

# 8

## Heavy-Duty Liquid Detergents

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## I. INTRODUCTION

Heavy-duty liquid detergents (HDLs) were introduced into the laundry market many years after the introduction of powder detergents. The first commercial heavy-duty liquid appeared in the U.S. in 1956. Liquid detergents were introduced in the Asia/Pacific region and Europe as recently as the 1970s and 1980s, respectively. A number of commercial heavy-duty liquids from the U.S., Europe, and Asia/Pacific are depicted in [Figure 8.1](#).

HDLs have several advantages when compared to powder detergents. Liquid detergents readily dissolve in warm or cold water, leaving no detergent residue on dark fabrics. They can be easily dispensed from the bottle or refill package, and their dispensing caps allow for the unused liquid to flow back into the container without spilling. In addition, liquids do not suffer from adverse effects after exposure to moisture (powders can “cake” in storage when exposed to high humidity). Furthermore, liquid detergents lend themselves to a pretreatment regimen at full strength by pouring directly on soils and stains, providing a convenient way to facilitate the removal of tough stains.

A typical heavy-duty liquid consists of all or some of the following components: surfactants, builders, enzymes, polymers, optical brighteners, and fragrance. In addition, it may contain other special ingredients designed for specific functions.

Both anionic and nonionic surfactants are used in the formulation of liquid detergents. Surfactants are primarily responsible for wetting the surfaces of fabrics as well as the soil (reducing surface and interfacial tension), helping to lift the stains off the fabric surface, and stabilizing dirt particles and/or emulsifying grease droplets [1–4]. The main anionic surfactants are sodium alkylbenzene sulfonates, alkyl sulfates, and alkylethoxylated sulfates. The nonionic surfactants used to formulate heavy-duty liquids are primarily ethoxylated fatty alcohols. Other surfactants are also used in HDLs and are discussed in a subsequent section.

Builders are formulated into detergents mainly to sequester hardness ions ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) found in water, as well as to disperse the dirt and soil particulates in the wash water. Common builders used in liquid detergents are sodium and potassium polyphosphates (except in the U.S.), carbonates, aluminosilicates (zeolite A), silicates, citrates, and fatty acid soaps [5].



**FIG. 8.1** Commercial North American (above) and European and Asia/Pacific HDLDs.

HDLs usually incorporate a protease and an amylase enzyme. In addition, a premium liquid detergent may also utilize lipase and cellulase enzymes to enhance performance. The function of the protease enzyme is to digest protein soils such as blood and proteinaceous food stains, while the amylase selectively acts on starchy soils (e.g., gravy). Lipase attacks fatty chains in greasy soils and facilitates the breakdown of these soils during the wash cycle. Cellulase is an enzyme that acts on cellulose, and is used in detergents for removing pills from cotton fabrics, thereby restoring the reflectance of the fabric surface and making colors look brighter [6].

Polymers now play an increasingly important role in heavy-duty liquids. Low-molecular-weight, water-soluble polyacrylate dispersants prevent clay/particulate soils from redepositing on fabrics. Dye transfer inhibitors (polyvinylpyrrolidone) help keep fugitive dyes well dispersed in the aqueous bath, delivering part of the color care benefit often found in premium liquids. Soil release polymers facilitate the removal of oily/greasy soils from synthetic fabrics and blends. Deflocculating (hydrophobically modified) polycarboxylates have found utility in “coupling” structured liquids. Recent patents depict novel polymeric technologies for reducing wrinkling (ease of ironing) and preventing fiber abrasion/wear (“liquifiber”). Rheology modifiers have also made dramatic inroads in recent years. These thickening agents can do more than simply increase viscosity, including stabilization of duotropic systems and suspending actives or visual cues to improve consumer acceptance.

Optical brighteners are colorless fluorescent whitening agents that absorb ultraviolet radiation and emit bluish light, making fabrics look whiter and brighter to the human eye. Most detergents contain optical brighteners in their composition. Their content is adjusted more or less to reflect regional consumer preferences and marketing claims.

Liquid laundry detergents may be classified into two main types: unstructured liquids and structured liquids. Unstructured liquid detergents typically are isotropic, have a large and continuous water phase, and are the most widespread type of liquid detergent sold on the U.S. market. Structured liquid detergents are those consisting of multilamellar surfactant droplets suspended in a continuous water phase. These structured liquids are capable of suspending insoluble particles such as builders (phosphates, zeolites). These liquids have had some commercial utilization in Europe and in Asia/Pacific and were formerly sold in the U.S. in the early to mid-1990s. A third type of liquid detergent is one where the continuous phase is nonaqueous. These products have seen limited distribution throughout the world, but remain a topic of interest for many detergent manufacturers.

This chapter first describes the physical characteristics of heavy-duty liquids, which is followed by a detailed description of typical formulation components and their functions. This is followed by a brief discussion of evaluation methodologies. Finally, the emerging trends in the formulation of heavy-duty liquids are reviewed. A comprehensive listing of the patents relevant to HDLDs is given in the Appendix.

## **II. PHYSICAL CHARACTERISTICS OF HDLDs**

The physical form and appearance of laundry liquids can vary greatly between different regions of the world. These variations in liquid types from region to region are largely dictated by the laundry habits and personal choices of the

consumers in that particular market. HDLDs can be broadly classified into two main types: structured and unstructured liquids. A third category, nonaqueous liquids, has been actively studied and is discussed in this chapter.

Structured liquids are opaque and usually possess a moderate viscosity. These products are formed when surfactant molecules arrange themselves as liquid crystals [7–9]. This form of liquid detergent is largely marketed in Europe and the Asia/Pacific region. Unstructured liquids, on the other hand, are usually thin, clear or translucent, and are formed when all ingredients are solubilized in an aqueous media. Nonaqueous liquids, where the continuous medium consists of an organic solvent, can be either structured or unstructured.

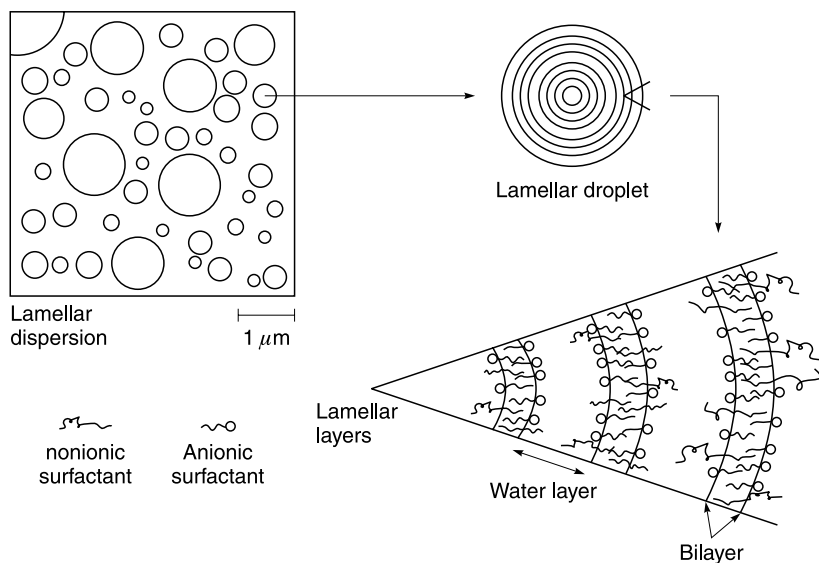
## A. Structured Liquids

### 1. Introduction

The general tendency of liquids containing high levels of anionic surfactants and electrolytic builders is to form liquid crystalline surfactant phases [7–12]. This trend can be accelerated with the use of longer or branched-chain alkyl groups and by using a higher electrolyte level [13]. The resulting liquid is opaque, extremely thick, unpourable, and frequently physically unstable. It may also subsequently separate into two or more layers or phases: a thick, opaque surfactant-rich phase containing the flocculated liquid crystals and a thin, clear electrolyte-rich phase. The challenge, therefore, in developing such a liquid is to not only to prevent phase separation of the product but also to reduce the viscosity to a “pourable” level. A pourable level depends, of course, on the preferences, requirements, and convenience of the consumer. Viscosities of commercially available structured liquids vary from 500 to 9000 cP.

### 2. Lamellar Structures

The liquid crystalline phase in a structured liquid is frequently in the form of spherical lamellar bilayers or droplets [14–18]. The internal structure of these droplets is in the form of concentric alternating layers of surfactant and water. This configuration is often compared to the structure of an onion, which also has a similar concentric shell-like structure (Figure 8.2). It has been previously determined that the physical stability of these types of liquids is achieved only when the volume fraction of these bilayer structures is high enough to be space-filling. This corresponds to a volume fraction of approximately 0.6 [7,8,19]. An excessively high value of this volume fraction, however, will lead to flocculation, high viscosity, and an unstable product. A stable dispersion of the lamellar droplets makes it possible to suspend solids and undissolved particles between the lamellae and in the continuous electrolyte phase. This allows the use of relatively high builder/electrolyte levels [20]. Many patents have been issued for structured liquids that have the capability of suspending undissolved solids. The suspended solids include bleaches [21,22], builders such as zeolites [23], and softeners [24,25].



**FIG. 8.2** Schematics of a nonflocculated lamellar dispersion, a lamellar droplet, and the internal structure of a lamellar droplet. (Reproduced from Sein, A., Engberts, J.B.F.N., Vanderlinden, E., and van de Pas, J.C., *Langmuir*, 9, 1714, 1993. With permission.)

There are a number of factors that determine whether or not a lamellar droplet can form. As a general rule these bilayer structures will develop if the surfactant head group is smaller than twice the trans cross-sectional area of the alkyl chains of the surfactants [8,13]. This ratio of the areas of the alkyl chain and the surfactant head group is referred to as the packing factor of the surfactant system. Among the factors that can accelerate the formation of these structures is the use of longer alkyl chains, branched alkyl groups, dialkyl groups, and higher levels of electrolytes. Conversely, by using short, straight-chain alkyl groups, lower electrolyte levels, or hydrotropes, the onset of the liquid crystalline phase can be delayed.

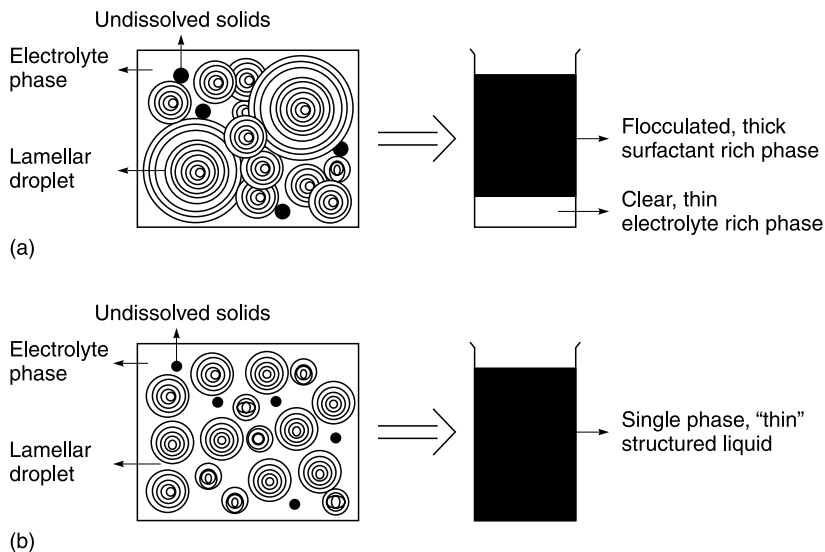
A lamellar droplet is held together by an intricate balance of various inter- and intradroplet forces [10,11]. Any alteration or imbalance in these forces can have a direct impact on the stability of the structured liquid. Electrostatic repulsion between the charged head groups of anionic surfactants is compensated for by attractive van der Waals forces between the hydrophobic alkyl chains of the anionic and nonionic surfactants. In addition, there are also osmotic and steric forces between the hydrated head groups of nonionic surfactants. These particular interactions can be either attractive or repulsive depending on the “quality” of

the solvent [8]. The resultant force has a direct influence on the size of the water layers, the size of the droplet, and eventually the stability of the liquid.

### 3. Stability of Structured Liquids

The balance of attractive forces between the surfactant layers and the compressive/repulsive forces due to steric/osmotic interactions makes highly concentrated formulations possible. However, a single-phase structured liquid, by its very nature, is never in a state of complete equilibrium. For practical purposes a stable structured liquid is achieved when the inter- and intralamellar forces are manipulated in such a way that phase separation is minimized or avoided. Depending upon the extent of concentration of the ingredients, various methods can be employed to stabilize these structured liquids (Figure 8.3).

The most basic means of stabilization and viscosity reduction is by the addition of electrolytes. The addition of cations in the form of electrolytes such as sodium citrate has the effect of screening out some of the repulsive forces between the negatively charged anionic head groups. Also, the electrolytes in the continuous layer provide an element of stability by giving it ionic strength. This screening out process reduces the size of the intralamellar water layer and consequently the size of the entire droplet. This reduction of the lamellae size frees up some



**FIG. 8.3** Schematics depicting the stability of (a) unstable and (b) stable structured HDLDs.

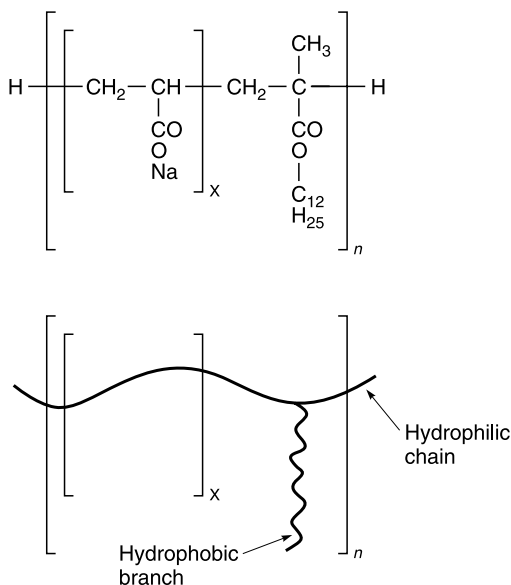
extra volume in the continuous phase and therefore provides an additional element of stability. Increasing the amounts of citrate works only up to a certain point beyond which there is a greater amount of undissolved salt which will be suspended *between* the lamellar droplets and can lead to excessive thickening. Another consequence of adding large amounts of electrolyte is the further erosion of the intralamellar water layer. This water layer has to be maintained at a level that is sufficient to hydrate the head groups of the nonionic surfactants. Salting-out electrolytes [26], of which sodium citrate is an example, also hydrate and therefore compete with the nonionics and other ingredients for the water. Excessive shrinkage of the water layer can, therefore, result in product instability.

(a) *Free Polymers.* The addition of electrolytes assists in lowering viscosities and in stabilizing a structured liquid only up to certain degree [27–29]. Polyethylene glycol and polyacrylates are examples of “free” polymers. These polymers are nonstructuring, and consequently they do not have the capability of adsorbing onto the lamellar dispersions. Instead, they function by means of osmotic compression which results in a shrinkage of the lamellar droplet. The consequence of this reduction in the volume of the individual droplets is a higher void fraction in the liquid. The polymer can therefore be used only up to the point at which the optimum void fraction is achieved. Further increases in the free polymer concentration often lead to depletion flocculation, which is also accompanied by large increases in viscosity as well as phase separation.

Concentrating the structured liquid by merely forming thinner lamellar layers and increasing the volume fraction of the lamellae can have implications for the rheology and pourability of the product. The best pourability characteristics are obtained when the volume fraction of the lamellar phase is as low as possible and the size of the lamellae is relatively large. A compromise between these two pathways/strategies has to be achieved in order to formulate a stable, concentrated liquid with acceptable rheological traits. This task becomes increasingly difficult at even higher concentrations. With only a limited void fraction available, the lamellar droplets, even though they are reduced in size, begin flocculating.

(b) *Deflocculating Polymers.* Free polymers are effective in reducing the sizes of the lamellar dispersion and thereby imparting stability. However, at ever increasing concentrations of surfactants and builders, simply reducing the intralamellar water layer is not sufficient to prevent flocculation. The problem was successfully addressed by researchers at Unilever who were able to prevent flocculation by altering the interlamellar forces [13,19,30–33]. This was achieved by means of a deflocculating polymer which can be considered as bifunctional. These polymers consist of a hydrophilic backbone that is attached to a hydrophobic side chain. The hydrophilic component is fundamentally like a free polymer or copolymer in structure as well as function. The hydrophobic side





Acrylate–laurylmethacrylate copolymer

**FIG. 8.4** Example of a deflocculating polymer. (Reproduced from Broekhoff, J.C.P. and van de Pas, J.C., presented at American Oil Chemists Society Conference, Anaheim, CA, April 1993. With permission.)

chain is typically a long alkyl group. Figure 8.4 shows a schematic of deflocculating polymer — an acrylate–laurylmethacrylate copolymer. The unique aspect of this polymer is its ability to not only utilize its hydrophilic component to induce osmotic compression within the lamellar bilayers, but also to employ its hydrophobic side chain to adsorb onto the surfactant layers. This hydrophobicity also permits the deflocculating polymer to attach itself to the outer surface of the lamellar droplet and consequently be able to influence the interlamellar interactions. This trait prevents or at least reduces the likelihood of flocculation occurring.

The stability of these structured liquids, therefore, is obtained when the lamellae are not only smaller in size but also well separated (Figure 8.4). This results in not only a single-phase, stable liquid but also a product with good flow properties. Table 8.1 lists the ingredients typically found in a structured HDLD.

## B. Unstructured Liquids

### 1. Introduction

The current U.S. market for HDLDs is predominantly low-viscosity, clear, isotropic compositions. Besides the obvious differences in the physical appearance

**TABLE 8.1** Example of a Structured HDLD Formulation

Ingredient	Function	%
Sodium Linear Alkylbenzene Sulfonate	Anionic Surfactant	0–30
Sodium Alkyl Ether Sulfate	Anionic Surfactant	0–10
Alcohol Ethoxylate	Nonionic Surfactant	0–10
Sodium Carbonate	Builder	0–25
Zeolite	Builder	0–25
Sodium Perborate	Bleach	0.0–10.0
Polymer	Stabilizer	0.0–1.0
Protease	Enzyme	0.0–1.5
Fluorescent Whitening Agent	Brightener	0.0–0.5
Boric Acid	Enzyme Stabilizer	0.0–5.0
Preservative		0.05–0.2
Fragrance		0.0–0.6
Colorant		0.00–0.2

and properties between the structured and unstructured liquids, there are other dissimilarities in the formulation of these liquids which can have a direct impact on the cleaning performance of the product. Unstructured liquids are commonly formulated with higher amounts of surfactants in conjunction with lower builder levels (see Table 8.2). This is in contrast to structured liquids, which utilize

**TABLE 8.2** Example of an Unstructured HDLD Formulation

Ingredient	Function	%
Sodium Linear Alkylbenzene Sulfonate	Anionic Surfactant	0–15
Sodium Alkyl Ether Sulfate	Anionic Surfactant	0–15
Alcohol Ethoxylate	Nonionic Surfactant	0–15
Sodium Citrate	Builder	0–10
Monoethanolamine	Buffer	0–5
Soap	Defoamer	0–5
Protease	Enzyme	0.0–1.5
Fluorescent Whitening Agent	Brightener	0.0–0.5
Boric Acid	Enzyme Stabilizer	0.0–5.0
Ethanol	Solvent	0.0–5.0
Sodium Xylene Sulfonate	Hydrotrope	0.0–10.0
Preservative		0.05–0.2
Fragrance		0.0–0.6
Colorant		0.0–0.2

more builders and electrolytes to sustain the structured phase. The physical appearance and stability of structured liquids are very dependent on surfactant ratios, whereas the clear, unstructured liquids allow far greater flexibility in choosing surfactant types/ratios as long as a single phase is maintained. The main advantage in structured liquids is their ability to suspend undissolved and insoluble solids. The unstructured clear liquids, on the other hand, by their very nature, typically do not permit the use of insoluble materials. This results in the use of only water-soluble builders at relatively low levels, and precludes the use of other useful builder ingredients such as zeolites. In the past few years there have been numerous research programs aimed at synthesizing modifiers with novel rheology that allow a formulator to suspend insoluble actives or visual cues in an unstructured (isotropic) liquid detergent matrix. These novel polymer chemistries are discussed in greater detail in [Chapter 5](#).

It cannot be said that one form of liquid has a distinct advantage over the other. The formulation and marketing of either form may be dependent on such factors as efficacy targets, consumer preferences and habits, choice and availability of raw materials, as well as cost considerations.

## 2. Stability of Unstructured Liquids

Unlike structured liquids, these unstructured, low-viscosity, clear liquids can be developed only if the onset of the formation of liquid crystals is hindered or they are broken up. This can be accomplished by two different methods: by the addition of hydrotropes and solvents which can disrupt or prevent any liquid crystal formation as well as aid in solubilizing the other components in the formulation or by increasing the water solubility of the individual components. More than likely a combination of both these techniques is used to develop a stable liquid. The respective costs of these approaches ultimately determine their usage in the final formulation. Some of the methods used to formulate stable, single-phase, clear unstructured liquids are summarized below.

Compounds such as sodium xylene sulfonate (SXS), propylene glycol, and ethanol are useful in disrupting and preventing the formation of lamellar structures which can opacify and thicken a liquid. SXS is especially useful in solubilizing linear alkylbenzene sulfonate (LAS). Propylene glycol and ethanol also have the additional benefit of contributing to enzyme stability. The main drawback of using these compounds is that they do not contribute to the detergency performance of the product. Their principal function is to aid in achieving the low viscosity and clear appearance by solubilizing various ingredients and preventing precipitation/phase separation.

It is possible to form concentrated liquid detergents that do not require additional ingredients to assist in the maintenance of a clear appearance. This is usually accomplished by minimizing the use of LAS and electrolytes and maximizing the use of nonionic surfactants.

The use of ingredients with increased water solubility is probably the most effective tool for producing a single-phase, low-viscosity clear liquid. Potassium salts generally tend to be more soluble than their sodium cation counterparts. In these formulations, a higher level of potassium citrate (as opposed to sodium citrate) can be successfully incorporated. Detergency performance is not affected by replacing the  $\text{Na}^+$  cation with  $\text{K}^+$ .

Citrate compounds are salting-out electrolytes — they tie up water molecules in the liquid and as a result help force the formation of liquid crystals or lamellar structures. It is sometimes possible to reverse this trend by the addition of “salting-in” electrolytes, compounds with high lyotropic numbers ( $>9.5$ ) which can raise the cloud point of a liquid formulation [26]. This permits increased concentration without the onset of structuring.

Ethanolamines such as monoethanolamine (MEA) and triethanolamine (TEA) can also be invaluable in enhancing the solubility of ingredients. These compounds are bifunctional in that they have characteristics common to both alcohols and amines. As a result, salts of MEA and TEA are more soluble than those prepared with  $\text{Na}^+$ . Neutralizing sulfonic acid with MEA is a very effective way of freeing up additional water to allow for higher surfactant concentrations. In addition, any free alkanolamine that is not tied up as a salt behaves in a similar fashion to an alcohol and can aid in solubilizing other ingredients. These compounds also provide detergency benefits by buffering the wash water on the alkaline side.

## C. Nonaqueous Liquids

Nonaqueous liquids may be classified as structured or unstructured depending on the level of surfactants and other components in their formulation [34]. These detergents have several advantages over aqueous formulations. Nonaqueous detergents can contain all the primary formulation components, including those that are not compatible with or difficult to formulate in aqueous systems. The liquid matrix is a nonionic surfactant or a mixture of nonionic surfactants and a polar solvent such as a glycol ether [35–38]. Builders such as phosphates, citrates, or silicates can be incorporated, although zeolites containing about 20% water are generally not recommended [39]. Phosphate-free formulations have also been reported [40]. Bleach systems such as TAED (tetraacetyethylene diamine) and activated sodium perborate monohydrate can be included in these formulations. Since these formulations do not contain water, enzymes may be added with minimal need for stabilizers. Softening ingredients can also be included [41,42].

Excellent flexibility in the concentration of the detergent can be attained since only the active cleaning ingredients are included in the formulation. The density of the finished product can be as high as 1.35 g/ml for these liquids, requiring lower dosages for equivalent cleaning. However, the two major challenges

facing this technology are physical stability and dispensability of the product and its rapid solubilization in the washing machine.

### III. COMPONENTS OF HDLDs AND THEIR PROPERTIES

Heavy-duty liquid laundry formulations vary enormously depending upon the washing habits and practices of consumers in a given geographic region. The degree of complexity can range from formulations that contain minimal amounts of cleaning ingredients to highly sophisticated compositions consisting of superior surfactants, enzymes, builders, and polymers. This section describes the ingredients found in typical HDLD formulations.

#### A. Surfactants

Surfactants are the major cleaning components of HDLD formulations throughout the world. Unlike powder detergents, physical and phase stability considerations greatly limit the usage of other cleaning ingredients, chiefly builders. Surfactants contribute to the stain removal process by increasing the wetting ability of the fabric surface and stains and by assisting in the dispersion and suspension of the removed soils.

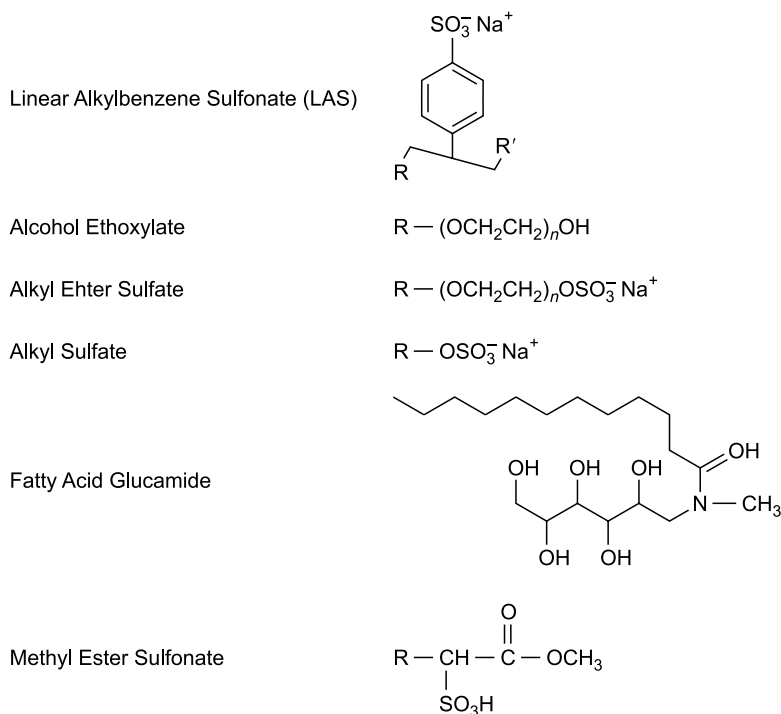
A HDLD formulator has a vast array of surfactants from which to choose [43]. A comprehensive listing and description of these surfactants are beyond the scope of this discussion. The choice and levels of surfactants used in commercial HDLD products depend not only on their performance and physical stability characteristics but also on their cost effectiveness.

This section briefly describes the anionic and nonionic surfactants commonly used in commercial HDLD formulations. Cationic surfactants, although used on a large scale, are found predominantly in rinse-added fabric softener products. LAS, alcohol ethoxylates, and alkyl ether sulfates are three of the most widely used surfactants in liquid laundry detergents [44]. Recently, various external considerations, such as environmental pressures, have prompted manufacturers to change their surfactant mix to include newer natural-based surfactants [45–47], including alkyl polyglucosides (Henkel) [48].

##### 1. Linear Alkylbenzene Sulfonate

The excellent cost–performance relationship of LAS makes it the dominant surfactant used in laundry detergents [49]. Recent trends in Europe and North America indicate a gradual reduction in its usage in HDLDs. Nevertheless, its use in laundry liquids globally is still substantial, especially in the developing regions of the world.

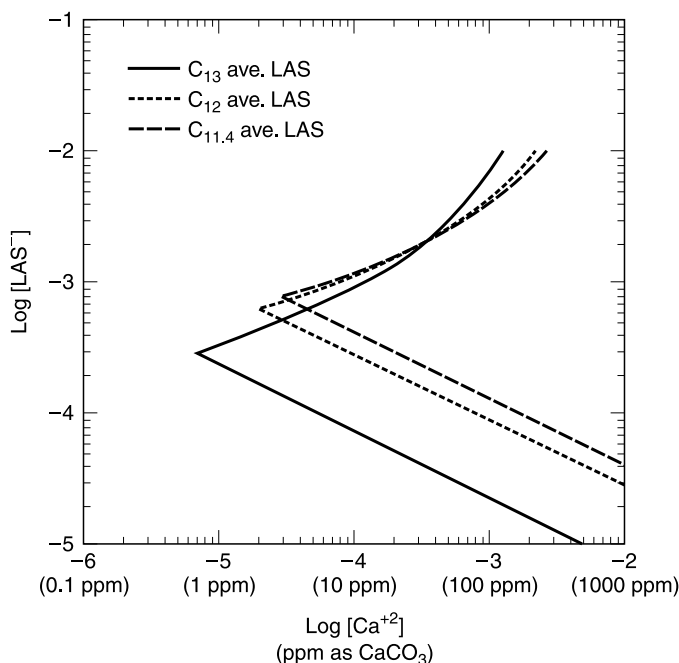
De Almeida *et al.* [50] and Matheson [51] provide a comprehensive examination of the processing, production, and use of linear alkylbenzene in the detergent



**FIG. 8.5** Structures of typical HDLD surfactants.

industry. LAS are anionic surfactants and are prepared by sulfonating the alkylbenzene alkylate and subsequently neutralizing it with caustic soda or any other suitable base. The alkylate group is typically a linear carbon chain of length ranging from C10 to C15, with a phenyl group attached to one of the secondary carbons on the alkyl chains (Figure 8.5). The alkylate portion of the molecule is hydrophobic whereas the sulfonate group provides the water solubility and the hydrophilicity. Most commercial alkylates are mixtures of various phenyl isomers and carbon chain homologs [52]. The position of the phenyl group depends on the manufacturing method. Systems using  $AlCl_3$  or HF catalysts are the most common.

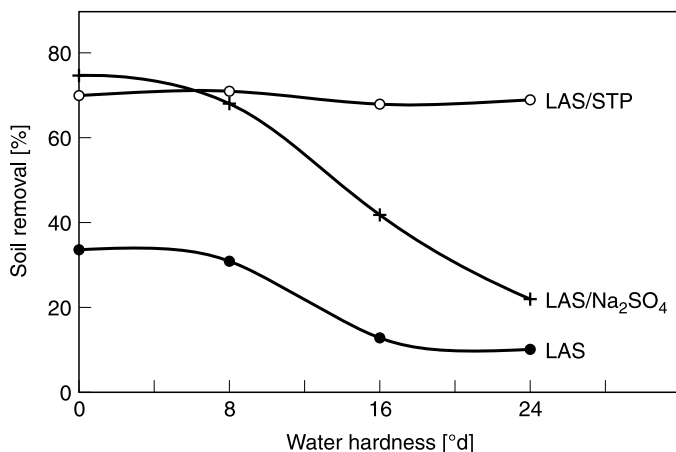
The length of the carbon chain and the isomeric distribution strongly influence the ease of formulation and performance of the surfactant. It has been determined that the surface activity of this surfactant increases with longer carbon chain lengths [53]. A longer alkyl chain increases the hydrophobicity of the molecule, lowers the critical micelle concentration (CMC), and generally provides better



**FIG. 8.6**  $\text{Ca}^{2+}$ -LAS precipitation boundary diagrams. (Reproduced from Matheson, K.L., Cox, M.F., and Smith, D.L., *J. Am. Oil Chem. Soc.*, 62, 1391, 1985. With permission.)

soil removal characteristics [54–57]. LAS offers superior and very cost effective detergency performance, especially on particulate soils. However, due to its high sensitivity to water hardness, it is best utilized only when used with an accompanying builder [58]. Figure 8.6 shows the increased sensitivity to hardness ions for LAS with longer carbon chain lengths. Without the assistance of builders, the soil removal efficacy of LAS drops rapidly with increasing water hardness [4,59] (Figure 8.7).

The amount and type of LAS in HDLDs depends largely on the physical form of the laundry liquid — unstructured or structured. In unstructured liquids, solubility considerations require the use of smaller carbon chain lengths ( $\sim\text{C}_{11}$ ). In addition, the choice of cations can also enhance solubility. Potassium and amine cations such as MEA and TEA can be used instead of sodium ions to improve stability [60]. An increased ratio of the 2-phenyl isomer in the LAS can also increase solubility [61] and sometimes improve the hardness tolerance of the surfactant [62]. In structured liquids, a longer alkyl chain can be more desirable for the formation



**FIG. 8.7** Soil removal data for LAS as a function of water hardness. Results are shown for surfactant with builder (sodium tripolyphosphate, STPP) and electrolyte. (Reproduced from Coons, D., Dankowski, M., Diehl, M., Jakobi, G., Kuzel, P., Sung, E., and Trabitzsch, U., in *Surfactants in Consumer Products: Theory, Technology and Application*, Falbe, J., Ed., Springer-Verlag, New York, 1987. With permission.)

of surfactant lamellae. The choice of the counterion can also affect stability since ions such as  $\text{Na}^+$  and  $\text{K}^+$  have different electrolytic strengths which can also have an impact on phase stability.

A disadvantage of using LAS in HDLDs is their detrimental effect on enzymes. With the increasing use of enzymes it becomes necessary to devote a sizable portion of the formulation space and cost to enzyme stabilization. Alternative approaches using surfactants that are more compatible with enzymes can be employed.

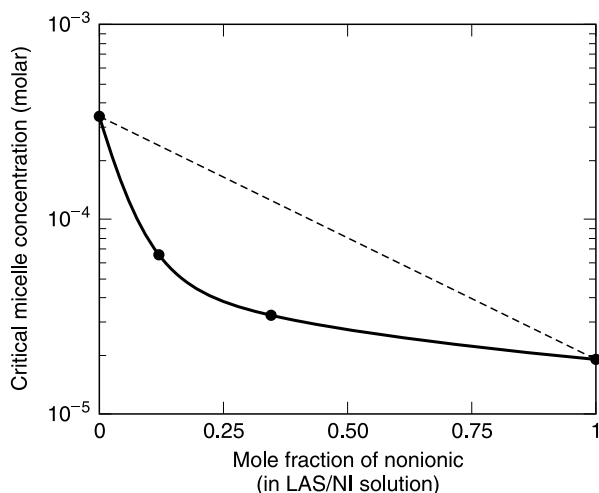
## 2. Alcohol Ethoxylates

Figure 8.5 shows the general structure of a nonionic alcohol ethoxylate surfactant. Its hydrophobic group is linear with the carbon chain length typically ranging from C10 to C15. The hydrophilic ethoxylate group can vary in size from an average of 5 to 12 moles of ethylene oxide [63–65]. Alcohol ethoxylates are marketed commercially under the trade names Neodol (Shell Chemical Co.), Bio-Soft (Stepan), Genapol (Clariant), Tergitol (Dow), Surfonic (Huntsman), and Alfonic (Sasol). The feedstock for the alcohol can be derived from natural coconut oil sources as well as from petroleum feedstock. These surfactants are usually sold at a 100% actives concentration and range in state from fluid liquids to soft solids.

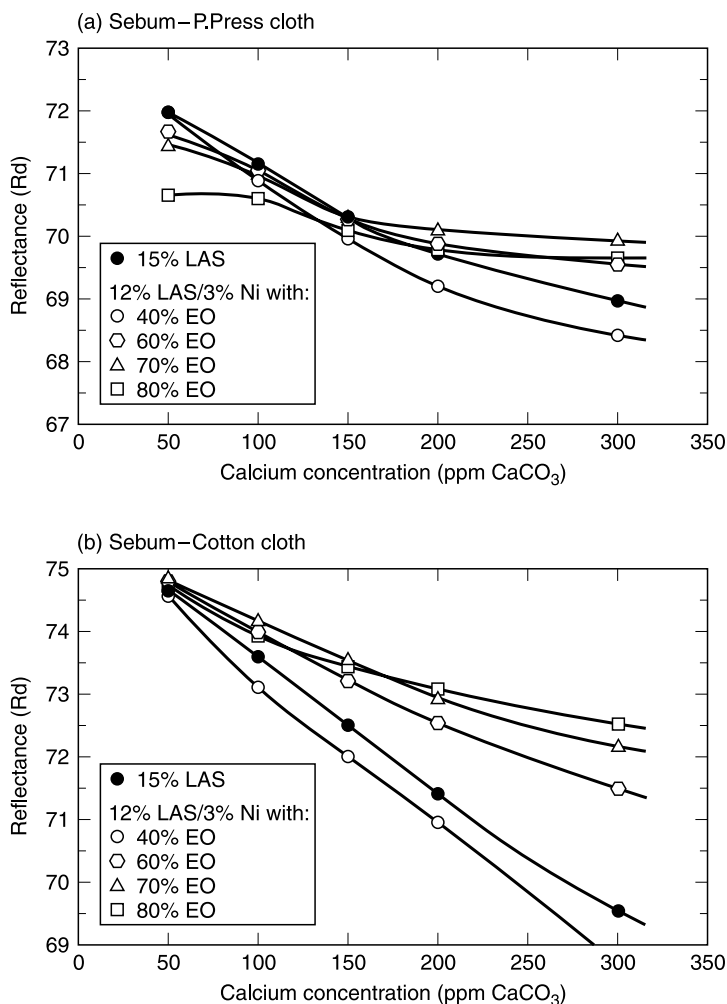


Alcohol ethoxylate usage in HDLDs depends on the type or the physical form of the liquid detergent. The high aqueous solubility of alcohol ethoxylates makes them a useful ingredient in unstructured liquids. This solubility can be further enhanced by increasing the degree of ethoxylation and decreasing the carbon chain length. However, these modifications can sometimes have negative ramifications on the cleaning performance. The choice of carbon chain length and the degree of ethoxylation depends on the physical stability and cleaning requirements of individual formulations. Structured liquids, in contrast, can only tolerate a limited amount of the nonionic alcohol ethoxylate surfactant since the stability of these liquids is dependent upon the optimum distribution of the size and packing configuration of lamellar droplets. Excessive use of nonionic surfactants can disturb this somewhat delicate equilibrium and cause phase separation of the HDLD.

Nonionic surfactants like alcohol ethoxylates demonstrate superior tolerance to hard water ions. This characteristic is especially useful in unstructured HDLD formulations because solubility constraints limit the amount of builder that can be incorporated. They also provide excellent cleaning benefits and are commonly used in conjunction with LAS in HDLD formulations [57,66]. Studies have shown that in LAS-containing products, alcohol ethoxylates can lower the critical micelle concentration (Figure 8.8) as well as provide improvements in the detergency [66]. Superior cleaning is observed, especially on oily soils such as sebum (body sweat) on polyester fabrics [67]. The presence of alcohol ethoxylates

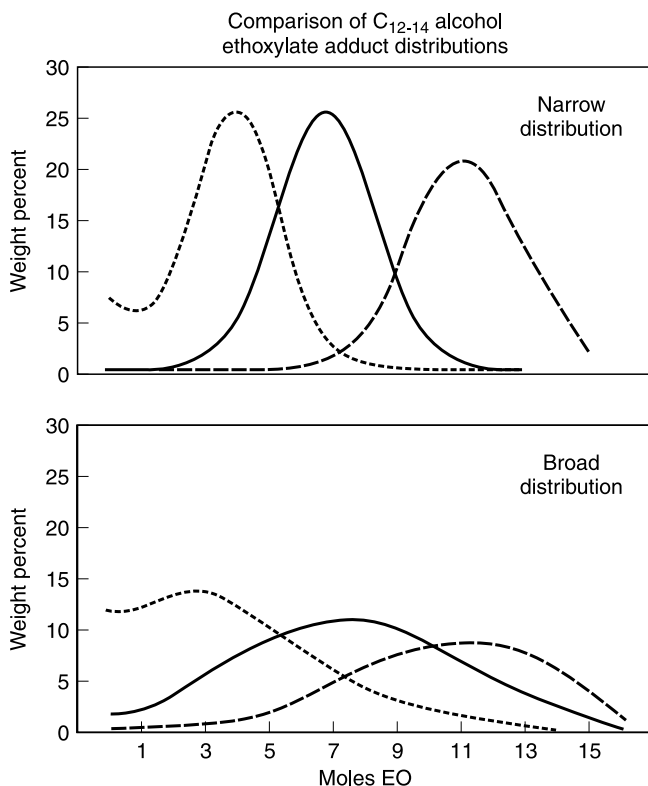


**FIG. 8.8** Critical micelle concentration (CMC) as a function of nonionic surfactant content in a LAS/NI solution. (Reproduced from Cox, M.F., Borys, N.F., and Matson, T.P., *J. Am. Oil Chem. Soc.*, 62, 1139, 1985. With permission.)



**FIG. 8.9** Detergency performance at 100°F (38°C) of LAS and LAS/alcohol ethoxylate blends. The formulation also contained 25% sodium tripolyphosphate, 10% silicate, and 35% sodium sulfate. (Reproduced from Cox, M.F., Borys, N.F., and Matson, T.P., *J. Am. Oil Chem. Soc.*, 62, 1139, 1985. With permission.)

in an LAS-containing formulation is found to improve detergency, especially at higher hardness levels (Figure 8.9). Improvements have also been detected when narrow distribution ethoxylate surfactants (Figure 8.10) are used [68].

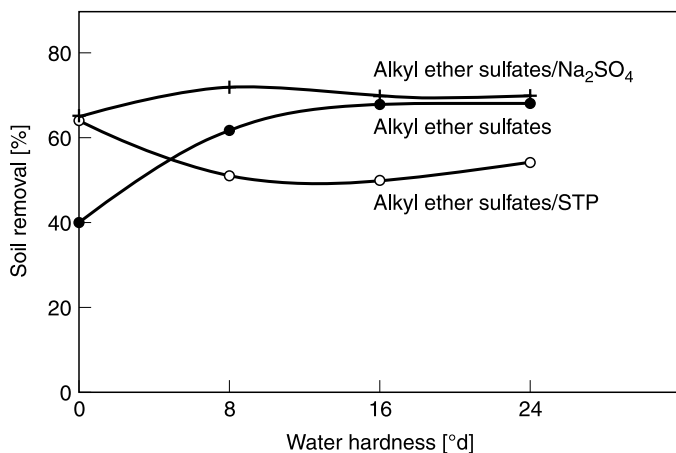


**FIG. 8.10** Typical ethoxylate adduct distributions in narrow range and broad range C12–C14 alcohol surfactants with similar cloud points. (Reproduced from Dillan, K.W., *J. Am. Oil Chem. Soc.*, 62, 1144, 1985. With permission.)

The insensitivity of nonionic surfactants to calcium ions also provides a very important benefit in the stabilization of enzymes (see Section III.C). It has been shown that these surfactants are not as detrimental to the preservation of enzymes in HDLDs as sodium LAS. With increasing reliance on the use of enzymes in the laundry cleaning process, nonionic surfactants like alcohol ethoxylates play an important role in enhancing enzyme stability.

### 3. Alkyl Ether Sulfates (AEOS)

These are also anionic surfactants which are manufactured by sulfating alcohol ethoxylate surfactants [69]. Figure 8.5 shows the structure of the molecule which consists of the alcohol ethoxylate connected to a sulfate group. The EO groups typically range in size from 1 to 3 moles.



**FIG. 8.11** Data showing the hardness tolerance of alkyl ether sulfate surfactants. (Reproduced from Coons, D., Dankowski, M., Diehl, M., Jakobi, G., Kuzel, P., Sung, E., and Trabitzzsch, U., in *Surfactants in Consumer Products: Theory, Technology and Application*, Falbe, J., Ed., Springer-Verlag, New York, 1987. With permission.)

These surfactants provide numerous benefits that make them an attractive option to HDLD formulators. They are commonly used in both structured and unstructured liquids. Their high water solubility makes it possible to use a wide range of levels in unstructured liquids. They can also be successfully incorporated in structured liquids.

Unlike sodium LAS, alcohol ether sulfates are more tolerant to hardness ions and as a result do not require an accompanying high level of builder in the formulation. Figure 8.11 shows the relative insensitivity of AEOS to hardness ions. Small amounts of AEOS when added to LAS were found to improve the interfacial properties. They are more compatible with enzymes, which can also reduce the cost of enzyme stabilizers in the formulation. They are also milder to the skin and, as a result, are frequently used in hand dishwashing applications. The superior detergency performance of this surfactant is demonstrated by its superior efficacy in most stain categories.

#### 4. Alkyl Sulfates

These anionic surfactants (Figure 8.5) are used primarily in Europe as a substitute for LAS [45]. Environmental considerations have prompted manufacturers to use surfactants of this type, which can be derived from oleochemical sources. The carbon chain length can range from C10 to C18. Tallow alcohol sulfate is the

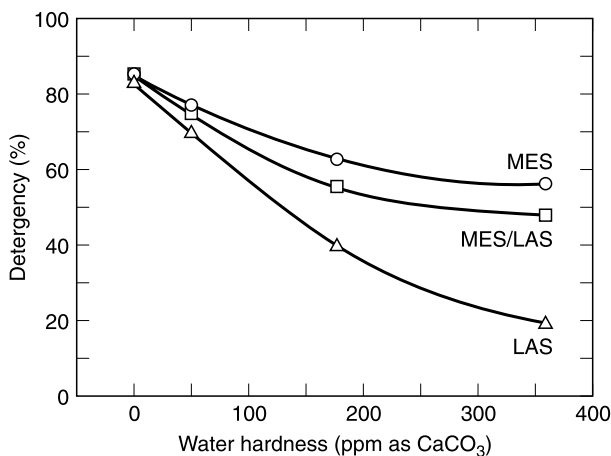
common form used in HDLDs. It provides excellent detergency, good foaming properties, and favorable solubility characteristics.

## 5. Polyhydroxy Fatty Acid Amides (Glucamides)

Polyhydroxy fatty acid amides (Figure 8.5) are currently used in light- and heavy-duty laundry liquids. Recent advances in the technology for the manufacture of these surfactants has made their use economically feasible [70–72]. The use of natural or renewable raw materials improves their biodegradation characteristics. Several patents have been filed for detergent formulations containing glucamides which claim superiority in cleaning efficacy for oily/greasy and enzyme-sensitive stains [73–76]. Synergies with other anionic and nonionic surfactants have also been reported [75,76]. Their improved skin mildness qualities can be useful in light-duty liquid applications [77]. Enzyme stabilization characteristics in glucamide formulations are also enhanced relative to LAS-containing HDLDs.

## 6. Methyl Ester Sulfonates

This anionic surfactant (Figure 8.5) is also derived from oleochemical sources and has a good biodegradability profile. It is currently used in only a limited number of markets (primarily in Japan), but has recently gained some prominence in the U.S. market. Its good hardness tolerance characteristics (Figure 8.12) and its ability to also function as a hydrotrope make this surfactant a good candidate



**FIG. 8.12** Detergency as a function of water hardness in methyl ester sulfonate/LAS formulations. Conditions: 25°C, surfactant 270 ppm, Na<sub>2</sub>CO<sub>3</sub> 135 ppm, silicate 135 ppm. (Reproduced from Satsuki, T., in *Proceedings of the 3rd World Conference on Detergents: Global Perspectives*, Cahn, A., Ed., AOCS Press, Champaign, IL, 1994, p. 135. With permission.)

for liquid detergents [78]. It has also been found to be a good cosurfactant for LAS-containing formulations. It can only be used in products with low alkalinity due to the likelihood of hydrolytic cleavage of the ester linkage under high pH conditions.

## 7. Other Surfactants

Once used as a major surfactant in detergent formulations, soap is now used only as a minor ingredient in HDLDs. Its function is primarily to provide foam control in the washing machine. European liquid formulations contain higher soap levels than their counterparts in North America because of increased foaming tendencies in European machines. Soap also aids in the cleaning process by chelating divalent cations (such as calcium and magnesium). When employed at high concentrations it behaves as a precipitating builder and can leave behind an organic complex (of soap scum) on fabric surfaces. A variety of other surfactants are also used primarily for specialty applications [79]. They include amine oxides, amphoterics, and betaines.

## B. Builders

The primary function of builders in the detergency process is to tie up the hardness ions,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , which are naturally found in water. They also provide other valuable benefits including maintaining the alkalinity of the wash solution, functioning as antiredeposition and soil dispersing agents and, in some cases, as corrosion inhibitors [80–84].

The level of builder usage in liquid formulations depends largely on three main criteria: (1) the aqueous solubility of the builder, (2) the physical form of the liquid, and (3) the cost effectiveness of the ingredient. Due to inherent solubility constraints in formulating stable liquid detergents, the usage level of builders in HDLDs is significantly lower than in granulated detergents. This is especially true in the case of unstructured liquids where the solubility limitations of the builder largely dictate its level in the formulation. In structured liquids, however, a certain amount of electrolytic builder is necessary to induce structuring which allows the incorporation of significantly higher amounts of builder. Insoluble builders can also be added by suspending them in the liquid. Builder ingredients such as zeolites, phosphates, silicates, or carbonates can account for 20% or more of the total formulation.

### 1. Mechanisms

Builder compounds decrease the concentration of the wash water hardness by forming either soluble or insoluble complexes with calcium and magnesium ions. The mechanisms by which these ingredients function can be broadly classified into three classes: (1) sequestration, (2) precipitation, and (3) ion exchange. All three methods have the ultimate effect of lowering the concentration of hardness

ions that could interfere with the cleaning process by rendering the surfactants less effective.

In sequestration (chelation) the hardness ions are bound to the builder in the form of soluble complexes. Phosphates, citrates, and nitrilotriacetic acid (NTA) are examples of this class of builder compound. Table 8.3 lists the calcium binding capacities of various builders. Other strongly chelating compounds exist, such as phosphonates and EDTA, but they are generally not extensively used in HDLDs. The most efficient builder is sodium tripolyphosphate (STPP). Unfortunately, tripolyphosphate has been identified as a possible cause of eutrophication in lakes and rivers. It is severely controlled and even banned in several countries. As a result, most countries in North America and Europe have converted to non-phosphate formulations. Other regions are also gradually imposing restrictions on the use of phosphates.

Carbonates are examples of builders that precipitate out the calcium ions in the form of calcium carbonate. Precipitating builders can leave behind insoluble deposits on clothes and washing machine components. Aluminosilicates such as zeolites are ion exchange compounds; they remove (predominantly) calcium and magnesium ions and exchange them with sodium ions.

Most builders also contribute significantly to detergency by providing alkalinity to the wash water. A high pH ( $>10$ ) solution aids in the removal of oily soils such as sebum by saponification. The insoluble fatty acids found in oily soils are converted to soluble soaps under alkaline conditions, facilitating their removal during the washing process.

## 2. Builder Classes

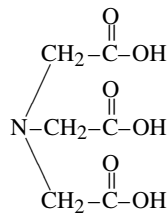
(a) *Inorganic.* In regions where phosphorous compounds are still permitted in detergent products, polyphosphates such as tripolyphosphates ( $P_3O_{10}$ ) and pyrophosphates ( $P_2O_7$ ) are unsurpassed in their cost effectiveness and cleaning ability. These ingredients are not only very good chelating agents but they also provide a soil suspending benefit. Stains, once removed from the fabric, can be suspended in the wash water by electrostatic repulsion, thereby preventing soils from redepositing onto clothing. To a certain extent phosphates also buffer the wash water. The solubility of tripolyphosphates can be enhanced by using the potassium salt. This would be more appropriate for unstructured liquids. In structured liquids, the sodium salt can be incorporated and at much higher levels.

Carbonate compounds offer an economical means of reducing the calcium content and also raising the alkalinity of the wash water. They lower the concentration of the calcium by precipitating it in the form of calcium carbonate. This could lead to fabric damage in the form of encrustation, which becomes especially apparent after repeated washing cycles under high water hardness conditions. Fortunately, this is not a major problem in unstructured HDLDs since the amount of carbonate used in the formulation is limited due to solubility restrictions. Compounds such

**TABLE 8.3** Sequestration Capacity of Selected Builders. Table Reproduced with permission from Jakobi, G. and Schwuger, M.J., *Chem. Z.*, 182, 1975.

Structure	Chemical name	Calcium binding capacity (mg CaO/g)	
		20°C	90°C
$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{NaO}-\text{P}-\text{O}-\text{P}-\text{ONa} \\   \quad   \\ \text{ONa} \quad \text{ONa} \end{array}$	Sodium diphosphate	114	28
$\begin{array}{c} \text{O} \quad \text{O} \quad \text{O} \\ \parallel \quad \parallel \quad \parallel \\ \text{NaO}-\text{P}-\text{O}-\text{P}-\text{O}-\text{P}-\text{ONa} \\   \quad   \quad   \\ \text{ONa} \quad \text{ONa} \quad \text{ONa} \end{array}$	Sodium triphosphate	158	113
$\begin{array}{c} \text{O} \quad \text{OH} \quad \text{O} \\ \parallel \quad   \quad \parallel \\ \text{HO}-\text{P}-\text{C}-\text{P}-\text{OH} \\   \quad   \quad   \\ \text{OH} \quad \text{CH}_3 \quad \text{OH} \end{array}$	1-Hydroxyethane-1,1-diphosphonic acid	394	378
$\begin{array}{c} \text{CH}_2-\text{PO}_3\text{H}_2 \\ \diagup \quad \diagdown \\ \text{N}-\text{CH}_2-\text{PO}_3\text{H}_2 \\ \diagdown \quad \diagup \\ \text{CH}_2-\text{PO}_3\text{H}_2 \end{array}$	Amino tris methylenephosphonic acid	224	224

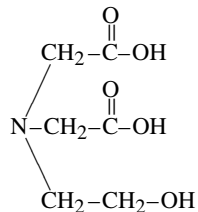




Nitrilotriacetic acid

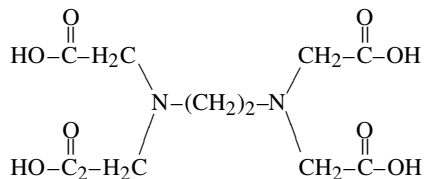
285

202

*N*-(2-Hydroxyethyl)imino diacetic acid

145

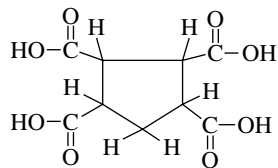
91



Ethylenediamine tetraacetic acid

219

154



1,2,3,4-Cyclopentane tetracarboxylic acid

280

235

*(continued)*

TABLE 8.3 (Contd.)

Structure	Chemical name	Calcium binding capacity (mg CaO/g)	
		20°C	90°C
$  \begin{array}{c}  \text{CH}_2 \text{---} \text{C} \text{---} \text{CH}_2 \\    \quad \quad   \quad \quad   \\  \text{C}-\text{OH} \quad \text{HO} \quad \text{C}-\text{OH} \quad \text{C}-\text{OH} \\     \quad \quad    \quad \quad    \\  \text{O} \quad \quad \text{O} \quad \quad \text{O}  \end{array}  $	Citric acid	195	30
$  \begin{array}{c}  \text{O} \\     \\  \text{C}-\text{OH} \\    \\  \text{CH}-\text{O}-\text{CH}_2-\text{C}-\text{OH} \\    \quad \quad    \\  \text{C}-\text{OH} \quad \text{O} \\     \\  \text{O}  \end{array}  $	<i>O</i> -Carboxymethyl tartronic acid	247	123
$  \begin{array}{c}  \text{O} \quad \quad \text{O} \\     \quad \quad    \\  \text{HO}-\text{C}-\text{CH}_2-\text{CH}-\text{C}-\text{OH} \\  \quad \quad   \quad \quad    \\  \quad \quad \text{O}-\text{CH}_2-\text{C}-\text{OH} \\  \quad \quad \quad    \\  \quad \quad \quad \text{O}  \end{array}  $	Carboxymethyl oxysuccinic acid	368	54

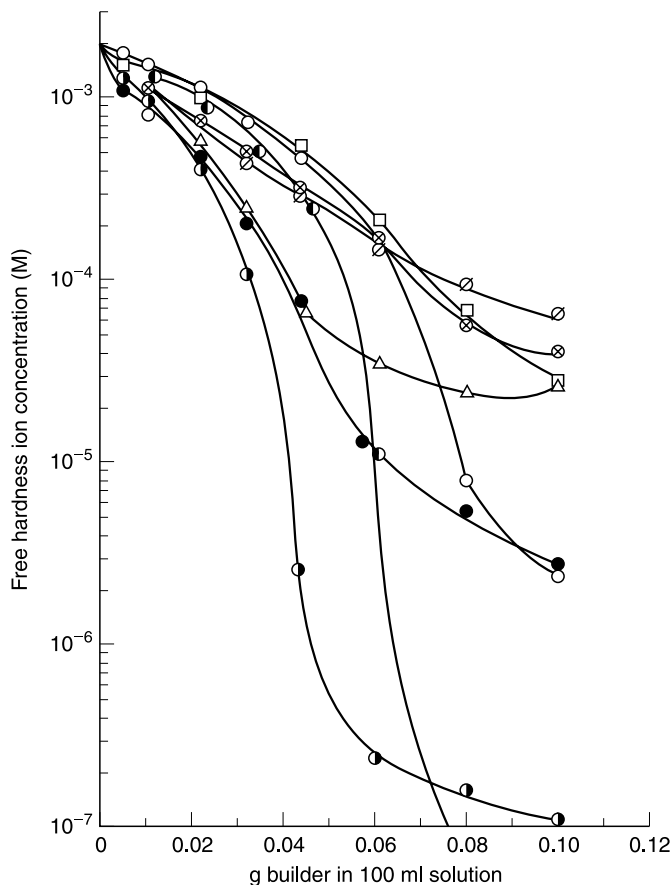
as sesquicarbonates and bicarbonates that are less likely to lead to the formation of calcium carbonate precipitates have better solubility characteristics and can be used to a larger extent in unstructured liquids. Structured liquids offer the potential of incorporating much higher amounts of these compounds. Carbonates are also good wash water buffers and can provide the alkalinity needed for improved efficacy.

Another class of ingredient that is effective at providing alkalinity is sodium silicates [86]. Although they can also be good sequestrants, and are used as such in powder formulations, they provide this benefit only at higher concentrations. Once again, solubility restrictions prevent the incorporation of any substantial amounts in unstructured liquids. At the low levels at which they can be used, they are valuable as alkaline buffers. The use of sodium silicates in HDLDs is typically limited to the liquid silicates which have  $\text{SiO}_2/\text{Na}_2\text{O}$  ratios from 3.2 to 1.8. Clariant recently introduced SKS-6, a pure sodium disilicate ( $\text{Na}_2\text{Si}_2\text{O}_5$ ) that softens tap water more efficiently than amorphous sodium silicates [87]. Although initially positioned for powder detergents (laundry and automatic dishwashing), its performance profile may entice a few manufacturers to look at potential utilization in liquid formulations.

Aluminosilicates [ $\text{M}_z(\text{zAlO}_2:\text{ySiO}_2)$ ] are another type of builder of which zeolite A is a common example [88]. Zeolite A is a sodium aluminosilicate, with an Al/Si ratio of 1:1 and a formula of  $\text{Na}_{12}(\text{SiO}_2 \times \text{AlO}_2)_{12} \times 27\text{H}_2\text{O}$ . It acts as a builder by exchanging sodium ions inside the lattice with calcium ions from the wash water. Zeolites are not effective in providing alkalinity and are normally used in conjunction with carbonates. They are insoluble in water and are not suitable for formulating unstructured liquids. In structured liquids, zeolites are suspended as solid particles.

(b) *Organic.* The restrictions placed on the use of phosphate compounds in detergent formulations have led to a variety of organic compounds that could function as builders but which also must be readily biodegradable. Although some of these compounds do approach the sequestration level of phosphates, they are not as cost effective [90].

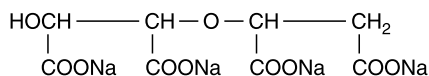
Various polycarboxylate compounds, those with at least three carboxylate groups, have now become widely used as replacements for phosphates as the builder component of HDLDs. In liquid detergent formulations citrate compounds have become commonplace. Although their chelating ability is relatively low (Figure 8.13), citrate is used in HDLDs for a variety of reasons. Citrate's high aqueous solubility makes it useful in unstructured liquids, whereas in structured liquids its high electrolytic strength can aid in salting out and stabilizing the formulation. In addition, it is also used in enzyme-containing formulations where the maintenance of the pH at less than 9.0 is crucial to the stability of the enzyme.



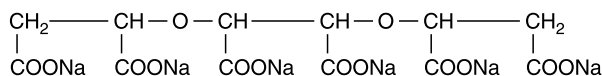
**FIG. 8.13** Sequestration of water hardness ions by detergent builders. Sodium polyacrylate  $M_w = 170,000$ , STPP (sodium tripolyphosphate), NTA (nitrilotriacetic acid), EDTA (ethylenediamine tetraacetic acid), sodium citrate, CMOS (sodium carboxymethoxysuccinate), sodium carbonate, zeolite A. (Reproduced from Nagarajan, M.K., *J. Am. Oil Chem. Soc.*, 62, 949, 1985. With permission.)

Citric acid itself has also been patented as an ingredient in protease stabilization systems [91].

Ether polycarboxylates have been found to provide improvements over the calcium and magnesium chelating ability of citrates. In a series of patents assigned to Procter & Gamble, it has been claimed that a combination of tartrate mono-succinates and tartrate disuccinates (Figure 8.14) delivers excellent chelating



Sodium Tartrate Monosuccinate (TMS)

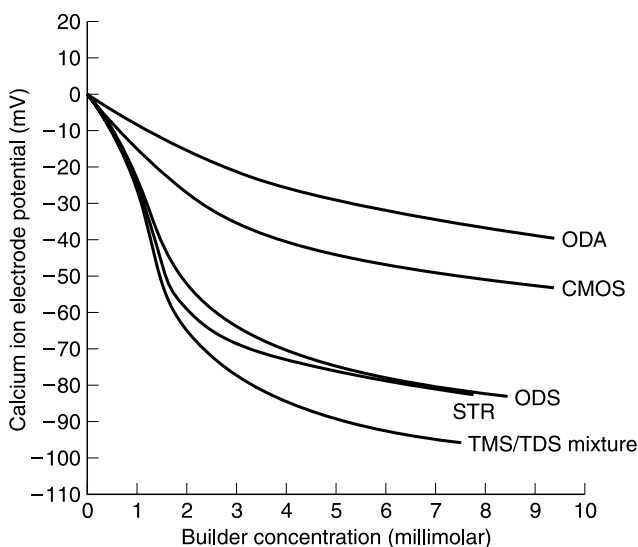


Sodium Tartrate Disuccinate (TDS)

**FIG. 8.14** Ether polycarboxylate builders.

performance [92–94]. Data represented in Figure 8.15 indicate a high calcium binding capacity.

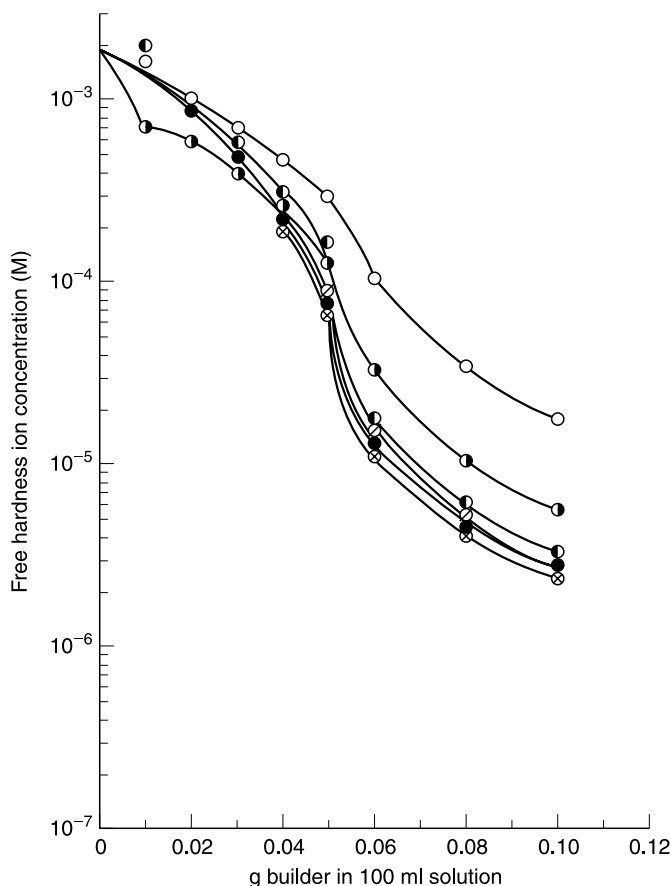
Salts of polyacetic acids, e.g., ethylenediamine tetraacetic acid (EDTA) and nitrilotriacetic acid (NTA), have long been known to be very effective chelating agents [95]. The chelating ability of NTA has been found to be comparable to that



**FIG. 8.15** Effect of builder level on calcium ion concentration. CMOS, sodium carboxymethoxysuccinate; ODS, sodium oxydisuccinate; STR, sodium triphosphosphate; TMS, tartrate monosuccinate; TDS, tartrate disuccinate. (From Bush, R.D., U.S. Patent 4566984 to Procter & Gamble Co., 1986.)

of STPP. Unfortunately, questions regarding the toxicity of this compound have all but prevented any large-scale use in HDLDs. Currently, NTA usage is primarily limited to a few powder and liquid detergent formulations in Canada. The high chelation power of EDTA has been used in compositions where metal impurities of iron and copper can be detrimental to the product stability, for example, in peroxygen bleach-containing liquids.

Polymeric polyelectrolytes have also found applications as alternative builder ingredients [96,97]. High-molecular-weight polyacrylate homopolymers and acrylic-maleic copolymers can be very effective in tying up calcium ions in the



**FIG. 8.16** Sequestration of water hardness ions by sodium polyacrylate polymers.  $M_w = 2,100, 5,100, 20,000, 60,000, 170,000, 240,000$ . (Reproduced from Nagarajan, M.K., *J. Am. Oil Chem. Soc.*, 62, 949, 1985. With permission.)

wash bath (Figure 8.16). However, concerns about their biodegradability and limited compatibility in most surfactant matrices have significantly limited their use in liquid formulations. The lower molecular weight polymer analogues can also aid in soil dispersancy and clay/particulate soil antiredeposition. In products containing moderate to high levels of carbonate, these polymers disrupt the nucleating calcium carbonate crystal structure, preventing the deposition of inorganic precipitates on fabrics.

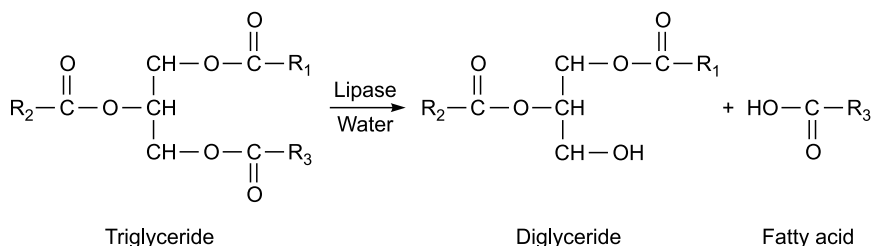
Fatty acids, such as oleic and coco fatty acid (saturation level) can serve a multifunctional role when added to HDLDs. Although they primarily provide a foam suppression capability, they can also precipitate out some of the calcium ions in the wash by forming calcium soap. This could, however, pose a problem, since soap scum, commonly known as lime soap, is insoluble and may have an impact on the overall cleaning result.

## C. Enzymes

Enzymes have become integral components of most liquid detergent compositions as they continue to play an increasing role in the stain removal process. This has come about due to many recent advances in enzyme technology and has resulted in more efficient and effective strains. The ability of these enzymes to target specific classes of stains can provide the formulator with the flexibility to tailor the development of products for consumers with different requirements and preferences. In addition, enzymes are especially effective when the liquid detergent is used as a prespotter.

There are four types of enzymes currently used in HDLDs: protease, lipase, cellulase, and amylase [6,98]. They are all proteins and are derived from various living organisms. Their role is to catalyze the hydrolysis of large biological molecules into smaller units which are more soluble and as a result are washed away relatively easily. The optimum conditions for the functioning of these enzymes depend on individual strains or types. Generally, the rates for enzymatic reactions rise with increasing temperatures, and are usually optimum within an alkaline pH range of 9 to 11.

Protease is by far the most widely used of all detergent enzymes. Introduced in the 1960s, it has since become one of the more important components of detergent formulations [6]. Proteases aid in the removal of many soils commonly encountered by the consumer, such as food stains (cocoa, egg yolk, meat), blood, and grass. This enzyme hydrolyzes or breaks up the peptide bonds found in proteins resulting in the formation of smaller and more soluble polypeptides and amino acids. Since most enzymes have to function under high pH conditions, subtilisin, a bacterial alkaline protease, is commonly used in laundry detergents. This particular protease does not hydrolyze any specific peptide bond in proteinaceous stains but cleaves bonds in a somewhat random manner.



**FIG. 8.17** Lipase-catalyzed conversion of insoluble oily (triglyceride) soils.

Amylase enzymes also work on food stains containing starches, such as rice, spaghetti sauce, potatoes, oatmeal, and gravy. These enzymes hydrolyze the 1–4 glucosidic bonds in starch, which leads to the formation of smaller water-soluble molecules.  $\alpha$ -Amylase randomly hydrolyzes the bonds in the starch polymer to form dextrin molecules.  $\beta$ -Amylase, in contrast, cleaves the maltose units that are situated at the end of the starch polymer.

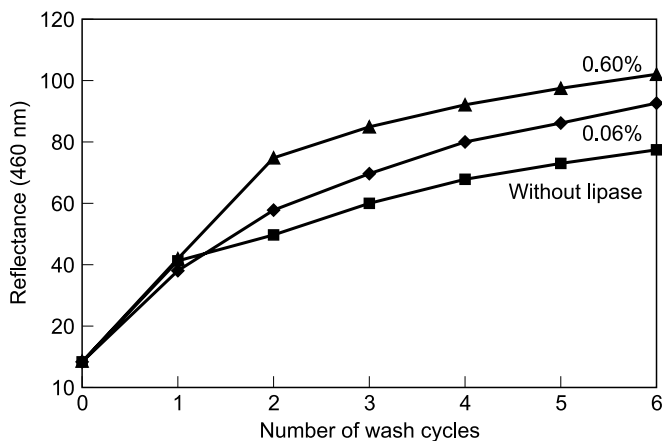
The use of lipase in detergents is a relatively recent occurrence. The first commercial detergent lipase was introduced in 1988 [6,98]. These enzymes target oily/greasy soils encountered with body sweat/collar soils, foods (butter, tallow, and sauces), and select cosmetics (lipstick, mascara) which are typically some of the most difficult stains to remove. The major components of most oily stains encountered in households are triglycerides. Lipases catalyze the hydrolysis of mostly the  $\text{C}_1$  and  $\text{C}_3$  bonds in the triglyceride molecule yielding soluble free fatty acids and diglyceride (Figure 8.17). In practice, it has been determined that lipases work best subsequent to the first wash (Figure 8.18). It is believed that the temperatures encountered in a typical drying process are needed to activate the enzyme. Although most oily stains can also be cleaned using traditional surfactant methods, the main benefit of lipases is their ability to perform at relatively low concentrations and low temperatures.

With greater emphasis being given to the care of fabrics, cellulase enzymes have become increasingly important in detergent products [98]. Repeated washing often leads to cotton fabrics looking faded and worn. This appearance is attributed to the damaged cellulose microfibrils on the fabric surface. Cellulase enzymes are able to hydrolyze the  $\beta(1-4)$  bonds along the cellulose polymer, resulting in smaller units which are carried away in the wash (Figure 8.19). The removal of these damaged microfibrils or “pills” gives the clothing a less faded appearance (Figure 8.20).

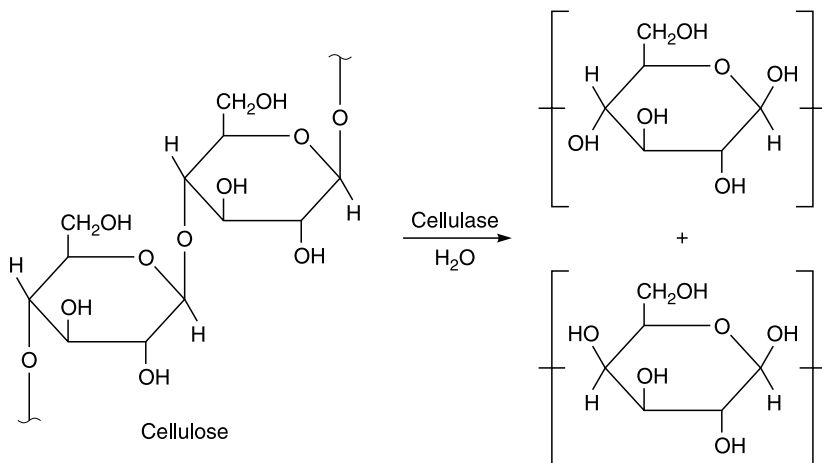
## 1. Enzyme Stabilization

Enzymes are highly susceptible to degradation in heavy-duty laundry liquids. With the increasing emphasis on the use of enzymes as cleaning agents, it becomes all

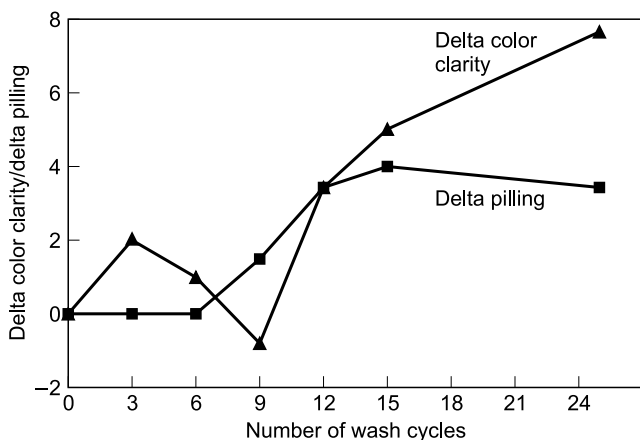




**FIG. 8.18** Effect of lipase enzyme (Lipolase<sup>TM</sup>) on lard/sudan red stains as a function of the number of wash cycles. Conditions: powder detergent, temperature = 30°C, tergotometer, pH = 9.7. (Reproduced from Gormsen, E., Roshholm, P., and Lykke, M., in *Proceedings of the 3rd World Conference on Detergents: Global Perspectives*, Cahn, A., Ed., AOCS Press, Champaign, IL, 1994, p. 198. With permission.)



**FIG. 8.19** Hydrolysis of cellulose fibers by the cellulase enzyme.

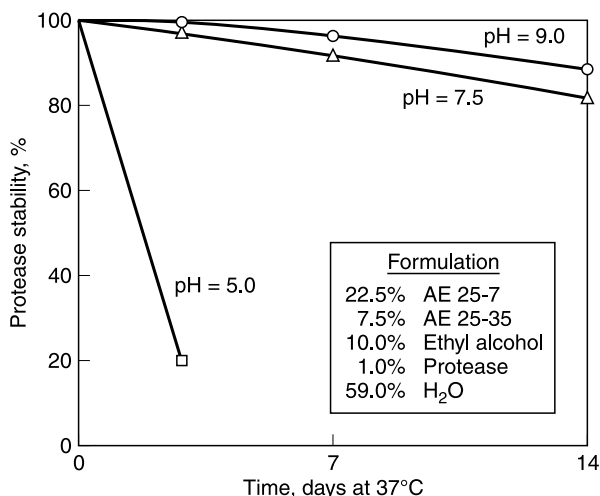


**FIG. 8.20** Effect of cellulase on the color clarity and pilling tendency of a cotton fabric. European machine at 40°C using a new black cotton fabric. (Reproduced from Gormsen, E., Roshholm, P., and Lykke, M., in *Proceedings of the 3rd World Conference on Detergents: Global Perspectives*, Cahn, A., Ed., AOCS Press, Champaign, IL, 1994, p. 198. With permission.)

the more important that these enzymes are protected against premature degradation or at least maintain their performance throughout the shelf life of the product.

Many factors contribute to the denaturation of enzymes in HDLDs. They include free water, alkalinity, bleaches, and calcium ion concentration. The presence of free water in the formulation is a major cause of enzyme degradation. This process is greatly accelerated at increasingly alkaline conditions. Generally, enzyme-containing commercial HDLDs are maintained within a pH range of 7 to 9 (Figure 8.21). However, this constraint can affect the detergency, as most enzymes attain their optimum efficacy at pH ranges from 9 to 11. Certain additional ingredients, especially bleaches, can also have a major detrimental effect on enzyme stability.

It is believed that those ingredients that are capable of depriving an enzyme's active site of calcium ions are detrimental to enzyme stability. It is hypothesized that calcium ions bind at the bends of the polypeptide chain, resulting in a more stiff and compact molecule [100–102]. Builders and surfactants that have affinities toward calcium ions are examples of such ingredients. The degree of stability also varies greatly with the type of surfactant or builder used. LAS and alkyl sulfate surfactants have been found to be more detrimental to enzymes than alcohol ethoxylates or alkyl ether sulfates [99]. The degree of ethoxylation also affects the status of the enzyme. In ether sulfates, improved stability is observed with increasing EO groups up to 5 to 7 EO groups [100]. LAS is more likely to bind



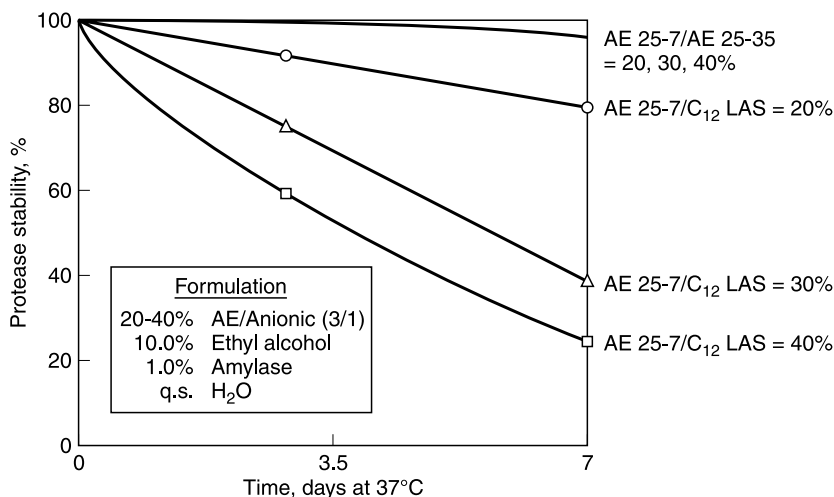
**FIG. 8.21** Effect of product pH on protease stability in a HDLD containing alcohol ethoxylate and alcohol ethoxy sulfates. (Reproduced from Kravetz, L. and Guin, K.F., *J. Am. Oil Chem. Soc.*, 62, 943, 1985. With permission.)

with the calcium ions in the product than other, more hardness-tolerant surfactants such as alkyl ether sulfates or the nonionic alcohol ethoxylate surfactants. This has been considered as a possible cause for faster enzyme degradation in LAS-containing HDLDs (Figure 8.22). Similarly, in formulations with builders or chelants, additional calcium is sometimes added to shift the equilibrium to favor the enzyme's active sites and prevent premature deactivation.

Other mechanisms for enzyme denaturation in the presence of surfactants have also been proposed. One hypothesis is that the high charge densities of ionic surfactants increase the probability of them binding strongly to protein sites. This causes conformational changes of the enzyme which subsequently leads to further enzyme deactivation [99,103].

The task of stabilizing enzymes is further complicated by the fact that HDLD formulations increasingly contain more than one enzyme (e.g., protease, lipase, and cellulase) system. In such systems, not only do the enzymes have to be protected against denaturation, but enzymes such as lipase and cellulase, which are themselves proteins, have to be shielded from the protease.

(a) *Protease-Only HDLDs.* All stabilization systems function by either binding to the active site of the enzyme or by altering the equilibrium of the formulation to favor the stable active sites. The system is effective in protecting the enzyme only if the stabilizing molecule binds strongly to the enzyme while in a formulation,



**FIG. 8.22** Effect of surfactant type on protease stability (AE, alcohol ethoxylate; AE25-3S, alcohol ethoxy sulfate; LAS, linear alkylbenzene sulfonate). (Reproduced from Kravetz, L. and Guin, K.F. *J. Am. Oil Chem. Soc.*, 62, 943, 1985. With permission.)

but easily dissociates from the enzyme's active sites when it encounters the dilute conditions in the wash.

Letton and Yunker [104] and Kaminsky and Christy [105] describe protease stabilization systems comprised of a combination of a calcium salt and a salt of a carboxylic acid, preferably a formate. These ingredients are moderately effective in enzyme stabilization and are relatively inexpensive. Care has to be taken, however, when adding divalent ions such as calcium to HDLDs to prevent the possibility of precipitation.

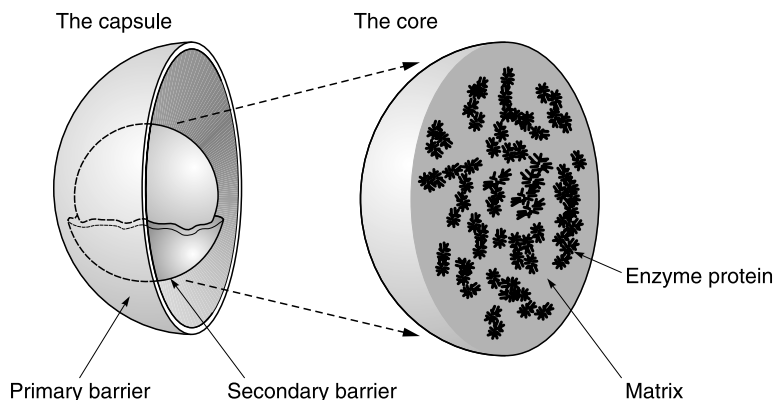
An improvement over this earlier system was attained with the addition of boron compounds such as boric acid or borate salts [106–108]. It has been hypothesized that boric acid and calcium form intramolecular bonds which effectively crosslink or “staple” an enzyme molecule together [107,108]. The use of polyols such as propylene glycol, glycerol, and sorbitol in conjunction with the boric acid salts further enhances the stability of these enzymes [109–111]. The patent literature contains numerous examples of enzyme stabilization systems that utilize borates, polyols, carboxylate salts, calcium, and ethanolamines, or combinations thereof [91,112–115].

(b) *Mixed Enzyme HDLDs.* In HDLD formulations with additional enzymes, it becomes increasingly difficult to stabilize all the enzymes. Amylases, lipases, and cellulases are themselves proteins and hence are susceptible to attack from

the protease. Various approaches to stabilizing a mixed enzyme system have been documented in the patent literature. One approach attempts to extend the stabilization techniques developed to stabilize protease-only formulations and apply them to mixed enzyme liquids [116–118].

Compounds that bind even more tightly to the protease active sites and as a result inhibit this enzyme's activity in the product during storage on the shelf have been identified. However, this method is effective only if this enzyme inhibition can be reversed under the dilute conditions of the wash water. Various boronic acids [119–123], such as arylboronic acids and alpha-aminoboronic acids, and peptide aldehyde [124], peptide ketone [125], and aromatic borate ester [126] compounds have been found which deliver this type of performance. It is believed that boronic acids inhibit proteolytic enzymes by attaching themselves at the active site. A boron-to-serine covalent bond and a hydrogen bond between histidine and a hydroxyl group on the boronic acid apparently are formed [122]. The patent literature also describes methods of stabilizing the cellulase enzymes in mixed enzyme systems with hydrophobic amine compounds such as cyclohexylamine and *n*-hexylamine [127].

Recently, alternative methods have also been developed to stabilize these complex enzyme systems. The technique of microencapsulation [128] is designed to prevent physically the protease enzyme from interacting with the other enzymes (Figure 8.23). This is accomplished by a composite emulsion polymer system which has a hydrophilic portion attached to a hydrophobic core polymer. The protease is stabilized by trapping it within the network formed by the hydrophobic polymer.

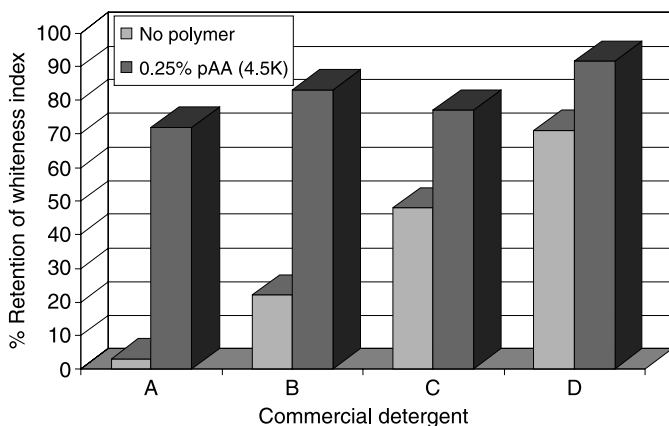


**FIG. 8.23** Enzyme microencapsulation. (Reproduced from Gormsen, E., Roshholm, P., and Lykke, M., in *Proceedings of the 3rd World Conference on Detergents: Global Perspectives*, Cahn, A., Ed., AOCS Press, Champaign, IL, 1994, p. 198. With permission.)

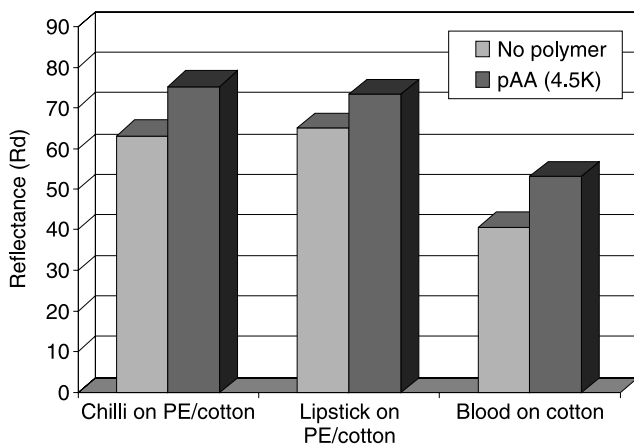
## D. Detergent Polymers

### 1. Polyacrylate Dispersants

Low- to moderate-molecular-weight polymeric dispersants have been utilized in powder laundry formulations for over 20 years. These polymers possess multiple benefits: (1) they act as crystal growth modifiers and prevent the formation and subsequent deposition of inorganic scale (i.e., calcium carbonate) on fabrics during the wash cycle, (2) they prevent the deposition of clay/particulate soils on fabrics, (3) they provide a modest increase in primary detergency on select soil/fabric combinations, (4) they reduce the viscosity of a high crutcher solids slurry, allowing easier processing, and (5) they improve particle integrity and the dissolution profile of spray-dried solids. In most isotropic liquid detergents, solubility limitations restrict the amount of inorganic builders incorporated into the formulation (so minimal inorganic scale is produced), and improvements in processing parameters are not warranted. The one measurable improvement has been attributed to clay soil antiredeposition, or enhanced whiteness maintenance. Incorporation of 3 to 5 ppm of active polymer into a liquid detergent can dramatically improve the whiteness index of a low- to moderate-cost formulation (Figure 8.24). These benefits are far less pronounced in systems utilizing high levels of surfactant with a modest builder system (citrate/fatty acid soap). Although these polymers are known to have modest sequestration properties for divalent metal cations (340 to 450 mg  $\text{CaCO}_3/\text{g}$  polymer), their use level in liquids is generally



**FIG. 8.24** Clay/oily soil redeposition of typical HDLDs. A, B, C, and D represent commercial liquid detergents, ranging from low-cost to premium brands, with and without the addition of a low-molecular-weight polyacrylate (pAA) homopolymer.



**FIG. 8.25** Effect of polymer incorporation in a commercial laundering application (35 lb machine, 100 ppm polyacrylate (pAA) homopolymer).

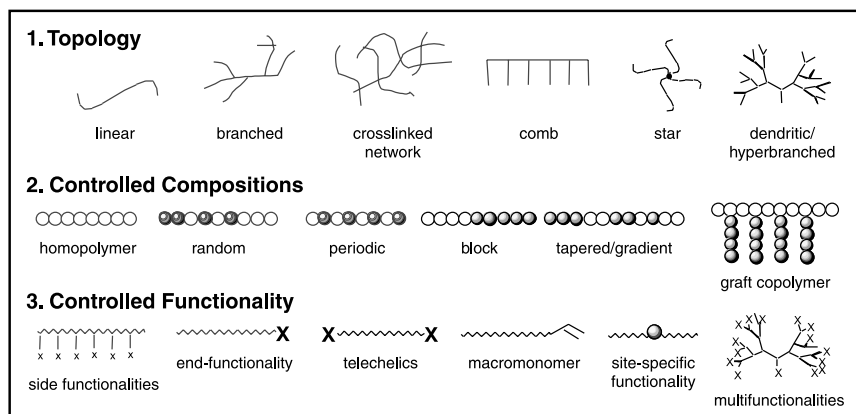
restricted to a fraction of a percent of the finished product. (Polyacrylates typically have limited compatibilities in surfactant matrices [129,130].) Studies have shown that these polymers are also effective in enhancing the primary detergency of select clay/oily soils, but this benefit is far more pronounced in industrial and institutional cleaning formulations than in heavy-duty liquids (Figure 8.25).

Polymer properties can be adjusted by modifying the polymer backbone through the introduction of alternative (hydrophilic/hydrophobic) monomers, adjusting the charge density (mono- versus dicarboxylic acids), varying the synthetic pathway (which can have an impact on polymer morphology), adjusting the molecular weight, or by utilizing different chain transfer (terminating) agents to cap the end functionality of the polymer chain, which changes the polymer's affinity and binding capacity for different substrates (Figure 8.26).

Carboxymethylcellulose (CMC) has also been widely utilized as an antiredeposition agent for cotton fabrics. It functions by forming a protective layer on the surface of the cellulosic fibers. However, the low aqueous solubility greatly limits its use in unstructured liquids.

## 2. Dye Transfer Inhibition: Polyvinylpyrrolidone (PVP)

Color-safe detergents are becoming a significant portion of the detergent market worldwide. Few technologies have been able to demonstrate real color safety in the washing cycle. Inhibition of dye transfer is one way whereby the color freshness of fabrics may be maintained after repeated washing. Polymers such as PVP are employed which inhibit transfer of fugitive dyes from colored fabrics onto other items in the washing machine [131,132].



**FIG. 8.26** Polymer morphology: production of polymers via alternative synthetic pathways.

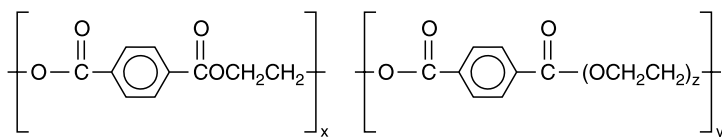
PVP is a nonionic water-soluble polymer that interacts with water-soluble dyes to form water-soluble complexes with less fabric substantivity than the free dye. Additionally, PVP inhibits soil redeposition and is particularly effective with synthetic fibers and synthetic cotton blends. The polymer comprises hydrophilic, dipolar imido groups in conjunction with hydrophobic, apolar methylene and methine groups. The combination of dipolar and amphiphilic character make PVP soluble in water and organic solvents such as alcohols and partially halogenated alkanes, and will complex a variety of polarizable and acidic compounds. PVP is particularly effective with blue dyes and not as effective with acid red dyes.

### 3. Soil Release Agents

Greasy and oily soils on polyester or polyester-containing fabrics are among the more difficult stains to displace. Removal of these soils from cotton fabrics, however, is far easier. This difference in cleaning can be attributed to the hydroxyl and carboxyl groups on the cellulosic fibers which give the surface of the cotton a hydrophilic nature and subsequently permit surfactants and water to more easily wash away adsorbed soils. The surface of polyester fabrics, in contrast, is hydrophobic since they are essentially composed of copolymers of terephthalic acid and ethylene glycol. This hydrophobicity not only creates an affinity towards oily soils, but makes them more difficult to remove.

The use of soil release agents in liquid laundry detergents is meant to address some of these issues [133]. These ingredients are usually polymeric and are composed of hydrophilic as well as hydrophobic segments. The hydrophobic functionality of the polymer allows it to be deposited and remain adsorbed onto the





Poly (Ethylene Terephthalate, Polyoxyethylene Terephthalate)  
(PET) (POET)

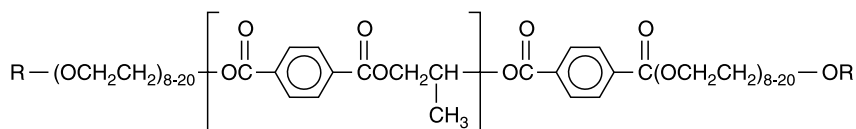
**FIG. 8.27** Polyethylene terephthalate (PET)–polyoxyethylene terephthalate (POET) soil release polymer. (Reproduced from Grime, K., in *Proceedings of the 3rd World Conference on Detergents: Global Perspectives*, Cahn, A., Ed., AOCS Press, Champaign, IL, 1994, p. 64. With permission.)

hydrophobic fibers of the polyester fabric during the washing and rinsing cycles. Once adsorbed the polymer can change the surface characteristics of the fabric to a more hydrophilic environment. In this way the polymer can not only make it easier for water and other cleaning agents to diffuse into the soil/fabric interface, but also prevents soils from adsorbing strongly onto the fabric. Consequently, soil release polymers are most effective only after the fabric has been treated with it. For this reason the largest impact is observed after several wash cycles.

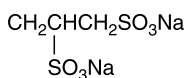
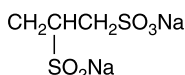
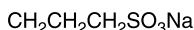
A typical soil release polymer consists of segments of hydrophobic ethylene terephthalate and hydrophilic polyethylene oxide (Figure 8.27). A major drawback initially with these polymers was the limited aqueous solubility. This, in turn, led to lower performance, especially in particulate soil removal, due to weaker adsorption on fabric surfaces. The low solubility also limited the use of soil release polymers in unstructured liquids and sometimes led to instability of the product. Some of these obstacles have been overcome by using lower molecular weight polymers and by introducing end-capping groups [98,134]. These changes have led to improved solubility and better soil removal characteristics (Figure 8.28).

#### 4. Rheology Modifiers

In recent years the use of rheology modifiers has taken on a more significant role in the formulation of unstructured liquid detergents. These polymers can improve product aesthetics, making the formulation more appealing to the consumer, and can enhance product stability by interacting with hydrophobic particles or pigments. The suspension of visual cues or actives has become a means of differentiating like products, and the combination of polymeric rheology modifiers and inorganic clays have produced systems with a yield stress. (This is discussed at greater length in Chapter 5.) Typically utilized rheology modifiers not only thicken the formulation but have an impact on liquid flow properties (i.e., pseudoplasticity, or shear thinning). These materials can be derived from organic compounds (natural or synthetic), can be nonassociative or associative (interact with surfactants or



Where R is a mixture of



**FIG. 8.28** Soil release polymer with end-capping groups. (Reproduced from Grime, K., in *Proceedings of the 3rd World Conference on Detergents: Global Perspectives*, Cahn, A., Ed., AOCS Press, Champaign, IL, 1994, p. 64. With permission.)

other hydrophobic moieties), or can be (relatively) simple inorganic compounds such as salts or clays.

## E. Bleaches

Bleaches play a significant role in detergent formulations since they can affect the cleaning efficacy which is easily consumer perceptible. Bleaching action involves the whitening or lightening of stains by the chemical removal of color. Bleaching agents chemically destroy or modify chromophoric systems as well as degrade dye compounds resulting in smaller and more water-soluble molecules which are easily removed in the wash. Typical bleach-sensitive stains include food/vegetable products, coffee, tea, fruits, red wine, and some particulate soils. Bleaches can also aid in minimizing “dinginess” which gives clothes a grayish/yellow tint caused by a combination of fabric fiber damage and dirt buildup. Bleaches also perform other functions in the wash liquor, namely improved sanitization and color protection (through oxidation of dyes and stains that have been solubilized during the cleaning process).

There are two types of bleaches used in the laundry process: hypochlorite and peroxygen bleaches. Although hypochlorite bleaches by themselves are effective bleaches, they lead to color fading and fabric damage and are difficult to incorporate into detergent formulations. Peroxygen bleaches, although not as effective, can be formulated into detergents and cause minimal color fading or fabric damage. They also bleach out food stains since the chromophores found in these soils are

susceptible to peroxide bleaches. Fabric dyes, however, are not as active as food dyes and are not easily affected by the peroxygen compounds.

Most detergents with bleach formulations are in the powder form. Unfortunately, the aqueous nature of HDLDs does not easily permit the formulation of bleach components. This is especially true in unstructured liquids where the stability of the peroxygen components is severely compromised. Nevertheless, attempts have been made to produce HDLDs that also contain bleaches.

## 1. Peroxygen Bleaches

Peroxide bleach-containing detergent formulations contain either hydrogen peroxide or compounds that react to form hydrogen peroxide in the wash. The most direct source for peroxide bleaching is hydrogen peroxide. Numerous attempts have been made to develop stable hydrogen peroxide-containing HDLDs [135–137]. The stability of this ingredient in aqueous formulations, however, is of concern. Hydrogen peroxide is very susceptible to decomposition in aqueous environments largely because trace impurities of metal ions such as iron, manganese, and copper can catalyze its decomposition [138]. Alkalinity also accelerates this process. For these reasons HDLDs containing hydrogen peroxide are maintained at an acidic pH and usually also contain a strong chelating agent to sequester metal ions. A free radical scavenger can also be added to further enhance stability. Polyphosphonate compounds, polycarboxylates, and butylated hydroxytoluene (BHT) are examples of chelating agents and free radical scavengers, respectively, which are used in hydrogen peroxide-containing formulations [139]. Still, the bleaching performance of these products is inadequate, particularly at low temperatures ( $<40^{\circ}\text{C}$ ). These limitations have prompted manufacturers to look at other methods to develop bleach-containing HDLDs.

Inorganic peroxygen compounds such as sodium perborate tetrahydrate or monohydrate and sodium percarbonate can also be used as sources for hydrogen peroxide. These insoluble compounds release hydrogen peroxide on contact with the wash water. The challenge is to stabilize them within a HDLD formulation. The ability of structured liquids to suspend solids between the surfactant lamellae or spherulites can be made use of in these products [140–143]. It is possible to suspend sodium perborate in highly concentrated structured liquids. The minimization of contact with water prevents the peroxygen compounds from decomposing prematurely. It has also been found that the use of solvents further improves the stability [144]. Hydrophobic silica can enhance stability in unstructured liquids [145]. The most effective method of formulating with perborates and percarbonates is with nonaqueous liquids. The complete absence of water and a high level of solvents significantly enhance the stability of bleaches in the product.

## 2. Peracid and Activated Peroxygen Bleaches

Peroxy-carboxylic acids or peracids are far more effective bleaching compounds than peroxygen compounds especially at low and ambient temperatures. The high reactivity and low stability of these compounds have so far prevented them from being used in commercial detergent bleach formulations. Peracids are somewhat stable in aqueous solutions of neutral pH and they equilibrate with water in acid pH to form hydrogen peroxide and carboxylic acids. However, in alkaline conditions these compounds undergo accelerated decomposition. Nevertheless, attempts have been made to develop HDLDs that take advantage of the ability of structured liquids to suspend insoluble solids. Patents have been issued for liquid detergent formulations which incorporate peroxy acids such as diperoxidodecanedioic acid [146,147] and amido and imido peroxy acids [148,149]. These product formulations are also maintained at an acidic pH to reduce the premature reaction of the peracid.

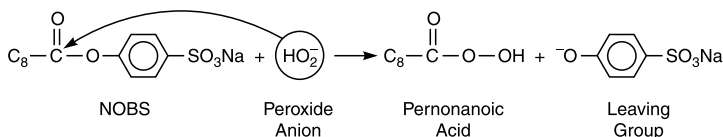
An alternative and more desirable method of bleaching is by forming the peracid in the wash water. This is accomplished by reacting a bleach activator compound with a source of hydrogen peroxide such as perborate, percarbonate, or hydrogen peroxide itself in an aqueous environment. In this reaction, referred to as perhydrolysis ([Figure 8.29](#)), the bleach activator undergoes nucleophilic attack from a perhydroxide anion generated from hydrogen peroxide, resulting in the formation of percarboxylic acid. This formulation strategy is effectively utilized in powder detergents where perborate and percarbonate compounds are used along with activators such as tetraacetylene diamine (TAED) and sodium nonanoyloxybenzene sulfonate (NOBS).

In liquid detergents the challenge is to incorporate hydrogen peroxide and an activator compound in an aqueous formulation and prevent these two components from reacting prematurely in the product itself. A novel method utilizes emulsions formed by nonionic surfactants with varying hydrophilic/lipophilic balance (HLB) values to protect a soluble activator, acetyltriethyl citrate, from other ingredients, including hydrogen peroxide, in the product [150–152]. An acidic pH and the addition of a strong chelating compound aid in product stability. Other patents using NOBS [153], glycol and glycerin esters [154], and a lipase–anhydride combination [155] have been issued.

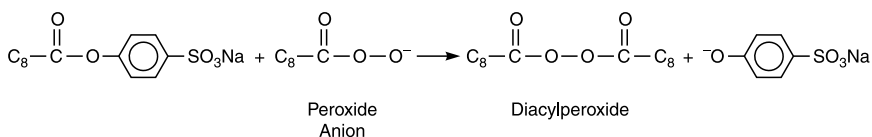
## F. Optical Brighteners

It has been found that fabrics, especially cotton, begin to appear yellowish after repeated washing cycles. Virtually all modern liquid detergent formulations contain very small amounts (<1.0%) of optical brighteners or fluorescent whitening agents which absorb ultraviolet light (300–430 nm) and reemit it as fluorescent visible blue light (400–500 nm) [156–159]. This visible blue light offsets some of

## Primary Reaction – Perhydrolysis



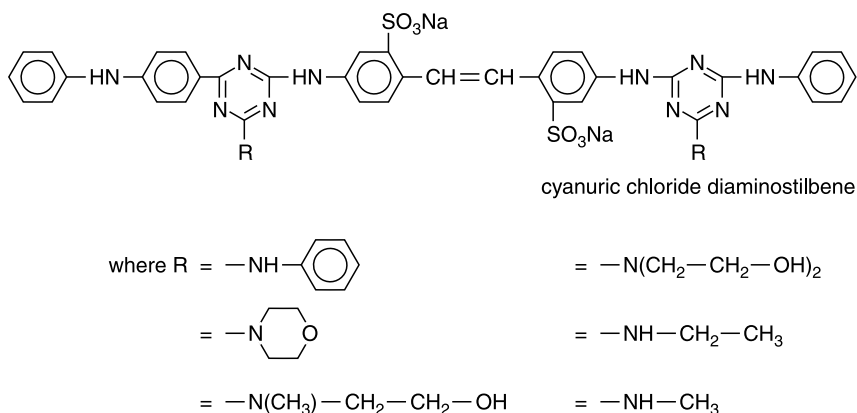
## Secondary Reaction – Formulation of Diacylperoxide



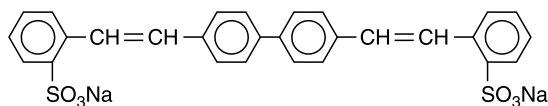
**FIG. 8.29** Bleach activator (nonanoyloxybenzene sulfonate) reactions. (Reproduced from Grime, K., in *Proceedings of the 3rd World Conference on Detergents: Global Perspectives*, Cahn, A., Ed., AOCS Press, Champaign, IL, 1994, p. 64. With permission.)

the yellow hues from the fabric and as a result provides a whitening/brightening effect as seen by the human eye.

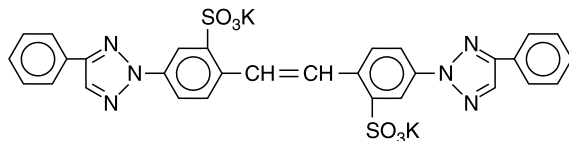
The most widely used class of fluorescent whitening agents (FWAs) are known as CC/DAS types or cyanuric chloride diaminostilbene. The chromophore in these molecules is triazinylaminostilbene (Figure 8.30). The basic molecule can



**FIG. 8.30** CC/DAS or DASC: bis-triazinyl derivatives of 4,4'-diaminostilbene-2,2'-disulfonic acid. (Reproduced from Whalley, G., *HAPPI*, Nov., 82, 1993. With permission.)



Disilyrylbiphenyl type



Triazolylstilbene type

**FIG. 8.31** Chlorine-stable fluorescent whitening agent: disodium 4,4'-bis(2-sulfostyryl)biphenyl and a triazolylstilbene type. (Reproduced from Whalley, G., *HAPPI*, Nov., 82, 1993. With permission.)

be altered by the addition of various substituent groups including alkoxy, hydroxy, or amino groups. The choice of these substituent groups can control the solubility, substantivity, and overall performance of the brightener. These brightener molecules are highly susceptible to electrophilic attack. As a result, they are ineffective and unstable in the presence of chlorine bleach. For this reason, it is common for detergent manufacturers to recommend that users add chlorine bleach at least five minutes into the wash. Another class of brighteners have been developed that are more resistant to chlorine bleach (Figure 8.31). These include distyrylbiphenyl derivatives such as disodium 4,4'-bis(2-sulfostyryl)biphenyl and triazolylstilbene.

## G. Miscellaneous Ingredients

A variety of other ingredients also serve valuable functions in HDLD formulations.

### 1. Buffers

An alkaline pH in the wash water can greatly improve the cleaning ability of the detergent. Certain oily/greasy soils can be removed from the fabric surface by saponification at high pH values. In addition, enzymes reach an optimum performance level within a pH range of 8 to 11. Examples of buffering compounds used in HDLDs include carbonates, liquid silicates, borates, and amines such as monoethanolamine (MEA) and triethanolamine (TEA). However, in enzyme-containing formulations care should be taken to prevent the product pH from exceeding a level that could lead to enzyme degradation.

## 2. Defoamers

Soap is used extensively to minimize excessive foaming in washing machines, particularly in European or horizontal axis machines where agitation is considerably higher and foam generation can become a significant problem. Long-chain fatty acids (palmitic/stearic) or their alkali metal salts (sodium or potassium) are typically incorporated into liquid formulations. Under high water hardness conditions the formation of lime soap (calcium fatty acids) presents a soil redeposition issue, and garments can become dingy and acquire an off odor. The problem can be mitigated by adjusting the surfactant system or incorporating a hydrophobically modified polymer to thoroughly disperse lime soap [160].

Silicone-based defoamers are also highly effective foam control agents. Marketed by Dow Corning, silicone foam control agents have a lower surface tension than most fluids, readily dispersing through the liquid film constituting a bubble, collapsing the soap bubble, and dramatically reducing the foam [161].

## 3. Hydrotropes

It is sometimes necessary to use hydrotropes to solubilize all ingredients in an unstructured liquid. Examples of hydrotropes include sodium xylene sulfonate (SXS), sodium cumene sulfonate (SCS), and sodium toluene sulfonate (STS). Alcohols (ethanol) and glycols (propylene glycol) are also commonly used to couple insoluble or incompatible actives to produce a homogeneous, isotropic liquid. An extensive description of these ingredients is presented in [Chapter 2](#).

## 4. Minors

A number of ingredients, although used in small amounts, serve very important roles. Preservatives are needed to inhibit the growth of microorganisms in aqueous products. Included in this long list of actives are formaldehyde or formaldehyde donors (imidazolidinyl compounds or dimethylhydantoin), isothiazolones, combinations of dimethylhydantoin and iodopropylbutylcarbamate (IPBC), and select cationic surfactants (when properly formulated with nonionics) [162]. Fragrances and dyes help cover the odor and color of the base liquid and enhance the aesthetics of the product. A fragrance is comprised of a blend of volatile organic chemicals (typically 20 to 100 ingredients), containing one or more functional groups such as aliphatic hydrocarbons, alcohols, aldehydes, terpenes, and natural extracts. Liquid detergents inherently possess a straw or amber color. Dyes are used to produce a brighter, more attractive appearance that will appeal to the eye of the consumer. In some cases, the detergent manufacturer will change the appearance of a liquid detergent by intentionally adding an opacifier into a clear, isotropic liquid. This can be done to provoke the concept of mildness (as evidenced in rinse-added fabric softeners) or to depict a highly concentrated formulation. The opacifiers that are commonly used in these systems are styrene/(meth)acrylate emulsion polymers (sold by Rohm and Haas) with a particle size between 150 and 400 nm [163].

## IV. PRODUCT EVALUATION METHODS

### A. Physical Properties

The acceptability and formulation success of a laundry liquid can depend on several important physical properties. Foremost among these characteristics is the physical stability of the product. The consumer expects the final product to be homogeneous and single phase. Accelerated aging tests at temperatures the product is likely to encounter in its lifetime are conducted to test the storage stability. In addition, a test to check the ability of the liquid to withstand repeated freeze–thaw cycles and still remain a single phase is generally carried out. Rheology and flowability tests are especially crucial in characterizing structured liquids. [Chapter 4](#) provides a good description of the basic rheological concepts. HDLDs have to maintain desirable pouring characteristics in order to be considered acceptable by the consumer. The stability of the fragrance is also of utmost importance to the product. Fragrance characteristics are analyzed in conjunction with the accelerated physical stability tests.

The importance of preserving enzymes has been discussed earlier in this chapter. The activity of enzymes is usually measured by performing an assay specific to the enzyme being tested. It is also recommended to conduct washing tests over an extended time period on enzyme-sensitive stained fabrics and determine the extent of enzyme loss as a function of time.

### B. HDLD Detergency Evaluation

The mechanisms underlying the detergency and soil removal process have been reviewed by many authors [164–172]. This section briefly summarizes the test methods used to characterize the performance of liquid laundry detergents. There are typically three stages of testing during product development: (1) laboratory evaluation, (2) practical evaluation, and (3) consumer tests.

#### 1. Laboratory Tests

(a) *Soil Removal.* Soil removal testing on a laboratory scale is conducted using specialized equipment, typically a tergotometer, which is designed to simulate the actual laundry process. The tergotometer consists of a series of 1 l stainless steel buckets, each with an agitation mechanism. Soiled fabric swatches are added into the wash solution in order to measure stain removal and other attributes of the detergent product. These instruments offer the advantage of providing a controlled environment in which the effects of various variables can be measured. The effects of water temperature, water hardness, agitation rate, detergent concentration, etc., can then be determined.

[Table 8.4](#) shows the categories and typical examples of soils that are artificially deposited on a range of fabrics such as cotton, polyester, and blends. These soils



**TABLE 8.4** Listing of Laundry Soils Used in Detergent Evaluations (Table reproduced with permission from Coons, D., Dankowski, M., Diehl, M., Jakobi, G., Kuzel, P., Sung, E., and Trabitzzsch, U., in *Surfactants in Consumer Products: Theory, Technology and Application*, Falbe, J., Ed., Springer-Verlag, New York, 1987.)

Water-soluble soils	Particulate soils	Fats/oils	Proteins source	Carbo-hydrates	Bleachable dye source
Inorganic salts	Metal oxides	Animal fats	Blood	Starches	Fruit
Sugar	Carbonates	Vegetable fats	Eggs		Vegetables
Urea	Silicates	Sebum	Milk		Wine
Perspiration	Humus	Mineral oils	Cutaneous scales		Coffee
	Carbon black	Waxes			Tea

represent stains that can be removed by physical as well as by chemical mechanisms. The removal of stains in the water-soluble and particulate categories are largely dependent upon mechanical agitation and the interfacial forces created by the detergent surfactants. Bleachable or oxidizable and enzymatic stains are examples of soils which are more responsive to the chemical nature of the wash liquor.

Detergency can be evaluated either visually by an expert experienced panel which rates the degree of soil removal or by instrumental techniques [173–175]. In the latter method, the stain removal  $R$  is expressed as:

$$R = 100 - \left[ (L_c - L_w)^2 + (a_c - a_w)^2 + (b_c - b_w)^2 \right]^{1/2}$$

where  $L$  = reflectance,  $a$  = redness/greenness,  $b$  = yellowness/blueness,  $c$  = unstained fabric washed in treatment conditions, and  $w$  = stained fabric washed in treatment conditions.

(b) *Brightening*. The brightening performance of detergent formulations is determined by washing a set of large unsoiled swatches representing various fabric types. These can include swatches of cotton, nylon, cotton blends, terry towels, and polyester fabrics. These swatches are washed for one to three cycles, and their brightness is subsequently measured using a reflectometer. The  $b$  component (blue/yellow) of the light reading is measured for this test.

(c) *Soil Release*. Clean swatches are first prewashed, typically for one to three cycles, using the detergents to be tested. After the prewash, the swatches are stained with a variety of soils, usually greasy particulate and food soils. Subsequently, the swatches are washed again. At each stage, the reflectance reading of the fabric swatches is recorded.

(d) *Antiredeposition.* Once soil removal has occurred, the possibility exists that this soil can redeposit onto the fabric. The likelihood or the extent of this occurring for a particular detergent product can be measured by an antiredeposition test. In this test clean swatches along with typical soils are added into the wash solution. Representative particulate soils include vacuum cleaner dirt and various colored clays (grayish-brown, reddish-brown, orange); a mixture of triolein and mineral oil as well as an artificial sebum (body sweat) composition serve as oily/greasy soils [176,177]. The washing experiments can be conducted using a laboratory-scale tergotometer or a commercial washing machine. Generally, one to three cycles for a laboratory scale and five to ten wash cycles for a washing machine are necessary for the entire test. The degree of soil deposited is measured instrumentally by reflectance readings.

(e) *Dye Transfer or Color Loss.* Colored fabrics tend to lose color and fade after repeated detergent washes. In addition, white or undyed fabrics can sometimes acquire a small degree of color from the transfer of dyes when washed with colored fabrics. Tests methods have been developed to measure the contribution of detergents to this color loss. Detergent manufacturers perform these tests on a laboratory scale as well as on a practical level.

In a typical laboratory-scale test [178,179] conducted using a tergotometer, a nylon fabric dyed red and cotton fabrics dyed different shades of blue are added to the wash bucket along with a clean undyed white cotton fabric. This white cloth is meant to be a scavenger of dyes lost in the wash and provides an indication of color transfer. Various detergents can be tested and ranked according to their color loss properties. After the wash, the fabric swatches are instrumentally evaluated with a colorimeter. The  $E$  value provides the degree of colorfastness of the fabric in a particular detergent:

$$E = \left[ (L_w - L_o)^2 + (a_w - a_o)^2 + (b_w - b_o)^2 \right]^{1/2}$$

where  $L$  = reflectance and the subscripts  $w$  and  $o$  signify after the wash and before the wash, respectively.

Practical evaluations utilize commercial washing machines and use actual colored clothing materials in the test. These clothes are then washed repeatedly with detergent over a 10- to 50-cycle range. The clothes are then evaluated visually using an expert panel. Instrumental measurements can also be taken.

## 2. Practical Evaluation

Additional performance evaluations are also conducted in commercial washing machines. Although this method does not permit testing in as controlled a fashion as the launderometers, they do predict consumer-relevant behavior. Soiled fabric

swatches when added to commercial washing machines also need to be accompanied by additional clothing as ballast to provide more realistic clothes-to-detergent and bath-to-fabric ratios.

Fabric bundle tests are also an effective and realistic method of evaluating detergency of HDLDs. In this test, clothing articles are distributed among volunteers to be used in their normal manner. They are periodically returned to be washed and evaluated. The evaluation can be conducted visually or instrumentally.

### 3. Consumer Tests

The final and most important component of the evaluation of laundry detergents is the consumer test. A select group of consumers is provided with a product and instructed to use it with their normal laundry loads. Their feedback on various aspects of cleaning and product aesthetics is collected and analyzed. These data play a significant role in any decision regarding the composition of the liquid laundry detergent.

## V. RECENT PATENT TRENDS

Several thousand patents have been issued over the past 7 or 8 years covering HDLDs. Many of these patents describe improvements in detergent efficacy via more conventional or accepted approaches, including optimized surfactant systems and “bleach alternative systems” (optical brightener/enzyme packages). In recent years there has been a greater emphasis on adjuvants or additives that are incorporated into detergent formulations at relatively low concentrations that deliver significant, consumer-perceptible benefits. High on that list are fabric and color care compositions, with the ultimate goal being focused on preserving fabric appearance after multiple launderings (“looks newer longer”) [180–185]. There has been a continuous effort to find/commercialize novel polymers (other than PVP and its associated derivatives) that reduce dye transfer in the wash or rinse cycle. Novel enzymes (peroxidases/oxidoreductases) are beginning to find utility in liquid detergents as alternative dye transfer inhibitors [186], with recent efforts aimed at reducing enzyme allergenicity by polypeptide modification [187]. Several patents on novel soil release technologies have also been granted, with the focus being shifted from synthetics and fabric blends to 100% cotton garments [189–193].

The market has also migrated towards consumer-friendly products that reduce fabric wrinkling and dramatically cut/eliminate ironing time [180,182,194,195]. Polymers have also been employed to build rheology (or structure) in various liquid formulations, with the objective of improved product aesthetics (through the suspension of actives or visual cues) [196]. Fragrance encapsulation and additives for masking malodors have also become topics of much interest [197,198].

Water-soluble packages or sachets have been launched commercially in Europe and the U.S., and several patents have also been published in this area [199,200].

These recent patent trends are described in greater detail in the following sections. A series of tables summarizing the principal advances in HDLDs are listed in the Appendix.

## **A. Polymers**

The incorporation of polymers into HDLDs is one of the areas where patent activity and manufacturer interest remain quite high. Polymers can attach to a fabric and facilitate the release of various soils (soil release polymers) [188–193], prevent the transfer of fugitive dyes onto clean fibers in the wash bath (dye transfer inhibitors) [201–205], improve the cleaning efficacy/antiredeposition properties of oily/particulate soils [206,207], act as suds enhancers/foam boosters [208,209], increase fabric yarn strength [210], reduce wrinkling/ease of ironing [180,194,195], and eliminate fabric pilling/fuzz on select garments [181–185].

### **1. Soil Release Polymers**

The concept of polymeric soil release agents has been around for well over 25 years. The initial polymer chemistries (polyethylene terephthalate–polyoxyethylene terephthalate, PET–POET) were designed to deposit on fabrics and facilitate oily soil removal upon subsequent washing [98,133,134]. The limitation of this chemistry was its effectiveness on synthetics (polyester) alone, with limited benefits being observed on cotton and synthetic blends. In recent years the focus has shifted to delivering soil release on cotton. Two classes of polymer chemistries have been disclosed in the recent patent literature for cotton soil release: one based on hydrophobically modified polycarboxylates derived from acrylic acid and hydrophobic comonomers at defined molar ratios [188] and the other based on modified polyamines [189–193].

### **2. Fabric Care**

During the laundering process, fabrics undergo mechanical and chemical changes that damage the fibers comprising a garment and adversely affect fabric integrity. These changes can be observed in the form of fiber deterioration (pilling/fuzz formation), fabric wrinkling, fabric stiffness, color fading, and poorer fabric appearance. There have been several patents/applications that have utilized cellulose-based polymers and their derivatives to negate this effect. Cellulose-based polymers or oligomers have been found to impart fabric appearance and integrity benefits (improved abrasion resistance) to textiles/fabrics washed in a conventional laundry composition without promoting any reduction in cleaning efficacy [183]. Cationic celluloses have also been employed as enhancing agents or deposition aids designed to facilitate the deposition of insoluble fabric care benefit agents such as dispersible polyolefins and latexes through the laundering

cycle [211]. Fabric care benefits have also been achieved via incorporation of fiber reactive additives (polyamide–polyamines) that provide several cleaning benefits (soil removal, soil dispersancy, and dye transfer inhibition) [184,185]. Polymers and prepolymers derived from polyoxyalkylene amines have also been utilized in a process to shrinkproof wool [212]. Yarn strength-enhancing agents selected from a group consisting of polysaccharides, clays, starches, chitosans, and mixtures of these materials have also been claimed [210]. The authors claim that strengthening the yarn reduces pilling and “wear and tear” by retarding/inhibiting fiber migration from within the yarn to the surface of the yarn.

Fabric care benefits have also extended to areas that simplify or reduce extra labor encountered by the consumer. The crease recovery of fabrics can be improved by using C20–C40 saturated or unsaturated aliphatic hydrocarbons which have melting points below 0°C [194]. These additives can be adopted into products for use in a tumble dryer (flexible sheets), sprayable formulations, or in fabric care compositions (such as rinse-added fabric softeners). Ease of ironing benefits have also been promoted by utilization of silicone gel compositions for ease of ironing (improved glide, wrinkles more readily removed) and improved appearance after ironing (less visible wrinkles) [195]. A recent patent application discloses the use of nanoparticles or nanolatexes (10 to 500 nm) as a crease resistance agent or additive for helping in the ironing of textiles in an aqueous or wet medium [180].

### 3. Color Care (Dye Transfer Inhibition)

PVP has been used for many years to inhibit dye deposition by complexing fugitive dyes during the washing of colored fabrics. The performance of PVP is adversely affected by the presence of anionic surfactants in the wash bath. Analogues of PVP, including poly(4-vinylpyridine-*N*-oxide) (PVPNO), polyvinylimidazole (PVI), copolymers of polyvinylpyridine and polyvinylimidazole (PVP–PVI), and polysulfoxide polymers, have also been employed in detergents to prevent dye redeposition onto garments [201,202]. Bleach-stable, modified polyamine additives have been found to inhibit dye transfer between fabrics during laundering [203], and poly(vinylpyridine betaines) containing a quaternary nitrogen and a carboxylate salt are also claimed [204]. A recent patent application has claimed that laundry detergent compositions with select, cationically charged dye maintenance polymers or oligomers (having a net positive charge) impart appearance and integrity benefits to fabrics and textiles [205]. These polymers (oligomers) or copolymers are comprised of one or more linearly polymerizing monomers, cyclic polymerizing monomers, or mixtures thereof. These additives associate with the fibers of the fabric, minimizing the natural tendency of the laundered garments to deteriorate in appearance over multiple wash cycles.

### 4. Enhanced Cleaning Efficiency

Polymers are not typically known for their cleaning prowess in detergent systems. Most of the observed benefits focus on preventing the formation or subsequent

redeposition of inorganic scale or clay soils back onto fabric. Premium liquid detergents often utilize a combination of citric acid/citrate and fatty acid soaps to chelate calcium ions in the wash bath. The presence of high concentrations of fatty acid soap and divalent metal ions ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) leads to the formation of lime soap, or the insoluble calcium salt of fatty acids. Incorporation of selected surfactant blends and polymeric additives (maleic/olefin copolymers) act as lime soap dispersants, controlling the formation/deposition of an organic “scale” on fabrics, resulting in improved whiteness maintenance [160]. Other polymeric additives have been shown to deliver enhanced whitening benefits. Blends of soil release copolymers and conventional dye transfer inhibitors (PVP, PVPNO) provide improvements in soil antiredeposition [207], and ethoxylated/propoxylated polyalkyleneamine polymers (e.g., polyethyleneimine, with a degree of substitution of 1.0) deliver enhanced soil dispersancy in fabric laundering, dishwashing, and hard surface cleaning applications [206].

## 5. Product Aesthetics

There are several advantages offered by polymer chemistries in this area which cover many different properties. Liquid detergent compositions comprising quaternary nitrogen-containing and/or zwitterionic polymeric suds enhancers and suds volume extender have been claimed [208,209]. These polymers also exhibit an increased effectiveness for preventing the redeposition of greasy soils during the cleaning process. Aqueous compositions (liquid detergents, shampoos, personal care products, etc.) designed to impart a “thick or rich” appearance perceived by the consumer can be achieved by incorporation of specialized synthetic or natural polymers. Systems exhibiting pseudoplasticity, or shear thinning behavior, are usually quite desirable. At high surfactant concentrations, many of these rheology modifiers fail to deliver sufficient viscosity build. The combination of a lipophilically modified copolymer (based upon acrylic acid residues) and a colloidal inorganic clay have been found to expand that surfactant range [111]. Other approaches have focused on polymer gums (carrageenans, gellans, and agars) capable of suspending relatively large size particles that remain pourable (with good shear thinning properties) [196].

## B. Enzymes

Enzyme cocktails are now commonly used in liquid detergents. Most products contain a minimum of a protease (for removal of proteinaceous soils) and an amylase (to facilitate starchy food-based soil removal) to assist cleaning. Several other formulations contain lipases (for degrading fatty/oily soils) and cellulases (to improve fabric appearance by cleaving the pills/fuzz formed on cotton and synthetic blends). Numerous patents were granted on enzyme stabilization packages during the 1980s and 1990s, but the recent focus has shifted toward novel enzymes for improved cleaning (xylogluconases, neopullulanase,

mycodextranase, and oxidoreductases) [213–216], reduced allergenicity [187], and the use of cellulose binding domains [217,218].

Currently, the generation of allergic responses to polypeptides is controlled by immobilizing, granulating, or coating the enzymes. The ability to reduce an allergic response by modifying the polypeptide (conjugating the enzyme with a polymer) allows the formulator to use enzymes in a wider range of products (light-duty liquids, personal care products).

The concept of utilizing cellulose binding domains to improve detergent efficacy is quite interesting. Cellulase enzymes are comprised, in part, of cellulose binding domains that have a high affinity for the surface of cotton. By linking a chemical entity to a cellulose binding domain, one can enhance/ensure deposition of actives (perfumes, polymers, bleaching or hygienic agents) onto the substrate through the wash.

### C. Fragrance Encapsulation/Odor Elimination

Although utilized in liquid detergents at relatively low concentrations, fragrances have become a critical selling feature of many cleaning products. The use of cyclodextrin molecules to reduce malodors generated by nitrogenous compounds (diamines) is just one example [197]. Instead of attempting to mask malodors with excess fragrance, the perfume is admixed with the cyclodextrin, which possesses an internal cavity capable of forming complexes. This technology delivers a fragrance to the wash cycle while the off odor emanating from other (undesirable) components is suppressed. Other mechanisms have been used in recent years to improve fragrance delivery or provide for controlled release. Fragrance raw materials can be delivered onto fabrics through the wash by way of a fragrance delivery system comprised of a single precursor pro-accord or pro-fragrance compound ( $\beta$ -ketoester) having higher fabric substantivity [219]. Compounds comprising at least one  $\beta$ -oxy or  $\beta$ -thio carbonyl moiety are capable of liberating an active molecule ( $\alpha$ , $\beta$ -unsaturated ketone, aldehyde, or carboxylic ester) into the surrounding environment [220]. Pro-perfume compositions comprising an amino functional component and a benefit agent (which is suspended in the liquid matrix) providing enhanced deposition and long-lasting fragrance release are also disclosed [221]. Lastly, polymeric nanoparticles including olfactive molecules having a defined glass transition temperature are also claimed [198]. The fragrance is contained inside the polymeric nanoparticle (core/shell technology), protecting the perfume and ensuring slow release during the washing process.

### D. Fabric Protection/Optical Whiteners

Consumers experience color damage to their personal garments from prolonged exposure to the sun (from line drying and everyday wear). The effect is more pronounced in tropical and subtropical climates around the globe. Visible light is

the largest contributor to fabric fading, and the incorporation of nonstaining, light-stable antioxidants into fabric care compositions has been achieved by addition of C8–C22 hydrocarbon fatty organic moieties [222]. A second approach involves novel compounds that are useful as ultraviolet absorbing agents and fluorescent whitening agents designed to improve the sun protection factor (SPF) of textile fibers, especially cotton, polyamide, and wool [223].

## E. Sachets/Unit Dose

Unit dose products have made impressive gains into the European marketplace, particularly the automatic dishwashing detergent market, in the form of compressed tablets. Polyvinyl alcohol (PVA) sachets containing powders and liquids have appeared in Europe and Asia/Pacific, but their presence has not been observed in the U.S. liquid detergent market. (Automatic dishwashing compositions containing liquids are being sold commercially in automatic dishwashing applications in the U.S.). The pouches must dissolve rapidly in the wash liquor, independent of water temperature and mechanical agitation, yet have enough structural integrity not to rupture upon handling by the consumer. Detergent components capable of crosslinking the water-soluble PVA film may alter the properties of the container, adversely affecting the sachet's solubility in water. The preparation of an essentially anhydrous liquid detergent composition (<5% free water by weight) allows the formulator more freedom to practice a wider variety of technologies [199].

## F. Surfactants

A series of patents covering novel anionic surfactants described as mid-chain branched surfactants deliver improved efficacy due to enhanced solubility (in cold water) and greater water hardness tolerance [224]. These surfactants could find greater utility in the U.S. with the growth of front loader washing machines and reduced washing temperatures. A second category of surfactants covers detergent compositions containing  $\alpha$ -sulfofatty acid esters and a process for synthesizing these materials [225]. These surfactants have performance comparable to other anionics in soft water, but exhibit better cleaning efficacy as water hardness increases.

## G. Builders

The use of builders in liquid laundry formulations has effectively been restricted to citrates and fatty acid soaps (in isotropic compositions sold in the U.S. and Europe). Although liquid laundry products can contain tripolyphosphate, soda ash, NTA, and other common builders found in powder laundry, limitations on solubility (in a surfactant matrix) or regulatory concerns have restricted their utilization. There is a finite number of patents covering zeolite-built HDLDs, but problems



relating to long-term stability of the slurry have always been a concern. A recent patent on the production of colloidal particles under 0.1  $\mu\text{m}$  (35 nm zeolite A) has rekindled interest in this application [226]. The drive is to mill zeolite particles even finer and reach a 15 nm particle size, where the zeolite suspension will become transparent. Theoretically, one could produce a “clear” zeolite slurry at a modest viscosity with a cost profile that is considerably more favorable than sodium citrate. Several articles/patents on nanoparticle technology are concerned with ultrafine particles (nanolatexes) capable of being suspended over time in a liquid detergent composition [190].

## VI. NEW PRODUCTS

As the twentieth century drew to a close, liquid detergents in the U.S. achieved a milestone to which no other global laundry market comes close — they surpassed the sales of powder detergents. This trend has continued unabated for the past 5 to 10 years, and in 2004 liquids accounted for close to 70% of detergent market sales.

A number of formulation revisions and advanced technologies have contributed to the rapid growth in liquids. In some cases the changes were directed at consumer needs/requirements and were relatively “low tech;” in other cases the market was driven by novel technologies developed by the detergent manufacturers in concert with other suppliers.

### A. High-Efficiency Detergents

In 1996 Frigidaire introduced a new extra large capacity, low-energy front loader clothes washing machine. The new machines, often referred to as horizontal axis washers, use considerably less water than comparable top loaders, and have performance features much like their European counterparts. The variation in mechanical agitation and fabric-to-water ratio necessitated the reformulation of the surfactant package to limit suds generation and prevent soil redeposition. Wisk HE and Tide HE were launched specifically to accommodate these new machines. Although these machines have been commercially available for close to eight years, the relatively high cost associated with front loaders has resulted in considerably less sales than anticipated, and the range of detergents manufactured for these types of machines remains limited.

### B. Line Extensions

An inherent weakness concerning liquid detergents is the inability to stabilize cost effectively an active oxygen bleach species in the liquid detergent matrix. Nearly every major detergent manufacturer has launched a line extension of its formulation with a *bleach alternative* variant. The consumer receives a product

with an improved cleaning and whiteness profile through the incorporation of an advanced enzyme/optical brightener package. All Free Clear, an enzyme-, dye-, and fragrance-free version of All, is a second example of targeting a niche market successfully without overhauling the existing formulation. Unilever was able to design an enzyme-linked immunosorbent assay to prove that All Free Clear effectively rids fabrics of dust mite matter, an allergen commonly found in the home. Procter & Gamble was able to leverage their cyclodextrin technology (first employed as a fragrance delivery vehicle) in their Febreze for the Wash laundry additive. Cyclodextrins are ring structures that are comprised of six, seven, or eight glucose monomers that can entrap small molecules [197]. Unwanted odors can be effectively removed from carpets and various textiles as opposed to masking the odor with perfumes that gradually lose their fragrance over time. (Henkel has recently introduced Fresh Magic, claimed to be the first detergent to neutralize unpleasant odors in synthetic garments as they are worn by the individual. The active ingredient, Neutralin, is a proprietary combination of a malodor absorber and a unique fragrance designed to deliver odor elimination and a long-lasting smell.)

### C. Color/Fabric Care

Several of the formulation improvements over the past few years have strong roots in research and development. ISP introduced a new dye transfer inhibiting polymer (Chromabond S-100) based upon poly(4-vinylpyridinium betaine) in a European color-safe detergent. This next generation dye transfer inhibitor is less likely than PVP, the industry standard, to interact with other ingredients (linear alkylbenzene sulfonate) in the detergent formulation. Procter & Gamble strengthened its claim as the market leader by releasing Tide Clean Rinse, a formulation designed to deliver enhanced cleaning, better stain removal, and brighter clothes. The product utilizes an alkoxyated polyalkyleneimine polymer to prevent soil from redepositing [206] onto fabrics and a proprietary mannanase enzyme designed to remove carbohydrates that physically attract/retain other soils. Procter & Gamble also introduced a novel, hydrophobically modified cellulosic material ("Liquifiber") into its Cheer liquid detergent with Colorguard. The product contains multiple ingredients to help protect and maintain the original color of garments [183–185]. The cellulosic polymer binds to the fabric and helps prevent cotton fibrils from breaking loose during mechanical agitation. This reduction in fabric abrasion prevents garments from prematurely looking worn after multiple wash cycles. Cheer with Colorguard also utilizes a peroxide to scavenge chlorine, a cationic polymer based upon imidazole and epichlorohydrin to fix dyes in place, and the vinylimidazole derivative of PVP to inhibit dye transfer from fugitive dyes in the wash bath. Henkel now markets a product called Black Magic that contains a dye fixative that keeps black clothes black longer by preventing color fading.

## **D. Wrinkling Reduction/Ease of Ironing**

Most consumers dread the idea of ironing their clothes after laundering. Unilever launched Wisk with Wrinkle Reducer in 2000 in an effort to reduce or eliminate the need for ironing, but product acceptance was not overwhelming. Procter & Gamble markets Downy Wrinkle Releaser as an auxiliary product that sprays directly onto garments. Although some benefits are realized on select fabrics, the premise of no ironing has not been achieved. (In Europe Procter & Gamble is marketing Bold Easy Iron with fabric softener. The product utilizes a combination of softening technologies and the hydrophobically modified cellulosic (Liquifiber) technology to reduce wrinkling concerns.)

## **E. Unitized Dose Products**

In the past three to four years alternative product forms have taken center stage. The reintroduction of detergent tablets has met with great success in Europe (in particular, the automatic dishwashing category), but has generated little interest in the U.S. Liquid-containing unitized dose sachets are successfully marketed in the U.S. automatic dishwashing category (Electrasol gelpacs and Cascade 2-in-1 action pacs, a powder encased in a liquid over wrap), but the market has not evolved to liquid-filled sachets for laundry. In Europe Persil Liquits (Henkel) is a water-free liquid detergent packaged in a polyvinyl alcohol wrap. The polyvinyl alcohol sachet is water soluble and dissolves in the wash bath within a few minutes, leaving no residue on clothing. The unitized dose concept has not met with overwhelming interest among consumers in the laundry area, so predicting its acceptance in the U.S. is anything but simple.

## **VII. FUTURE TRENDS**

During 2003 and 2004 the price of oil and natural gas increased dramatically. This in turn has resulted in significant increases in detergent raw material costs, and considerable emphasis has been placed on controlling product spend. With the prospect of higher prices persisting for the next few years, where will the detergent manufacturers focus their research efforts? Will the consumer be content with the status quo, or continue to demand additional benefits without incurring added costs?

### **A. Detergent/Fabric Softener Combinations: Return of the Two-in-Ones**

One concept that appears to be of interest is the formulation of “two-in-one” or softergent liquids. This idea has seen its popularity rise and fall over the past two decades. The prospect of delivering fabric softening in a liquid detergent has often met with consumer pessimism. Most liquid detergent/fabric softener

combinations are based upon cationic surfactants (to provide fabric softening and antistatic properties). In the past these products often had associated negatives with respect to primary detergency (removal of clay/particulate soils) and problems with clay soil redeposition during the wash cycle, leading to poor whiteness maintenance of cotton garments. In addition, the (ion pair) complex formed between the anionic and cationic surfactants resulted in less than desirable softening properties. In August 2004 Procter & Gamble introduced Tide with a Touch of Downy, a “pseudo” two-in-one composition. This product is not targeted as a replacement for rinse-added fabric softeners (as was the case with earlier attempts), but is being launched as a line extension to the current Tide formulation. The consumer gets a minimal enhancement of softening/antistatic properties, and the high level of cleaning performance anticipated from the market leader is maintained without any noticeable downsides in detergent efficacy. Unilever recently filed a U.S. patent application with its own version of a two-in-one formulation based upon a very high-molecular-weight cationic homo/copolymer as the active softening agent [227]. These cationic polymers have been used extensively in personal care applications (hair and skin), and have a high affinity for negatively charged surfaces (like cotton). It will be interesting to watch how this market evolves over the next 6 to 12 months from a technical and consumer perspective.

## **B. Suspension of Visual Cues**

One of the recent trends in personal care products is to deliver a “visual cue,” or stated in a more definitive way, a consumer-perceptible point of differentiation. For the most part, this has been accomplished by the introduction of a polymeric rheology modifier (organic gums, cellulose, hydrophobically modified alkali-soluble emulsions (HASE), polyacrylates, or carbomers) and/or an inorganic (clay) to clear, gel formulations to establish a yield point. These thixotropic, highly pseudoplastic systems allow the suspension of various “actives” which are visible to the consumer. The list of actives can encompass substances ranging from air particles to insoluble builders to moisturizing beads to stabilized (micro)emulsions. This concept could be a way to promote a unique advantage offered by a cleaning product, even if the visual cue is actually inert in reality. The majority of liquid detergents sold in the U.S. are currently homogeneous, clear, single-phase products, so adapting this technology to a HDLD, although not trivial, is potentially viable.

## **C. Fabric/Color Care**

Fabric and color care are areas that have received considerable emphasis over the past decade. The introduction of hydrophobically modified cellulose (Liquifiber), multiple variants based upon derivatives of PVP technology for dye transfer inhibition, and a wealth of recent patent applications on polymeric additives to improve

fabric appearance (looking newer longer, reduced pilling, fuzz reduction) will set the tone for the next round of product improvements.

## **D. Ultraviolet Protection**

Another area that has received considerable attention, although mainly outside of the U.S. and Europe, is ultraviolet light protection for garments (and skin). Ciba Specialties has marketed ultraviolet absorbing products under the Tinosorb tradename that boost the sun protection factor (SPF) of a typical cotton T-shirt from a value of 5 to 8 to at least 15 after 5 wash cycles. Although this technology has not been embraced in the more temperate regions of the world, climate changes and the impact of global warming will make these materials more popular, with rinse-added fabric softeners the likely delivery vehicle.

## **E. Enhanced Detergency: Several Potential Approaches**

Improvements in detergent efficacy will continue to capture the undivided attention of detergent manufacturers. There are multiple approaches that encompass a wide variety of current and novel technologies. Examples of these types of approaches range from unique combinations of enzymes (pectate, lyase, and mannanase) to facilitate the removal of food soil residues, to ethoxylated quaternized amines to improve soil suspension and cleaning of outdoor soils/stains, to nanoparticle technologies to deliver crease resistance properties in tumble dry additives and aqueous ironing formulations [180].

As discussed in Section V, detergent manufacturers have begun utilizing cellulose binding domains to enhance the deposition of actives onto fabric surfaces. Will this open a unique window into alternate biotechnology advances/ approaches? Can the emergence of water-soluble silicate builders (e.g., SKS-6) as replacements for zeolites (in Europe) translate to liquid detergent formulations? HDLDs have been formulated with zeolite 4A as the builder of choice, but hard packing and viscosity build upon aging have made these products very difficult to formulate successfully, and these liquids have not gained consumer acceptance. Despite the wealth of patent activity on soil release polymers for cotton, will these technologies become commercially viable (from a performance and cost/use standpoint)? Can encapsulation technologies be expanded beyond fragrances/odor protection to include actives such as bleaches?

## **F. New and Developing Markets**

Most of the emphasis in this section has focused on the expanding boundaries of patent art and technology, and ascertaining its impact on future (liquid) detergent compositions. The laundry detergent markets in the U.S., Europe, and Japan

are well established, so where will the next influx of new products occur? The answer will probably be in emerging countries, where consumers will gradually upgrade from generic, low-cost domestic products to more high-tech offerings. Although liquids will not be the principal product form utilized by the consumer, limitations on phosphate levels (environmental pressures) and the implementation of alternative, poorer performing builders may lead the market back toward liquids. Eastern Europe (Poland, Hungary, the Czech Republic, and Slovakia), China, India, and parts of Latin America (Mexico, Brazil) will likely spur rapid growth and new product entries, further diversifying the variety and compositions marketed globally.

## APPENDIX

**TABLE A** Recent HDLD Patents (1994–2004) Related to Fabric Care

Patent no.	Issue date	Inventor/company	Technology
U.S. 2004/0038851	02/2004	Aubay <i>et al.</i>	Deliver crease resistance/ease of ironing properties to fabrics by a treatment comprising nanoparticles
U.S. 6696405	02/2004	Mooney/Unilever	Improved crease recovery of fabrics utilizing C20–C40 saturated or unsaturated aliphatic hydrocarbons. For use in fabric conditioning formulations used in the dryer cycle (sheets, liquids for rinse-added fabric softeners)
U.S. 2002/0016276	02/2002	Spendel/Procter & Gamble	Yarn strength-enhancing agents suitable for laundry and/or fabric care compositions. The additives that improve yarn strength can include polysaccharides, clays, starches, chitosans, and mixtures thereof
U.S. 5336419	08/1994	Coffindaffer <i>et al.</i> / Procter & Gamble	Silicone gel for ease of ironing and improved fabric after treatment

(continued)

**TABLE A** (Contd.)

Patent no.	Issue date	Inventor/company	Technology
U.S. 2004/0121930	06/2004	Wang <i>et al.</i> / Procter & Gamble	Cationic celluloses for enhanced delivery of fabric care benefits (softening, color protection, pill/fuzz reduction, antiabrasion, antiwrinkle). One water-insoluble fabric care benefit agent in combination with at least one delivery-enhancing agent (dispersible polyolefins and latexes)
WO 2003/027219	04/2003	Cooke <i>et al.</i> / Unilever	Polymeric material comprising one or more poly(oxyalkylene) amine groups and an epihalohydrin-derived terminal group that acts as a lubricant to reduce fabric abrasion during the tumble dryer/wash cycle, decreasing fabric wear and color loss on collars and cuffs
GB 2360792	04/2003	Hopkinson <i>et al.</i> / Unilever	Fiber rebuild polymers (cellulosics/polysaccharides with pendant ester groups) that impart unique properties to the fabric. These properties include replacing lost fiber weight (on cellulose), repair/rebuild fiber strength, enhance fabric body/smoothness, reduce fading, improve appearance and fabric comfort, control dye transfer, and can increase fiber stiffness, deliver antiwrinkling benefits, and ease of ironing properties. The polymers undergo a chemical change in the wash bath (hydrolysis of ester groups) that enhances their affinity for the fabric surface

(continued)

**TABLE A** (Contd.)

Patent no.	Issue date	Inventor/company	Technology
WO 98/29530	07/1998	Randall <i>et al.</i> / Procter & Gamble	Laundry detergent compositions containing fiber reactive additives (polyamide–polyamines) to improve fabric appearance and integrity
WO 97/42287	06/1994	Pramod <i>et al.</i> / Procter & Gamble	Laundry detergent compositions containing fiber reactive additives (modified polyamines) to improve fabric appearance and integrity
WO 99/14245	03/1999	Leupin <i>et al.</i> / Procter & Gamble	Laundry detergent compositions containing cellulosic-based polymers to improve fabric appearance and integrity Laundering of fabric/textiles with the additive leads to overall improvements in fabric appearance, pill/fuzz reduction, antifading properties, improved abrasion resistance, and enhanced softening
U.S. 5571286	11/1996	Connell <i>et al.</i> / Precision Process Ltd	Polymers and prepolymers derived from polyoxyalkylene amines and their use in a process for shrinkproofing wool

**TABLE B** Recent Patents (1993–2004) on HDLDs with Enzymes

Patent no.	Issue date	Inventor/company	Technology
U.S. 2003/ 0022807	01/2003	Wilting <i>et al.</i> / Novozymes North America, Inc.	Removing or bleaching soils/stains derived from xyloglucan-containing food or plants, select binding of soils on cellulosic fabrics
U.S. 6015783	01/2000	Von der Osten <i>et al.</i> / Novo Nordisk A/S	Removal or bleaching of soils/stains from cellulose with an enzyme hybrid comprised of a catalytically activated amino acid sequence from a noncellulytic enzyme

(continued)



TABLE B (Contd.)

Patent no.	Issue date	Inventor/company	Technology
			linked to an amino acid comprising a cellulose binding domain. The enzyme hybrid in combination with a surfactant in a detergent formulation
WO 99/32594	07/1999	Duval <i>et al.</i> / Procter & Gamble	Cleaning compositions containing a neopullulanase for improved stain removal, enhanced overall cleaning, and sanitization of treated surface
WO 98/13457	04/1998	Ohtani <i>et al.</i> / Procter & Gamble	Cleaning compositions containing a mycodextranase for improved stain removal, enhanced overall cleaning, and sanitization of treated surface
EP 0603931	07/1993	Pramod/Procter & Gamble	Liquid laundry detergents containing stabilized glucose/ glucose oxidase as a hydrogen peroxide generation system
U.S. 6734155	05/2004	Herbots <i>et al.</i> / Procter & Gamble	Cleaning compositions containing an oxidoreductase to facilitate the removal of colored and/or everyday body stains/soils
U.S. 6114509	09/2000	Olsen <i>et al.</i> / Novo Nordisk A/S	Modified polypeptides with reduced allergenicity
WO 00/18897, EP 1119613, EP 1117770	04/2000	Smets <i>et al.</i> / Procter & Gamble	Detergent compositions containing a chemical component linked to a cellulose binding domain. These materials deliver a higher effective concentration of the active to the fabric surface
U.S. 5981718	11/1999	Nielsen <i>et al.</i> / Novo Nordisk A/S	4-Substituted phenyl boronic acids as enzyme stabilizers
U.S. 5834415	11/1998	Nielsen <i>et al.</i> / Novo Nordisk A/S	Naphthalene boronic acids

**TABLE C** Recent Patents (1996–2004) on HDLDs with Polymers

Patent no.	Issue date	Inventor/company	Technology
U.S. 6372708	04/2002,	Kasturi <i>et al.</i> / Sivik <i>et al.</i> / Procter & Gamble	Polymeric additives (possessing a cationic charge) that deliver enhanced suds duration and suds volume
U.S. 6645925	11/2003		
U.S. 5854197	12/1998	Duccini <i>et al.</i> / Rohm and Haas	Cleaning compositions containing a lime soap dispersant (maleic/hydrophobe) that delivers improved whiteness maintenance in liquid detergents built with modest levels of fatty acid soaps
U.S. 6451756	09/2002	Shulman <i>et al.</i> / Rohm and Haas	Hydrophobically modified polycarboxylates that deliver soil release benefits on cotton and cotton-containing blends. These polymers are effective on oil/greasy soils through the wash or during the rinse cycle
U.S. 6291415	09/2001	Gosselink <i>et al.</i> / Procter & Gamble	Cotton soil release polymers from modified polyamines having functionalized backbones and improved stability to bleach. Laundry detergent compositions comprising these polymers possessing enhanced hydrophilic soil removal benefits
U.S. 6191093	10/2001		
U.S. 6087316	07/2000		
U.S. 6071871	06/2000		
U.S. 6057278	05/2000		
EP 1402877	03/2004	Tepe/Rohm and Haas	Composition containing at least one lipophilically modified copolymer (acrylic residues) and a colloidal inorganic clay. Thickener for high surfactant concentrations (>18%)

(continued)

TABLE C (Contd.)

Patent no.	Issue date	Inventor/company	Technology
U.S. 5565145	10/1996	Watson <i>et al.</i> / Procter & Gamble	Cleaning and soil dispersing compositions comprising ethoxylated/propoxylated polyalkyleneamine polymers
U.S. 6369018	04/2002	Hsu <i>et al.</i> / Unilever	Easy pouring (high shear thinning), transparent liquid capable of suspending particles in the presence of high levels of surfactant and electrolyte. Polymer gum solution selected from carrageenans, gellans, and agars
U.S. 2003/0186832	10/2003	Padron <i>et al.</i> / Unilever/Procter & Gamble	Isotropic liquid detergents containing a soil release polymer and an antiredeposition enhancer (PVP, PVPNO) delivering a synergistic improvement in soil antiredeposition
U.S. 6664223	12/2003	Zappone <i>et al.</i> / Colgate- Palmolive	Fabric treatment composition that contains a polyfunctional molecule, such as derived from polyacrylic acid, in combination with a urea-derived compound. During pressing or ironing of the fabric, the urea-derived compound is said to crosslink the polyfunctional molecule and thereby provide crease resistance to the fabric

**TABLE D** Recent Patents (1998–2003) on HDLDs with Optical Brighteners/Antioxidants/Fabric Protection

Patent no.	Issue date	Inventor/company	Technology
U.S. 6482241	11/2002	Metzger <i>et al.</i> /Ciba Specialty Chemicals	Method of improving the sun protection factor (SPF) of textile fabrics (cotton, polyamide, wool) using asymmetric stilbene derivatives
U.S. 5854200	12/1998	Severns <i>et al.</i> /Procter & Gamble	Rinse-added fabric softeners containing antioxidants for sun fade protection of fabrics. Nonfabric-staining, light-stable antioxidant compounds comprising C8–C22 hydrocarbon fatty organic moieties
U.S. 6015504	01/2000	Reinehr <i>et al.</i> /Ciba Specialty Chemicals	New compounds (triazinyl diaminostilbenes) that are useful as ultraviolet absorbing agents and increase the SPF of textile fibers
U.S. 6613340	09/2003	Koshti <i>et al.</i> /Galaxy Surfactants	Substantive hydrophobic cationic UV absorbing compounds

**TABLE E** Recent Patents (1995–2004) on HDLDs with Dye Transfer Inhibition

Patent no.	Issue date	Inventor/company	Technology
U.S. 5855621	01/1999	Damhus <i>et al.</i> /NovoNordisk A/S	Reduce DTI through the addition of a peroxidase/oxidase during the wash/rinse cycle
WO 99/15614	04/1999	Shih <i>et al.</i> /ISP Investments	Poly(vinylpyridine betaines)
WO 97/42291	11/1997	Panandiker <i>et al.</i> /Procter & Gamble	Modified polyamines
U.S. 5880081	03/1999	Gopalkrishnan <i>et al.</i> /BASF	Hydrophilic copolymer (unsaturated “philic” copolymer with an oxyalkylated monomer)

(continued)

**TABLE E** (Contd.)

Patent no.	Issue date	Inventor/company	Technology
U.S. 2004/0038852	02/2004	Brown <i>et al.</i> / Procter & Gamble	Chlorine scavenger in concert with a polymeric DTI and less than 0.02% of a triazinylaminostilbene optical brightener
U.S. 6733538	05/2004	Panandiker <i>et al.</i> / Procter & Gamble	Dye maintenance polymer comprising one or more linearly polymerizing monomers, cyclically polymerizing monomers and mixtures thereof
U.S. 5466802, WO 95/27038	11/1995	Panandiker <i>et al.</i> / Procter & Gamble	PVPNO and PVP-VI
EP 664335	07/1995	Abdennaceur <i>et al.</i> / Procter & Gamble	Polysulfoxide polymers

**TABLE F** Recent HDLD Patents (1997–2003) Related to Surfactants

Patent no.	Issue date	Inventor/company	Technology
WO 97/39089	10/1997	Connor <i>et al.</i> /Procter & Gamble	Liquid cleaning compositions containing selected mid-chain branched surfactants and cosurfactants. These surfactants deliver enhanced cleaning in cold water and in the presence of hard water
WO 01/90293	11/2001	Libe <i>et al.</i> /Huish Detergents	Compositions containing $\alpha$ -sulfofatty acid ester surfactants and hydrotropes and method of manufacture
U.S. 6596680	07/2003	Kott <i>et al.</i> /Procter & Gamble	Specific alkylbenzene surfactant mixtures to improve detergency

**TABLE G** Recent HDLD Patents (2001–2004) on Perfume Adjuvants

Patent no.	Issue date	Inventor/company	Technology
U.S. 6184188	02/2001	Severns <i>et al.</i> / Procter & Gamble	Fragrance delivery system for liquid detergent compositions comprising a $\beta$ -ketoester
U.S. 2004/0018955	01/2004	Wevers <i>et al.</i> / Procter & Gamble	Pro-perfume composition comprising an amino functional component and a benefit agent that is stably suspended in a liquid detergent. Provides enhanced deposition and a long-lasting release on the treated fabric
WO 02/077150	10/2002	Pashkovski <i>et al.</i> / Colgate- Palmolive	Fragrance-containing gel delivering enhanced deposition and retention of said fragrance (from structured liquids)
EP 1146057	10/2001	Quellet <i>et al.</i> / Givaudan	Polymeric nanoparticles that incorporate olfactive components into an emulsion polymer and act as an efficient delivery system for these fragrances. Perfume is gradually released over a period of time, preventing “top notes” from volatilizing too quickly
WO 03/049666	06/2003	Fehr <i>et al.</i> / Firmenich	Compounds comprising one $\beta$ -oxy or $\beta$ -thio carbonyl moiety capable of liberating a perfume molecule ( $\alpha,\beta$ -unsaturated ketone, aldehyde, or carboxylic ester)
WO 01/23516	04/2001	Foley <i>et al.</i> / Procter & Gamble	Compositions that are particularly effective at masking malodors or odor suppression. Complexing agents (cyclodextrins) that have an internal cavity, forming complexes that incorporate the malodor
WO 2003015736	02/2003	Ness <i>et al.</i> /Quest International	Aqueous fabric care composition comprises surfactant, silicone insoluble in water, and perfume having a solubility parameter (SP) not exceeding about 20. By using a perfume with a low SP value, the invention enables good partitioning of perfume into the silicone of the composition, which means that the perfume will be associated with the silicone and deposited onto fabric in use

**TABLE H** Recent Patents (2000–2004) on Unit Dosed HDLDs

Patent no.	Issue date	Inventor/company	Technology
WO 02/097026	12/2002	Fregonese/Reckitt Benckiser	Liquid detergent compositions encapsulated in a polymer (especially compositions that contain ingredients capable of crosslinking a water-soluble polymer)
U.S. 6448212	07/2000	Holderbaum <i>et al.</i> /Henkel KgaA	Laundry detergent portion for use in a washing/dishwashing machine for a program taking place in an aqueous phase
WO 02/16541	02/2002	Kaiser <i>et al.</i> /Reckitt Benckiser	Aqueous liquid detergent packaged in a water-soluble or water-dispersing package having an improved stability. Composition contains 20–50% water, at least one polyphosphate, and potassium and/or sodium ions
EP 1378564	01/2004	Bonastre <i>et al.</i> /Cognis Iberia	Laundry detergent portion
EP 1319706	06/2003	Ramcharen <i>et al.</i> /Unilever	Dispersed solid in a liquid detergent in a water-soluble pouch

**TABLE I** Recent Patents (1993–2004) Related to Builders

Patent no.	Issue date	Inventor/company	Technology
U.S. 5704556	01/1998	McLaughlin/DevMar	Process for rapidly producing finely divided aluminosilicate particles by media grinding techniques
U.S. 6699831	03/2004	Takano <i>et al.</i> /Kao Corporation	Liquid detergent composition comprising an aluminosilicate or crystalline silicate
U.S. 5252244	10/1993	Beaujean <i>et al.</i> /Henkel KgaA	Aqueous zeolite-containing liquid detergent stabilized with an electrolyte mixture

**TABLE J** Recent HDLD Patents (1995–2004) with Nonaqueous Liquids

Patent no.	Issue date	Inventor/company	Technology
U.S. 2003/0100468	05/2003	Smerznak <i>et al.</i> / Procter & Gamble	Nonaqueous particulate-containing liquid laundry detergents comprising a peroxygen bleaching agent and an organic detergent builder
U.S. 6770615	08/2004	Aouad <i>et al.</i> /Procter & Gamble	Nonaqueous liquid laundry detergent compositions with a suspended solid particulate phase comprised of low-density particles (binding agent, alkalinity source, a chelant, and builder or mixtures thereof). Ingredients that are insoluble in the surfactant-rich phase can be incorporated into the liquid phase without segregation or separation
U.S. 5441661	08/1995	Beaujean <i>et al.</i> / Henkel KgaA	Nonaqueous liquid detergent containing a hydrated zeolite stabilized by a polar deactivating agent

**TABLE K** Recent Patents (2004) with Fabric Softeners

Patent no.	Issue date	Inventor/company	Technology
U.S. 2004/0152617	08/2004	Murphy <i>et al.</i> / Unilever	Cationic polymers and anionic surfactants that provide optimal cleaning and fabric softening properties. High-molecular-weight cationic polymers are used in place of conventional quats (cationic surfactants) to provide the softening benefit on cotton cloth



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