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Liquid Automatic Dishwasher Detergents

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I. INTRODUCTION

The concept of using mechanical devices for dishwashing was documented as early as 1865 with the issuance of a U.S. Patent to J. Houghton [1]. Subsequently several companies tried to manufacture and market automatic dishwashing machines for home as well as for institutional use [2,3]. However, it was not until the early 1950s that both detergents and mechanical dishwashers became widely available to consumers. By the early 1990s, an estimated 50% of the households in the U.S., 25% in Europe, and 8% in Japan had automatic dishwashers [4].

The focus of this chapter is on the U.S. market, as this is still the major market for liquid automatic dishwasher detergents (ADDs). However, we will touch briefly on the global situation that prevailed in the late 1990s. During that period, the global dishwashing market was divided between hand dishwashing and automatic machine dishwashing. The split was about 70% for hand dishwashing, and 30% for machine dishwashing. About 90% of ADD sales worldwide were concentrated in five countries: the U.S., France, Germany, the U.K., and Italy. The greatest incidence of households with dishwashing machines was in the U.S., with more than 50%, followed by France with more than 30%. In Europe the predominant form of ADD was unit dose, followed by powder, then liquid. In contrast, in the U.S. powder dominated at about 60%, followed by liquid at about 30%, and unit dose at about 10%. By 2004, the market in the U.S. had begun to shift more toward unit dose, although liquids continued to rise. The form distribution was about 40% powder, 40% liquid, and 20% unit dose.

The ADDs originally introduced into the U.S. market were in the powder form. These products have subsequently undergone major changes in composition to deliver better cleaning performance. Typical compositions of powder ADDs sold in the U.S. and Europe are shown in [Table 9.1](#).

Attempts have been made to produce and market phosphate-free detergents with minimal success. Two proposed compositions, which might also be suitable for tablet making, are shown in [Table 9.2](#).

In North America enzyme-based powder formulas have come to dominate the powder market.

Today, powders no longer dominate the U.S. market. While ten years ago they commanded nearly 70% of the market share [6], today they represent only about

TABLE 9.1 Conventional Machine Dishwashing Powder Formulation [4]

Ingredient	% by weight
Sodium tripolyphosphate (STPP)	15–45
Sodium silicate	15–60
Sodium carbonate	0–25
Chlorocyanurates	0–7
Nonionic surfactant	0–6
Sodium sulfate	0–40
Water	Balance

TABLE 9.2 Nonphosphate Machine Dishwashing Formulation [5]

Ingredient	Composition 1 (wt %)	Composition 2 (wt %)
Na citrate 2 H ₂ O	35	35
Na disilicate (granular)	30	30
Na perborate 1 H ₂ O	10	10
TAED ^a	3	3
Acrylic-salt D	10	0
Acrylic-salt G	0	10
Na carbonate	10	10

^aTetraacetylene diamine.

40% of the U.S. market. About 20 years ago the marketplace saw the advent of liquid automatic dishwasher detergents (LADDs). Clarification of what constitutes a “liquid” is worth mentioning here. Commercially, the products are marketed under different names such as: liquids, liquigels, liquid gels, or gels. Technically, these products are concentrated suspensions. The liquid matrix predominantly comprises an aqueous phase and thickening or structuring agents. The latter are typically either swellable clays or water-dispersible polymers and optionally a cothickener. The mechanical properties of these products are such that the product can be dispensed from the container without prior shaking.

ADDs in the liquid form offer the following advantages over powders:

1. They offer convenience in dispensing and dosing.
2. They dissolve quickly in the wash water, providing a residue-free wash.
3. They are free from lumping or caking during storage.
4. They do not release irritating dust upon handling.

The market entry of first-generation automatic dishwasher liquids dates back to 1986 in the U.S. and 1987 in Europe with the introduction of Palmolive Automatic and Galaxy, respectively, by Colgate-Palmolive [7]. Soon afterwards, Procter & Gamble and Lever Brothers introduced similar liquid products. The category has since been steadily growing. Today LADDs account for about 40% and 15% of total sales of the automatic dishwasher detergent market in the U.S. and Europe, respectively [8].

There has been an evolution of LADD technology over the years. This consists of clay hypochlorite bleach form, gel hypochlorite bleach form, and enzyme no bleach form. The first-generation LADDs were essentially powder compositions in the liquid form, in which functional components were suspended or dispersed in a structured liquid matrix. The liquid matrix consisted of water and the common structuring additives used were bipolar clays and a cothickener comprising a metal salt of a fatty acid or hydroxy fatty acid. These liquid products, although minimizing some of the shortcomings of the powders, suffered from two major disadvantages. First, the rheological properties of these products were such that the bottle needed to be shaken prior to dispensing of the product. This was due to phase separation and the production of "free" bleach solution. Second, the shelf life stability of the products did not meet consumer expectations. This problem was shortly recognized by the manufacturers and aesthetically superior, nonshake, stable, and translucent products were introduced to the market in 1991 as "gels." All the liquid products marketed today in U.S. are essentially in gel form using polymeric thickeners.

A new form of ADD (Electrasol), as a tablet, appeared in the U.S. in 1997. This was the first tablet for use in dishwashing machines. It was a pressed powder. It contained a disintegrant to help the tablet break apart and dissolve in the wash water. This form was based on both enzyme/oxygen bleach technology as well as chlorine bleach technology. In 2002 the next generation of unit dose products appeared (Electrasol). This was a "gel pac" that was based on enzyme technology. It consisted of a gel suspension in a water-soluble sachet. This was soon followed by a dual-compartment, water-soluble sachet. One compartment contained a typical enzyme/oxygen bleach cleaning system, while the second contained a liquid. The liquid was typically a nonionic or solvent system that contributed to cleaning and acted as a humectant to control moisture in the powder compartment.

By 2004, the ADD market was segmented in three forms: powder, gel, and unit dose. Approximate market share for these forms in the U.S. was 40, 40, and 20% respectively. While liquid gel systems continued to grow, they were challenged by the unit dose segment that consisted of solid, liquid, or hybrid products.

The discussion of this chapter focuses on the technology behind the development of currently marketed LADDs in either gel or unit dose form. Powder ADDs, which in most areas utilize analogous technology, will not be discussed except for comparison.

II. MECHANICS AND CHEMISTRY OF AUTOMATIC DISHWASHING

Cleaning in an automatic dishwasher is accomplished by a combination of three types of energy: mechanical, thermal, and chemical. In general, a combination of machine (mechanical), hot water (thermal), and detergent (chemical) is necessary for complete cleaning of dishware. Before these effects are discussed in more detail, the basic components and mechanics of an automatic dishwasher are described.

A. Components of Automatic Dishwashing Machines

Concurrent with the evolution and advancement in dishwasher detergents, automatic dishwashers have been improving over time in order to offer the consumer greater convenience and performance. European machines are similar to North American machines except for some minor but important differences. These differences allow for the use of different detergent technologies in the two markets. In recent years the machine technologies as well as the chemical technologies of Europe and North America have become closer and may merge. It is more cost effective for manufactures to offer machines with common components.

Ten years ago the European market was dominated by machines that heated the water and had stainless steel interiors. The North American market was dominated by machines that received hot water from the house plumbing, did not heat the water, and had plastic interiors. Today, high- and middle-tier North American machines are sensor controlled (water temperature and wash time) and come in stainless steel options ([Figure 9.1](#)).

Automatic dishwashing machines typically contain two racks that hold the items to be washed. All machines contain at least one spray arm, which spins due to the pressurized wash solution being pumped through the arm nozzles. This allows for an even distribution of the wash liquor over all the items being washed. The main spray arm is located underneath the bottom rack and directs the water pumped through it upwards. In some machines, a second and even a third spray arm are located below and above the top rack, respectively. Water can be delivered to the spray arms either through a “tower” which extends during the wash cycle, or through a “pipe” that runs along the back of the machine to deliver water to the upper spray arms. This is typical of a three-spray-arm machine. The wash liquor is recycled throughout the complete cycle by means of a pump which continually circulates it through the spray arms. A strainer in the wash tank removes large soil particles throughout the recirculation process. For each program cycle (wash or rinse) a new water supply is introduced. The amount of water introduced is a function of machine type and wash setting. As machines have become more energy and environmental friendly, less water is used. The cost to operate the machine is also lower.



FIG. 9.1 Stainless steel inside of an automatic dishwashing machine. (Courtesy of the General Electric Co.)

Machines generally contain two detergent dispensing cups, one of which has a lid and is therefore closed through part of the machine cycle. Newer machines have the “open” and “closed” cups side by side with one gasketed cover. The part of the cover that is over the open cup has vents to allow the dish liquid to be washed into the prewash cycle. As machines have become “smarter” the size of the second or prewash cup seems to be shrinking. With the new unit dose technologies, it may disappear altogether. A significant difference between American and European machines used to be that the latter contained a gasketed closed cup. This prevents the detergent from prematurely leaking out of the cup. The detergent is formulated as a viscous gel which will not flow unless stressed. As American machines evolve toward a more common structure with their European counterparts, this difference will probably disappear.

All European machines, and some American ones, also contain a rinse aid dispenser, which provides a dose of rinse aid during the final cycle. These dispensers only have to be filled about once a month. Rinse aids are especially useful in hard water areas (see [Section VII](#)).

A typical dishwashing program consists of several cycles of differing function. The number of each type of cycle and their order depends on the brand of

machine and the wash program selected. Today's machines offer a wide selection of washing programs. The simpler machines may offer a few programs, such as heavy wash, normal wash, short wash, rinse only, plate warmer, and hot start. More elaborate machines offer a greater number of programs, such as antibacteria, cookware (pots and pans), normal wash, speed cycle, china crystal, glasses, plastics cycle, and rinse only. Additionally, options such as heated dry (on/off) delay hours, added heat (wash), prewash, control lock, and reset may be available. All washing programs consist of at least a rinse, a main wash, one rinse after the main wash, and a drying cycle, which is optionally heated. The rinse cycles are mechanically similar to the wash cycles, except that no detergent is present. In programs containing two wash cycles (heavy or pot-scrubber cycle), both dispensing cups are filled with detergent. If only a main wash cycle is to be used (normal or light cycle), only the closed cup is filled. In either case, it is essential that the detergent be structured so that it will not leak out of the closed cup before the cup opens. Otherwise, the main wash will be under dosed and will not result in effective cleaning. Proper structuring of gel detergents is discussed in Section IV.

The most important differences between European and North American machine designs are in the condition of the incoming wash water. As discussed later in this chapter, the presence of hardness ions (Ca^{2+} and Mg^{2+}) in the wash decreases the overall effectiveness of cleaning. This is a problem especially in hard water areas and can only be overcome by softening of the water. Water hardness varies by country. The United States and Japan have water that would generally be considered soft. Most European countries, in contrast, have water that is considered to be hard [9].

European machines circumvent the problem of hard water by softening the water before it is introduced into the wash. This is accomplished by a built-in ion exchanger which works by replacing the hardness ions with sodium ions. Regeneration of the ion exchanger with sodium chloride is required periodically. In contrast, North American machines contain no water softening device and must therefore rely on the detergent for sequestration of the hardness ions. The presoftening of the wash water by European machines allows for detergents to be formulated that contain lower builder levels.

Another difference between North American and European dishwashing programs concerns the temperature of the incoming water. In North America the wash water is preheated by the household water heater and is introduced into the machine at temperatures of 110 to 140°F, typically 120°F (49°C). Newer machines may then heat the water in the various wash and rinse cycles. In contrast, European machines receive cold water and heat it via machine heating coils during the wash and rinse cycles. The final temperature that the water reaches in this manner is therefore higher than American machines, reaching 115 to 170°F (46 to 77°C), depending on the program selected. Schematic profiles of water temperature vs. time for U.S. and European machines are shown in [Figure 9.2](#) and [Figure 9.3](#), respectively.

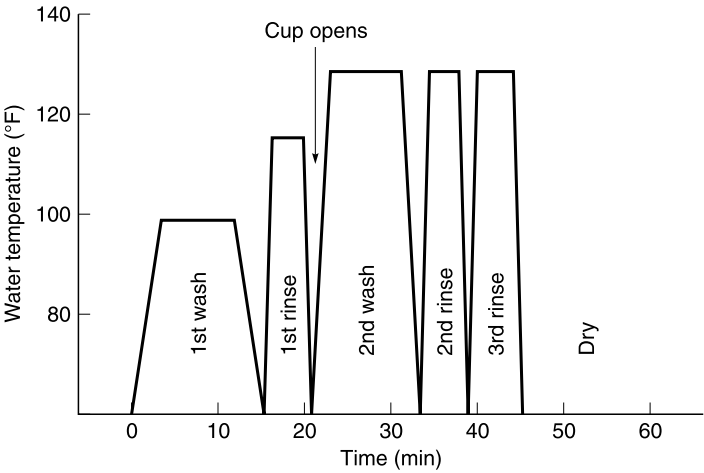


FIG. 9.2 Typical U.S. dishwashing cycle.

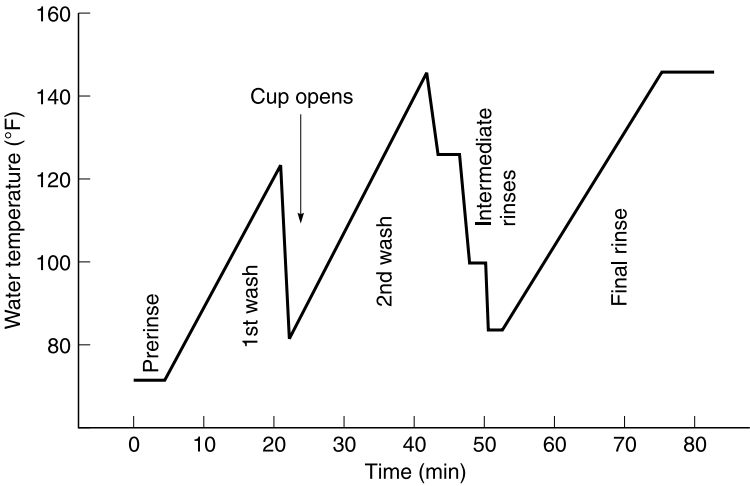


FIG. 9.3 Typical European dishwashing cycle.

B. Mechanical Cleaning

Probably the most important component of cleaning in automatic dishwashing is the mechanical component, which primarily arises from the kinetic energy of the water being pressurized through the rotating spray arm nozzles. As the wash water is pumped through the spray arms, the water jets sprayed from the rotor arms help to dislodge soils adhered to the dishware. Better machines with three spray arms and a more efficient water feed will naturally be more efficient. Therefore, an increase in kinetic energy, which can be accomplished by either more water or higher pressure, will result in more efficient removal of soils from substrates [10]. It has been suggested that mechanical energy of the machine itself is responsible for 85% of the soil removal during the cleaning cycle; the detergent contributes the other 15% [11]. Thermal energy is in a sense a secondary effect, contributing to the effectiveness of both the mechanical and chemical components of cleaning.

C. Thermal Cleaning

Most soil removal during an automatic dishwashing cycle is positively affected by thermal energy, which is delivered by hot water. In the past the wash water temperature was dictated by the incoming water temperature. Modern machines sense the wash water temperature and adjust it according to the program selected. In contrast, the wash temperature in European machines approaches 170°F (77°C). This is because the machine itself contains a heating element that heats the water.

Elevated temperatures have some advantageous effects on chemical processes involved in cleaning. For example, the solubility of slightly soluble salts increases with temperature. Otherwise, the deposition of such salts on glassware is the cause of much of the inorganic filming observed in hard water regions. Thermal energy also aids in the removal of fatty soils from items being washed. Above their melting points, fats are more easily removed since the interfacial forces binding them to the dishware and the cohesive forces of the soil are both lower. The activity of most oxidizing agents also increases with temperature. Conversely, higher temperatures can have a negative effect on fine china and crystal, causing etching. Some machines compensate for this by having a glass or crystal wash program.

D. Chemical Cleaning

A typical wash load consists of several types of soils which must be solubilized or degraded by a combination of the detergent and machine. Detergents must control both food soils introduced by the items washed and inorganic scale produced by hardness ions in the wash water. Food soils consisting of either proteinaceous, starchy, or fatty materials must not only be effectively removed from the dishware, but they must also be prevented from redepositing on items being washed.

The composition of soils on the washware surface may vary both before and during machine washing. Heat during cooking or machine washing may cause a redistribution of fats on the surfaces, for example. Redeposition on glasses is of particular importance as it leads to undesirable spotting and filming which is easily consumer perceivable. Soils that produce stains are also a problem in automatic dishwashing. For example, coffee, tea, wine, and tomato sauce leave highly visible stains on wash items unless properly treated during the wash.

Removal of food soils from wash surfaces can only be accomplished once the attractive forces between surface and soil are overcome. Generally, dehydrated soils interact more strongly with surfaces due to stronger van der Waals interactions between soil and surface [10]. In contrast, the soil-surface interaction decreases as the surface becomes more hydrophobic due to less available polar sites. Exceptions are hydrophobic soils such as fats, which interact strongly with hydrophobic surfaces [10].

III. COMPONENTS OF LIQUID AUTOMATIC DISHWASHER DETERGENTS AND THEIR FUNCTIONAL PROPERTIES

LADDs are chemically complex mixtures, consisting of a variety of components working in unison to clean the items placed in the dishwashing machine. Each component performs a vital function, either alone or in conjunction with others. LADD ingredients can be broadly classified into two categories: those that perform a cleaning function and those that modify the rheology or aesthetics of the liquid. In this section the typical components found in LADDs are discussed.

A typical LADD composition and the functions of the individual components are shown in [Table 9.3](#). Two examples of specific gel LADD formulas are shown in [Table 9.4](#) [12].

A. Builders

Builders as a class perform several essential functions in the automatic dishwashing process. Ideally, a builder should possess the following properties: a high and rapid sequestration capacity for hardness ions in the wash water, soil dispersing properties, chemical stability and compatibility with other detergent components, low toxicity, high biodegradability, and low cost. The chemical structures of some common builders are shown in [Figure 9.4](#).

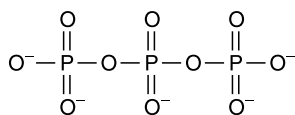
The presence of alkaline earth (Ca^{2+} and Mg^{2+}) ions during an automatic dishwashing cycle can lead to undesirable spotting and filming on items being washed. This occurs through the formation of insoluble metal complexes with proteinaceous soils, fatty acids, anionic surfactants, and carbonate. Research in

TABLE 9.3 Typical Compositions and Functions of LADD Products

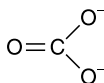
Component	Typical	Amount (%)	Function
Builder	Sodium tripolyphosphate (STPP)	5–30	Sequestration
	Low-molecular-weight acrylate		Soil suspension, alkalinity, emulsification
	Citrate		
	Silicate		Anticorrosion, alkalinity, sequestration
Surfactant	Dowfax		Spot/film prevention, sheeting action, soil dispersion
Bleach	Sodium hypochlorite	0.5–2	Stain removal, soil removal, disinfectant
Caustic	Perborate	1–5	Alkalinity
	NaOH		
	KOH		
Defoamer		0–1	Foam prevention
Thickener	Carbopol	0.5–2	Gel structure
	Polygel		
Enzymes	Protease	<1.0	Food removal
	Amylase	<1.0	
Color/fragrance		<0.5	Aesthetics
Water		Balance	Solubilizer, flow properties

TABLE 9.4 Examples of Gel LADD Formulas [12]

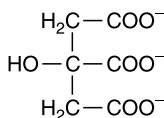
Ingredient	Formula A (%)	Formula B (%)
Sodium tripolyphosphate	6	6
Sodium disilicate	12	12
Potassium hydroxide	3.89	3.89
Sodium hydroxide	0.87	0.87
Acusol 445N	1.92	1.92
Carbopol 617	0.7	0.7
Dowfax 3B2	0.23	0.23
LPKn 158	0.16	0.16
Sodium hypochlorite (13% solution)	9.2	9.2
Stearic acid	0.11	0.16
Perfume	0.1	0.1
Water	Balance	Balance



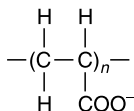
Tripolyphosphate (TPP)



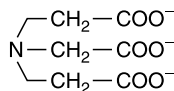
Carbonate



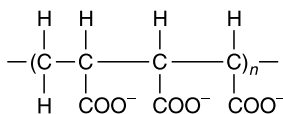
Citrate



Polyacrylate



Nitrilotriacetate (NTA)



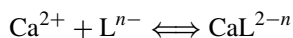
Acrylic/maleic copolymer

FIG. 9.4 Chemical structures of selected builders.

the field has led to a better understanding as to the causes of spotting and filming on items being washed, especially glassware [13,14]. Fatty soils, in combination with calcium ions, result in filming of glasses. However, organic soils do not deposit as film in soft water. In addition, inorganic filming (as CaCO_3) is also a problem in hard water conditions. Both types of film can be controlled or even prevented by efficiently sequestering the hardness ions in the wash water. This problem is obviously of greater concern in hard water areas. Spotting, in contrast, cannot be controlled by sequestration of hardness ions. Both fatty and proteinaceous soils can deposit as spots under all water conditions.

Because of the different mechanisms responsible for soil deposition on glassware, formulators of LADD products rely on two different approaches to control this problem. First, compounds that sequester the hardness ions (builders) are used. In this manner, the calcium and magnesium form water-soluble complexes and are removed with the wash water. In general, Ca^{2+} sequestration is of greater importance than that of Mg^{2+} . This is not only due to the fact that Ca^{2+} is generally present in higher concentrations in water supplies, but also because Ca -soil and CaCO_3 complexes are more stable and less soluble than the magnesium analogs. An important factor in the selection of builders is therefore their calcium binding affinity, K_{Ca} , usually reported as the $\text{p}K_{\text{Ca}}$ [15].

The equilibrium present in solution is as follows:



$$K_{\text{Ca}} = [\text{CaL}^{2-n}]/[\text{Ca}^{2+}][\text{L}^{n-}]$$

$$\text{p}K_{\text{Ca}} = -\log K_{\text{Ca}}$$

where L is the complexing ligand. The $\text{p}K_{\text{Ca}}$ of builders typically used in LADDs are listed in Table 9.5. Also listed are the calcium binding capacities in terms of mg CaO per g of builder [16]. For two molecules with equal binding constants, the one with the lower molecular weight will be more efficient.

The second approach to spot/film prevention involves the use of compounds that either inhibit the deposition and precipitation of Ca^{2+} complexes by slowing down crystallization or reduce the growth of existing crystallites, known as the threshold effect.

Generally, combinations of builders are used in LADD products, the reason being that some builders are more effective sequestrants of calcium, others more effectively bind magnesium, and yet others provide soil dispersion. Studies have also shown synergistic effects in many cases. For example, Lange has reported that interactions between silicate and phosphate show surface activity greater than that which each component alone would contribute [17]. Experiments have shown that combinations of low-molecular-weight polyacrylates and soda ash tolerate higher concentrations of Ca^{2+} in the wash water than equal amounts of either sequestrant individually [15,18]. Builders also work synergistically with surfactants to increase the detergency of the liquid. By tying up free hardness ions, they prevent the formation of insoluble Ca–surfactant complexes.

TABLE 9.5 Values of $\text{p}K_{\text{Ca}}$ and Calcium Binding Capacity for Typical ADD Builders

Builder	$\text{p}K_{\text{Ca}}$	Ca binding capacity (mg Ca^{2+} /g)
Sodium tripolyphosphate	6.0	198
Nitrilotriacetic acid	6.4	448
Sodium citrate	3.6	400
Sodium carbonate	?	286
Low-molecular-weight polyacrylate	4.5	440
Acrylate–maleic copolymers	4.5	480
Zeolite A		198

1. Phosphates

Details of the chemistry of phosphorous compounds pertinent to detergent applications are discussed in a comprehensive review by van Wazer [19]. Phosphates are the universal builder in LADDs due to their high performance-to-cost ratio. The term “phosphate” when used in reference to LADDs actually refers to oligophosphate ions, most common being the tripolyphosphate pentaanion (TPP), the pyrophosphate tetra-anion, and the cyclic trimetaphosphate trianion. The structure of TPP is shown in Figure 9.4. All polyphosphates hydrolyze to simple orthophosphate (PO_4^{3-}) over time. The rate of hydrolysis increases with increasing temperature or decreasing pH [19]. For tripolyphosphate under typical LADD conditions, the hydrolysis half-life is very long, on the timescale of years [18], and is thus of little concern for typical alkaline LADD compositions.

These builders are generally available as sodium, potassium, or mixed-metal salts, the latter being more soluble in water but also more costly. The widespread use of sodium TPP (STPP) in LADD formulations can be attributed to the many functions it performs during the wash cycle. Besides its efficient sequestration of hardness ions, STPP works to disperse and suspend soils, enhance the surface action of anionic surfactants, solubilize proteinaceous soils, and provide alkalinity and buffering action. Pyrophosphates have been included in some LADD formulations because of its better solubility properties relative to tripolyphosphate [20].

Phosphates are currently the primary builder in all LADD products sold in North America, although various regulations limiting their use have been in place for the past 20 years. The concern with phosphates is that large amounts of them in waste water results in the eutrophication of lakes and ponds, leading to excessive algal growth. Because of this concern, government regulations banning their use in laundry detergents and limiting their use in ADD products were passed in the early 1970s.

2. Silicates

After phosphates, silicates are the most ubiquitous builders used in LADD formulations. Like tripolyphosphates, silicates are multifunctional. They are, however, better sequestrants of magnesium ions. A combination of phosphate and silicate is therefore generally used in ADD formulations. In addition to their sequestering properties, silicates provide alkalinity, soil suspension, and anticorrosion properties. A detailed treatment of the synthesis, chemistry, and applications of silicates has been undertaken by Iler [21]. Other reviews are also available [22,23].

Silicates used in detergents vary according to the $\text{SiO}_2\text{:Na}_2\text{O}$ ratio present. They are synthesized by the reaction of sand and sodium carbonate at elevated temperatures. Commercially, ratios of 0.5 to 4 are available, depending on the

ratios of starting materials used [24]. An important transition occurs at a mole ratio of about two. Below an $\text{SiO}_2\text{:Na}_2\text{O}$ mole ratio of two, monomeric or dimeric silicate tetrahedra exist [23]. In contrast mole ratios greater than two result in higher molecular weight silicates due to polymerization. The equilibrium between monomeric and polymeric silicate is affected by the pH of the solution. As the solution becomes more alkaline, the amount of monomeric species increases. For LADD formulation purposes, disilicates with an $\text{SiO}_2\text{:Na}_2\text{O}$ ratio of 1:2 to 1:3 are generally used. At lower ratios, metasilicates form which render the detergent too alkaline, at which point safety problems due to their corrosiveness may become a concern.

An interesting study was reported in 2003 examining the cause of a cloudy, milky ring that can form in soda-lime-silicate glassware [25,26]. This ring was particularly noticed in the bowl of wineglasses that had undergone many washings in an automatic dishwasher. Under microscopic examination grooves and scratches were noted in the unwashed glassware that were not visible to the unaided eye. The glassware was then washed 100 times in an automatic dish washing machine. Glassware washed with solutions containing no sodium disilicate remained clear and transparent. Glasses washed with harsher, sodium disilicate solutions (0.7–1.5 g/l) became visibly corroded around the bowl where the microscopic scratches were noted. Interestingly, the most aggressive dish-washing solutions did not appear to produce this ring. This was attributed to a higher, more uniform rate of corrosion, which left the glass clear but thinner. These glasses may be more prone to breakage in subsequent washings.

3. Zeolites

A related class of siliceous builders are the aluminosilicates (zeolites). Zeolite A, in particular, has been studied as a builder in detergent formulations, generally as a phosphate replacement. It consists of alternating SiO_2 and AlO_2^- building blocks forming a three-dimensional cage structure, with sodium ions balancing the charge. It works by ion exchange, replacing Ca^{2+} in solution with Na^+ . This is a different mode of action compared to the other builders, which form soluble complexes with calcium and magnesium. Because of the relatively small pore size of zeolite A (4.2 Å), the larger, hydrated Mg^{2+} dications cannot be efficiently exchanged.

Studies have shown zeolites to be slower than STPP at removing Ca^{2+} from the wash solution [27]. In addition, their insolubility in aqueous solutions has limited their use to powder detergents, especially in the laundry industry. A comprehensive review of the chemistry of aluminosilicates in detergent compositions is available [28]. Patents for LADD products utilizing zeolites have appeared in the literature [29–31]. The attraction is due to their low cost and low toxicity.

4. Carbonate

Sodium carbonate (Na_2CO_3) has been used in detergent formulations for many years both to sequester calcium ions (at $\text{pH} > 9$) in the wash water and as an alkalinity source. The structure of the carbonate dianion is shown in Figure 9.4. Currently, all powder ADDs contain high levels of sodium carbonate (15 to 40%), mainly as a source of alkalinity. In LADDs, where caustic can be incorporated into the compositions, the need for sodium carbonate is less important.

Because complexation with Ca^{2+} results in insoluble CaCO_3 , which deposits on items being washed, carbonate alone is not an effective builder system. In contrast, tripolyphosphate forms a soluble calcium salt, preventing deposition of insoluble salts. Sodium sesquicarbonate ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$) and sodium bicarbonate (NaHCO_3) have not been used in LADD formulations, except where buffering action is needed.

5. Citrate

A builder that has been studied as a possible phosphate replacement is sodium citrate. The structure of the citrate trianion is shown in Figure 9.4. Several properties of sodium citrate restrict its use in LADD formulations. First, it is incompatible with hypochlorite, precluding its use in most LADD compositions. It is also inferior to STPP in its sequestration efficiency for calcium ions. Finally, it is almost three times more expensive than STPP. This combination renders citrate unsuitable as a replacement for STPP. In Europe, where the different wash conditions allow for the use of milder peroxygen bleaches or enzymes and the water is presoftened, citrate-built products are possible.

6. Organic Polymers

Polymers of carboxylic acids are being increasingly used in LADD formulations since they can perform several functions necessary of ADD components. Low-molecular-weight polycarboxylates ($< 250,000$ a.m.u.) are useful both as builders and soil dispersing agents. Since these latter two functions in LADD formulations are usually performed by STPP, much effort has been directed toward the use of low-molecular-weight polycarboxylates as phosphate replacements. In particular, the soil dispersing properties of low-molecular-weight polycarboxylates makes them very attractive in LADD formulations since other builders such as carbonate, silicate, aluminosilicates, nitrilotriacetate, citrate, and even tripolyphosphate act mainly as sequestrants.

The most often used polycarboxylates consist of acrylic, maleic, and olefinic monomers, either as homo- or copolymers. Modifications to the side groups can be made in order to alter the hydrophobicity of the polymer. In addition, the

relative ratios of monomers in copolymer structures can be varied in order to control the properties of the polymer. Both acrylic acid homopolymers and acrylic acid–maleic anhydride copolymers are commercially available in a wide range of molecular weights (1,000 to 250,000 a.m.u.). The structures of both types are shown in [Figure 9.4](#). They are sold under the trade names Acusol® (Rohm & Haas) [32] and Sokalan® (BASF) [33], among others.

As calcium sequestering agents the copolymers are generally better than analogous acrylic homopolymers due to their greater concentration of COO^- groups per monomeric unit. The differences are rather small, though. In addition, the calcium binding capacity increases with increasing molecular weight [18]. The degree to which the carboxylate groups are ionized also affects the polymer properties. Polycarboxylates that exhibit only partial ionization in the wash have been found to be better sequestrants [34]. The degree of ionization determines the amount of association between COO^- groups and the degree to which the polymer coils. Two mechanisms have been proposed for sequestration of Ca^{2+} and Mg^{2+} by polycarboxylic acids [35]. Through electrostatic binding, the hardness ions interact with electrostatic fields created by the polymer. In contrast, site binding relies on preferential binding of large cations (e.g., Ca^{2+}) over smaller ones (e.g., Na^+ or K^+) along specific binding sites [35].

Ca–polycarboxylate complexes are not very soluble, and will precipitate and deposit on glassware under high Ca^{2+} concentrations. In fact, research at BASF [15] has shown that a combination of soda ash and low-molecular-weight polycarboxylates works better at preventing filming on glassware than either soda ash or the polymer alone. This is because soda ash will bind the calcium but will not be deposited as CaCO_3 due to the dispersing properties of the polymer. In this manner, a higher concentration of Ca^{2+} can be tolerated.

In addition to their role as calcium sequestrants, polycarboxylates perform two other major functions [15]. In fact, because they are usually used in combination with other sequestrants (phosphate, carbonate, citrate) which behave more as sequestrants of hardness ions, it is this property that makes them so important. First, they prevent crystal growth of calcium precipitates, especially CaCO_3 (threshold effect). They also reduce the growth of crystallites already formed. In general, low-molecular-weight polycarboxylates (<10,000 a.m.u.) are more effective than high-molecular-weight ones. Second, and equally important, polycarboxylates are effective dispersants of particulate soils. In this role, low-molecular-weight polymers are again more efficient than high-molecular-weight analogs.

7. Other Builders

A very effective STPP replacement not used in LADD compositions is nitrilotriacetic acid (NTA), commonly manufactured as the monohydrate. Its structure

is shown in [Figure 9.4](#). It is superior to STPP in sequestration of hardness ions, contribution to the alkalinity of the detergent, and solubility at high pH conditions. Because of these properties, it was once considered for use in phosphate-free LADD products. However, concerns about its toxicity have prevented widespread use. There is some controversy regarding its possible role as a carcinogen [36,37]. Several states have classified this material as a potential carcinogen, discouraging its use. Only sporadic use in the laundry detergent category is now observed in Canada and parts of Europe.

The last class of builder to be mentioned here is the ether carboxylates, or oxydicarboxylates. These have not found use in marketed LADD products mainly due to their high cost and incompatibility with hypochlorite. Nonetheless, some favorable characteristics have been identified for effective Ca^{2+} binding [38]:

1. A $\text{pK}_{\text{Ca}} \geq 5$ is desired with minimum molecular weight.
2. Carboxylate and ether oxygens on α -carbons are preferred.
3. Ether oxygens are preferred over ketal oxygens.
4. The order of preference is substituted malonate > malonate > succinate > acetate > propionate.
5. The total ionic charge should be >2 but <5, except for 2:1 complexes.
6. A close steric fit of ≥ 4 donor oxygens around Ca^{2+} is desired.
7. A minimum number of degrees of freedom in the carbon backbone is desired.

B. Surfactants

The role of surfactants in the automatic dishwashing process is very different from their role in the hand dishwashing process. In contrast to light-duty liquid detergents (LDLDs) (see [Chapter 7](#)), which consist mainly of and rely on a combination of surfactants for foaming, grease cutting, and soil removal, LADDs contain surfactants only as a minor additive. The grease and soil removal is instead accomplished by the high alkalinity and bleach present. In addition, the high wash temperature helps to melt fatty soils and to denature proteinaceous soils. Surfactants do provide sheeting action on the items being washed to prevent soils from depositing as spots or film. However, their tendency to produce a large amount of foam is detrimental to the automatic dishwashing process. The reason is that dishwashing machines work by pumping the wash solution through spray arms, which spin because of the water pressure. Foam decreases the water pressure and therefore the cleaning efficiency of the machine (see [Section II](#)). In surfactant-containing compositions, defoamers are often used which reduce foaming by interfering with the formation of micelles (see [Section III.C](#)).

Surfactants suitable for LADD formulations must be low foaming. In addition, if the product is to contain chlorine bleach, the surfactants must be resistant

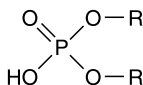
to oxidation. In LADD formulations only anionic and nonionic surfactants have found use. Cationic or amphoteric surfactants have not been used because of their relatively high cost and/or incompatibility with other detergent ingredients. Anionic surfactants are available as alkali metal salts which dissociate in aqueous solution. Typical hydrophilic “head groups” useful in LADD formulations include carboxylates, sulfonates, sulfates, phosphates, and phosphonates. These surfactants are bleach stable unless the hydrophobic tail is oxidizable. A drawback to the use of anionics in LADDs is that they produce too much foam. Nonetheless, because of their bleach stability, alkyl ether sulfonates such as the Dowfax® line (Dow Chemicals) have been used at low concentration in LADD products. The bleach compatibility of a series of anionic surfactants is reported by Rosen and Zhu [39] and in a Dow Chemical bulletin [40].

Nonionic surfactants have also been investigated as components of LADD compositions. The hydrophilicity of nonionic surfactants arises from the polar linkages within the molecule. Typical nonionic surfactants include polyethylene glycol ethers, fatty acid alkanol amides, amine oxides, and ethylene oxide/propylene oxide (EO/PO) block polymers. The last mentioned are especially effective in LADD formulas, although their incompatibility with chlorine bleach has restricted their use to powder or bleach-free gel formulas. The relative hydrophobicity of the EO/PO polymeric surfactants can be controlled by variations in the EO:PO ratio, with hydrophobicity increasing with PO content. Nonionic surfactants possess several advantages over anionics as far as automatic dishwashing is concerned. At temperatures above their cloud points, foaming is reduced to nearly zero. In addition, nonionics are much more effective at lowering the surface tension of water and are therefore much better detergents.

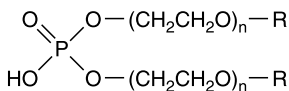
C. Defoamers

The formation of foam during the automatic dishwashing cycle is detrimental to the mechanical washing efficiency of the machine. To prevent foaming, LADD products often contain defoamers. The most commonly used hypochlorite-stable defoamers in LADDs are anionic surfactants such as alkyl phosphate esters and ethoxylated esters [41–43] and silicone oils [44]. The structures of the first two types are shown in Figure 9.5. Also described in the patent literature is the use of aliphatic alcohols or acids as defoamers [45].

The wash temperature has a significant effect on foaming due to its effect on the solubility of the defoaming surfactant. Nonionic surfactants are only effective above their cloud points. Careful consideration must therefore be taken when formulating with nonionics. Water hardness also plays a role in foam formation. In hard water, Ca^{2+} and Mg^{2+} form complexes with fats or anionic surfactants. These insoluble complexes interact with the foam, breaking up the micellar structure.



Phosphate Diesters



Ethoxylated Phosphate Diesters

FIG. 9.5 Chemical structures of phosphate ester defoamers.

D. Oxidizing Agents

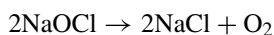
The primary role of bleach in automatic dishwashing is in the removal of food-based stains by oxidation of the responsible molecules. These include anthocyanins (berries), humic acid polymers (coffee, cocoa), tannins (tea, red wine), and carotinoid dyes (carrots, tomatoes). In addition, bleaches contribute to overall cleaning and disinfecting of dishware. They accomplish this by oxidizing food soils, thereby solubilizing them. Several factors contribute to the bleaching activity in the automatic dishwashing process. The most important ones are listed below [46]:

1. All bleaches work faster with increasing temperature.
2. Trace amount of metal impurities dramatically increase the rate of catalytic decomposition of bleaches.
3. The rate of bleaching increases with increasing bleach concentration. However, bleach self-decomposition also increases.
4. The bleach activity is often dependent on pH.

Two general types of bleaches have been used in ADDs: hypochlorite and peroxygen bleaches. Chlorine bleaches refer here to complexes that either contain or deliver hypochlorite (OCl^-) in solution. The compounds used in detergent products are typically alkali metal or alkaline earth hypochlorites, with liquid sodium hypochlorite being the most common. Solid calcium hypochlorite has also received attention, although its low solubility and its contribution of Ca^{2+} to the wash liquor has limited its use in LADD products. Generally, NaOCl is added in amounts resulting in 1 to 2% available chlorine.

One drawback to the use of chlorine bleaches is that in addition to oxidizing soils the bleach also oxidizes some ingredients often used in the formulations. Because

of these unwanted side reactions, care must be taken when formulating with chlorine bleaches. For example, enzymes, nonionic surfactants, sodium citrate, and other useful LADD components are easily and rapidly oxidized by hypochlorite. A study of the stability of sodium hypochlorite in the presence of surfactants has been published by Rosen and Zhu [39]. Even when using only bleach-stable detergent ingredients, the bleach present will decrease over time due to autodecomposition. Two different pathways contribute to bleach degradation [46]:



The first pathway accounts for about 95% of the consumption of OCl^- in the absence of metallic catalysts [47]. The decomposition is affected by pH, concentration, temperature, salt content, and photolysis [39,47] and can lead to loss of product performance upon prolonged storage.

The peroxygen bleaches, typically perborate or percarbonate salts, produce peroxide in aqueous solutions. The effectiveness of peroxide as an oxidizing agent at relatively low wash temperatures (120 to 140°F) is unfortunately minimal. Peracids (RC(O)OOH), which can be generated by the activation of carboxylic acids by peroxide or can be added directly, have not found use in LADD compositions in spite of their relatively high oxidation potentials because of their instability in aqueous solution.

As mentioned earlier, European wash conditions are somewhat different from those encountered in the U.S. In particular, the water temperature during the wash cycles is higher in Europe. This difference has important consequences regarding the formulation of detergents. The higher wash temperatures of European dishwashing also allow for the use of milder oxygen bleaches in place of chlorine bleaches. As bleaching agents, the activity of peroxides and peracids increases with temperature. Under typical North American conditions, they are not suitable replacements for hypochlorite. However, they are more effective under European conditions. The use of oxygen bleaches allows for more freedom in formulations since many LADD components are incompatible with hypochlorite but not with peroxide. Because of the instability of peroxide in alkaline aqueous systems, their use is limited to nonaqueous LADDs. Unfortunately, these are not currently economically feasible.

E. Enzymes

The use of enzymes in detergent formulations became a practical matter in the mid-1960s when Novo Industry began production of proteases by microbial fermentation. These enzymes were stable at the high temperatures and alkalinity encountered in dishwashing.

Several types of enzymes have found uses in LADD compositions [4,48]. Most common are proteases, amylases, and lipases, which attack proteinaceous, starchy, and fatty soils, respectively. Proteases work by hydrolyzing peptide bonds in proteins. Proteases differ in their specificity toward peptide bonds. The typical protease used in LADD formulations, bacterial alkaline protease (subtilisin), is very nonspecific. That is, it will attack all types of peptide bonds in proteins. In contrast to proteases, amylases catalyze the hydrolysis of starch. They attack the internal ether bonds between glucose units, yielding shorter, water-soluble chains called dextrans. Lipases work by hydrolyzing the ester bonds in fats and oils. Often, combinations are used because of the specificity of each kind to one type of soil. The commercially available enzymes are listed in Table 9.6.

While enzymes have played a role in powder detergents in the U.S. market over the years, more recently they have started to emerge as additives in LADD formulations. Both proteases and amylases have appeared in LADDs in spite of the fact that, unlike powders, oxygen bleaches could not be incorporated for stain removal. They first appeared in bottled liquid/gel products in 2000 in the U.S. These were introduced as premium products, with dual enzymes, and captured about 5% of the total automatic dishwashing market.

The first automatic dish gel pac was introduced in 2002. This was a dual enzyme-based formula that was packaged in a water-soluble sachet. This form of unit dose followed on the relative success of pressed powder (tablet) unit dose products in the market. This also captured about 5% of the total automatic dishwashing market.

TABLE 9.6 Commercially Available Detergent Enzymes

Type	Trade name	Manufacturer
Protease	Esperase	Novo
	Savinase	
	Alcalase	
	Everlase	Genencor
	Kannase	
	Purfect® L	
	Purafect® L	
Amylase	Properase® L	Novo
	Termamyl	
	Duramyl	
	Purastar® HPAm L	
Lipase	Lipolase	Novo
	Lipolase Ultra	
	Lipo Prime	

As enzyme technology improves, the share of enzyme-containing products can be expected to grow in the liquid LADD market. New forms will probably help support this move, and may ultimately lead to a dual enzyme, oxygen bleach technology.

F. Structuring Agents

LADD products currently in the marketplace are not real liquids, but are gels thickened by a structuring agent. Two main kinds of materials are used in LADD products currently available to consumers: water-swallowable, high-molecular-weight ($>1,000,000$) crosslinked polyacrylates and clays such as bentonite or laponite. Often, cothickeners are added to improve the stability of the gel. For example, colloidal alumina or silica [49–51], fatty acids or their salts [50,52–63], and others have been described in the patent literature as being effective additives. It has also been found that incorporated air bubbles can also contribute to the stability of polyacrylate-thickened gels [71–74]. The effect of such thickening systems is to make the gel viscoelastic and thixotropic. This means that the gel is viscous when unstressed, but the viscosity decreases due to shear thinning upon application of an applied stress. The rheological properties of LADD products are discussed in Section IV. When LADD products contain bleach, potential structuring agents are very limited. They must be chemically stable to bleach for the life of the product.

Currently, products in the market are thickened mainly by polyacrylic acids, although some use a mixture of polymer and a clay. This is in contrast to the early LADD products, which used exclusively clay thickeners and therefore suffered from stability problems [7]. The products, being clay suspensions in an aqueous medium, tended to separate in a relatively short period of time. The introduction of bleach-compatible polymeric thickeners in the early 1990s overcame this problem [75].

IV. RHEOLOGY AND STABILITY OF LADDs

As discussed earlier, LADDs are complex, multicomponent mixtures consisting of both organic and inorganic compounds dispersed in a liquid matrix. Such compositions can exhibit a broad range of rheological characteristics from simple Newtonian to complex pseudoplastic flow. Shown in [Figure 9.6](#) and [Figure 9.7](#) are flow and viscosity profiles of Newtonian and non-Newtonian fluids as a function of applied shear rate. A number of mathematical models have been proposed [76] to describe the flow characteristics of various systems. These equations are called constitutive equations and are used to predict flow behavior in complex systems.

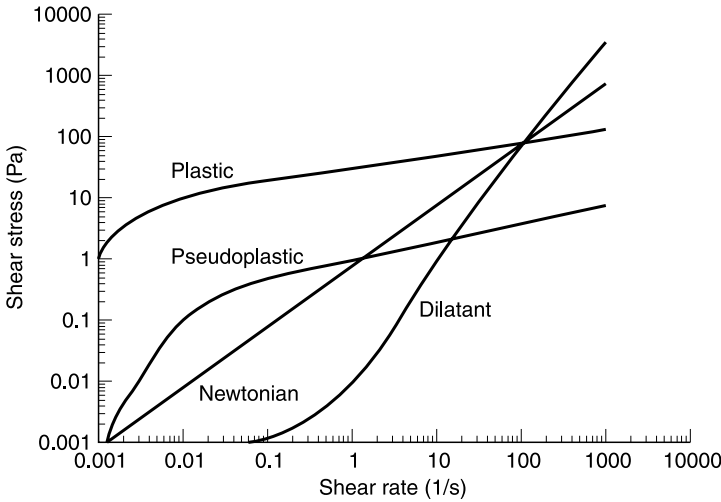


FIG. 9.6 Generic examples of shear stress vs. shear rate plots for different rheological systems. (Reproduced from Laba, D., Ed., *Cosmetic Science and Technology Series*, Vol. 13, Marcel Dekker, New York, 1993. With permission.)

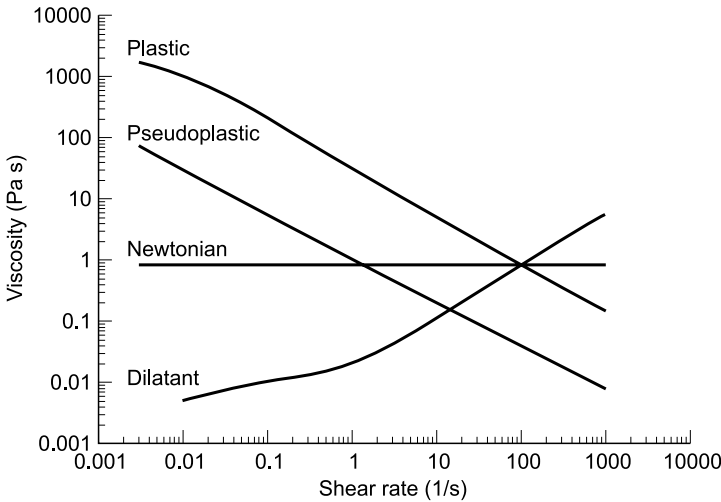


FIG. 9.7 Generic examples of viscosity vs. shear rate plots for different rheological systems. (Reproduced from Laba, D., Ed., *Cosmetic Science and Technology Series*, Vol. 13, Marcel Dekker, New York, 1993. With permission.)

Clearly, the response of fluids to an applied shear can be linear or nonlinear and depends on two major factors: shear rate and structural or mechanical properties of the system, which in turn depend upon the interaction between the components including the rheological additives. It is the latter that primarily determines the flow properties of LADDs. The intent of this section is to discuss various rheological properties and test methods pertinent to LADDs. Interested readers are referred to [Chapter 4](#), which deals with the rheology of complex liquids and suspensions, and other books [76–79] and review articles [80–82] covering this subject. Heywood [83] discusses the criteria for selecting various commercial viscometers.

The ideal rheological characteristics of LADDs from the consumer point of view are:

1. The product must be homogeneous and phase-stable.
2. The flow properties of the product should be such that it can be readily dispensed to the dishwasher cup from the bottle without dripping.
3. Once the product is in the dishwasher cup it should recover its structure/viscosity such that the product stays in the cup until the wash cycle begins.

The third attribute is the most important for dishwashers sold in the U.S. since a majority of dishwasher cups are primarily designed for powders. They are therefore ungasketed and will not prevent improperly structured gel products from prematurely leaking out.

A. Flow Properties

1. Viscosity

This is a fundamental rheological property that is universally measured and reported for all liquid products. Viscosity is resistance to flow. Different types of viscometers are used to measure this property. A major disadvantage of determining the viscosity of complex fluids is that the value obtained depends on the instrument, type of spindle, and rotational speed. Therefore, one should be extremely careful when comparing the viscosities of liquid products described in the literature.

2. Yield Value

Another rheological attribute of LADDs commonly referred to in the patent literature is yield value (also referred to as yield stress). The significance of the yield value is that it indicates shear stress or shear rate necessary to induce flow which is a characteristic of the system. This is only an apparent yield stress, since everything will flow even at zero stress if given enough time.

Several methods based on viscometers [84,85] and stress rheometers [86,87] have been proposed and described for measuring this parameter. One of the methods described [88] utilizes a Brookfield RVT model viscometer and a T-bar spindle.

The viscometer readings are recorded at 0.5 and 1.0 r/min after 30 seconds or after the system is stable. Shear stress at zero shear is equal to two times the 0.5 r/min reading minus the reading at 1.0 r/min. The yield value is then calculated as follows:

$$\text{Yield value} = 18.8 \times \text{stress at zero shear}$$

According to this patent, the yield value for LADDs should be in the range 50 to 350 dyn/cm².

Another method described in the literature [85] is based on the Brookfield viscosity measurements at two different shear rates and the yield value is calculated according to the following equation:

$$\text{Yield value} = 2r_1(\eta_1 - \eta_2)/100$$

where r is the shear rate and η_1 and η_2 are viscosities at shear rates of r_1 and $2r_1$, respectively.

3. Thixotropy

The most desirable rheological behavior for LADDs is thixotropy. Such systems follow a shear-thinning pattern very similar to pseudoplastic systems, but when the shear is removed the structure rebuilds in a time-dependent manner instead of instantaneously. A rheological profile of a thixotropic liquid shows a characteristic hysteresis loop, the size of which is related to the degree of thixotropy and structure recovery time. A typical thixotropic loop shows the relationship between the viscosity or stress vs. shear rate. An example of such a plot for a commercial LADD is shown in [Figure 9.8](#). Such flow curves are typically obtained by plotting viscosity or shear stress with increasing shear rate (up curve) followed by decreasing shear rate (down curve).

Some systems exhibit flow behavior opposite of thixotropic systems, that is, viscosity increases with increasing shear rate. Such fluids are referred to as dilatant or rheopectic. This type of behavior is not common for liquid products containing a low concentration of the dispersed phase.

4. Dynamic Properties

The vast majority of concentrated dispersions, such as LADDs, exhibit both viscous and elastic properties. These systems are therefore referred to as viscoelastic. The flow properties discussed in the previous section are not sufficient for complete rheological characterization of viscoelastic fluids. Dynamic mechanical properties, characterized by the storage modulus (G') and loss modulus (G''), are normally

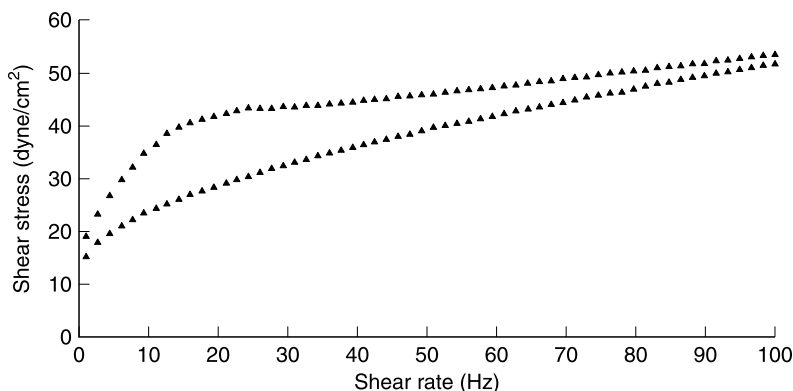


FIG. 9.8 Plot of shear stress vs. shear rate for a commercial LADD. The rheograms were recorded on a Carri-Med CSL 100 stress-controlled rheometer using a 4 cm acrylic parallel plate configuration with gap setting of 1000 μm .

measured to quantify the viscoelastic properties. The storage modulus represents the mechanical energy stored and recovered and is a direct measure of the elasticity of the fluid. The loss modulus is a measure of mechanical energy lost thermodynamically as heat. This type of energy dissipation occurs when the sample is undergoing viscous flow. For predominately elastic materials $G' > G''$, and for predominately viscous materials $G'' > G'$.

Both G' and G'' are related to the complex modulus G^* and complex viscosity η^* by the following relationships:

$$G^* = G' + iG''$$

$$\eta^* = [(G'/\omega)^2 + (G''/\omega)^2]^{1/2}$$

where ω is the angular frequency of the oscillation.

The relative magnitudes of the two moduli provide significant information regarding strength of internal association or structure in fluids and dispersions. These moduli are measured as a function of strain, frequency, or time. For some dispersions, the magnitudes of G' and G'' may remain constant as a function of either frequency or strain. Such materials are referred to as linearly viscoelastic.

Plots of G' and G'' vs. % strain for the three major commercial gel LADDs sold in the U.S. are shown in Figure 9.9, Figure 9.10, and Figure 9.11. For these plots, a strain is applied to the sample and the stress response is measured.

The elasticity and viscosity of a gel are essential criteria for ease of dispensing and cup retention in the dishwasher. For example, a patent [89] claims that

viscosities of 1000 to 20000 cP under 5/sec shear, 200 to 5000 cP under 21/sec shear, and a steady-state viscoelastic deformation compliance value of at least 0.01 are ideal for product dispensability and cup retention (as measured on a Haake Rotovisco RV-100 viscometer). A series of patents issued to Dixit and co-workers

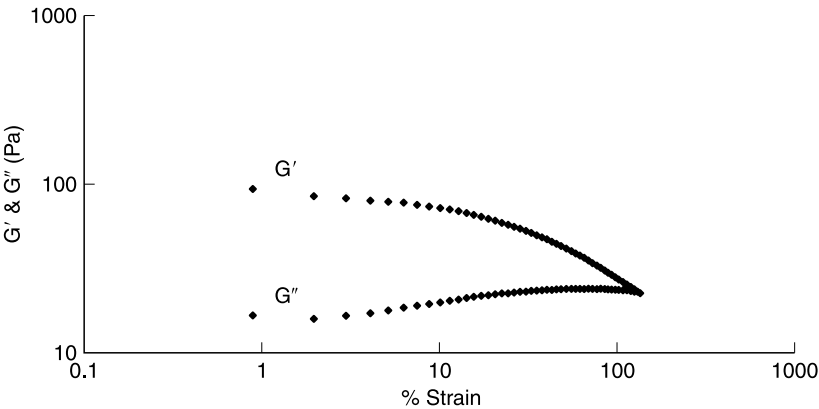


FIG. 9.9 Plots of G' and G'' vs. % strain for a commercial LADD. The rheograms were recorded on a Carri-Med CSL 100 stress-controlled rheometer using a 4 cm acrylic parallel plate configuration with gap setting of 1000 μm .

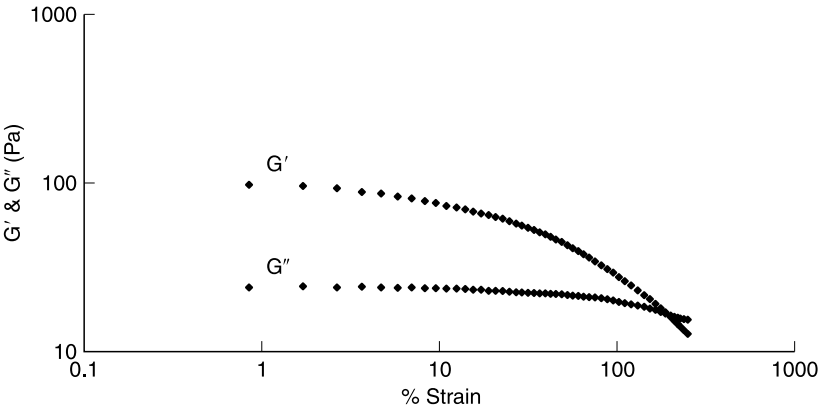


FIG. 9.10 Plots of G' and G'' vs. % strain for a commercial LADD. The rheograms were recorded on a Carri-Med CSL 100 stress-controlled rheometer using a 4 cm acrylic parallel plate configuration with gap setting of 1000 μm .

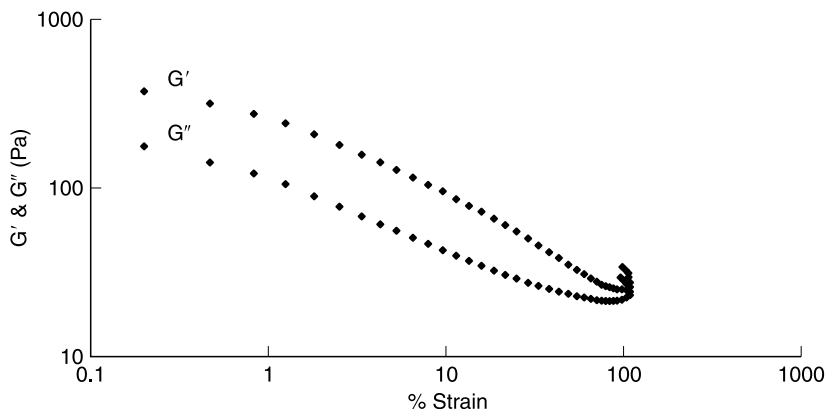


FIG. 9.11 Plots of G' and G'' vs. % strain for a commercial LADD. The rheograms were recorded on a Carri-Med CSL 100 stress-controlled rheometer using a 4 cm acrylic parallel plate configuration with gap setting of 1000 μm .

[55,56,59,71,72] emphasize the importance of linear viscoelasticity as defined by $\tan(\delta)$ as an important rheological characteristic for LADDs.

V. EVALUATION OF THE PERFORMANCE OF LADDs

Essential to the development of new LADD products is the evaluation of their performance. It is important that the test conditions closely reproduce the conditions encountered by the consumer under typical household situations; therefore, prototype formulas are usually tested in actual dishwashing machines using real food soils.

Typically, performance evaluation tests are run using a variety of soiled items, since a combination of soils is typically encountered by consumers. For example, spotting and filming tests on standard glass tumblers are run in conjunction with plates and cutlery soiled with egg, oatmeal, spinach, tomato sauce, and various other common food soils. In addition, the ability of the ADD product to remove tough stains such as coffee, tea, or blueberry is assessed on a variety of substrates during these multi-soil test cycles.

Ideally, testing should be conducted using machines from all major manufacturers, as differences exist in detergent dosing amounts, water fill amounts, and lengths and orders of cycles. It is also important that performance tests be carried out at different water hardnesses, since regional variations exist. Water hardness for testing purposes can be controlled by the addition of simple salts of calcium and magnesium to deionized water. A 2:1 mole ratio is commonly used since that is the $\text{Ca}^{2+}:\text{Mg}^{2+}$ ratio encountered in most water supplies.

A. Spotting and Filming

The standard method for the testing of ADD products as regards spot/film prevention on glassware is described in ASTM D 3556 [90]. The test entails the washing of glass tumblers using commercial automatic dishwashing machines. A soil consisting of margarine and powdered, nonfat milk (40 g, in an 8:2 ratio) is added prior to starting the cycle. The soil can be introduced by spreading onto dinner plates or by adding directly into the wash. This combination of soils provides the fats and proteins generally present during typical household wash cycles. Optionally, a similar soil mixture which also contains cooked cereal can be added, providing a source of starch. For completeness, dinner plates, dessert plates, and silverware are placed in the machine for ballast.

It is recommended that at least five complete cycles be run during a test, adding the soil at the beginning of each cycle. This is to ensure that product performance remains acceptable after repeated cycles. Detergents that are underbuilt, for example, will lead to heavy filming on the glasses only after several cycles. The test parameter that is typically varied during this spot/film test is the hardness. Spotting tends to occur under lower water hardness conditions, while film formation tends to happen more under harder water conditions.

To discriminate between similar products, it is often useful to run the tests under stress conditions; that is, low temperature and high water hardness. In contrast, to see how a detergent might perform under normal household conditions, higher temperatures and lower water hardness should be explored.

The ASTM procedure also describes a rating method for judging the spotting and filming on glasses. The readings are done visually, using a fluorescent light box to highlight spotting and filming on the glasses being inspected. The performance of a product is rated on a 1 to 5 scale for both spotting and filming, as shown in Table 9.7.

The use of photometry to rate the spotting and filming on glassware eliminates the possibility of subjective judging by humans. Several systems have been

TABLE 9.7 Rating Scale for Spotting and Filming of Glassware

Rating	Spotting	Filming
1	No spots	None
2	Random spots	Barely perceptible
3	¼ of surface covered	Slight
4	½ of surface covered	Moderate
5	Virtually completely covered	Heavy

described in the literature that take advantage of this technique [91]. As of this writing, the ASTM D 3556 test is under review.

B. Soil Removal

When testing the performance of ADD products it is often useful to determine the ability of the detergent to remove tough food soils from items being washed. In selecting the soils to be used, the following criteria must be met. The soils must be representative of those encountered by consumers, but they must not be removed so easily as to render all products equal in cleaning efficiency. The soils can be roughly divided into two classes: water-soluble and water-insoluble soils. Examples of the former are sugars, starch, flour, or egg white, while the latter might be animal or vegetable fats.

Egg yolk has proven to be an especially useful soil for performance testing of ADD products, provided that it is prepared in a way that gives meaningful and reproducible results. This soil contains a very high protein content, and thus is not saponified by the heat and alkalinity during the wash cycle as fatty soils are. The efficient removal of egg yolk from dinner plates can only be accomplished by detergents that target proteinaceous soils. Often, CaCl_2 is mixed into the egg mixture to make a cohesive–adhesive egg complex capable of remaining on the dishes throughout the complete cycle [92]. Otherwise, the mechanical energy from the water jets alone will remove the egg from the plate. Typically, 2 to 3 g of CaCl_2 /25 g of egg yolk are added. This more closely simulates typically soiled plates, which might derive a small amount of calcium from milk or salts present. A known weight of the egg soil should be spread onto dinner plates. The degree of egg removal after the cycle is determined either visually or by weight difference. An added bonus of this test is that it provides a proteinaceous soil to the wash liquor, making the spotting and filming scores obtained more realistic. Studies have shown proteinaceous soils to be a source of spotting on glasses [13]. It is important to place consistently the egg plates in the same position in the dishwasher in order to minimize spray arm effects.

The Association of Home Appliance Manufacturers (AHAM) has published a set of standards for testing of automatic dishwashers [93]. Although the focus of this test is the dishwasher performance, it can also be applied to the product performance.

The test procedure also describes how to load the items into the dishwasher and other test parameters. Variations in the types and number of soils and items used for a multi-soil test are permissible. It is desirable, though, to use a soil combination that contains the major types of soils (proteinaceous, fatty, and starchy), as some ADD products might effectively remove some but not others. This is especially true for formulas that contain enzymes.

C. Stain Removal

Besides the prevention of spots and film and the removal of food soils from items being washed, LADD products must also effectively remove stains. For this purpose, LADDs often employ bleaching agents which act by oxidizing the chromophore responsible for the stain color. Generally, as the oxidizing potential of the bleach increases, its effectiveness also increases. The common method employed to gauge stain removal is to allow either coffee or tea to dry in a porcelain, plastic, or glass cup. The cups are then run in a standard soil test [93]. Additionally, coffee- and/or tea-stained melamine tiles can be used in evaluating stain removal. These types of tiles can be obtained from companies such as Test Fabrics in West Pittston, PA.

D. Foaming

The minimization of foam generated by detergent and food soils during the wash cycles in the automatic dishwashing process is a prerequisite for efficient mechanical cleaning by the machine spray arms. Foam decreases the water pressure pumped through the rotors, decreasing the kinetic energy of the water jets. As stated in Section II, mechanical action has been estimated to be responsible for 85% of the cleaning in a machine dishwashing cycle. A lowering of the wash pressure therefore will have a noticeable effect on overall cleaning. Because of this, ADD formulations, especially those containing anionic surfactants, often contain defoamers.

A standard test method has been developed for the measurement of foam during an automatic dishwashing cycle. This method is described in the CSMA Compendium, Method DCC-001 [94]. The test involves the measurement of the machine spray arm rotational velocity (in r/min) at one-minute intervals over a ten-minute wash cycle. The rotor r/min will decrease in the presence of foam since the water pressure being pumped through the spray arm will be lower. In order to measure the revolutions per minute, a magnetically activated reed switch is used and the spray arm is fitted with a magnet. The detergent is dosed normally, and a high-foaming soil is added before the cycle begins. The recommended soil is nonfat powdered milk (10 g) or a powdered milk and egg white combination (1:1).

The efficiency score for a particular detergent is obtained by taking the average of the arm speed readings and dividing by the average reading for the control. In this experiment, the control is the same experiment without the detergent or soil. As in other performance tests, it is good practice to use the same machine for all comparative experiments in order to eliminate variations due to the use of different machines. Different machines will have slightly different motors which will produce slightly different rotor velocities.

E. Fine China Overglaze and Glass Corrosion

Fine china is often decorated with colored patterns made from various metal salts or oxides. Two methods are commonly used: underglaze, in which the color is put on before the glaze, and overglaze, in which it is applied after the glaze. The overglaze pattern on fine china is incompatible with the high alkalinity characteristic of ADD products. Unless the china is somehow protected from hydroxide ions during the wash, the overglaze and the color will be attacked and destroyed. To protect against this, LADDs are generally formulated with sodium silicate, which acts by coating the china with a protective siliceous layer, preventing the alkali from coming in contact with the overglaze itself. Silicate works in a similar manner to protect metal machine parts from corrosion.

A procedure has been developed to test the effectiveness of ADD products in fine china overglaze protection. This method is described in ASTM D 3565 [95]. Segments of a china plate are soaked in a 0.3% ADD solution held at 96.0 to 99.5°C in a steam bath. Two controls are also set up consisting of a sodium carbonate solution and water only. The segments of the china plate are placed on wire mesh supports to avoid contact with the bottom of the steel beakers used. The solutions are heated for six hours, after which the china segments are removed and rubbed vigorously with a 1.5 inch square of muslin. The plate segment is then washed, dried, and visually inspected for fading. An effective detergent should prevent any sign of wear.

Additional information about glass corrosion can be obtained from the research done by Sharma and Jain [25,26]. Although they evaluated the visible effect of wine glass corrosion over the course of 100 machine washings, a similar visible irreversible clouding of the wineglasses can be demonstrated by a modification of the ASTM D 3565 glaze test. The test can be modified by using soda-lime-silicate wine glasses in place of the china plate segments. The ring effect can be seen in as little as three hours.

VI. FORMULATION TECHNOLOGY

A. Cleaning

Consumers have several criteria for accepting a LADD. Some of these are listed in [Table 9.8](#). The formulator must strike a balance among performance, aesthetics, convenience, and cost to meet consumer requirements. While cleaning dishware is the most important element, shine and spot and film prevention are also strongly desired. Corrosion protection, particularly related to glasses and china, is also an important attribute for a successful LADD. Formulators use a combination of components to achieve these goals. These include, but are not limited to, alkalinity, bleach, silicates, phosphates, polymers (both low and high molecular weight), and enzymes.

TABLE 9.8 Important Attributes of LADDs

Effective cleaning
Shine
Spot and film prevention
No powder residue
Convenient to use
Safe to dishes and tableware
Safe to dishwasher
Stable upon storage
Safe to humans
Economic to use

Aside from mechanical action, the bulk of the food removal from soiled dishes is accomplished by two mechanisms. Fatty soils are removed by a combination of the high temperature and alkalinity present, which melts and saponifies fats. Proteinaceous and starchy soils, in contrast, are solubilized by oxidation and hydrolysis. More effective soil removal is accomplished by the use of enzymes, which selectively and efficiently attack fats, starches, or proteins. Stain removal is another aspect of cleaning that is addressed by different technologies. A recent technology, based on benzoyl peroxide, has been shown to be effective against red tomato stains on plastic. The removal of tough stains such as coffee or tea can only be accomplished by strong bleaching agents such as hypochlorite. Hypochlorite also has a sanitizing effect on the washed items. Listed in [Table 9.9](#) are relevant patents that disclose novel cleaning technologies in LADDs.

B. Thickeners

Equally important when formulating LADDs is making a stable and easy-to-handle product. LADDs are concentrated suspensions which must be properly structured so as to prevent separation upon storage. The product must also be thickened for two reasons: to prevent it from prematurely leaking out of the machine dispenser cup and to make it easier to control when dosing. However, the product must be shear thinning so that it will easily flow under an applied stress. Early LADDs were thickened by clay thickeners. More recently, the use of high-molecular-weight polymeric thickeners, optionally with fatty acid or other surfactant cothickeners, has solved the separation problems. Composition patents in this area are listed in [Table 9.14](#). Patents that disclose processing or manufacturing methods used in LADD production are listed in [Table 9.10](#).

TABLE 9.9 Patents Relating to Cleaning Technology in LADDs

Patent no. and year	Inventor(s) and company	Technology	Claimed benefits
U.S. 6602837 (2003) [96]	Patel (Procter & Gamble)	Nonaqueous; diacyl peroxide	Plastic stain removal especially carotenoids
U.S. 5929008 (1999) [98]	Goldstein (Procter & Gamble)	Perborate bleach	Improved cleaning at pH > 11.4
U.S. 5858944 (1999) [105]	Keenaqn <i>et al.</i>	Polycarboxylates	Low film/spot
U.S. 5698507 (1997) [99]	Gorlin <i>et al.</i> (Colgate-Palmolive)	Dual enzyme	Soil removal
U.S. 5618465 (1997) [100]	Durbut <i>et al.</i>	Dual enzyme	Soil removal
U.S. 5597789 (1997) [101]	Sadlowsk	Polymer	Hard water film performance
U.S. 5545344 (1996) [102]	Durbut <i>et al.</i>	Enzymes, no phosphate, nonaqueous	Concentrated
U.S. 5527483 (1996) [103]	Kenkare <i>et al.</i>	Nonaqueous, enzymes	Soil removal
U.S. 5372740 (1994) [104]	Fair <i>et al.</i>	<i>In situ</i> TPP, Na/K balance	No added silicate
U.S. 5318715 (1994) [106]	Krishnan (Colgate-Palmolive)	Nonaqueous, dual enzymes	Improved cleaning at pH < 10.5
WO 94/25557 (1994) [107]	Sadlowski (Procter & Gamble)	Modified polyacrylate copolymer	Enhanced hard water filming
WO 94/17170 (1994) [108]	van Dijk <i>et al.</i> (Unilever)	Itaconic acid–vinyl alcohol copolymer	Improved scale prevention; biodegradable
U.S. 5308532 (1994) [109]	Adler <i>et al.</i> (Rohm & Haas)	Water-soluble carboxylate terpolymers	Reduced spotting and filming

(continued)

TABLE 9.9 (Contd.)

Patent no. and year	Inventor(s) and company	Technology	Claimed benefits
U.S. 5240633 (1993) [110]	Ahmed <i>et al.</i> (Colgate-Palmolive)	Nonaqueous; protein-engineered enzymes	Improved protein and carbohydrate soil removal; improved low-temperature cleaning
U.S. 5164106 (1992) [111]	Ahmed <i>et al.</i> (Colgate-Palmolive)	Nonaqueous; dual bleach system	Improved cleaning against proteinaceous and starchy soils
U.S. 5094771 (1992) [112]	Ahmed <i>et al.</i> (Colgate-Palmolive)	Nonaqueous; silica, alumina, or titanium dioxide	Readily dispersible in water; improved spotting and filming in hard water
U.S. 5076952 (1991) [113]	Ahmed <i>et al.</i> (Colgate-Palmolive)	Dual bleach sysactem	Improved cleaning
U.S. 4971717 (1990) [30]	Dixit (Colgate-Palmolive)	Aluminosilicate	Improved filming and spotting
U.S. 4970016 (1990) [114]	Ahmed <i>et al.</i> (Colgate-Palmolive)	Alumina or titanium dioxide	Improved filming in hard water
U.S. 4968446 (1990) [115]	Ahmed <i>et al.</i> (Colgate-Palmolive)	Alumina or titanium dioxide	Improved filming
U.S. 4968445 (1990) [116]	Ahmed <i>et al.</i> (Colgate-Palmolive)	Silica	Improved filming
U.S. 4931217 (1990) [117]	Frankena (Lever Bros.)	Quaternary ammonium salts	Enhanced fat removal at low temperature
EP 271155 (1988) [118]	van Dijk (Unilever)	Bacterial lipases	Improved spotting and filming
U.S. 4753748 (1988) [119]	Laitem <i>et al.</i> (Colgate-Palmolive)	Nonaqueous; stable polyphosphate builder suspension	Improved rinse properties
U.S. 4597886 (1986) [120]	Goedhart <i>et al.</i> (Unilever)	Enzymes and layered clay	Improved spotting and filming
U.S. 4539144 (1985) [121]	de Ridder <i>et al.</i> (Lever Bros.)	Modified polyacrylate; phosphate-free	Improved filming, spotting, streaking
U.S. 4306987 (1981) [122]	Kaneko (BASF Wyandotte)	Block polyoxyalkylene nonionic surfactant	Effective foam control; spot-free wash items; effective against encrusted protein soils

TABLE 9.10 Patents Relating to Thickeners in LADDs

Patent no. and year	Inventor(s) and company	Technology	Claimed benefits
U.S. 5691292 (1997) [53]	Marshall <i>et al.</i> (Procter & Gamble)	Thixotropic liquid; chlorine bleach free	Thickener for enzyme-based ADDs; enzyme stabilizing
U.S. 5427707 (1995) [52]	Drapier <i>et al.</i> (Colgate- Palmolive)	Thixotropic thickener; long-chain fatty acids	Thixotropy with lower thickener levels
U.S. 5413727 (1995) [54]	Drapier <i>et al.</i> (Colgate- Palmolive)	Thixotropic thickener; long-chain fatty acids	Thixotropy with lower thickener levels
U.S. 5368766 (1994) [71]	Dixit (Colgate- Palmolive)	High-molecular-weight crosslinked polymer thickener; K/Na ratio > 1:1; incorporated air bubbles	Physical stability; low bottle residue; low cup leakage; improved cleaning
U.S. 5298180 (1994) [72]	Dixit (Colgate- Palmolive)	High-molecular-weight crosslinked polymer thickener; K/Na ratio > 1:1; incorporated air bubbles	Physical stability; low bottle residue; low cup leakage; improved cleaning
U.S. 5336430 (1994) [123]	Bahary <i>et al.</i> (Lever Bros.)	Polysaccharide thickener; encapsulated bleach and chlorine scavenger	Biodegradable structurant
U.S. 5252241 (1993) [55]	Dixit <i>et al.</i> (Colgate- Palmolive)	High-molecular-weight crosslinked polymer thickener; long-chain fatty acid; incorporated air bubbles	Physical stability; low bottle residue; low cup leakage; improved cleaning
U.S. 5252242 (1993) [56]	Dixit <i>et al.</i> (Colgate- Palmolive)	High-molecular-weight crosslinked polymer thickener; long-chain fatty acid; incorporated air bubbles	Physical stability; low bottle residue; low cup leakage; improved cleaning
U.S. 5229026 (1993) [57]	Dixit <i>et al.</i> (Colgate- Palmolive)	High-molecular-weight crosslinked polyacrylic acid; K:Na ratio > 1:1; incorporated air bubbles; fatty acid or salt	Exceptional physical stability; low bottle residue; low cup leakage; improved cleaning

(continued)

TABLE 9.10 (Contd.)

Patent no. and year	Inventor(s) and company	Technology	Claimed benefits
U.S. 5229026 (1993) [31]	Dixit (Colgate- Palmolive)	High-molecular-weight crosslinked polyacrylic acid; K:Na ratio > 1:1; incorporated air bubbles; aluminosilicate	Exceptional physical stability; low bottle residue; low cup leakage; improved cleaning
U.S. 5205953 (1993) [73]	Dixit (Colgate- Palmolive)	High-molecular-weight crosslinked polyacrylic acid; K:Na ratio > 1:1; incorporated air bubbles; polymeric chelating agent	Exceptional physical stability; low bottle residue; low cup leakage; improved cleaning
U.S. 5188752 (1993) [58]	Prencipe <i>et al.</i> (Colgate- Palmolive)	Crosslinked methyl vinyl ether-maleic anhydride copolymer; fatty acid/salt	Linear, viscoelastic
U.S. 5169552 (1992) [64]	Wise (Procter & Gamble)	Polymeric thickener; stabilizing agent; buffering agent	Improved bleach stability; improved rheology; shear thinning
U.S. 5135675 (1992) [65]	Elliot <i>et al.</i> (Lever Bros.)	Swellable clay, sulfonated polymer, and multivalent cations	Good salt tolerance; bleach stability; shear thinning
U.S. 5130043 (1992) [66]	Prince <i>et al.</i> (Procter & Gamble)	Polycarboxylate and phosphate esters	Enhanced stability and cohesiveness
U.S. 5098590 (1992) [59]	Dixit <i>et al.</i> (Colgate- Palmolive)	Thixotropic thickener; long-chain fatty acid/salt; equal specific gravities for bulk and liquid phases	Improved stability
U.S. 5057237 (1991) [60]	Drapier <i>et al.</i> (Colgate- Palmolive)	Clay thickener; polyvalent metal salts of long-chain fatty acids	Improved stability
U.S. 4950416 (1990) [50]	Baxter (Vista Chemical)	Thixotropic liquid; aqueous alumina dispersion; long-chain fatty acid or salt and mixtures	Nonpolymeric and nonclay compositions

U.S. 4941988 (1990) [51]	Wise (Procter & Gamble)	Polyacrylate thickener and alkali metal silica colloid; optimized thickening system	
WO 89/04359 (1989) [67]	Donker (Unilever)	Thixotropic gel with alkyl phosphate, phosphonate, sulfate, or sulfonate	Improved stability against phase separation
U.S. 4836946 (1989) [61]	Dixit (Colgate-Palmolive)	Clay thickener; alkali metal fatty acid salt	Lower clay levels needed
U.S. 4824590 (1989) [74]	Roselle (Procter & Gamble)	Shear-thinning gels with incorporated air	Improved stability
U.S. 4801395 (1989) [62]	Chazard <i>et al.</i> (Colgate-Palmolive)	Clay thickener and long-chain fatty acids	Improved stability against phase separation; increased viscosity; lower clay levels needed
EP 304328 (1989) [124]	Kreischer (Unilever)	Nonsoap anionic surfactant and soap; electrolyte level > 20%	Thixotropic liquid structured by surfactants only
U.S. 4752409 (1988) [63]	Drapier <i>et al.</i> (Colgate-Palmolive)	Inorganic colloid-forming clays or other thixotropic thickener; polyvalent metal salts of long-chain fatty acids	Phase stability for more than 12 weeks; lower clay levels needed
U.S. 4740327 (1988) [68]	Julemont <i>et al.</i> (Colgate-Palmolive)	Clay thickener and anionic surfactant	Improved dispensability and processing; improved cup retention
GB 2168377 (1985) [69]	Taraschi (Procter & Gamble)	Water-insoluble abrasive colloidal clay; water-insoluble low-density particulate filler	Low yield value; phase stability due to the filler material
WO 83/03621 (1983) [70]	Kolodny <i>et al.</i> (American Home Prod.)	Xanthan gum thickener; mixture of anionic and nonionic surfactants	Viscosity 3000–6000 cP; yield point 250–825
U.S. 4260528 (1981) [125]	Fox <i>et al.</i> (Lever Bros.)	Natural or synthetic gum thickener, urea and polyhydric alcohol	Good viscosity and flow control
U.S. 4226736 (1980) [126]	Bush <i>et al.</i> (Drackett)	Thixotropic gel	Reduced cup leakage; low foaming

TABLE 9.11 Patents Relating to LADD Processing

Patent no. and year	Inventor(s) and company	Technology	Claimed benefits
U.S. 5624892 (1997) [128]	Angevaare <i>et al.</i> (Lever Bros.)	Aluminum sequestrant	Inhibits lead corrosion
U.S. 5395547 (1995) [129]	Broadwell <i>et al.</i> (Colgate-Palmolive)	Fatty acid/surfactant/defoamer	Improved stability predisposition
U.S. 5366653 (1994) [127]	Corring (Lever Bros.)	Dry-blending thickening polymer and sodium trimetaphosphate	Concentrated liquid
U.S. 5246615 (1993) [130]	Broadwell <i>et al.</i> (Colgate-Palmolive)	Preneutralization of polymeric thickener with alkali metal silicate or builder	Pumpable polymer gel premix
WO 93/21298 (1993) [131]	Gabriel <i>et al.</i> (Procter & Gamble)	Premix made, mixed aerated to increase density and aesthetics	Increased product density; enhanced aesthetics; improved rheological efficiency of polymer
U.S. 5075027 (1991) [132]	Dixit <i>et al.</i> (Colgate-Palmolive)	High shear dispersing to entrain air; in-line mixing	Stable product
U.S. 4927555 (1990) [133]	Colarusso (Colgate-Palmolive)	Wet grinding with high-speed disperser	Manufacture of thixotropic gel

C. Processing

The manufacture of stable, rheologically built products is not as simple as mixing the ingredients. Proper processing is required to provide the right rheology and density. Both of these attributes are required for a successful LADD. Table 9.11 provides a list of patents related to this subject.

D. Corrosion

Other important considerations must be taken into account when formulating LADDs. Because of the corrosiveness of typical LADDs, ingredients must be added which protect both the machine itself and fine items such as china and silverware. Generally, silicate is added for this purpose, but its inherent alkalinity in aqueous solutions is not always desired. In [Table 9.12](#) several patents are listed which describe other anticorrosion agents.

TABLE 9.12 Patents Relating to Corrosion Inhibition in LADDs

Patent no. and year	Inventor(s) and company	Technology	Claimed benefits
U.S. 6448210 (2002) [135]	Keyes <i>et al.</i> (Johnson Diversey)	Zinc (gluconate)	Glassware protection
U.S. 6083894 (2000) [138]	Keyes <i>et al.</i> (S.C. Johnson)	Zinc (gluconate)	Glassware protection
U.S. 5731277 (1998) [136]	Gary <i>et al.</i> (Lever Bros.)	Aluminum tetrahydroxide	Tableware protection
U.S. 5783539 (1998) [137]	Angevaere <i>et al.</i> (Lever Bros)	Aluminum complex	Tableware protection
U.S. 5698506 (1997) [139]	Angevaere <i>et al.</i> (Lever Bros.)	Aluminum salt	Tableware protection
U.S. 5374369 (1994) [134]	Angevaere <i>et al.</i> (Lever Bros.)	Cyanuric acid and chloroamines, etc.	Prevents tarnishing of silver items
U.S. 4992195 (1991) [140]	Dolan <i>et al.</i> (Monsanto)	Sulfamic acid or water-soluble salts	Protection of silver items; stabilizes bleach present
U.S. 4933101 (1991) [141]	Cilley <i>et al.</i> (Procter & Gamble)	Insoluble inorganic zinc salts	Inhibits glassware corrosion
U.S. 4859358 (1989) [142]	Gabriel <i>et al.</i> (Procter & Gamble)	Long-chain hydroxy fatty acid salts	Protection of silver items

E. Surfactants

Surfactants can provide greasy soil removal, and spot and film benefits to LADDs. The main restriction of surfactants is their ability to create foam. While this is a desirable property in hand dishwashing, it can create significant problems in automatic dishwashing products. They can cause foam which reduces the amount of energy delivered by the spray arms. Additionally, the foam can rise above the machine lip and cause external flooding. The foam can be controlled by using defoaming agents in conjunction with the surfactants, or selecting appropriate nonionic surfactants. Patent examples of these technologies are listed in [Table 9.13](#).

F. Stability

As previously mentioned, a hurdle in formulating bleach-containing LADD products is that many useful ingredients are not stable toward hypochlorite. Table 9.13 lists patents that claim bleach-stable nonionic surfactants and [Table 9.14](#) contains patents relating to the stabilization of LADD components.

TABLE 9.13 Patents Relating to Surfactants in LADDs

Patent no. and year	Inventor(s) and company	Technology	Claimed benefits
U.S. 6034044 (2000) [97]	Scheper <i>et al.</i>	Nonionic surfactants	Superior grease cleaning
WO 94/22800 (1994) [143]	Bunch <i>et al.</i> (Olin)	Epoxy-capped poly(oxyalkylated) alcohol	Reduction in spotting and filming; biodegradable; low foaming
U.S. 4988452 (1991) [144]	Kinstedt <i>et al.</i> (Procter & Gamble)	Capped polyakylene oxide nonionics	Bleach stable
EP 337760 (1989) [145]	Gabriel <i>et al.</i> (Unilever)	Capped polyalkylene oxide nonionics	Bleach stable
U.S. 5073286 (1989) [146]	Otten <i>et al.</i> (BASF)	Sterically hindered polyether polyol nonionics	Bleach stable
U.S. 4438014 (1984) [147]	Scott (Union Carbide)	EO/PO adducts of alkoxylates	Bleach compatible; enhanced low foaming and wetting
U.S. 4436642 (1984) [148]	Scott (Union Carbide)	EO/PO adducts of alkylphenols	Bleach compatible; enhanced low foaming and wetting

G. New Forms

The last few years have seen the introduction of new forms for LADDs. These include both a solid tablet form and, perhaps more importantly, a liquid form delivered in a water-soluble sachet. [Table 9.15](#) lists patents relating to some of these novel products.

VII. AUXILIARY PRODUCTS FOR DISHWASHERS

A. Liquid Prespotters

The automatic dishwasher detergents in today's marketplace, both liquid and powder versions, deliver cleaning performance that is acceptable to most consumers. However, one area in which consumers would like to see product improvement is in cleaning of baked-on, cooked-on, and dried-on food soils. These soils are tenaciously stuck to surfaces and are hard to remove unless strong mechanical forces are applied. To make the cleaning task of such hard-to-remove soils easier, special liquid formulations, often referred to as "prespotters," have been developed.

The idea of a prespotter is to apply the product onto the soiled surface and allow it to stand at ambient temperature over a period of 30 to 60 minutes before cleaning in the dishwasher. This process allows the soil to soften and debond or the adhesive forces between the soil and the substrate to loosen. The conditioned soiled substrate can be easily removed by mechanical and chemical forces in the dishwasher.

TABLE 9.14 Patents Relating to Stabilization of LADD Components

Patent no. and year	Inventor(s) and company	Technology	Claimed benefits
U.S. 5384061 (1995) [149]	Wise (Procter & Gamble)	Chlorine bleach ingredient, phytic acid, rheology stabilizing agent	Enhanced chemical and physical stability
U.S. 5258132 (1993) [150]	Kamel <i>et al.</i> (Lever Bros.)	Wax encapsulation of bleach, enzymes, or of bleach catalysts	Allows for stabilization of incompatible materials in liquid products
U.S. 5230822 (1993) [151]	Kamel <i>et al.</i> (Lever Bros.)	Wax encapsulation of bleach, enzymes, or of bleach catalysts	Allows for stabilization of incompatible materials in liquid products
U.S. 5225096 (1993) [152]	Ahmed <i>et al.</i> (Colgate- Palmolive)	Alkali metal iodate	Improved hypochlorite stability and efficacy
U.S. 5185096 (1993) [153]	Ahmed (Colgate- Palmolive)	Alkali metal iodate	Improved hypochlorite stability and efficacy
U.S. 5229027 (1993) [154]	Ahmed (Colgate- Palmolive)	Water-soluble iodide/iodine mixture	Improved hypochlorite stability and efficacy
U.S. 5200236 (1993) [155]	Lang <i>et al.</i> (Lever Bros.)	Solid core particles encapsulated in wax coating	Coat prolongs time that encapsulated particles remain active in water
EP 533239 (1993) [156]	Tomlinson (Unilever)	Encapsulated bleach	Excellent enzyme stabil- ity; reducing agent
U.S. 5141664 (1992) [157]	Corring <i>et al.</i> (Lever Bros.)	Encapsulation of bleach, bleach precursor, enzymes, surfactants, or perfumes	Uniformly dispersed active particles in a clear gel
EP 414282 (1991) [158]	Behan <i>et al.</i> (Quest)	Encapsulation of perfume in microorganism cells	Protects perfume from oxidizing agents
U.S. 4919841 (1990) [159]	Kamel <i>et al.</i> (Lever Bros.)	Blend of hard and soft waxes for coating bleach, perfumes, enzymes, or surfactants: process for encapsulation	Capsules useful for cleaning compositions

Several prespotter formulations are disclosed in the patent literature. Acidic compositions that contain a mixture of nonionic surfactants and hydrotropes [163], thickened alkaline products with hypohalite bleaches [164,165], and enzyme-containing formulas [166] have all been developed for use as prespotters. Although

TABLE 9.15 Patents on New Forms of LADD

Patent no. and year	Inventor(s) and company	Technology	Claimed benefits
U.S. 6632785 (2003) [161]	Pfeiffer <i>et al.</i> (Unilever)	New form: sachet	Water-soluble sachet; encapsulated bleach
U.S. 6605578 (2003) [160]	Fleckenstein <i>et al.</i> (Colgate-Palmolive)	New form: sachet	Water-soluble container; liquid composition
U.S. 6228825 (2001) [162]	Gorlin <i>et al.</i> (Colgate-Palmolive)	New form: sachet	Water-soluble package; nonaqueous

these products are effective at cleaning tough soils, no product has made it to the marketplace, possibly due to economic factors. However, LADD products can be used as prespotters by applying directly to soiled items.

B. Rinse Aids

As discussed before, consumers judge the performance of automatic dishwasher detergents based on the overall cleaning, filming, and spotting on dishware, glasses, and utensils. Spots and film on glass surfaces are readily noticeable due to the differences in the refractive indices of the glass and the deposits. It is generally recognized that the deposits on glasses are predominantly water-soluble minerals such as salts of alkaline earth metal ions present in the water with proteins and fats of the soil as minor components. Clearly, the condition of the final rinse cycle water largely determines the degree of spotting and filming on glasses. Laboratory assessment indicates that water hardness exceeding 200 ppm as CaCO_3 results in poor performance on glasses and silverware unless the calcium ions are sequestered.

To minimize the mineral deposits and surface-active soil components on articles cleaned in the dishwasher, special formulations called rinse aids are often used for both home and institutional dishwashers. In the U.S. an estimated 40% of households use rinse aids [167]. Rheologically, rinse aid liquids are Newtonian type with viscosities in the range 50 to 200 cP. Their role is to reduce the interfacial tension between the dish- and glassware and the wash water. In this way, a uniformly draining film of the wash water is achieved on the items. Otherwise, uneven wetting will result in spotting and filming or on the items being dried.

Typically, rinse aid formulations for household dishwashers are composed of aqueous solutions containing a nonionic surfactant(s), a complexing agent such as citric acid or polyphosphate, hydrotropes (also known as coupling agents), fragrance, and color. Suitable preservatives are also added to the formulations to prevent the product from bacterial and fungal growth [168]. The pH of the formulations ranges from acidic to alkaline. Normally the rinse aid solution is

injected during the final rinse cycle of dishwashing. A typical dosage of the product per rinse is about 0.3 to 1.0 g/l depending upon the level of nonionic surfactant in the formulation. Most rinse aids contain between 20 and 40% surfactant levels. Excessive or underdosage may have an adverse effect on the spotting and filming on glasses.

1. Ingredients for Rinse Aids

(a) *Nonionic Surfactants.* The heart of the rinse aid formulation is the surfactant and virtually all formulations contain nonionic surfactants. The primary function of the nonionic surfactant is to produce rapid sheeting action, achieving a quick and uniformly draining film which prevents the nonuniform drying of the hard water minerals on the utensil surfaces. Systematic studies have shown that the nonionic surfactants must satisfy the criteria for rinse aid applications, the most important ones of which are discussed below:

1. The nonionic surfactant must be an efficient wetting agent with low foaming characteristics, since excessive foaming not only influences the cleaning but also the rinsing effectiveness.
2. The foaming properties of the nonionic surfactants depend upon the temperature because of their inverse solubility temperature relationship. Above the cloud point they are nonfoamers and some nonionic surfactants may even function as defoamers above their cloud point temperature. Therefore, the nonionic surfactant selected for rinse aid formulations must have a cloud point below the temperature of the rinse water.
3. The aqueous surface tensions of the surfactant solutions must be low, in the range 30 to 40 dyn/cm². The surface tensions should be preferably measured at temperatures close to rinse water temperatures.

The nonionic surfactants commonly used in rinse aid formulations along with their structures are shown in [Table 9.16](#).

(b) *Sequestering Agents.* Sequestering agents such as polyphosphates are added to the rinse formulations in order to condition the rinse cycle water (deactivation of alkaline earth metal ions) and to prevent or delay the formation of water-insoluble compounds like calcium bicarbonate or carbonate. These insoluble precipitates may deposit on glasses and appear as spots or film.

The addition of acidic additives such as citric acid is very popular in European formulations. The theory behind their use is that if sufficient acid is present in the final rinse solution, the acid converts the carbonate and bicarbonate ions into water and carbon dioxide, preventing the formation of insoluble salts. Citric acid formulations may also keep the dishwasher surfaces and nozzle of the spray arms free of limescale deposits. It is also believed that citrate may contribute to the brilliancy or shiny appearance of siliceous surfaces [175].

TABLE 9.16 Nonionic Surfactants for Rinse Aids

Surfactant	Structure
Alkylphenoxy polyethenoxyethanol [169]	$R(C_6H_4)O(CH_2CH_2O)_nCH_2CH_3$
Block polymers of ethylene and propylene oxide [170–172]	$RO(CH_2CH_2O)_n(CH_2CH[CH_3]O)_mH$
Alkylphenoxy polyethenoxybenzyl ethers [173]	$R(C_6H_4)O(CH_2CH_2O)_nCH_2C_6H_5$
Alkyl polyethenoxybenzyl ethers [174]	$R(CH_2CH_2O)_nCH_2C_6H_5$
Ethoxylated alcohols	$R(OCH_2CH_2)_nOH$

(c) *Hydrotropes*. Hydrotropes (Chapter 2) or coupling agents play an important role in formulating rinse aid products. Their main functions include increasing the solubility of the nonionic surfactant in water and thus maintaining the clarity of the formulations. Judicious selection of hydrotropes is important since they may contribute to the foaming and potentially reduce the sheeting efficiency of the nonionic surfactant. Most effective are certain alkylnaphthalene sulfonates and sulfosuccinate esters, since they increase the solubility of the nonionic surfactants without leading to excessive foaming. Other hydrotropes utilized in rinse aid formulations include propylene glycol, isopropanol, and urea. In general, alcohols are not effective solubilizers in rinse aid formulas [175].

2. Typical Rinse Aids

Typical examples of rinse aid formulations are shown in Table 9.17 [176]. Several patents describing rinse aid compositions have been issued. These are listed in Table 9.18.

TABLE 9.17 Examples of Rinse Aid Formulations [176]

Ingredient	I (wt %)	II (wt %)
Plurafac® RA 30 ^a	50	17.5
Plurafac® RA 40 ^a	1	17.5
Isopropanol	24	12
Citric acid, dehydrated	—	25
Deionized water	16	28

^aBASF Corporation.

TABLE 9.18 Patents Relating to Rinse Aids

Patent no. and year	Inventor(s) and company	Technology	Claimed benefits
WO 94/07985 (1994) [177]	De Smet <i>et al.</i> (Procter & Gamble)	Lime soap dispersant; lipase enzyme	Improved spotting and filming
U.S. 5294365 (1994) [178]	Welch <i>et al.</i> (BASF)	Hydroxypolyethers	Low foaming; improved spotting and filming
U.S. 5104563 (1992) [179]	Anchor <i>et al.</i> (Colgate-Palmolive)	Low-molecular-weight polypropylene which interacts with anionic or nonionic surfactants	Improved spotting and filming
GB 2247025 (1992) [180]	van Dijk <i>et al.</i> (Unilever)	Phospholipase A ₁ and/or A ₂	Improved cleaning, filming, and spotting
EP 252708 (1988) [181]	van Dijk <i>et al.</i> (Unilever)	Nonplate-shaped colloids such as silica	Reduced drying time; improved spotting
U.S. 4443270 (1984) [182]	Biard <i>et al.</i> (Procter & Gamble)	Ethoxylated nonionic; organic chelating agent; water-soluble Mg, Zn, Sn, Bi, or Ti salts	Improved spotting and filming
U.S. 4416794 (1983) [183]	Barrat <i>et al.</i> (Procter & Gamble)	Ethoxylated nonionic; organic chelating agent; aminosilane	Improved spotting and filming

VIII. FUTURE TRENDS

The majority of LADDs marketed today deliver performance that is acceptable to consumers. However, economic, environmental, and regulatory pressures necessitate formulators of LADDs to continue to improve the products. Over the last dozen years, machine redesign has consistently improved performance. Recent developments have led to smarter and more efficient machines. Microprocessors and sensors determine most of the washing conditions in modern machines. This has been driven by the need for more energy- and water-efficient machines. Both Europe and the U.S. have seen an explosion of unit dose products that are essentially concentrates, as they are only single-cup products. Exploration in the area of phosphate-free products continues, as state legislatures continue to be under pressure to ban their use in automatic dish detergents. Legislative pressure has also encouraged the exploration of nonchlorine bleaches. The use of enzyme-based formulas has continued to grow, and they now account for about 10% of the LADD market in the U.S.

A. Reduction in Dose Size

Recommended inlet water temperature has dropped as much as 20°F, from 140 to 120°F (60 to 50°C). Sensors then adjust the water temperature, monitor the cleaning, and extend the cycles as needed. The amount of water used has also been reduced. Dishwashers have two cups for dosing detergent: a main wash cup and a prewash cup. The prewash cup has been reduced in size over recent years. All of these changes have led to a more consistent performance for the consumer, and the ability to use less automatic dishwasher detergent. This has also presented the product formulator with a challenge.

One solution for this has been the advent of unit dose. This generally consists of a tablet or sachet form. The sachet form may contain a liquid gel [184]. This is a water-based, enzyme-containing system in a water-soluble polyvinyl alcohol pouch. Recently a new variant has emerged. This is a combination liquid and powder in two separate compartments in a polyvinyl alcohol pouch [185,186]. The powder portion contains traditional enzyme, oxygen bleach chemistry, while the liquid portion contains an organic solvent that enhances “baked-on, burnt-on” cleaning. The liquid can also act as a humectant to control the stability of the active components of the powder portion. These provide about one half the weight of product that would be used for a single closed-cup wash. In the last few years these forms have grown to about 20% of the U.S. market.

The development of more sophisticated unit dose forms continues. An aqueous gel containing encapsulated bleach has been developed [187–189]. It is claimed that these have excellent cleaning properties with minimal spot and film formation.

B. Nonphosphate Products

The low cost-to-performance ratio of phosphates, especially alkali metal triphosphates, makes them the “work-horse” of detergents. Although phosphate builders are safe for humans, they are unfortunately beneficial to algae growth. Therefore, large amounts of phosphate in waste streams lead to eutrophication of lakes and streams. For this reason there have been concerns, especially in Europe, about the heavy use of phosphates in detergent products. In certain regions of the U.S. the quantity of phosphates used in LADDs is regulated by local governments. Therefore, one of the challenges that the automatic dishwasher detergent manufacturers face today is finding a substitute for polyphosphate. Ideally, the phosphate substitute must satisfy several criteria such as:

1. Free from phosphorous and nitrogen.
2. Soluble in water with readily biodegradable characteristics.
3. Chemically stable and compatible with oxygen and/or chlorine bleach
4. Cleaning performance characteristics equal to phosphates.

5. Safety to humans.
6. Economically practical.

Although many builder systems meet most of these criteria, they provide inferior performance. In particular, filming and spotting on glasses is a concern in hard water areas. This is probably the primary reason that nonphosphate liquid products have not found their way into the marketplace.

The search for an alternative to phosphates will continue as evident from the patent activity in the last 5 to 10 years. Many reviews have appeared which compare the characteristics of the more heavily studied alternatives [18,29,38,190–206]. [Table 9.19](#) lists the recent patents on phosphate-free LADD formulations.

C. Hypochlorite-Free Products

Another trend appears to be the formulation toward products containing no hypochlorite bleach. The reason is that the strong oxidizing nature of hypochlorite makes it incompatible with other easily oxidized components, such as nonionic surfactants, fragrances, and enzymes. There is also some concern regarding the possible formation of chlorinated organics [8]. Oxygen bleaches, such as perborates or percarbonates, which liberate peroxide in solution, are being studied to replace chlorine bleach. Being weaker oxidizing agents than halogen bleaches, they are compatible with some oxidizable LADD components. However, there are two main disadvantages of oxygen bleaches. First, they display acceptable performance only at elevated temperatures. Second, they are difficult to formulate in liquid products due to chemical stability problems.

The search for chlorine bleach alternatives as well as development of technologies for stabilizing peroxide bleaches will continue. Microencapsulation technology for formulating LADDs containing chlorine bleaches has shown limited success [150,151,155,159].

D. Enzymatic Products

Although enzyme-based systems comprise the bulk of the powder market, it has only been in recent years that they have emerged in automatic dishwasher gels. Currently enzyme-based liquid products comprise about 10% of the ADD market. This comprises both bottled gels and unit dose sachets. Unlike the powder formulas, liquid enzyme formulas with bleach have not been successfully delivered. Efforts in this area include the development of a gel containing encapsulated bleach [187–189]. New enzymes are continuously being developed that are more bleach stable. As these become commercially viable, new aqueous gel products that provide the benefits of both bleach and enzyme cleaning will be available to the consumer.

TABLE 9.19 Patents Relating to Phosphate-Free LADDs

Patent no. and year	Inventor(s) and company	Technology	Claimed benefits
U.S. 6602837 B1 (2003) [191]	Patel (Procter & Gamble)	Diacyl peroxide	Stain removal from plastics
U.S. 5545344 (1996) [192]	Durbut <i>et al.</i> (Colgate-Palmolive)	Nonaqueous; enzyme	Long-term stability
U.S. 5510048 (1996) [193]	Durbut <i>et al.</i> (Colgate-Palmolive)	Enzyme; nonaqueous	Concentrated; stability
EP 0703974 B1 (1998) [194]	Ambuter <i>et al.</i> (Procter & Gamble)	Enzyme	Concentrated; free of bleach and silicate
EP 0625567 B1 (2001) [195]	Beck <i>et al.</i> (Stockhausen)	Anhydrous	Free of bleach
EP 0530635 B1 (1997) [196]	Golz <i>et al.</i> (Benkisser)	Neutral; carboxylic acid	Free of bleach and silicate
EP 0518721 B1 (1995) [197]	Burbut <i>et al.</i> (Colgate-Palmolive)	Enzyme; nonaqueous	Free of bleach; stability
WO 94/29428 (1994) [190]	Ambuter <i>et al.</i> (Procter & Gamble)	Concentrated; enzymes and stabilizing system	Long-term stability; free of chlorine bleach and silicate
WO 94/05763 (1994) [198]	Rattinger <i>et al.</i> (Unilever)	Pyridine carboxylates	Hypochlorite resistant; biodegradable
EP 561452 (1993) [207]	van Dijk <i>et al.</i> (Unilever)	Biodegradable polyamino acid	Improved scale prevention
U.S. 5169553 (1992) [208]	Durbut <i>et al.</i> (Colgate-Palmolive)	Binary mixture of protease and amylase; nonaqueous	Free of phosphates
WO 91/03541 (1991) [29]	Beaujean <i>et al.</i> (Henkel)	Aluminosilicate; stabilizing electrolyte system	Stable during storage and transport; do not sediment between 5 and 60°C
EP 476212 (1990) [199]	Boutique <i>et al.</i> (Procter & Gamble)	Citrate; C10–C16 alkyl- or alkenyl-substituted succinic acid	Physically stable; good building capacity
DE 3832478 (1988) [209]	Dixit (Colgate-Palmolive)	Aluminosilicate; polycarboxylates	Free of phosphates

REFERENCES

1. Houghton, J., U.S. Patent 7,365, 1865.
2. Meeker, D.A., *The Story of the Hobart Manufacturing Co.*, Newcomer Publications, Princeton University Press, Princeton, NJ, 1960.
3. Morrish, D.H., *History of Dishwashers*, General Electric Co., Louisville, KY, 1967.
4. Cater, D.H., Flynn, M.H., and Frank, P.F., *Inform*, 5, 1095, 1994.
5. Gauthier, F., Schneegans, W., Bernard, L., and Reeve, P., Rohm and Haas France, Sepawa, October 2003.
6. Branna, T., *HAPPI*, 18, 56, 1990.
7. Whalley, G.R., *HAPPI*, 23, 71, 1995.
8. Lake, R.F., in *Proceedings of the 3rd World Conference on Detergents: Global Perspectives*, Montreux, Switzerland, 1993, pp. 108–110.
9. Werdelmann, B., *Soap Cosmet. Chem. Specialties*, 50, 36, 1974.
10. Mizuno, W.G., Detergency, Theory and Test Methods, in *Surfactant Science Series*, Vol. 5, Part III, Marcel Dekker, New York, 1981.
11. Oberle, T.M., *Detergents in Depth*, The SDA, New York, 1974.
12. Gorlin, P., U.S. Patent 6,258,764 to Colgate-Palmolive, 2001.
13. Shulman, J.E., *HAPPI*, 20, 130, 1992.
14. Shulman, J. E. and Robertson, M.S., *Soap Cosmet. Chem. Specialties*, 68, 46, 1992.
15. Richter, F.H., Winkler, E.W., and Baur, R.H., *J. Am. Oil Chem. Soc.*, 66, 1666, 1989.
16. McGrew, G.T., *HAPPI*, 14, 66, 1986.
17. Lange, K.R., *J. Am. Oil Chem. Soc.*, 45, 487, 1968.
18. Hudson, A.P., Woodward, F.E., and McGrew, G.T., *J. Am. Oil Chem. Soc.*, 65, 1353, 1988.
19. van Wazer, J.R., in *Phosphorous and its Compounds*, Interscience, New York, 1958.
20. Shen, C.Y., *J. Am. Oil Chem. Soc.*, 45, 510, 1968.
21. Iler, R. K., *The Chemistry of Silica*, John Wiley, New York, 1979, p. 21.
22. Falcone, J.S., Ed., *Soluble Silicates*, ACS Symposium Series 194, Washington D.C., 1982.
23. Coffey, R. and Gudowicz, T., *Chem. Ind.* 6, 169, 1990.
24. The PQ Corp., Multi-Functional Characteristics of Soluble Silicate, 17-101/1291, 1991.
25. Sharma, A. and Jain, H., *J. Am. Ceram. Soc.*, 86, 1669, 2003.
26. Sharma, A. and Jain, H., *J. Surfactants Detergents*, 7, 111, 2004.
27. The PQ Corp., New Dimensions in Zeolite Detergent Chemistry, VAL-100/1192, 1992.
28. Schwuger, M.J. and Smulders, E.J., in *Surfactant Science Series*, Vol. 20, Marcel Dekker, New York, 1987, p. 371.
29. Beaujean, H.F., Bode, J., Paasch, S., Schwadtke, K., Smulders, E., and Sung, E., WO Patent 91/03541 to Henkel, 1991.
30. Dixit, N.S., U.S. Patent 4,971,717 to Colgate-Palmolive, 1990.
31. Dixit, N.S., U.S. Patent 5,229,026 to Colgate-Palmolive, 1993.
32. Rohm & Haas, Acusol 445 Series Detergent Polymers for Machine Dishwashing, FC-131, 1993.
33. BASF Specialty Chemicals, Sokalan Polymeric Dispersing Agents, 49.
34. Schaffer, J.F. and Woodhams, R.T., *Tenside Det.* 16, 240, 1979.

35. Hunter, M., da Motta Marques, D.M.L., Lester, J.N., and Perry, R., *Environ. Technol. Lett.*, 9, 1, 1988.
36. Dwyer, M., Yeoman, S., Lester, J.N., and Perry, R., *Environ. Technol.*, 11, 263, 1990.
37. Grilli, M.P. and Capucci, A., *Toxicol. Lett.*, 25, 137, 1985.
38. Crutchfield, M.M., *J. Am. Oil Chem. Soc.*, 55, 58, 1978.
39. Rosen, M.J. and Zhu, Z.H., *J. Am. Oil Chem. Soc.*, 69, 667, 1992.
40. Dow Chemicals, Dowfax Anionic Surfactants for High-Performance Products, 1994.
41. Scardera, M. and Scott, R.N., U.S. Patent 4,070,298 to Olin, 1978.
42. Jeschke, R., Schmidt, K., Lange, F., and Koren, K., WO Patent 92/20768 to Henkel, 1992.
43. Dahanayake, M. and Hashem, M., *Soap Cosmet. Chem. Specialties*, 65, 39, 1989.
44. Surutzidis, A. and Fisk, A.A., European Patent 593841 A1 to Procter & Gamble, 1994.
45. Kurzendörfer, C., Seiter, W., Beaujean, H., Block, C., and Holderbaum, T., WO Patent 94/12603 to Henkel, 1994.
46. Coons, D.M., *J. Am. Oil Chem. Soc.*, 55, 104, 1978.
47. Church, J.A., *Ind. Eng. Chem. Res.*, 33, 239, 1994.
48. Dalgaard, L.H., Kochavi, D., and Thellersen, M., *Inform*, 2, 532, 1991.
49. Farooq, A., Mehreteab, A., Broze, G., Dixit, N., and Hsu, D., *J. Am. Oil Chem. Soc.*, 72, 843, 1995.
50. Baxter, S.L., U.S. Patent 4,950,416 to Vista Chemical, 1990.
51. Wise, R.M., U.S. Patent 4,941,988 to Procter & Gamble, 1990.
52. Drapier, J., Gallant, C., Laitem, L., Delsignore, M., Shevade, M., Rounds, R., Kenkare, D., Davan, T., and Dixit, N.S., U.S. Patent 5,427,707 to Colgate-Palmolive, 1995.
53. Marshall, J.L., Hall, D.L., Ambuter, H., and Fitch, E.P., U.S. Patent 5,691,292 to Procter & Gamble, 1997.
54. Drapier, J. and Dixit, N.S., U.S. Patent 5,413,727 to Colgate-Palmolive, 1995.
55. Dixit, N.S., Shevade, M., Rounds, R., and Delsignore, M., U.S. Patent 5,252,241 to Colgate-Palmolive, 1993.
56. Shevade, M., Delsignore, M., Dixit, N.S., and Kenkare, D., U.S. Patent 5,252,241 to Colgate-Palmolive, 1993.
57. Dixit, N.S., Farooq, A., Rounds, R.S., and Shevade, M., U.S. Patent 5,232,621 to Colgate-Palmolive, 1993.
58. Principe, M., McCandlish, E.F., and Loprest, F.J., U.S. Patent 5,188,752 to Colgate-Palmolive, 1993.
59. Dixit, N.S., and Davan, T., U.S. Patent 5,098,590 to Colgate-Palmolive, 1992.
60. Drapier, J., Gallant, C., Wouters, F., and Laitem, L., U.S. Patent 5,057,237 to Colgate-Palmolive, 1991.
61. Dixit, N.S., U.S. Patent 4,836,946 to Colgate-Palmolive, 1989.
62. Chazard, G., Drapier, J., Gallant, C., and van De Gaer, D., U.S. Patent 4,801,395 to Colgate-Palmolive, 1989.
63. Drapier, J., Gallant, C., van De Gaer, D., and Delvenne, J., U.S. Patent 4,752,409 to Colgate-Palmolive, 1988.
64. Wise, R.M., U.S. Patent 5,169,552 to Procter & Gamble, 1992.
65. Elliot, D.L., and Sisco, R.M., U.S. Patent 5,135,675 to Lever Brothers, 1992.

66. Prince, M.J., and Glassco, T.H., U.S. Patent 5,130,043 to Procter & Gamble, 1992.
67. Donker, C.B., WO Patent 89/04359 to Unilever, 1989.
68. Julemont, M. and Marchal, M., U.S. Patent 4,740,327 to Colgate-Palmolive, 1988.
69. Taraschi, F.A., U.K. Patent GB 2168377 A to Procter & Gamble, 1986.
70. Kolodny, E.R. and Liebowitz, E., WO Patent 83/03621 to American Home Products, 1983.
71. Dixit, N.S., U.S. Patent 5,368,766 to Colgate-Palmolive, 1994.
72. Dixit, N.S., U.S. Patent 5,298,180 to Colgate-Palmolive, 1994.
73. Dixit, N.S., U.S. Patent 5,205,953 to Colgate-Palmolive, 1993.
74. Roselle, B.J., U.S. Patent 4,824,590 to Procter & Gamble, 1989.
75. Lockhead, R.Y., Sauer, C.E., and Nagarajan, M.K., Hypochlorite Tolerant Polymeric Rheology Modifiers, presented to the American Oil Chemists Society, Baltimore, MD, 1990.
76. Laba, D., Ed., *Cosmetic Science and Technology Series*, Vol. 13, Marcel Dekker, New York, 1993.
77. Ferry, J.D., in *Viscoelastic Properties of Polymers*, 3rd ed., John Wiley, New York, 1980, p. 40.
78. Sherman, P., in *Industrial Rheology*, Academic Press, London, 1970.
79. Walters, K., in *Rheometry: Industrial Applications*, Wiley, New York, 1980.
80. Tadros, T.F., *Colloids Surf.*, 18, 137, 1986.
81. Russell, W.B., *J. Rheology*, 24, 287, 1980.
82. Goodwin, J.W., in *Surfactants*, Tadros, T.F., Ed., Academic Press, New York, 1984.
83. Heywood, N., *Chem. Eng.*, 415, 16, 1985.
84. Dzwj, N.Q. and Boger, D.V., HaakeBuchler Instruments Inc., technical bulletin PB-856.
85. Bowles, R.L., *et al.*, *Modern Plastics*, 32, 142, 1955.
86. Casson, N., in *Rheology of Dispersed Systems*, Miles, C.C., Ed., Pergamon Press, New York, 1959.
87. Asbeek, A.W., *Official Digest*, 33, 65, 1961.
88. Gabriel, S.M. and Roselle, J., U.S. Patent 4,859,358 to Procter & Gamble, 1989.
89. Corring, R. and Gabriel, R., U.S. Patent 5,141,664 to Lever Brothers, 1992.
90. ASTM method D 3556-85 (Reapproved 1995), 2000, V15.04, p. 367.
91. Mausner, M. and Schlageter, M., *Household Personal Prod. Ind.*, Jan., 59, 1982.
92. Peart, M.V.K., Ph.D. thesis, Purdue University, 1969.
93. Association of Home Appliance Manufacturers, ANSI/AHAM DW-1-1992.
94. Chemical Specialties Manufacturers Associations, Inc., Detergents Division Test Methods Compendium, 1985.
95. ASTM method D 3565-89, 2000, V15.04, p. 372.
96. Patel, R.N., U.S. Patent 6,602,837 to Procter & Gamble, 2003.
97. Scheper, W.M., U.S. Patent 6,034,044 to Procter & Gamble, 2000.
98. Goldstein, A.S., U.S. Patent 5,929,008 to Procter & Gamble, 1999.
99. Gorlin, P., Kenkare, D., and Phillips, S., U.S. Patent 5,698,507 to Colgate-Palmolive, 1997.
100. Durbat, P., Fahim, F.U., and Drapier, J., U.S. Patent 5,618,456 to Colgate-Palmolive, 1997.
101. Sadlowski, E., U.S. Patent 5,597,789 to Procter & Gamble, 1997.

102. Burbut, P., Ahmed, F., and Drapier, J., U.S. Patent 5,545,344 to Colgate-Palmolive, 1996.
103. Kenkare, D., Dixit, N., and Durbut, P., U.S. Patent 5,527,483 to Colgate-Palmolive, 1996.
104. Fair, M.J. and Nicholson, J.R., U.S. Patent 5,372,740 to Lever Brothers Co., 1994.
105. Keenan, A.C., Kirk, T.C., McCallum, T.F., III, Shulman, J., Tallent, R.J., and Weinstein, B., U.S. Patent 5,858,944, 1999.
106. Krishnan, S., U.S. Patent 5,318,715 to Colgate-Palmolive, 1994.
107. Sadlowski, E.S., WO Patent 94/25557 to Procter & Gamble, 1994.
108. van Dijk, W.R. and Khoshdel, E., WO Patent 94/17170, 1994.
109. Adler, D.E., McCallum, T.F., Shulman, J.E., and Weinstein, B., U.S. Patent 5,308,532 to Rohm & Haas, 1994.
110. Ahmed, F.U., Durbut, P., and Drapier, J., U.S. Patent 5,240,633 to Colgate-Palmolive, 1993.
111. Ahmed, F.U. and Bochis, K., U.S. Patent 5,164,106 to Colgate-Palmolive, 1992.
112. Ahmed, F.U., Buck, C.E., and Jakubicki, G., U.S. Patent 5,094,771 to Colgate-Palmolive, 1992.
113. Ahmed, F.U. and Bochis, K., U.S. Patent 5,076,952 to Colgate-Palmolive, 1991.
114. Ahmed, F.U. and Buck, C.E., U.S. Patent 4,970,016 to Colgate-Palmolive, 1990.
115. Ahmed, F.U. and Buck, C.E., U.S. Patent 4,968,446 to Colgate-Palmolive, 1990.
116. Ahmed, F.U. and Buck, C.E., U.S. Patent 4,968,445 to Colgate-Palmolive, 1990.
117. Frankena, H., U.S. Patent 4,931,217 to Lever Brothers, 1990.
118. van Dijk, W.R., European Patent 271155 A2 to Unilever, 1988.
119. Laitem, L., Delvaux, M., Broze, G., and Bastin, D., U.S. Patent 4,753,748 to Colgate-Palmolive, 1988.
120. Goedhart, M., Gortemaker, F.H., Kemper, H.C., and Kielman, H.S., U.S. Patent 4,597,886 to Lever Brothers, 1986.
121. de Ridder, J.J.M., Hollingsworth, M.W., and Robb, I.D., U.S. Patent 4,539,144 to Lever Brothers, 1985.
122. Kaneko, T.M., U.S. Patent 4,306,987 to BASF Wyandotte, 1981.
123. Bahary, W.S. and Hogan, M.P., U.S. Patent 5,336,430 to Lever Brothers, 1994.
124. Kreischer, P.H., European Patent 304328 A2 to Unilever, 1989.
125. Fox, D.J., van Blarcom, D., and Rubin, F.K., U.S. Patent 4,260,528 to Lever Brothers, 1981.
126. Bush, W.G. and Braun, V.D., U.S. Patent 4,226,736 to Drackett, 1980.
127. Corring, R., U.S. Patent 5,366,653 to Lever Brothers, 1994.
128. Angevaere, P.A. and Gary, R.G., U.S. Patent 5,624,892 to Lever Brothers, 1997.
129. Broadwell, R. and Shevade, M., U.S. Patent 5,395,547 to Colgate-Palmolive, 1995.
130. Broadwell, R., Shevade, M., and Kenkare, D., U.S. Patent 5,246,615 to Colgate-Palmolive, 1993.
131. Gabriel, S.M., Glassco, T.H., Ambuter, H., and Fitch, E.P., WO Patent 93/21298 to Procter & Gamble, 1993.
132. Dixit, N.S. and Davan, T., U.S. Patent 5,075,027 to Colgate-Palmolive, 1991.
133. Colarusso, R.J., U.S. Patent 4,927,555 to Colgate-Palmolive, 1990.
134. Angevaere, P.A. and Gary, R.G., U.S. Patent 5,374,369 to Lever Brothers, 1994.
135. Keyes, G.B., Seaman, C.E., and Kasson, J.K., U.S. Patent 6,448,210 to Johnson Diversey, 2002.

136. Gary, R.G., Angevaare, P.A.J.M., Jensen, A.O., and Van Gorkom, L., U.S. Patent 5,731,277 to Lever Bros., 1998.
137. Angevaare, P.A. and Gary, R.G., U.S. Patent 5,783,539 to Lever Bros., 1998.
138. Keyes, G.B., Seaman, C., and Kassen, J.K., U.S. Patent 6,083,894 to S.C. Johnson Commercial Markets, Inc., 2000.
139. Angevaare, P.A. and Gary, R.G., U.S. Patent 5,698,506 to Lever Bros., 1997.
140. Dolan, M.J. and Jakse, F.P., U.S. Patent 4,992,195 to Monsanto, 1991.
141. Cilley, W.A. and Wise, R.M., U.S. Patent 4,933,101 to Procter & Gamble, 1991.
142. Gabriel, S.M. and Roselle, B.J., U.S. Patent 4,859,358 to Procter & Gamble, 1989.
143. Bunch, H.S., Groom, T., Grosser, F.R., Scardera, M., Targos, T.S., and Vanover, A.R., WO Patent 94/22800 to Olin, 1994.
144. Kinstedt, G.C. and Myers, S.L., U.S. Patent 4,988,452 to Procter & Gamble, 1991.
145. Gabriel, R., Aronson, M.P., and Steyn, P.L., European Patent 337760 A2 to Unilever, 1989.
146. Otten, J.G., Parker, E.J., and Kinnaird, M.G., U.S. Patent 5,073,286 to BASF, 1989.
147. Scott, R.J., U.S. Patent 4,438,014 to Union Carbide, 1984.
148. Scott, R.J., U.S. Patent 4,436,642 to Union Carbide, 1984.
149. Wise, R.M., U.S. Patent 5,384,061 to Procter & Gamble, 1995.
150. Kamel, A.A., Lang, D.J., Hanna, P.A., Gabriel, R., Theiler, R., and Goldman, A.S., U.S. Patent 5,258,132 to Lever Brothers, 1993.
151. Kamel, A.A., Lang, D.J., Hanna, P.A., Gabriel, R., and Theiler, R., U.S. Patent 5,230,822 to Lever Brothers, 1993.
152. Ahmed, F.U. and Shevade, M., U.S. Patent 5,225,096 to Colgate-Palmolive, 1993.
153. Ahmed, F.U., U.S. Patent 5,185,096 to Colgate-Palmolive, 1993.
154. Ahmed, F.U., U.S. Patent 5,229,027 to Colgate-Palmolive, 1993.
155. Lang, D.J., Kamel, A.A., Hanna, P.A., Gabriel, R., and Theiler, R., U.S. Patent 5,200,236 to Lever Brothers, 1993.
156. Tomlinson, A.D., European Patent 533239 A2 to Unilever, 1993.
157. Corring, R. and Gabriel, R., U.S. Patent 5,141,664 to Lever Brothers, 1992.
158. Behan, J.M., Birch, R.A., and Perring, K.D., European Patent 414282 A1 to Quest International, 1991.
159. Kamel, A., Hurckes, L.C., and Morelli, M.M., U.S. Patent 4,919,841 to Lever Brothers, 1990.
160. Fleckenstein, M. and Zyzyck, L., U.S. Patent 6,605,578 to Colgate-Palmolive, 2003.
161. Pfeiffer, N., Ghatlia, N.D., and Secemski, I.I., U.S. Patent 6,632,785 to Unilever Home & Personal Care USA, 2003.
162. Gorlin, P., Calabro, D., Martin, E., Fiore, M., and Canady, V., U.S. Patent 6,228,825 to Colgate-Palmolive, 2001.
163. Altenschoeper, T., Jeschke, P., and Wisotzki, K., U.S. Patent 4,818,427 to Henkel, 1989.
164. Rupe, L.A., Tuthill, L.B., and Leikhim, J.W., U.S. Patent 4,116,851 to Procter & Gamble, 1978.
165. Leikhim, J.W., U.S. Patent 4,116,849 to Procter & Gamble, 1978.
166. McCandlish, E., Canadian Patent 2,093,783 to Colgate-Palmolive, 1993.
167. Roberts, G. and Welch, M.C., *Soap Cosmet. Chem. Specialties*, 71, 58, 1995.
168. Stache, H., in *Tensid-Taschenbuch*, Stache, H., Ed., Hanser, Munich, 1981, p. 484.

169. Wilson, J.L., Mizuno, W.G., and Crecelius, S.B., *Soap Cosmet. Chem. Specialties*, 34, 48, 1958.
170. Wyandotte Chemical Pluronic Grid, bulletin 189-61.
171. Reich, H.E., Patton, J.T., and Francis, C.V., *Soap Cosmet. Chem. Specialties*, 37, 55, 1961.
172. Fischer, W. K., in *Fatty Alcohols*, Henkel, Dusseldorf, 1982, p. 187.
173. Niederhauser, W. D. and Smialkowski, E.J., U.S. Patent 2,856,434 to Rohm & Haas, 1958.
174. Rue, L.M., Brunelle, T.E., and Mizuno, W.G., U.S. Patent 3,444,242 to Economics Laboratory, 1969.
175. Parker, E. J. and Schoene, K.F., *HAPPI*, 25, 83, 1988.
176. Heitland, H. and Marsen, H., in *Surfactants in Consumer Products*, Falbe, J., Ed., Springer-Verlag, Heidelberg, 1987, p. 321.
177. De Smet, B.L.A., Pluyter, J.G.L., and Jones, L.A., WO Patent 94/07985 to Procter & Gamble, 1994.
178. Welch, M.C., Otten, J.G., and Schenk, G.R., U.S. Patent 5,294,365 to BASF, 1994.
179. Anchor, M.J. and Roelofs, R.R., U.S. Patent 5,104,563 to Colgate-Palmolive, 1992.
180. van Dijk, W., Gerardus, A., and Bastein, T.M., British Patent GB 2247025 to Unilever, 1992.
181. van Dijk, J., Kielman, H.S., Los, L., and Verheul, R.C.S., European Patent 252708 A2 to Unilever, 1988.
182. Biard, D. and Lodewick, R., U.S. Patent 4,443,270 to Procter & Gamble, 1984.
183. Barrat, C.R., Walker, J.R., and Wevers, J., U.S. Patent 4,416,794 to Procter & Gamble, 1983.
184. Kaiser, R., Guzman, M., and Wiedmann, R., WO Patent 02/16541 to Reckitt Benckiser, 2002.
185. Sharma, S., Kinloch, J.I., Greener, S.J., and Lynde, K.R., U.S. Patent Application 2002/0137648 A1 to Procter & Gamble, 2002.
186. Smith, D.J., Sharma, S., Kinloch, J.I., and Greener, S.J., U.S. Patent Application 2002/0142930 A1 to Procter & Gamble, 2002.
187. Pfeiffer, N., Ghatlia, N.D., and Secemski, I.I., U.S. Patent 6,475,977 B1 to Unilever, 2002.
188. Pfeiffer, N., Ghatlia, N.D., and Secemski, I.I., U.S. Patent 6,492,312 B1 to Unilever, 2002.
189. Pfeiffer, N., Ghatlia, N.D., and Secemski, I.I. U.S. Patent 6,632,785 B2 to Unilever, 2003.
190. Ambuter, H. and Alwart, T.S., WO Patent 94/29428 to Procter & Gamble, 1994.
191. Patel, R.H., U.S. Patent 6,602,837 B1, to Procter & Gamble, 2003.
192. Durbot, P., Ahmed, F.U., and Drapier, J., U.S. Patent 5,545,344 to Colgate-Palmolive, 1996.
193. Durbot, P., Ahmed, F.U., and Drapier, J., U.S. Patent 5,510,048 to Colgate-Palmolive, 1996.
194. Ambulter, H. and Todd, S., EP 0703974 B1 to Procter & Gamble, 1998.
195. Beck, R., Krause, F., and Shouenkaes, U., EP 0625567 B1 to Stockhausen, 2001.

196. Golz, K., Hertling, L., Magg, H., and Washenbach, G., EP 0530635 to Benkisser, 1997.
197. Durbut, P., Ahmed, F., and Drapier, J. EP 0518721 B1 to Colgate Palmolive, 1997.
198. Rattinger, G.B., Cotter, B., and Fair, M.J., WO Patent 94/05763 to Unilever, 1994.
199. Boutique, M.J., and Depoot, K.J.M., European Patent 476212A1 to Procter & Gamble, 1992.
200. Matzner, E.A., Crutchfield, M.M., Langguth, R.P., and Swisher, R.D., *Tenside Deterg.*, 10, 239, 1973.
201. Niewenhuizen, M.S., Kieboom, A.P.G., and van Bekkum, A.P.G., *J. Am. Oil Chem. Soc.*, 60, 120, 1983.
202. Kemper, H.C., Martens, R.J., Nooi, J.R., and Stubbs, C.E., *Tenside Deterg.*, 12, 47, 1975.
203. Santhanagopalan, S., Raman, H., and Suri, S.K., *J. Am. Oil Chem. Soc.*, 61, 1267, 1984.
204. Madden, R.E., Edwards, T.G., Kaiser, C.B., and Jaglowski, R.G., *Soap Cosmet. Chem. Specialties*, 50, 38, 1974.
205. Trulli, F. and Santacesaria, E., *Chimoggi*, 8, 13, 1993.
206. Gauthier, F., *Comun. J. Com. Esp. Deterg.*, 24, 109, 1993.
207. van Dijk, W.R., Rocourt, A.P.A.F., and van Drunen, R.W.P., European Patent 561452 A1 to Unilever, 1993.
208. Durbut, P., Ahmed, F., and Drapier, J., U.S. Patent 5,169,553 to Colgate-Palmolive, 1992.
209. Dixit, N.S., German Patent DE 3832478 A1 to Colgate-Palmolive, 1988.