1
Liquid Detergents: An Overview

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I. INTRODUCTION

Liquid detergents provide convenience in our daily life ranging from personal care of hand and body cleansing and hair cleaning and conditioning to home care in dishwashing and cleaning of various household surfaces to fabric care in laundering and fabric softening. Compared with powdered detergents, liquid detergents dissolve more rapidly, particularly in cold water, they generate less dust, and they are easier to dose. It is not surprising, therefore, that liquid forms of cleaning products have been gaining in popularity since their introduction in the late 1940s.

With the exception of fabric softeners and shampoos, the solid form of cleaning products preceded the liquid form. This is true of manual and automatic dishwashing, laundering, and general personal cleansing products. As a result, the technical history of liquid detergents is to a large extent one of emulating the performance features of the powder models.

[†]Dr. Cahn passed away on October 26, 2004. This overview chapter is based on his earlier work in the first edition with an update since that time. We would like to acknowledge Dr. Cahn for the enormous contributions that he made to the detergent industry over the last few decades.

All other factors — soiling, water hardness, and temperature — being equal, cleaning performance is a function of concentration and type of active ingredients that are delivered into the cleaning bath. Almost by definition, the liquid form involves a dilution of the active ingredients, that is, a given volume of a powdered detergent can generally deliver more active ingredients than an equal volume of a liquid detergent. The task of providing performance equality with powders is therefore not insignificant. It is made even more difficult when salts often pose problems of solubility and compatibility with any organic surfactants of the formulation. Finally, formulation problems are most severe when the active components are less stable in an aqueous environment than in a solid matrix.

These considerations apply principally to the heavy-duty liquids, the largest of the liquid detergent categories, but they also come into play with automatic dishwasher liquid detergents.

The situation is different for products designed for light duty, such as for hand dishwashing and softening fabrics. These liquids are generally superior in performance to their powder counterparts to the extent that these existed in the first place. This is also true of shampoo formulations, for which there is no common solid equivalent.

Since the mid-1990s there have been numerous new products launched around the world and there have been many advances in technology in this field. Liquid detergents have further gained popularity around the world replacing many traditional products in solid, powder, or other forms. Detergent manufacturers have introduced a large number of new products in every category. These products not only offer continuous improvement in cleaning performance but also incorporate more and more additional benefits. This is true for all products. Chapters 7 to 14 provide a detailed review of these new products and the advances in new technologies in every area.

This chapter is intended to give readers a historical overview of the various products as well as the new developments in the last decade (1995–2004).

II. LIGHT-DUTY LIQUID DETERGENTS

On a truly commercial scale, the age of liquid detergents can be said to have begun in the late 1940s when the first liquid detergent for manual dishwashing was introduced. This liquid consisted essentially of a nonionic surfactant, alkylphenol ethoxylate. It produced only a moderate amount of foam when in use.

This proved to be a serious detriment. To be successful, consumer product innovations must show a large measure of similarity to the conventional products they are intended to displace. In this case, copious foam was the essential performance attribute that needed to be as close as possible to that generated from powders and soap chips.

The requirement for copious foam levels has a technical basis and is more than a mere emotional reaction to a visual phenomenon. With soap-based products the appearance of a persistent foam signals that all hard water ions have been removed by precipitation as calcium and magnesium caboxylates and that excess soap is available to act as a surfactant.

The foaming requirements for light-duty liquids were met by the next series of product introductions in the early 1950s. These formulations were based on high-foaming anionic surfactants. They were capable of maintaining adequate levels of foam throughout the dishwashing process and possessed sufficient emulsifying power to handle any grease to produce "squeaky clean" dishware. This was accomplished by a mixture of anionic surfactants — alkylbenzenesulfonate, alcohol ether sulfate, and alcohol sulfate — sometimes in combination with nonionic surfactants. To maintain foam stability alkanolamides were incorporated. In some products alkanolamides were subsequently replaced by long-chain amine oxides.

The formulation of light-duty liquids overcame a second major technical hurdle inherent in the formulation of all liquid detergents: to maintain homogeneity in the presence of significant levels (about 30% or more) of moderately soluble organic surfactants. Coupling agents or hydrotropes (see Chapter 2) were introduced for this purpose, specifically short-chain alkylbenzenesulfonates, such as xylene-, cumene-, and toluenesulfonate, as well as ethanol.

Light-duty liquids have maintained a significant market volume to this day. This is in spite of the introduction and increasing popularity of automatic dishwashing machines and the detergents formulated for these machines. In fact, the use of both has increased greatly since their introduction in the late 1950s. This can be explained in part by the fact that some consumers use the light-duty liquids for washing delicate laundry items by hand in addition to continued use of them for washing small loads of dishes.

Over the years, minor additives have been incorporated into light-duty liquid formulations, principally to support marketing claims for special performance features. For a period in the 1960s, antimicrobials were incorporated into some products designed to prevent secondary infections of broken skin during dishwashing. After an absence of some 30 years antimicrobials are again appearing in light-duty liquids, and antimicrobial-containing formulations have become an important product segment. This is clearly a result of the increasing awareness of the possible presence of bacteria in foods, especially in chicken.

Improving the condition of skin as a result of exposure to light-duty liquid solutions proved to be technically very difficult. Exposure times are relatively short, about 20 minutes, three times a day in the best circumstances, and use concentrations are low, about 0.15%. The combination of low use levels and short exposure times makes it difficult to overcome the adverse effects of skin exposure to other influences, such as dry air in heated homes and strong household chemicals.

Generally speaking, light-duty liquid compositions are relatively nonirritating to skin. Mildness to skin could therefore be claimed for these products with reasonable justification. During the 1960s and 1970s the cosmetic image was further enhanced by making light-duty liquids more opaque, and imparting to them the ability to emulsify grease, combined with a persistent foam, has been the main objective of technical improvement.

In line with cleaning efficacy, solid particles have also been incorporated into some light-duty liquid formulations with the objective of increasing the effectiveness of the products in removing solid caked-on or baked-on soiling from articles.

Since the mid-1990s a great wave of evolution has taken place in the hand dishwashing liquid detergent market. The new products not only include "smarter" surfactants and surfactant mixtures, but also address multiple consumer needs offering multidimensional benefits. While consumers are in general quite satisfied with the primary cleaning function of dishwashing detergents, they have started looking for additional benefits beyond cleaning. New products introduced to the market incorporate various benefits including antibacterial and hand care properties and cleaning of tough-to-remove soiling.

A number of nontraditional ingredients have been introduced to light-duty liquid detergent formulations. These include some novel surfactants, antimicrobial agents, special polymers, and enzymes. Novel surfactants such as mid-chain branched ethoxy sulfates, ethylene diaminetriacetate, ethoxylated/propoxylated nonionic surfactants, Gemini surfactant, bridged polyhydroxy fatty acid amides, and the amphoteric surfactant sultaine are used for enhancement of cleaning or foaming performance.

The antimicrobial agent most commonly used in light-duty liquid detergents is triclosan (2,4,4′-trichloro-2′-hydroxydiphenyl ether). Other antimicrobial agents such as triclorocarban (TCC) and *para*-chloro-*meta*-xylenol (PCMX) are also used in some products, although to a much lesser extent.

Many polymers are used in light-duty liquid detergents to give various benefits. For example, polyoxyethylene diamine is used to increase grease cleaning, polyacrylate to aggregate and suspend particles, amino acid copolymer to tackle resistant soiling, polyethylene glycol to increase solubility, and ethylene oxide–propylene oxide copolymer to increase solubility, grease cleaning, or foam stability, or to improve mildness.

The other major development in light-duty liquid detergents since 2000 has been the introduction of experiential products, with different colors and fragrances that enhance a cleaning task. Colgate-Palmolive launched the Spring Sensations line in the U.S. market in the spring of 2000. New variants in colors and fragrances such as Orchard Fresh and Green Apple have been added to the line. Procter & Gamble followed with Joy Invigorating Splash and Tropical Calm and in the spring

of 2001 with Dawn Fresh Escapes featuring Citrus Burst Apple Blossom and Wildflower Medley.

More recently, the aromatherapy benefit offered by personal care products has been extended to hand dishwashing products. Colgate-Palmolive launched Ultra Palmolive Anti-Stress Aromatherapy Dish Liquid with lavender and ylang-ylang extracts claiming "a whole new sensation in dishwashing."

III. HEAVY-DUTY LIQUID DETERGENTS

Once light-duty liquid products had established an attractive market position, the development of heavy-duty liquids could not be far behind. As with light-duty liquids, the requirement of similarity to existing products also had to be met. In this case these products were powdered laundry detergents. The powdered laundry detergents of the 1950s were characterized by the presence of high levels of builder, specifically pentasodium tripolyphosphate (STPP), and relatively low levels, about 15%, of surfactants. In formulating a heavy-duty liquid, therefore, the major technical objective was to find ways of stably incorporating maximum levels of builder salts.

The first commercially important heavy-duty liquid was introduced into the U.S. market in 1958. The product incorporated tetrapotassium pyrophosphate, which is more soluble than STPP. Even so, in the presence of a surfactant system of sodium alkylbenzenesulfonate and a mixture of alkanolamides the formulation could tolerate only 15 to 20% of tetrapotassium pyrophosphate.

Incorporation of an antiredeposition agent, another ingredient present in laundry powders, proved to be another major technical hurdle. Antiredeposition agents, generally carbohydrate derivatives such as carboxymethylcellulose, had been introduced into laundry powders to prevent graying after a number of repeat wash cycles. In one product the patented solution to this problem consisted of balancing two antiredepostion agents of different specific gravity such that the tendency of one to rise in the finished product was counterbalanced by the tendency of the second to settle in the product [1].

Although the first major commercial heavy-duty liquid composition was formulated with a builder system, the concentrations of builders and surfactants it delivered into the washing solution were lower than those provided by conventional detergent powders. As a liquid, however, the product possessed a unique convenience in use, particularly for full-strength application to specific soiled areas of garments. Convenience was accompanied by effectiveness, because the concentration of individual ingredients in the neat form approached that of a nonaqueous system.

This is illustrated by the following consideration. Recommended washing product use directions lead to washing solutions with a concentration of about

0.15% of the total product. At a surfactant level of about 15% in the product, the final concentration of surfactant in the wash solution is about 0.0225%. The efficacy of surfactants in providing observable cleaning at such a low concentration attests to the power of the interfacial phenomena that underlie the action of surfactants.

By contrast, a heavy-duty liquid containing 20% surfactant, applied full strength, leads to a surfactant concentration of 20%, some three orders of magnitude larger than in the case discussed above. At these (almost nonaqueous) concentrations solution phenomena, such as those occurring in nonaqueous dry cleaning, are likely to be responsible for cleaning efficacy. The popularity of heavy-duty liquids for pretreating stains was thus based not only on convenience but also on real performance.

In the mid-1960s branched-chain surfactants were replaced by more biodegradable analogs in all laundry products. In heavy-duty liquids sodium alkylbenzenesulfonate, derived from an alkylbenzene with a tetrapropylene side chain, was replaced by its straight-chain analog, referred to as sodium linear alkylbenzesulfonate (LAS).

The conversion to more biodegradable surfactants was prompted by the appearance of foam in rivers. The appearance of excessive algal growth in stagnant lakes prompted a second environmental development that proved to be beneficial to the expansion in use of heavy-duty liquids: the reduction or elimination of the sodium tripolyphosphate builder in laundry detergents. Restrictions on the use of phosphate in laundry detergents were imposed by a number of states and smaller administrative agencies beginning in 1970. Because no totally equivalent phosphate substitute was immediately available, the performance of heavy-duty laundry powders was adversely affected. As the whole-wash performance differential between powders and liquids narrowed, the usage of heavy-duty liquids for the whole wash expanded, markedly so in areas where phosphate had been banned.

In the first nonphosphate version of a commercial product, phosphate was replaced by NTA (trisodium nitrilotriacetate), a powerful builder, comparable to condensed phosphate in its efficacy in sequestering calcium ions in the washing solution. Because of reports of adverse teratogenic effects in laboratory experiments, this builder was withdrawn from the market toward the end of 1971. It was replaced by sodium citrate, an environmentally more acceptable but inherently less powerful calcium sequestering agent. At the same time surfactant levels were increased by a factor of about three. What had happened in practice (if not in theory) was that higher levels of surfactants had been introduced to compensate for the loss in the builder contribution to washing efficacy provided previously by phosphate.

The 1970s saw the introduction of several heavy-duty liquids that carried this substitution to its limit, being totally free of builder and consisting solely of

surfactants at levels ranging from 35 to 50%. These compositions were distinguished from light-duty liquids by the presence of laundry auxiliaries, such as fluorescent whiteners and antiredeposition agents. With the exception of a few products based on surfactants only, most heavy-duty liquids are formulated with a mixture of anionic and nonionic surfactants, with anionics predominating.

The steady expansion of the banning of phosphate across the U.S. accompanied by an increase in the convenience and efficacy of heavy-duty liquids led to an expansion in the use of this product category in the 1970s and 1980s. This expansion was fueled not only by the publicity that normally accompanies the introduction of new brands but also by some significant product improvements. The first of these to appear in the early 1980s was the incorporation of proteolytic and, later, amylolytic enzymes. In liquid detergents, with their relatively high amounts of water, proteolytic enzymes must be stabilized to prevent degradation during storage [2,3]. Enzymes make a significant and demonstrable contribution to washing efficacy, not only in the removal of enzyme-specific stains, such as grass and blood, by proteinases, but also in an increase in the level of general cleanliness. The latter effect is the result of the ability of a proteolytic enzyme to act upon proteinaceous components of the matrix that binds soils to fabrics.

Enzymes had been used in detergent powders in the U.S. and Europe as early as 1960. They were subsequently withdrawn in the U.S., but not in Europe, when the raw proteinase used at the time proved to have an adverse effect on the health of detergent plant workers. Improvements in the enzymes, specifically encapsulation, eliminated their dustiness and made it possible to use these materials in detergent plants without adverse health effects.

Since the 1990s enzyme mixtures have been commonly used in heavy-duty liquids. Most products contain a minimum of a protease for removal of proteinaceous soils and an amylase to facilitate starchy food-based soil removal. Some products contain lipases for degrading fatty or oily soils and cellulases to improve fabric appearance by cleaving the pills or fuzz formed on cotton and synthetic blends.

The second product innovation was the incorporation of a fabric-softening ingredient. Again, a powdered version of a "softergent" that had been on the market for some time served as the model product. In a powder the mutually antagonistic anionic surfactants and cationic softening ingredients could be kept apart so that they would not neutralize their individual benefits in the wash cycle. In a liquid this proved to be unattainable. As a result, the choice of surfactants in liquid softergents was restricted to nonionics.

Although the incorporation of enzymes and fabric softeners strengthened the market position of heavy-duty liquids, it did not solve the basic problem of limited general detergency performance in normal washing. As noted earlier, heavy-duty liquids came close to the performance of the first nonphosphate laundry powders. With time, however, the performance of nonphosphate laundry powders improved

as new surfactant systems and new nonphosphate builders, notably zeolite in combination with polycarboxylate polymers, were introduced.

From the mid-1980s to the mid-1990s some major brands of heavy-duty liquids were converted from builder-free to builder-containing compositions. The first of these products employed a builder system consisting of sodium citrate in combination with potassium laurate [2]. Later, potassium laurate was replaced by a small-molecule ether polycarboxylate sequestrant, a mixture of sodium tartrate monosuccinate and sodium tartrate disuccinate [3]. In these builder-containing products the stabilization of enzymes is technically more difficult than in builder-free systems. A combination of low-molecular-weight fatty acids, low-molecular-weight alcohols, and very low levels of free calcium ions proved to be the solution to this problem.

In the U.S. heavy-duty liquids have grown at about 3% volume share of market a year in the last decade replacing powder laundry detergents that have dominated the market for years. By 1998 liquids had surpassed powders for the first time, and by 2001 liquid products accounted for 72% volume share of the U.S. laundry detergent market while powder laundry detergents declined to only 28% [4]. In Canada the heavy-duty liquid detergent volume share of the market grew from 15% in 1997 to 35% in 2001 [4]. In other parts of the world the volume share of heavy-duty liquid detergents grew at varying degrees.

There has been a significant technological development in heavy-duty liquid detergents in the last decade. Several thousand patents in this area were granted during this period. While many of these advances continue to focus on improvement in cleaning efficacy with conventional approaches using alternative surfactant systems, optical brighteners, or enzymes, there has been a greater emphasis on additives incorporated into the detergent formulation at low concentrations that deliver other significant, consumer-perceivable benefits. A strong emphasis in recent years has been on fabric and color care benefits, with the goal of preserving fabric appearance after multiple launderings. The market has also shifted toward consumer-friendly products that reduce fabric wrinkling and eliminate the need for ironing or reduce ironing time. Procter & Gamble developed a "Liquifiber" technology using a hydrophobically modified cellulosic to help reduce wrinkles in clothes. There has also been a continuous effort to find novel polymers that reduce dye transfer in the wash or rinse. Several patents on soil release technologies have been granted, with the focus being shifted from synthetics or blends to cotton garments. Novel enzymes are routinely finding new uses in liquid detergents, with efforts aimed at reducing allergenicity also being actively pursued. Polymers have been employed to modify the rheology of various liquid formulations for improving product aesthetics through suspension of visual cues. Incorporating encapsulated fragrances and additives into heavy-duty liquids for masking or eliminating malodors is another important development in recent years.

IV. LIQUID AUTOMATIC DISHWASHER DETERGENTS

Liquid automatic dishwasher detergents (LADDs) were first introduced to the U.S. and European markets in 1986. Prior to that, all dishwasher detergents were in powder form. LADDs have slowly gained popularity since their introduction. At the same time there has been an increase in the number of households with dishwashers, especially in the U.S. and Europe. By the early 2000s about half of U.S. households had dishwashers. LADDs account for about 40% of the dishwasher detergent market; 40% is accounted for by the powder form and 20% by the new unit-dosed form.

There has been an evolution in the technology of LADDs from clay hypochlorite bleach form to gel hypochlorite bleach form to gel enzyme nonbleach form.

The first LADDs were essentially powder compositions in a liquid form, in which functional components were suspended or dispersed in a structured liquid matrix. The liquid matrix consisted of water and the common structuring additives used were bipolar clays and a co-thickener comprising a metal salt of a fatty acid or hydroxy fatty acid. These liquid products, although minimizing some of the shortcomings of powders, suffered from two major disadvantages. First, the rheological properties of these products were such that the product needed to be shaken prior to dispensing. Second, the shelf life stability of these products did not meet consumer expectations. These problems were recognized by the manufacturers and aesthetically superior, non-shake, stable, and translucent products were introduced to the market in 1991 as "gels." All the liquid products marketed in the U.S. today are essentially in "gel" form using polymeric thickeners.

V. SHAMPOOS AND CONDITIONERS

Shampoos are liquid detergents designed to clean hair and scalp. They bear some resemblance to hand dishwashing liquids in that they are essentially builder-free surfactant solutions.

The history of shampoos is long, beginning well before the days of synthetic surfactants. The advent of synthetic surfactants greatly expanded the options for formulators and at the same time improved the aesthetics of the products.

Aesthetic properties, such as appearance (clear or pearlescent), viscosity, and fragrance, are perhaps more important in this product group than in any other product category discussed in this book. Development and maintenance of an adequate foam level is a performance property and also an aesthetic property in that it is noticed and evaluated by users.

Shampoos almost always contain additives with activity in areas other than cleaning and foaming, designed to provide specific performance attributes such as hair luster and manageability and elimination of dandruff.

The use concentration of shampoos is estimated as near 8%. This is an order of magnitude greater than that of laundry and dishwashing liquids. Mildness to skin and low irritation to eyes are therefore important requirements for shampoos.

Salts, generally sodium but also triethanolammonium, of long-chain alcohol sulfates and alcohol ether sulfates are the most widely used surfactants in shampoo formulations. Alkanolamides act as viscosity regulators and foam stabilizers.

The most general benefits associated with the use of conditioners are a reduction in static charge on hair and hence a greater ease of combing, that is, improved manageability. Cationic, quaternary surfactants and cationic polymers provide these benefits as a result of electrostatic adsorption on hair. Analogous to "softergents," the mutual antagonism of the cationic conditioners and the anionic surfactants that provide the primary shampoo function of removing oily deposits on hair presents a problem in the development of conditioning shampoos. Some anionic surfactants, notably carboxylated nonionics, have been found to be more tolerant toward cationic surfactants than alcohol sulfates or alcohol ether sulfates.

Like all other liquid detergents, shampoos have evolved from basic cleaning products into products with multiple benefits. "Two-in-one" shampoos that combine cleaning and conditioning benefits in one product have gained increasing acceptance since their development in the late 1980s and have become the major product type on the market. Consumers like the convenience and the savings from this kind of product in contrast to using shampoo and conditioner separately. The primary conditioning agent used in most two-in-one shampoos is dimethicone. Other related silicones such as dimethiconol, amodimethicone, and dimethicone copolyol have also been used, either in a primary or secondary capacity. Because many of these materials are not soluble in water, it is necessary to incorporate these ingredients into the product with emulsifying agents or stabilizers. Therefore, two-in-one shampoos are typically oil-in-water emulsions. There have been significant technological advances in two-in-one shampoos focusing on improving cleaning or conditioning benefits and improved stability. There have been numerous patents relating to these kinds of products, especially since the 1990s.

Shampoos are also formulated with antidandruff agents. Water-insoluble antidandruff agents, such as zinc pyrithione (ZPT), selenium sulfide, climbazole, coal tar derivatives, and sulfur, have been used in many products for treating dandruff. In the last decade there have been many new developments in this kind of product providing improved antidandruff efficacy. Three-in-one shampoos are also available, which provide cleaning, conditioning, and antidandruff benefits in one product.

Shampoos for particular individual needs have been increasing in acceptance among consumers with specific cosmetic or health concerns. The demand for specialty products is driven by race, age, gender, image, personality, lifestyle, health, well-being, fashion, etc. New specialty shampoos that have been developed and are appearing on the market include those offering volume control,

color protection, sun protection, revitalization or repair of damaged hairs or split-ends, frizz and flyaway reduction, and styling control.

The growing trend of using natural ingredients in personal care products in recent years also holds true for shampoos and conditioners. Keratins, vitamin E, essential oils, green tea, rosemary, grapefruit, grape seeds, saw palmetto, lotus, honey, chitosan, and ginseng are examples of some of the ingredients used in "natural" shampoos. Some of these shampoos only contain minute amounts of these ingredients for making "ingredient claims" with no real substantiated benefits.

VI. LIQUID HAND SOAP AND BODY WASH

The initial development of liquid hand soap may be dated to as early as the 1940s. In the 1960s and 1970s liquid soaps started to appear as institutional and hospital health care hand washing products, some using simple liquid fatty acid coco soaps and some using blends of synthetic surfactants. In the late 1970s liquid soap was developed and launched on the mass market in the U.S. With the advantages liquid soaps offer over conventional bar soaps, they soon gained consumer acceptance and became increasingly popular.

Liquid soap can be stored and dispensed with the convenience characteristics of all liquids. Beyond these generic attractions, they possess an aesthetic advantage over conventional bar soaps in that during use, and particularly during occasional use, they are not subject to the visual and physical deterioration in appearance of bar soaps. Stored in an aqueous matrix (residual water from washing), soap bars tend to slough and crack to various degrees. The cracks, in turn, can collect dirt, which leads to a less than attractive appearance.

As liquid soap has gained popularity, its application has extended beyond washing hands to body cleansing and liquid body wash/shower gel products. These have become a growing product subcategory.

Since the mid-1990s liquid hand soap and body wash/shower gel products have experienced probably the biggest increase in use among all the liquid detergents. This is especially true for liquid body wash/shower gel products. While there has not been a dramatic change in the cleaning chemistry and formulation, this product category has expanded with ever-growing new consumer benefits. The growing usage of liquid soap and body wash products is not merely at the expense of traditional bar soaps but is an additional usage. Consumers started using these new products for benefits that they did not get or expect to get from traditional bar soaps.

New liquid hand soap products introduced to the market in the last decade continue to focus on superior cleaning plus antibacterial and skin moisturizing benefits. Triclosan is the universal choice of antimicrobial agent for these products.

With the advent of liquid body wash or shower gel, the rapid pace of innovation in the bath and shower market in the last decade has transformed traditional

bathing and showering practice from the necessity of basic cleaning and hygiene to pampering and caring for the well-being of body and mind. The skin care benefits that were being delivered via products sold only in specialty stores and for indulgences such as spas are now coming onto the mass market. Relaxation of body and mind is being offered in the shower with the introduction of aromatherapy shower gels based on essential oils, traditionally known to soothe the nerves and relax the muscles. A desire for youthful appearance and willingness to pay for products that promise such a benefit are leading to the development and introduction of a multitude of antiaging shower products based on firming, exfoliation, etc. (see Chapter 11).

VII. FABRIC SOFTENERS

Fabric softeners or conditioners are designed to deliver softness to washed clothes and to impart a pleasant smell. They first made their appearance in the U.S. market in the 1950s. The softening effect is typically accomplished using cationic surfactants, "quats" (quaternary ammonium surfactants), which adsorb onto fabric surfaces. Di-hard tallow dimethylammonium chloride (DHTDMAC) has been the most commonly used softening ingredient for several decades. The positive charge on the nitrogen atom combined with the high molecular mass associated with the long alkyl chain ensure adsorption of the compound on the substrate and a soft feel of the conditioned fabric.

In contrast to most other liquid detergents, fabric softeners are not true solutions. The long-chain quaternary salts do not dissolve to form an isotropic solution.

Cotton is the primary target substrate for fabric softeners. With repeated washing the fine structure of cotton at the surface of a fabric becomes dendritic, that is, many fine spikes of cotton fibers are formed that protrude from the surface of the textile. Electrostatic repulsion holds these spikes in place, but in the presence of a cationic softening agent they are smoothed out. Synthetic fabrics, such as polyester and nylon, are not subject to this phenomenon. Much of the "softening" with these substrates is provided by the mechanical flexing action in the drier. However, the mechanical action of the drier causes a buildup of static electricity on synthetic fabrics, which can result in considerable sparking when garments made of synthetic fibers are withdrawn from the clothes drier. Fortunately, the agents that confer softening to cotton fibers also reduce the buildup of static charges on synthetics.

In a conventional fabric softener formulation the level of the quaternary surfactants is about 5%. Low concentrations of leveling agents can also be present. These materials, often nonionic surfactants, assist in the uniform deposition of the softening quats. In addition, a buffering system is used to ensure an acidic pH. Finally, a solvent, such as isopropanol, present at a level of about 10 to 15%, ensures a viscosity range suitable for easy dispensing from the bottle.

As additives to improve ease of ironing and to reduce the wrinkling tendencies of a treated textile, silicone derivatives, such as polydimethyl siloxanes, have been incorporated into liquid fabric softener compositions [5].

As alternative softening quaternaries, imidazolinium compounds have been introduced with a claim of superior rewet performance. This can be a useful performance feature because with continuing usage and buildup of cationics on the substrate, the water absorption of the substrate can be adversely affected. The use of anionic detergents in the main wash can mitigate this phenomenon because the anionic surfactant can combine with the cationic fabric softener to form a combination that is removed as part of the oil on the fabric.

Since the late 1970s concentrated fabric softener products have been marketed in the U.S. and Europe. The concentration of the softening cationic in these products is about three times as high as in conventional products.

As more and more attention was paid to the environmental impact of every product, the biodegradability profile of DHTDMAC was scrutinized. In the early 1990s, as the result of changes in European regulations, fabric softener manufacturers in Europe voluntarily replaced DHTDMAC with the more biodegradable esterquats. Since 1996 manufacturers in the rest of the world have also started to remove DHTDMAC from products and to replace it with esterquats. Replacing DHTDMAC with esterquats is not a simple one-to-one replacement in a formula. It requires full reformulation to maintain product aesthetics and performance. This is discussed in detail in Chapter 12.

Over the years consumers' expectation of and demand for this kind of product have been increasing. Like all other liquid detergents, more and more benefits have been added to fabric softener products. These added benefits include ease of ironing, wrinkle reduction, fiber care and protection, antibacterial properties, color protection, long-lasting freshness, deodorization, soil release, and dye transfer inhibition. There are significant differences in consumer needs and expectations from different parts of the world. In spite of all these developments, fragrance remains the most important attribute of the product on which consumers base their purchasing decision. Manufacturers offer products with various new fragrance variants as line extensions on a continuing basis.

VIII. SPECIALTY LIQUID HOUSEHOLD SURFACE CLEANERS

Detergents for cleaning various household surfaces are considered specialty cleaners. These include all-purpose cleaners for floors and surfaces, and cleaners for bathrooms, kitchens, toilet bowls, and glass.

Early versions of specialty liquid cleaners were based on low levels of tetrapyrophosphate builder and surfactant, and additions such as alkanolamides and a

sufficient amount of hydrotrope to keep the composition homogeneous. For sanitizing products, the additions included compounds with antimicrobial efficacy, such as pine oil or antimicrobial cationics. With the advent of phosphate bans, sodium citrate has emerged as the most common phosphate replacement in these products.

For increased efficacy in removing particulates adhering to substrates, some general-purpose cleaners incorporate a soft abrasive, such as calcium carbonate. The resulting products are milky suspensions with about 40 to 50% of suspended calcium carbonate [6]. Keeping these compositions homogeneous through extended storage is a technical challenge. One approach to solving this problem is to provide "structure" to the liquid medium. Surfactants present as a lamellar phase are capable of structuring liquids. U.S. patent 4,695,394 discloses a composition containing both soft abrasive and bleach.

Solvent cleaners are generally free of builder salts. The cleaning efficacy depends on solvent-type compounds, such as glycol ethers. Solvent cleaners are less effective on particulate soiling, such as mud on floors; however, they are effective against oily soiling, particularly on modern plastic surfaces.

Window cleaners constitute a specialty within the solvent cleaner category. Because any residue left on glass after drying leads to streaking or an otherwise undesirable appearance, these products are highly dilute aqueous solutions containing extremely low surfactant levels — most often nonionic surfactants — and a combination of glycol ethers and isopropyl alcohol as the solvent system.

Bathroom cleaners, sometimes referred to as tub-tile-and-sink cleaners, represent "subspecialty" liquids that must be effective against a combination of sebum soil deposited from skin detritus during bathing or showering and the hardness deposits deriving from hard water or from the interaction of hard water with soap, that is, calcium salts of fatty acids (soap scum). One subset in this group depends on acids for removing this combination of soiling. The acids contained in these products range from strong hydrochloric and phosphoric acids to moderately strong organic acids such as glycolic acid. Other products are formulated at a basic pH, incorporating calcium sequestrants, such as the sodium salt of ethylenediaminetetraacetic acid (EDTA), surfactants, and, in the case of products with disinfecting action, antimicrobial quaternaries.

Toilet bowl cleaners, like bathroom cleaners, are formulated to remove mineral deposits, principally iron salts that form an unsightly deposit at the water level. Again, acids ranging in strength from hydrochloric to citric are found in these products.

Like other liquid detergents, household surface cleaners have been produced in recent years with added benefits beyond their simple cleaning action. These added benefits include disinfection, surface shine, prevention of tenacious soil adhesion, and reduced fogging.

With so many different kinds of cleaning tasks in the home, consumers are looking for convenience, efficiency, and time savings from products. To satisfy these needs many products are moving toward more dilute, ready-to-use form. Sprays are popular forms to meet these needs. There is a large array of spray cleaners now available, including all-purpose cleaners and cleaners for bathrooms, kitchens, furniture, and glass.

The biggest change in household cleaners around the turn of the millennium, largely in the developed markets of Europe and North America, was the rise of wipes as a product form. These take the convenience factor even further, presenting the cleaner at its use concentration (like spray cleaners) but already impregnated in the cleaning implement. Wipes constitute yet another delivery system for liquid cleaners.

The use of wipes eliminates the need to rinse the surfaces on which they are used. Consumers expect wipes to give streak-free cleaning and quick drying of surfaces. The use of volatile solvents is an easy way to achieve effective cleaning with no residue, but the solvents contribute significantly to the odor of the product and can be limited by volatile organic compound considerations. Therefore, some developments are concerned with lower levels of solvent.

The area in which these types of wipe products have made the biggest impact is that of floor cleaning. The main advantage of these systems is that they represent an essentially "bucketless" floor cleaning method, which was first mentioned in the literature almost 10 years ago. There are wet and dry wipes. Both are used in conjunction with a resilient slightly spongy pad on the end of a long handle. In the wet system, wipes are supplied saturated with the cleaning solution. The wet wipe is secured to the bottom of the pad to clean the floor. In the dry system, dry nonwoven wipes are supplied separately from the cleaning solution, which is bottled. The dry nonwoven wipe is attached to the bottom of the pad at the end of the handle, and the cleaning solution is fixed in some way to the handle, either in a holder for the bottle or in a reservoir.

This type of system has led to one of the biggest changes in consumer cleaning habit and practice in the last decade. First, the system makes floor cleaning immediately available, cutting out the setup phase of getting out a bucket, cleaner, and mop and then making the solution. Second, it eliminates the need to clean the mop and bucket. Third, because minimal solution is used on the floor and the wipe is highly absorbent, the cleaned floor does not need rinsing. For many consumers this has completely changed the way they clean floors.

The formulations of the liquids impregnated in the wipes and the liquids supplied in bottles are similar. Typically, foam suppressors such as silicones are added to minimize foaming during the cleaning so as not to leave consumers with the impression that rinsing may be needed.

There have also been significant packaging innovations that have contributed to the new products in terms of convenience and aesthetics.

TABLE 1.1 Major Raw Materials Used in Various Liquid Detergents

Product	Surfactants	Foam stabilizers	Hydrotropes/ solvents	Builders/ sequestrants	Other additives
Light-duty liquids	Linear alkylbenzenesulfonate salts (LAS), alkyl ether sulfate salts (AEOS), betaines, alkylpolyglycoside (APG), paraffin sulfonate salts, alcohol ethoxylates, fatty acid glucoamides, alkyldimethylamine oxides	Fatty acid alkanolamides, alkyldimethylamine oxides	Sodium xylenesulfonate, sodium cumenesulfonate	EDTA, sodium citrate	Triclosan (antibacterial), enzymes (cleaning aid), lemon juice (cleaning aid), protein (skin care), abrasives (cleaning aid), polymers (skin care)
Heavy-duty liquids	Linear alkylbenzenesulfonate salts (LAS), alkyl ether sulfate salts (AEOS), alkyl sulfate salts, alcohol ethoxylates, *N*-methylglucamides		Sodium xylenesulfonate, sodium cumenesulfonate	Sodium citrate, sodium tripolyphosphate	Enzymes (stain remover), borax (cleaning aid), sodium formate, calcium chloride (enzyme stabilizing system), hydrogen peroxide (bleach), soil release polymers (soil release), polyvinylpyrrolidone (dye transfer inhibition)
Liquid automatic dishwasher detergents	Alkyldiphenyl oxide disulfonate salts, hydroxy fatty acid salts			Pentasodium tripolyphosphate, tetrasodium pyrophosphate, sodium carbonate, sodium silicate, sodium citrate	Sodium hypochlorite (bleach), polyacrylate sodium salts (rheology modifier), carbopol (rheology modifier), enzymes (cleaning aid), monostearyl acid phosphate (suds depressant)

Shampoos and conditioners	Alkyl sulfate salts, alkyl ether sulfate salts (AEOS), betaines, alpha-olefinsulfonate salts (AOS), polysorbate 20, PEG-80 sorbitan laurate	Fatty acid alkanolamides, amine oxides		Citric acid, EDTA, polyphosphates	Polyquaternium 7 (conditioner), polyquaternium-10 (conditioner), fatty alcohols (conditioning aid), silicones (conditioner), climbazole (antidandruff), zinc pyrithione (antidandruff), glycol monostearate (opacifier), aloe vera (luster promoter), jojoba (luster promoter)
Liquid hand soap and body wash	Alcohol sulfate salts, alcohol ether sulfate salts, alpha-olefinsulfonate salts (AOS), alkylbenzenesulfonte salts (LAS), sodium isethionate, fatty acid salts, alkylpolyglucoside, betaines	Fatty acid alkanolamides		EDTA, sodium citrate	Triclosan (antibacterial), glycerin (moisturizer), essential oils (aromatherapy), glycol distearate (pearlescent agent), citric acid (pH adjuster), sodium chloride (viscosity adjuster), microparticles (exfoliant), dried fruit particles (exfoliant), vitamins (antioxidant)
Fabric softeners	Di-hard tallow dimethylammonium chloride (DHTDMAC), esterquats, imidazolinium salts, diamido quaternary ammonium salts		Ethanol, isopropanol, polyethylene glycol		Fatty alcohol (co-softener), fatty acid ester (co-softener), fatty amides (co-softener), amido amines (co-softener), polyethylene terephthalate (soil release agent), PVP-type polymers, (dye transfer inhibitor)
Specialty liquid household surface cleaners	Linear alkylbenzenesulfonate salts (LAS), alcohol sulfate salts, alkylsulfonate salts, alkyl ether sulfate salts (AEOS), alkylphenol ethoxylates, alcohol ethoxylates		Glycol ether, ethanol, isopropanol, sodium xylenesulfonate, sodium cumenesulfonate	Sodium carbonate, sodium sesquicarbonate, sodium citrate, EDTA	Pine oil (disinfectant), orange oil (cleaning), benzalkylonium cationics (antimicrobial), sodium hypochlorite (bleach), calcium carbonate (cleaning), acids/alkalis (cleaning)

IX. MANUFACTURE AND RAW MATERIALS

In principle, the manufacture of unstructured liquid detergents in general is relatively simple, as it involves mainly good mixing of aqueous solutions. For light- and heavy-duty liquids, which contain sodium salts of surfactant acids, neutralization can be carried out *in situ*, that is, as a first step in the mixing process. The heat of neutralization must be dissipated before addition of more temperature-sensitive ingredients such as the fragrance. Heat must also be dissipated in the manufacture of products that require heat input to solubilize individual ingredients. In contrast, the manufacture of structured liquid detergents can be quite difficult because of the complexity of their rheological profiles. Both structured and unstructured liquids can be manufactured using either batch or continuous processes depending on the specific production and volume requirements. There can be significant manufacturing challenges, such as overfoaming, aeration of product, and long batch cycle times. Detailed discussions on all aspects of liquid detergent manufacture can be found in Chapter 14.

The raw materials used in the production of liquid detergents are discussed in some detail in Chapters 7 to 13. Table 1.1 provides a summary of the major raw materials used for various product categories. The similarities and differences between these products are evident.

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