10].

Softener antistatic activity is easily quantified by measuring the electrostatic charge or the surface resistance of items directly after the drying cycle. It depends on several parameters:

1. The chemical structure of the cation, which determines the ionic and hygroscopic characteristics. Enhancing the hydrophilicity, e.g., by introducing double bond(s), ethylene oxide chain(s), or hydroxyl group(s) in the molecular structure, can increase the antistatic efficacy of an active [20].
2. The type of counterion. Methylsulfate derivatives are somewhat more efficient than chloride ones [1].
3. The amount present on fabrics. The higher the content, the better the static control.
4. The particle size of the softener dispersion, since the coating is more homogeneous when the dispersion is micronized [92].
5. The type of fiber [36].

Softening actives exhibit the following sequence of increasing antistatic activity in rinse cycle products: tallow imidazolinium < tallow ammonium chloride < tallow diamidoalkoxylated quat. Triethanolammonium oleate has also been reported to be a very efficient antistatic agent [20].

The type of softener is also important. Williams [9] proposed the following sequence of decreasing efficacy: dryer softener \geq (liquid nonionic) wash cycle softener > rinse cycle softener.

The difficulties encountered by the textile industry are even greater. The friction of hot air moving along fibers produces static electricity. Besides electric shocks, the problems caused by static electricity are twofold: it may cause malfunctions in the operation of electronic equipment and it generates sparks that may be hazardous in the presence of flammable vapor [20]. Here also, softeners are extremely efficient in fighting static charges on fibers.

E. Others

1. Ironing

Because of their long fatty chains that form a film at the fiber surface, softening actives work as lubricants and decrease the frictions between fibers. As a result,

they facilitate the flexibility of the fibers and their sliding over each other, thereby improving fabric smoothness. Many [2,26,112] but not all [34] authors found the effect perceivable. The discrepancy is probably due to differences in experimental conditions, such as a different number of cumulative launderings. Even more efficient than the usual softener actives in improving fabric smoothness are polydimethylsiloxane and partially oxidized polyethylene [17].

The antiwrinkle effect of softeners is usually quantified by the wrinkle recovery angle, the residual angle exhibited by a fabric after having been creased and compressed. Better results are usually observed for softener-treated fabrics [34].

Softeners also reduce the dynamic friction coefficient between the fabrics and the iron, thereby making gliding easier [27]. The resistance to an iron is easily quantified by measuring the height of an inclined plane at which the iron starts to move: it decreases as the number of rinses with a fabric softener increases; the opposite is observed in the absence of softener [4].

2. Wettability of Softened Textiles

The intrinsic affinity of fibers for water is easily quantified by measuring the sinking time of a piece of fabric carefully deposited on water. A better alternative is the dye wicking method in which a fabric strip is suspended with the extremity dipping in a 0.05% aqueous solution of methylene blue. The rise of the liquid is recorded as a function of time and compared to that of a control without softener.

Water absorption by porous solids depends on the water–solid contact angle and on the liquid surface tension. The spreading of water in fabrics is the result of wetting the fiber surface, penetration into the fibers, and capillary pressure [20]. The wetting of yarns depends on their surface energy and the interfiber space.

The elaboration of a model to describe cotton wicking is very complicated, although the effect of quaternaries on the wetting of fibers is easily seen: the softener enhances the interfacial tension strongly. Since the fiber surface energy and the surface tension of water are not affected, the spreading coefficient is decreased, and so is the wetting of the fiber surface.

The spreading coefficient is given by:

$$S_{L/S} = - \left(\frac{\Delta G_{\text{spreading}}}{S} \right) = \gamma_{SA} - (\gamma_{SL} + \gamma_{LA})$$

where S = surface area of the fiber, γ_{SA} = surface energy of the fiber, γ_{SL} = fiber–water interfacial tension, and γ_{LA} = water surface tension. When an angle is formed between the solid and the liquid, the equation is:

$$\gamma_{LA} \cos \theta = \gamma_{SA} - \gamma_{SL} \text{ or } S_{L/S} = \gamma_{LA} (\cos \theta - 1).$$

Because of the presence of pores in cotton, no real capillary exists in or between the yarns and no true meniscus is formed. Consequently, Jurin's law does not apply. This explains why the elaboration of a model to describe cotton wicking is so complicated.

In real life, the decrease of water absorbency by fabrics is significant only when an excess of fabric softener is present on the fibers. Modifying the structure of the softening active to make it less hydrophobic restores the wettability. For example, one can use actives bearing shorter or unsaturated alkyl chains; the former approach is much more efficient than the latter. Introducing ether groups in the structure also helps in restoring the fiber affinity for water. All these modifications, however, induce a loss of softening efficacy! As a general rule, any structure modification that enhances the affinity of the softened fabric for water impairs its softness. The only exception is silicones, which, at low levels, increase both softness and water absorption.

An alternative way of restoring the affinity of cotton for water is to introduce small amounts of nonionic surfactant in the softener composition.

3. Perfume

Perfumes are a key ingredient of fabric softeners. They are complex mixtures of water-insoluble organic molecules, which remedy the intrinsic malodor of the product by integrating the base odor in the scent. They do not cover the base odor, they eliminate it [21].

When dispersed in water together with the melted cationic active, the perfume is solubilized in the hydrophobic area of the softener particles, which transport it onto fabrics.

Upon storage of the laundered garments, the perfume is slowly released into the air. As the release of the volatile components from the fatty layer at the fiber surface is slower than when the perfume is simply sprayed on the fabrics, the pleasant smell lasts longer.

Escher and Oliveros systematically studied the effect of various parameters on fragrance adsorption onto fabrics [113]. They found that the affinity of fragrance for fabrics is mainly determined by the type of fiber (cotton > polyacrylonitrile) and, to a lesser extent, by the type of single-chain surfactant (cationic > anionic and nonionic). These factors are interdependent (the effect of the type of surfactant on the affinity for polyacrylonitrile is weak). The effect of temperature and of surfactant concentration is less.

The tenacity of an ingredient, defined as the proportion of product present on wet laundry that remains after drying, essentially depends on the type of fabric and is much larger on cotton. This is tentatively assigned to the swelling of cotton fibers, leading to a better penetration of the fragrance into the fibers.

It would have been extremely interesting to include DHTDMAC in the study, as it is expected to outperform CTAB in transporting fragrance onto fabrics.

4. Antibacterial Activity

Cationic surfactants are extremely harmful to enzymes. The most efficient germicidal agents are single alkyl chain derivatives of ammonium or pyridinium [18]. They are known to interact immediately with the negatively charged amino acid residues of proteins. As a result, the electrostatic repulsion between the charged groups at the enzyme surface is lost and its structure collapses. This and the neutralization of the ionized groups in the enzyme active center cause the complete loss of the catalytic activity [69].

This is the mechanism proposed by Datyner to account for CTAC antibacterial, and antifungal to a lesser extent, activity he reports [20]. Martins *et al.* invoke the ability of the surfactant to disrupt the cell membrane and form mixed micelles with its lipids to account for CTAB and SLS antibacterial activity [29]. In contrast, the bacteria-killing efficacy of double-chain surfactants such as DHTDMAC is assigned to an alteration of the membrane protein function resulting from the adsorption of vesicles onto the bacterial membrane. This study was carried out under laboratory conditions (very low ionic strength), and the antibacterial efficacy of fabric softeners under realistic use conditions remains highly questionable.

5. Color Protection

Fabric softeners exhibiting color protection properties are also found on the market. Some contain ingredients that prevent dye bleeding or dye transfer from colored items onto whites. Others keep dissolved minerals in solution, thereby preventing their deposition onto the fabric and the resulting dull look [35].

IX. FUTURE TRENDS

Trends for future fabric softeners may, to some extent, be found in the patent literature [10]. In a worldwide survey of 280 patents related to fabric softeners, 151 (54%) cover new softening molecules (Figure 12.10a). The main claims are color protection (color fading, dye transfer inhibition, and ultraviolet protection) and better fragrance perception (new perfume or improved delivery or longer lasting). Miscellaneous benefits cover improved aesthetics, increased convenience (ease of ironing and reduced wrinkling), soil release, and enhanced wettability. Reduction of malodor and disinfection are also claimed; they are particularly critical in equatorial areas (Figure 12.10b) [16].

Many of the new molecules are claimed to deliver more softness, leading to more cost effective or more easily concentrated products. To be considered for incorporation in a softening composition, the candidates must be available to the manufacturer on an industrial scale and cannot be hindered by patents. They must fulfill the human safety requirements and in Europe the environmental regulations.

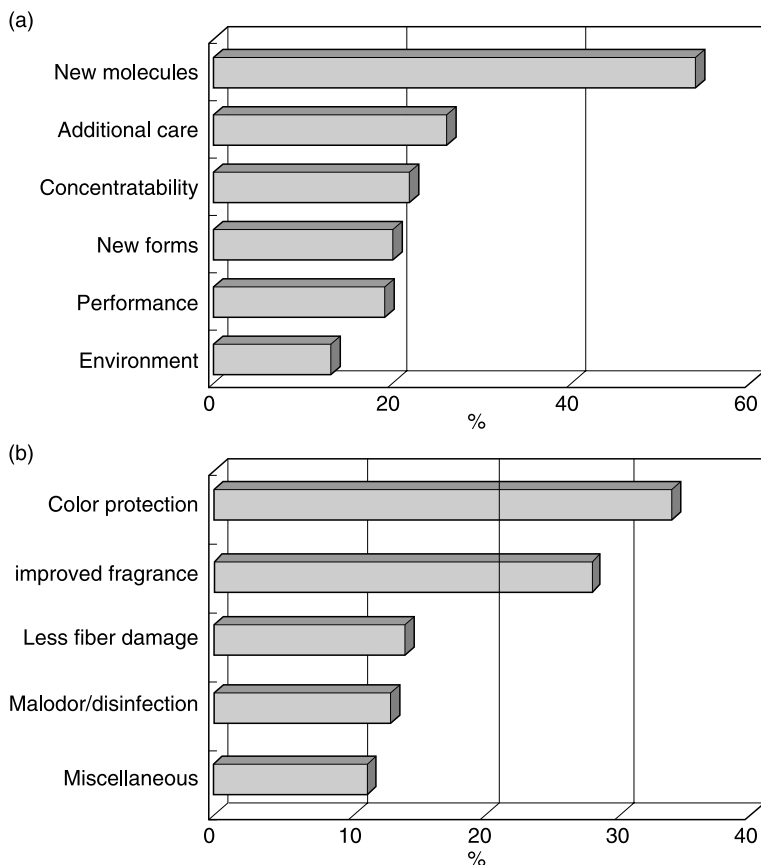


FIG. 12.10 Trends for the future, as estimated from a patent literature survey. The survey involved 280 patents; percentages are the proportion of patents claiming the corresponding benefit. (a) Softener characteristics; (b) Softener attributes.

The cost of testing safety and environmental risk is high, usually over U.S.\$200,000 or €155,000 [3].

Another important driver of the softener market is the globalization of formulations to reduce costs. Besides scale reduction, globalization enables the centralization of product development. Habits, preferences, and devices, however, vary from country to country. A global technology has to be adjusted to local habits as well as the different washing equipment.

Another source of growth may be found in concentrates, which enable a reduction of the packaging material. They also deliver more convenience and exhibit a

TABLE 12.2 Levinson's Vision of the Future for Fabric Softeners [3]

	Europe	North America	Latin America	Asia
Expected growth rate (%/year)	2	3	>5	1–2
Primary market driver	New softening molecules	Cost/performance ratio	Performance; strong fragrance	Biodegradation ^a
Remarks	Esterquat fulfills environmental profile requirements	Actives are removed by waste treatments and considered as biodegradable	Line drying predominates; refill to reduce packaging waste	Japan accounts for 50% consumption

^a Biodegradation is a concern because of the high individual consumption and population density.

better environmental profile, but they may be perceived as offering less value for money (small bottle, thin product when diluted).

Major volume and value growths in the future are expected to take place in high-growth markets: Asia, Latin America, and Eastern Europe. The present consumption for these markets is low. The fabric softener in-home penetration is less than 30% and the consumption is only 7 l/user household/year. For fabric softener use to increase requires a certain economic well being for consumers to spend their income on products that go beyond their basic needs, which is simply cleaning [16].

In mature markets, added-value benefits may become a must for further business growth [16]. A complementary vision of the future of fabric softeners has been proposed by Levinson [3]. This is summarized in Table 12.2.

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