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Light-Duty Liquid Detergents

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I. INTRODUCTION

Light-duty liquid detergents (LDLDs) are mixtures of surfactants dispersed in water and, as opposed to heavy-duty liquid detergents (HDLDs), are free of builders or alkaline inorganics. They are used primarily for hand washing of dishes, glasses, pots and pans, and other cooking and serving utensils. They are also used for washing hands, cleaning kitchen countertops, cutting boards, stove surfaces, and less often for washing delicate fabrics and general household cleaning.

Consumers expect LDLDs to clean, foam, and be mild to their hands. In addition, many consumers have come to want long-lasting foam, pleasing appearance and fragrance, ease of rinsing, safety for dishes, consumers, and the environment, convenient packaging and ease of dispensing, and good value. In the developed markets, LDLDs are now more and more concentrated, some are antibacterial for those concerned about family health, and some are more experiential. With the introduction of these “ultras,” antibacterial, and sensorial variants of LDLDs in the 1990s, the face of the hand dishwashing liquid market in the developed markets has changed significantly. In the developing markets, LDLDs are in general more dilute with lower active levels and generally do not have the added benefits (such as antibacterial ability or the “aromatherapy” experience). However, the fundamental consumer need is still a dishwashing liquid that cleans fast, is convenient to use, and is not too expensive.

The LDLD market is worth over $900 million in the U.S. [1]. In a recent Habits and Practices study [2] conducted by Colgate-Palmolive in the U.S., it was found that an average household has on average 6.8 main meals per week. An LDLD is used to some extent after 94% of these meals. This is despite the fact that 60% of households have an automatic dishwasher (which is the highest incidence of these appliances in homes in the world). Even with the popularity of automatic dishwashers, a great deal of dishwashing is still performed manually; in particular the toughest to clean items are mostly washed by hand rather than in a dishwasher (86% vs. 16%).

The literature specifically devoted to the discussion of LDLDs is limited [3–11]. The advances in technology in this area are primarily documented in patents.

This chapter attempts to provide a thorough review of all aspects of LDLDs, including discussions on typical compositions and ingredients, the hand dishwashing process and the chemistry involved, test methods and performance evaluations, formulation technology, and new products and future trends. The LDLD chapter from the first edition [11] has been updated and sections rewritten to reflect the recent advances in technology and new products and future trends in the markets.

II. TYPICAL COMPOSITION AND INGREDIENTS

A. Typical Composition

LDLDs consist of a mixture of ingredients designed to provide cleaning, foaming, solubilization, preservation, fragrance, color, and in some cases antibacterial action. A typical light-duty liquid composition is detailed in Table 7.1.

Surfactants are the main active ingredients in an LDLD formulation and usually make up the bulk of the solids. Surfactants are surface-active agents and

TABLE 7.1 Typical Light-Duty Liquid Composition

Ingredient	Content (%)	Purpose
Surfactants	1–50	Cleaning, foaming
Hydrotrope	0–10	Phase stability, solubility
Salts	<3	Viscosity control
Preservative	<0.1	Micro stability
Fragrance	0.1–1	Aesthetics
Dye	<0.1	Aesthetics
Other Additives	0–3	Chelant, antibacterial agent, enzymes, divalent ions, UV stabilizer
Water	Balance	

TABLE 7.2 Typical Physical and Chemical Characteristics of Light-Duty Liquid Detergents

Characteristic	Typical value
Viscosity, cP	100–500
pH	5–8
Cloud point, °C	<5
Clear point, °C	<10
Solids level, %	10–50
Specific gravity	1.0–1.1

their function is to penetrate and loosen soil, enhance water absorption and wetting of surfaces, suspend, disperse, and emulsify soil in water, and generate and stabilize foam.

Typical physical characteristics of LDLDs are summarized in Table 7.2. They are generally slightly viscous, Newtonian fluids with viscosities in the range 100 to 500 cP. The pH has always typically been near neutral (pH = 5 to 7) to match the natural pH range of the skin. Very recently more extremes in product pH have come onto the market with the relaunch of some of Procter & Gamble's products in the U.S. (pH = 8 to 8.5) and new antibacterial products by Colgate-Palmolive in Europe (pH = 3.5). LDLDs are usually between 10 and 50% solids in water.

B. Ingredients

1. Surfactants

The primary cleaning ingredients in hand dishwashing liquids are surfactants. Surfactants are also responsible for providing the foaming, which is an important sensory indicator of efficacy for consumers. Another factor that is important to the consumer is mildness to the skin, as hand dishwashing is one cleaning task in which the hands are exposed to the cleaning solution for an extended time. Surfactants, since they are present in the formula in the largest amount, contribute the most to the irritation or lack of irritation of a product. The type of surfactants typically used in LDLDs are anionics and to a lesser degree nonionics and amphoterics. Cationics have not been used historically because of their lesser cleaning ability and incompatibility with anionic surfactants. Table 7.3 summarizes some of the surfactants and their structures falling into these three classes (anionic, nonionic, and amphoteric) that are found in LDLDs.

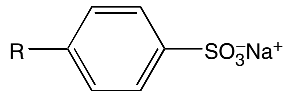
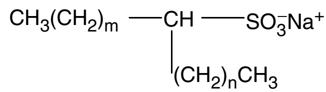
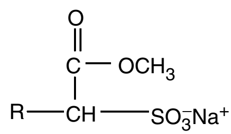
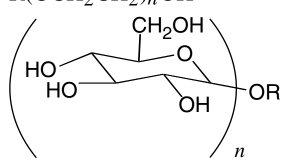
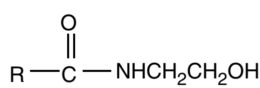
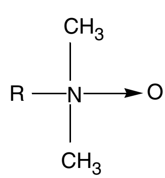
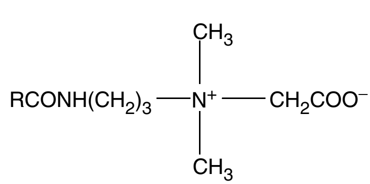
Anionic surfactants have been used predominantly because of their availability, good cleaning properties, excellent foaming properties, and low cost [12]. The anionics that have been most widely used either have a sulfonate (SO_3^-) or sulfate (OSO_3^-) head group. Some common sulfonates are linear alkylbenzene sulfonate (LAS), α-olefin sulfonate (AOS), and paraffin sulfonate (PS, also referred to as secondary alkane sulfonate, SAS). Some typical sulfates are alkyl sulfate (e.g., sodium lauryl sulfate, SLS) and alkylethoxy sulfate (AEOS or more specifically sodium lauryl ethoxy sulfate, SLES), which differ only by the number of moles of ethylene oxide groups. Another anionic surfactant used on a limited scale is alpha sulfomethyl ester (ASME). In general, ASMEs have excellent detergency and are potential substitutes for LAS [13]. In the U.S. (and much of the rest of the world) LAS and AEOS are the most commonly used anionics, while in Europe PS is the major anionic used.

Nonionic surfactants have been used to a lesser extent because of their lower foaming performance and higher cost [14]. However, when used in combination with anionic surfactants they provide benefits to the overall formulation, such as mildness, improved wetting, foam boosting, and foam stabilization. Some nonionics that are found in LDLDs are ethoxylated alcohols, in particular 11-carbon chains with 9 moles of ethoxylation (e.g., Neodol 1-9 from Shell). Surfactants derived from sugar, such as alkylpolyglycosides (APG) [15] and fatty acid glucamides [16], are also used in many hand dishwashing formulations.

Another important class of nonionics are amine oxides, such as DMDAO (dimethyldodecyl amine oxide) and CAPAO (cocoamidopropyldimethyl amine oxide). This type of surfactant is nonionic at pH values above its pK_a and cationic below that point. When functioning as a nonionic, amine oxides have many useful properties. They interact strongly with anionics which can result in performance benefits [17]. Amine oxides help to mitigate anionic surfactant irritation, act as foam stabilizers, and can also function to improve grease removal.

Amphoteric surfactants, in particular betaines, especially cocoamidopropyl betaine, typically provide synergistic benefits with anionic surfactants [18]. Similar to the benefits of amine oxides, they have been found to mitigate the inherent

TABLE 7.3 Surfactants Commonly Used in Light-Duty Liquid Detergents

Chemical description	Chemical structure
Anionic surfactants	
Alkylbenzene sulfonate	
Paraffin sulfonate	
α-Olefin sulfonate	$R–CH_2–CH{=}CH–H_2–SO_3^-\ Na^+$
Alkyl sulfate	$R–OSO_3^-\ Na^+$
Alkylethoxy sulfate	$R–(OCH_2CH_2)_n–OSO_3^-\ Na^+$
Alpha sulfomethyl ester	
Nonionic surfactants	
Alcohol ethoxylate	$R(OCH_2CH_2)_nOH$
Alkylpolyglycoside	
Fatty acid glucamide	
Amine oxide	
Amphoteric surfactants	
Cocoamidopropyl betaine	

irritation of anionics, boost foaming and foam stability, and enhance grease removal. Taking proper advantage of positive surfactant interactions allows for the use of overall less total surfactant for similar performance benefits.

Surfactant suppliers [19] are concentrating their research on improving the cost/performance attributes of the surfactants. Their efforts have been and are focused on:

- The ability to remove and emulsify the suspended soil.
- Foaming and foam stability in the presence of soils.
- Solubility in the aqueous phase.
- The ability to coexist with other ingredients under extreme conditions as well as at room temperature.
- A good environmental profile.

2. Foam Stabilizers

Foam is an important visual signal for LDLDs. While there is no direct correlation between foam and cleaning, consumers in general use foam volume and foam persistence to judge the performance of an LDLD. There is a wide variety of stabilizers for foam [20]. Among the most commonly used in LDLDs are the following:

- Fatty alkanol amides, such as LMMEA (lauric/myristic monoethanol amide), LMDEA (lauric/myristic diethanol amide), CDEA (cocodiethanol amide), and CMEA (cocomonoethanol amide). (Although recently there have been negative reports about DEA, diethanol amides [21].)
- Amine oxides, such as DMDAO (dimethyldodecyl amine oxide) and DMMAO (dimethylmyristyl amine oxide).

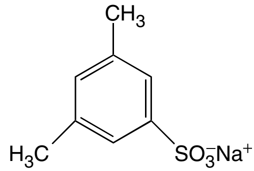
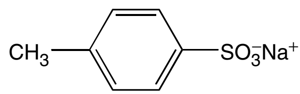
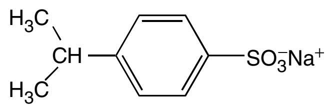
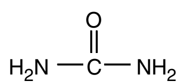
Details of fatty alkanol amides and amine oxides commonly used as foam stabilizers in LDLDs can be found in the literature [22].

3. Hydrotropes

Hydrotropes are often added to an LDLD to help solubilize certain surfactants or other materials that are not easily soluble in water to ensure the stability of the formulation. The fundamental properties of hydrotropes and their hydrotropic action in liquid detergents are discussed in Chapter 2. The addition of a hydrotrope affects the formula viscosity and cloud/clear points.

The hydrotropes most widely used in LDLDs are sodium xylene sulfonate (SXS), sodium cumene sulfonate (SCS), sodium toluene sulfonate (STS), urea, and ethanol, as shown in Table 7.4. SXS, SCS, and ethanol are the most often used hydrotropes in LDLDs since they are nearly odorless and colorless. Urea is an effective and cheap hydrotrope; however, it has been found to raise the pH

TABLE 7.4 Hydrotropes Commonly Used in Light-Duty Liquid Detergents

Hydrotrope	Chemical structure
Sodium xylene sulfonate (SXS)	
Sodium toluene sulfonate (STS)	
Sodium cumene sulfonate (SCS)	
Urea	
Ethanol	CH_3CH_2OH

of a formulation upon aging, which could potentially result in an ammonia odor. Urea is also a good nutrient for bacteria. With proper attention toward pH and preservation, urea can be utilized. Other molecules used as hydrotropes include isopropanol, propylene glycol, and polyethylene glycol ethers.

4. Minor Ingredients

Many minor ingredients are added at the level of less than 1% and mainly to affect product aesthetics. Examples of these include fragrances, dyes, preservatives, chelators, viscosity modifiers, and pH modifiers. The fragrance and color of an LDLD are of critical importance to its success. The selection of these, together with packaging, creates the image for the product.

Preservatives are often needed to prevent microbial and fungal growth in LDLDs. Preservatives commonly used are formaldehyde, gluteraldehyde, benzoic acid, Kathon®, Dowicil®, Bronopol®, various esters of hydroxybenzoic acid, and others.

Chelants are used to ensure that no precipitation occurs on aging. The most common problem is iron, which is introduced as an impurity from surfactants and salts. The chelants most commonly used are EDTA, HEDTA, citrate salts, and disodium diethylene pentaacetate.

Viscosity modifiers are used to achieve the desired product viscosity. These include alcohols, salts, polymers, and hydrotropes. Viscosity adjustment with polymers, particularly in the high surfactant concentrations of "ultra" LDLD formulations, can be challenging. Acids, such as citric or sulfuric acids, or bases, such as hydroxide, are also added to bring the product pH to the desired level.

In certain products, specialty ingredients are also added for extra benefits, specific aesthetic effects, or for marketing claims. Some examples of these ingredients include antibacterial agents, enzymes, protein, lemon juice, opacifier, abrasives, polymers, bleach, and aloe. Antibacterial agents, such as triclosan, are popular in U.S. hand dishwashing liquids and provide a benefit to consumers of killing germs on hands. Recently, Procter & Gamble has introduced enzymes into two of its hand dishwashing liquids for cleaning or skin conditioning benefits. Polymers have been added to LDLDs in order to improve foaming, or grease release, or to enhance mildness.

III. HAND DISHWASHING

A. Variables

1. Mechanical Action

Mechanical action is very important in hand dishwashing. When people wash dishes they actively rub the surface. This mixes the surfactants with the soils and accelerates the cleaning. It also physically removes the soil.

The amount of mechanical action used in hand dishwashing is extremely variable and hard to quantify. This is typified by the large number of dishwashing performance tests that are used (see Section IV). Consumers may soak items that are difficult to clean in a low mechanical action environment. Under these conditions, surface chemistry is very important. Consumers may also scrub vigorously directly on the soiled area, break up the soil particles, and suspend them. At this point interfacial processes become important again. All individuals have their own techniques. Individuals vary the amount of effort they use depending on the type and distribution of the soil on the item. However, they usually do not use enough sustained mechanical action to make a stable oil-in-water emulsion.

Much of the cleaning occurs from water, heat, and mechanical action alone, as is true in automatic dishwashing machines. Large food particles, sugars, many starches, and some protein soils are readily removed by rinsing or soaking with plain hot water. However, some food soils, such as baked-on starches or polymerized fats, are extremely resistant. These require vigorous, direct mechanical action. In some cases vigorous chemical action is used, as in oven cleaners, but this mechanism is not within the scope of typical LDLDs.

2. Washing Methods

Dishwashing methods are extremely diverse and vary greatly according to geography, local tradition, and individual person, lifestyle, and diet.

Neat dishwashing. Neat dishwashing refers to the practice of placing the dishwashing liquid directly on the item to be washed or directly on the washing tool (sponge, brush, rag, etc.). The item is usually rinsed first. In neat dishwashing the surfactant concentration ranges from a few percent to 30% or more, depending on the active ingredient level of the product. In developed countries neat dishwashing is used when there are only a few dishes to wash or when one particular item is especially soiled. Neat dishwashing is also a common habit in places such as Brazil, India, and Japan [23].

Dilute methods. Dilute dishwashing is the widely used practice of filling a tub, sink, or pot with water and adding the dishwashing liquid (1 to 10 g) to make a solution [24]. The dishes are either submerged in the solution all at once or submerged one at a time and then washed. Typical surfactant concentrations range from 0.06 to 0.2% for U.S. consumers (using an "ultra" concentrated product) and from 0.06 to 0.3% for European consumers. The sinks range in size from 5 to 20 liters [25].

Soaking. The soaking method is used for hard-to-clean, baked-on grease and soils. One or two squirts of the product are added directly to the cookware, which is filled with hot water and left to soak for a period of time. After soaking, the items are cleaned with much less effort since the soils have been loosened. Typical soak concentrations are 0.2 to 0.5%, temperatures are usually those of domestic hot water supplies (40 to 50°C), and time is 10 to 15 minutes.

Dip and dab methods. The dip and dab method consists of adding product (10 to 100 g) to a small bowl and filling the bowl with water. The soiled item is then washed with this solution, but not submerged as in the dilute method. The dip and dab method generally has much higher concentrations (1 to 3%) than the dilute method and is generally only used in developing countries.

Rinsing. Once items are washed, they are generally rinsed with clean water. This is especially important when higher concentrations of dishwashing liquid are used. Some consumers in German-speaking countries do not rinse. They scrape the plates thoroughly so there is a minimum soil load, wash in very dilute solutions, and dry with a towel.

3. Soils

Many food soils are encountered in hand dishwashing, such as grease, carbohydrate, protein, dairy, and mixed soils. Baked-on soil requires more vigorous treatment, either mechanical or chemical [26]. The type of oily soil is almost exclusively triglycerides. The hydrocarbon chains in food triglycerides are predominantly C12 to C16, although higher and lower chains are also present.

When heated by cooking these fats and oils can undergo significant chemical changes due to oxidation and polymerization.

4. Surfaces

In dishwashing, one must consider soil and surfactant adsorption to both polar and nonpolar surfaces. Metals (aluminum, stainless steel, carbon steel, cast iron, silver, and tin), siliceous surfaces (china, glass, and pottery), and organics (polyethylene, polypropylene, polyethylene terephthalate (PET), polytetrafluoroethylene (PTFE), and wood) present a wide variety of surface characteristics. They span the range of high interfacial free energy (metals and many ceramics) to low interfacial free energy (hydrocarbon polymers) surfaces [27,28].

5. Water Temperature and Hardness

The water temperature used in hand dishwashing is highly variable and depends on the climate and the availability of hot water. In tropical places the ambient temperature of water is 30 to 37°C. Many edible fats are at least partly liquefied at this temperature. In some temperate zones the water can be close to 0°C, depending on its source and time of year. A source of hot water is essential under these conditions. A typical wash temperature is usually between 32 and 43°C. The maximum wash temperature is about 50°C due to the previously mentioned exposure of the consumer's skin during the washing process. Above this temperature the water becomes dangerously hot. Hotter water is used for tough jobs, but the items are left to soak and are not handled, unless perhaps gloves are used. Raising the washing temperature can markedly increase the amount of cleaning [29].

The amount of hardness ions in the water can vary greatly according to geographic location. Typical values in the U.S. are around 50 ppm (soft water) to 300 ppm (hard water). Water hardness can be beneficial or detrimental to performance, depending on the application and the product composition. In hand dishwashing, water hardness generally increases the efficacy of LDLDs. High water hardness increases grease removal and increases the number of items washed with a given amount of surfactant. Water hardness has a variable effect on foam depending on the range of hardness and the anionic or nonionic nature of the surfactants. Hard water can also increase the likelihood of spotting on articles when they are left to air dry.

B. Mechanisms of Performance and Relevant Physical and Chemical Properties

1. Cleaning Mechanisms

The three main mechanisms for soil removal from hard surfaces are chemical, mechanical, and detergent action [30]. Cleaning of dishes by hand is accomplished primarily by mechanical action, warm water, and the detergent. The role of the

LDLD, through the use of surfactants, is to provide the detergency. Different surfactant physicochemical processes are relevant depending on whether the soil is a liquid or a solid.

Liquid soil is usually removed by roll-up, emulsification, direct solubilization, and possibly formation of microemulsion or liquid crystalline phases. The oil emulsification capability of the surfactant solution and the oil–water interfacial tension are relevant physicochemical parameters.

The first mechanism of cleaning hard surfaces is the roll-up of liquid soils or soils that have been liquefied by heat or surfactant penetration [31]. The mechanism involves successive steps. The first step is the wetting step in which the washing solution adsorbs on the grease and the substrate. The interfacial tensions of the grease–water and substrate–water interfaces are reduced to the same range as that of the substrate–grease interface. At this point, convection or mild mechanical agitation can be enough to detach the grease droplet from the surface. If the substrate–grease interfacial tension remains lower than the substrate–water tension, then all the grease cannot be removed. A portion is removed, however, and the remainder can be emulsified or solubilized.

Above the critical micelle concentration (CMC), surfactant molecules aggregate into structures called micelles. The hydrophobic portion of the surfactant molecule occupies the core of the aggregate and the hydrophilic head groups point toward the water phase. Solubilization is the spontaneous dissolving of grease in the hydrophobic core of the micelles. This results in swollen micelles, the size of which is still well below the wavelength of light, resulting in transparent systems. Swollen micellar systems are thermodynamically stable and can be considered oil-in-water microemulsions. The extent to which the LDLD can solubilize oily soil depends on the chemical structure of the surfactants, its use concentration, and the temperature. High concentrations of surfactants can accommodate much larger amounts of oil.

When insufficient surfactant is present to solubilize all of the oily soil, the remainder can be suspended in the bath by emulsification. An emulsion is a thermodynamically unstable suspension of liquid particles in a second liquid phase. Emulsion particles are much larger than micelles, about 500 nm or greater. The fact that emulsions are not thermodynamically stable is irrelevant since the dirty suspension is drained down the sink and the dishes are rinsed.

A recent review [32] describes several cases in which the maximum soil removal occurs when the soil is incorporated into an intermediate phase, such as a microemulsion or lamellar liquid crystals. These intermediate phases form at the interface between the soil and the washing bath. The phases grow up to a point and then, as a result of agitation, break off into the bath, where they are emulsified into the aqueous solution.

Solid inorganic soils, such as dust particles, are removed through a wetting and suspension mechanism. Solid organic soils, such as greases, are broken up and suspended in the bath by the LDLD. Penetration into the solid grease can cause it to swell and liquify. The relevant physicochemical processes are wetting and adhesion tension. The first step in cleaning hard surfaces is the adsorption of the surfactants at the soil interface. The cleaning solution first must effectively wet the surface. Wetting involves the interaction of a liquid with a solid. For dishwashing, it is usually the spreading of a liquid over a surface. Wettability can be measured by the contact angle (θ), which is the angle that the liquid makes when it is in equilibrium with the other phases in contact with it. A low contact angle means high wettability and a high contact angle means poor wettability.

The work required to separate a unit area of liquid from a solid is called the work of adhesion. Adhesion tension is found from the product of surface tension and the cosine of the contact angle made by a drop of surfactant solution on a solid surface. Adhesion tension measurements have been conducted at a model grease surface–water interface and used to design superior consumer products [33]. Nonionic surfactants are useful in solid grease removal because they are efficient at covering the grease substrate and reducing the interfacial tension even at very low surfactant concentrations. Anionic surfactants are necessary, however, to disperse and emulsify the soil. It has been shown that by making adhesion tension measurements and using predictive diagrams the optimum ratio of anionic to nonionic surfactants can be formulated for superior cleaning [33].

2. Foaming

The foam of LDLDs is an important signal to the consumer of product efficacy. High sudsing signals good detergency and suds decrease signals detergency decrease to the consumer. Today, nearly all LDLDs are formulated to deliver long-lasting foam. Even though high foaming is not necessarily related to a product's actual cleaning ability (e.g., nonionic surfactants offer good cleaning but in general they do not foam well), modern products deliver both good cleaning and long-lasting foam to meet consumer expectation.

Consumers evaluate several different properties related to foam. The amount of foam formed when the water and product are first introduced into the wash basin or sink is referred to as the flash foam or the initial foam volume. The persistence of the foam in the presence of food soils is also judged. This is referred to as foam stability in the presence of soils. Foam must be present until the end of the dishwashing process. This performance measure is referred to as foam mileage or longevity. For some consumers, the quality of foam might also be important. This is particularly true for those consumers that use LDLDs to wash their hands. The quality or hand feel of the foam should be rich and thick; however, the foam must rinse quickly from the dishes.

The different properties of foam find their origin in different physicochemical phenomena. The amount of mechanical energy introduced can be the most important factor in determining foamability and in fact may play a greater role than the actual surfactant properties. Surfactant systems perform differently depending on whether the foam is generated with high shear or low shear. The relationship between a surfactant's chemical structure and its foaming ability can be quite complex. Also, there is not always a direct relationship between a surfactant's performance in foam volume and foam stability. A surfactant's foaming ability depends on its ability to lower the surface tension of the solution, its ability to diffuse to interfaces, the packing or structure it takes at the interface, the elastic properties it imparts on interfaces, and its ability to stabilize thin films.

In a homologous series of surfactants, the foam volume will generally go through a maximum as the chain length increases with C12 often providing the best foaming. This is due to a balance between conflicting effects. As the chain length increases, the CMC decreases and surface tensions are lowered. In contrast, as the chain length increases the solubility and speed of diffusion to interfaces is reduced.

In general, surfactants with lower CMCs are more *efficient* foamers [34]. Foam heights generally increase with an increase in concentration below the CMC and level off near the CMC. Thus the CMC of a surfactant system gives an indication of its foam efficiency. Above the CMC, different surfactants are able to foam to different heights, i.e. the effectiveness. The *effectiveness* of a surfactant system depends on both its ability to reduce the surface tension and the magnitude of intermolecular forces. Researchers from Exxon found that foam heights (effectiveness) correlate with the effectiveness of surface tension reduction at the CMC [35]. Foam stability correlated with the rate of surface tension reduction at the air–water interface [35]. Other researchers have also found correlations between dynamic surface tension and foam height generated in a kinetic manner [36]. In studies of SDS modified with long-chain alcohols it was found that foamability exhibits opposite behavior depending upon the rate of foam generation [37]. In slow gentle foam generation, more foam was generated with a system of lower equilibrium surface tension. In vigorous foam generation, more foam was generated with a system of lower dynamic surface tension.

Foams become unstable due to three basic mechanisms: drainage (gravity), film rupture (coalescence), and coarsening (Laplace pressure). Coarsening is driven by surface tension and causes gas to diffuse from small to larger bubbles. Effective methods for stabilizing foams attempt to overcome one or more of these mechanisms. All three phenomena depend on the elasticity and viscosity of the foam surface. Thus surface rheology measurements are becoming of increasing importance [38].

LDLDs are mixtures of surfactants. Surfactant mixtures often perform better than the sum of the individual surfactant contributions, or perform synergistically. The origin of this synergistic interaction is head group interactions and is dipolar in nature. The surfactant pairs having the greatest dipolar forces have the largest synergies: anionic–cationic > anionic–amphoteric > anionic–nonionic. However, anionic–cationic surfactant pairs tend to have solubility issues. For this reason, amphoteric surfactants, such as betaines, are often used in surfactant systems to improve foamability and foam stability. Rosen and Zhu have studied the relationship between synergism in foam height (by the Ross–Miles test) and synergism in surfactant adsorption properties [39]. The only correlation they were able to establish was between synergism in initial foam heights and surface tension reduction effectiveness. This term refers to the surface tension at the CMC of the mixture being lower than either pure component. However, no relationships for foam stability were found with equilibrium surface adsorption properties.

3. Mildness

The mildness of an LDLD is important since consumers spend time with their hands exposed to the product either neat or soaking in diluted product. Negative signals can be a redness or roughness feeling. Skin feel can change with time. Surfactants are the ingredients primarily responsible for the lack of mildness in a product, although there is irritation to the skin just from soaking in hot water.

There are several known mechanisms of surfactant-induced skin irritation [40]. The first is by binding of surfactants to sites on the stratum corneum. The second is swelling of the membrane in response to binding. Stratum corneum swelling studies have shown that swelling increases over time, consistent with a diffusion process [41]. The rate of swelling changes with concentration after the CMC is reached. This contributes to the commonly held belief that it is surfactant monomers and not micelles that contribute to surfactant irritation. Swelling has been found to be a maximum for C12 or C14 isomers for various anionic surfactant series. Again this is probably due to a balance between opposing forces: decreasing CMC with increasing chain length but a decrease in water solubility. Nonionics have been found not to swell the stratum corneum significantly. The third mechanism is release of mediators of inflammation or removal of biomolecules. The release of inflammatory mediators is essentially from living cells, the Langerhans cells present in the epidermis and the keratinocytes, also in the epidermis. These mediators initiate a cascade of release and other cell types also participate in this release, such as macrophages, lymphocytes, leucocytes that are present in the dermis. The removal of biomolecules refers to the NMF (natural moisturizing factor) molecules that are extracted from the corneocytes and the stratum corneum and cause the stratum corneum to dehydrate. The fourth mechanism is the denaturation of proteins (discussed in Section IV.C). The fifth mechanism is permeability of surfactants through membranes. Finally, surfactants may be responsible for removal of skin lipids.

Surfactant mixtures have been shown to counter irritation. The explanation for this phenomenon is that the two or more surfactant types compete for a limited number of binding sites on the stratum corneum. Also, the two surfactants can form a complex that is less irritating. A mixture of surfactants very often has different solutions properties, as, for example, the CMC might be lowered. Adding an amphoteric surfactant, such as a betaine, to an anionic-based product can result in reduced skin irritation [42].

4. Rheology

Concentrated LDLDs, or "ultra" dishwashing liquids, typically contain 40 to 45% of surfactants and are isotropic, Newtonian liquids with viscosity in the range 100 to 500 cP. For most ionic surfactant systems, if the viscosity is plotted against the salt concentration the curve is found to increase to a maximum and then decrease again with higher salt concentration. Most concentrated LDLDs are already on the side of the salt curve where viscosity decreases with added salt. Therefore, salt can be used to reduce the viscosity of the concentrated surfactant system to the desired level. Alcohols such as ethanol are also used to reduce the viscosity. The addition of solvents such as alcohols or glycols also helps to solubilize and lower cloud/clear points. However, this needs to be done with care to avoid imparting undesirable odor to the product.

In some cases it has been observed that concentrated LDLDs thicken upon dilution. This would indicate that the micelles in the system are becoming elongated and entangled. This could be a potential problem for consumers who add water as the LDLD product bottle becomes empty in an attempt to wash out the remaining amounts of product.

5. Antibacterial Properties

There are two kinds of antibacterial effects: bacteriostatic, which means to stop bacteria growth; and bacteriocidal, which means to kill bacteria. In the U.S. the claims are bacteriocidal and specific to the hands. While there is no real signal of antibacterial action, consumers believe the claims that reputable dishwashing liquid manufacturers make. Claims are government regulated which helps justify consumer belief. The U.S. Food and Drug Administration (FDA) regulates claims regarding human skin (and therefore claims for hand washes), while the Environmental Protection Agency (EPA) regulates claims regarding surfaces (i.e., hard or porous). An FDA-regulated product must contain an antibacterial ingredient covered by an NDA (New Drug Application) of the Tentative Final Monograph, and efficacy of the product must be shown versus the vehicle (product without antibacterial ingredient). An EPA-regulated product must contain an active that is approved by the EPA and all other ingredients must be present on an EPA inert-ingredient list. Data must be presented on the product's efficacy and safety. In Europe there are different regulations, as discussed in Sections IV.C and VI.A.

IV. TEST METHODS AND PERFORMANCE EVALUATION

There are a number of laboratory tests used by formulators to evaluate the various performance aspects of an LDLD. These tests use a variety of soils and washing conditions (e.g., temperature, time, water hardness, mechanical action or not). A detailed description of various test methodologies is given in the literature [11]. Some of those methodologies are reviewed in this section. In addition, a subsection on antibacterial test methodology is included.

The test methods discussed below are classified in five categories: evaluation of cleaning performance; evaluation of foam performance (volume and stability); evaluation of mildness; evaluation of antibacterial efficacy; and other tests.

A. Cleaning Performance

Cleaning performance is the most important characteristics of a dishwashing liquid since consumers purchase the product for washing dishes, and their principal expectation is the removal of greasy soils. As stated previously, many food soils such as carbohydrates can be effectively removed sometimes with just plain hot water. However, this is not true of greasy soils which tend to pose more of a cleaning challenge. Consequently, the literature is replete with formulations directed at efficacious grease cleaning. Test methods for cleaning performance have mainly focused on greasy soils.

1. Baumgartner Test

The Baumgartner test was originally developed by Hoechst AG Chemical Company [43]. This test attempts to mimic actual dishwashing by incorporating physical energy into the grease removal process. Polypropylene test tubes are coated with a thin layer of Armour lard (about 60 to 70 mg) and repeatedly dipped, at a controlled rate, in and out of the test detergent solution. The weight of the soil removed from each tube is measured. Test solutions contain 0.667 g LDLD/l of 150 ppm artificially hardened water for ultra formulas, corresponding to about 0.30 g/l surfactant for a 45 AI product. The experiment is executed at 300 or 600 dips and the temperature of the test solutions is held at 108°F (42°C).

Results are reported as % soil removed calculated using the following formula:

$$\%\ \text{Soil removed} = \frac{\text{Amount of soil removed}}{\text{Original amount of soil}} \times 100$$

A higher percentage soil removed reflects better greasy soil cleaning ability.

2. Cup Test

Another test used to assess the grease-removing ability of test solutions is the cup test. This test is based on Procter & Gamble's grease removal test [44] with a few modifications. The test consists of solidifying about 6.5 g of beef tallow in the bottom of a tripour cup. Test cleaning solutions are heated to 115°F (46°C) and then poured into the soiled cup and allowed to soak for 15 minutes. The cleaning solution is then poured out of the cup with any soil it has removed. It is important that the temperature of the solution in the cup be below that of the melt temperature of the greasy soil or combination of soils (e.g., chicken, beef, pork fat) otherwise a true reading of the product's performance will not be obtained, as the soil will melt.

The evaluation of the product can be done by either gravimetric or turbidity means. The gravimetric method is preferred since it is simpler. Cups are allowed to dry overnight and the final weight of the grease remaining measured and used to calculate the % grease removed. The amount of grease is determined before and after the solution is added. Results are reported as % soil removed, as described above for the Baumgartner test.

The test concentration is 2.67 g/l for an "ultra" dishwashing liquid, or 1.2 g/l of surfactant and 4.0 g/l for regular products. Six replicas are usually measured.

3. Hand Dishwashing Test (Plate Count)

Hand dishwashing tests provide the best performance information about the entire product as they use soils and wash conditions as close as possible to those encountered by consumers under normal conditions. The indicator of a product's performance is the number of plates washed. In this test [46] the product is placed directly onto a sponge and soiled plates are washed until they cannot be cleaned any further (greasy residue on the plate). Performance is equated to the number of plates washed: the greater the number of plates washed, the better the product.

Although this test provides a more accurate assessment of a product's performance, it has some drawbacks. This type of test usually takes a long time to complete. Another limitation of this test is that it is subjective, and thus can vary from operator to operator.

4. Static Soaking Test [46]

This test measures the amount of soil (Crisco®, a vegetable shortening derived from cotton seed and soy bean oils and manufactured by Smucker Co.) removed from a plate after soaking for 30 seconds in a test solution of 0.1% detergent, 150 ppm hardness, 100 ppm alkalinity, and at 50°C. The plates are transferred to an ice bath following immersion in the warm test solution to stop the soil-removing process. The plates are dried and weighed. The % percent soil removal is calculated as:

$$\% \text{ Soil removal} = \frac{\text{Amount of soil removed}}{\text{Original amount of soil}} \times 100$$

The higher the % soil removal, the better the performance of the dishwashing detergent.

5. Emulsion Stability Test [47]

This test measures a liquid detergent composition's ability to keep greasy soils emulsified. The test is performed by placing an oil, like corn oil, into a vial containing a solution of detergent. The vial is agitated for a fixed number of rotations at a fixed rate and let stand for a fixed time. Readings are taken with a turbidity meter or colorimeter at given time intervals. Higher turbidity values indicate more stable emulsions and lower colorimetry values indicate more stable emulsions.

B. Foam Performance

Foam volume and foam mileage tests are widely used for evaluating LDLDs. Foam volume tests measure the amount of foam a composition can generate with and without soil. Foam mileage, sometimes referred as foam stability, measures the ability of a detergent to maintain its foam with soil present or while it is introduced. This attribute is extremely important, because it constitutes a powerful signal to the consumer that it is time to add more detergent during the dishwashing process, and therefore influences consumers' estimation of the cost per use of the product.

1. Foam Volume Tests

Foam volume is an important characteristic of light-duty dishwashing detergents. Higher foam heights are desirable, as consumers generally equate foaming with cleaning performance [4]. An ASTM method [48] for foam volume evaluations of light-duty dishwashing liquids is more commonly known as the Ross–Miles foam test. This method is widely used for evaluating the foaming ability of detergents or surfactants in general. Numerous other foam volume tests are cited in the patent literature that often differ significantly from the Ross–Miles test. These test methods are faster and easier for foam volume evaluation [49,50].

Foam volume tests can be conducted with soil or without soil. One foam volume test without soil [51], called the shake foam test or inverted cylinder test, is conducted by placing a solution of a composition into a cylinder. An amount of 100 g of LDLD solution (0.33 g/l concentration for an ultra formulation) is placed in a 500 ml graduated cylinder. The cylinder is shaken or inverted a fixed number of times or for a set amount of time (e.g., 40 rotations at 30 r/min). The foam height is measured in centimeters or milliliters, which are conveniently measured if graduated cylinders are used. A foam volume test with soil is conducted the same way but soil is placed into the cylinder. The soil can either be added with the solution initially or added after foam is generated. The cylinder is rotated or inverted the desired number of times and the resultant foam height is measured in milliliters or centimeters; usually at least three replicas are recorded.

2. Foam Stability Tests

Various types of foam mileage or foam stability tests are found in the literature. All use the same basic theme of generating foam under constant agitation and introducing soil until the foam collapses. Foam mileage tests measure a product's ability to resist foam depletion in the presence of soil. The amount of soil needed to break the foam is an indication of the product's ability to keep foaming while the consumer is washing dishes. The more soil it takes to break the foam the better the product's performance. Examples of some foam mileage tests are briefly described here.

(a) Miniplate Test. The Miniplate test [52] is an automated test designed to measure foam mileage. Foam is generated in a vessel and titrated to an endpoint with soil. The Miniplate apparatus consists of a computer system connected to an experimental chamber. The experimental chamber contains a thermostatically regulated water bath that is supplied with deionized water, a thermostatically controlled plate on which the reaction vessel sits, a motorized pump used to inject the soil, a brush with a system of gears to control its movement, a turbidity meter, and a photocell used to measure electronically the foam endpoint.

Concentrated LDLD solutions are prepared at 5% for regular and at 3.33% for ultra products in deionized water. A mixture of hard water concentrate, LDLD solution, and deionized water from the thermostat bath in the instrument is stirred by the motorized brush to generate the foam in the vessel. The final LDLD concentration is 0.083% for ultra products and 0.125% for regular products. The soil used in all Miniplate experiments is Crisco shortening (other soils can also be used) filled into plastic syringes. The amount of soil as well as the time required until the foam fully disappears is used to calculate the theoretical amount of plates washed. This method has been found to be correlated with a hand dishwashing procedure.

(b) Shell Test. The Shell test is a similar method to the Miniplate test, in that it is used to evaluate the foam performance of light-duty dishwashing liquid in the presence of soil [53]. Initial foam is generated in the test vessel by stirring a dilute solution of the test LDLD product. The soil is then titrated into the vessel, under constant-rate stirring, until the foam endpoint is reached. The quantity measured is the weight of soil added to reach the foam endpoint. This value can then be normalized to determine a foam performance rate (FPR). FPR [54] is the ratio of the weight of the soil used in the test formula to the average weight of the soil used in the standard LDLD formula under the same test conditions (e.g., temperature, test soil, water hardness):

$$\text{FPR} = \frac{\text{Weight of test product}}{\text{Weight of control}} \times 100$$

FPR can be used in comparing different products. A higher FPR value indicates better foam stability. The soil used is a mixed soil consisting of Crisco vegetable shortening, Pillsbury brand instant mashed potatoes, Progresso olive oil, homogenized milk, formaldehyde, and water. (The formaldehyde is added so that the soil mixtures are preserved from microbial degradation when a batch is stored for use over a period of days.) The solution concentration for ultra LDLDs is 0.0266% and for regular LDLDs is 0.04%.

(c) Tergotometer Test. The tergotometer test is commonly used in evaluating detergency of laundry products. It was modified [55] for the evaluation of LDLDs. The tergotometer provides constant agitation where a dilute solution of test composition is added and foam is generated. Planchets covered with soil are periodically added until the foam height is reduced to a foam endpoint or to a fixed height. The number of small metal plates added to the foam endpoint reflects the foam stability of a composition.

(d) Piston Plunger Test. Another foam mileage test is referred to as the piston plunger test [56]. In this test, similar to the tergotometer test, foam is generated and soil is added until the foam is depleted. The soil used in this test is a mixture of the commercial foods Crisco shortening and Ragu spaghetti. The amount of soil needed to break the foam is an indication of a product's efficacy.

(e) Dishwashing Test (Foam Endpoint). An ASTM method [57] exists for the evaluation of foam stability of hand dishwashing detergents that uses foam endpoint to indicate a products' performance. The objective of this test is to provide a standard test for formulators and suppliers, a screening test for formulations, and quality control. One method described uses a dishcloth to wash the front and back of a series of soiled dishes at 30-second intervals. Dishes are continually washed to a foam endpoint as determined by an originally uniform layer of foam in a dishpan solution becoming a thin layer of foam covering half the surface. Standard soils are described, an example being a mixture of oils (Wesson and corn), grease (lard), oleic acid, gelatin, salt, flour, and water.

Another example of a plate wash test [56] consists of soiling dishes with a fixed amount of Crisco shortening. A basin of water is prepared where the temperature, water hardness, and product concentration are adjusted to meet the habits and practices for the intended market. Foam is generated by a mixer or by manual agitation. The plates are washed using standard washing implements like sponges or cloths. It is common to fix the time and number of strokes used to wash the plates to minimize variability. The cleaned plate is then stacked and the process continues until the foam endpoint is reached. Again, the foam endpoint is when half the surface of the water is covered with foam. The plates washed are counted and used as a relative measure of a product's performance.

(f) Modified Schlachter–Dierkes Test [58]. In this test the product is placed in a graduated cylinder and inverted to generate foam. Soil increments are added at fixed intervals until the foam collapses. The results are recorded as the number of soil increments, with a higher value indicating better foam stability.

(g) Total Suds and Suds Mileage [59]. Four graduated cylinders are charged with a test solution consistent with conditions for the intended market. The cylinders are stationed side-by-side, rotated to generate foam, and initial foam heights are measured. Soil is added and the cylinders are again rotated. The foam height is again recorded. Soil is repeatedly added to a low foam height. A control is tested with each run and compared to the test product. Total suds and suds mileage are determined as follows:

$$\text{Total suds} = \frac{\text{Overall suds of test product}}{\text{Overall suds of control}} \times 100$$

$$\text{Total mileage} = \frac{\text{Overall mileage of test product}}{\text{Overall mileage of control}} \times 100$$

C. Mildness Evaluation

Mildness has become an important attribute of LDLDs. Assessments typically involve clinical and sensory evaluations of skin irritation. Mildness evaluations are usually conducted in both *in vivo* and *in vitro* testing.

1. *In Vivo* Tests

(a) Frosch–Kligman Soap Chamber Test. The Frosch–Kligman soap chamber test [60] is designed to evaluate the mildness of surfactant compositions (8% solution) for panelists with hypersensitive skin. It is one of the most popular tests and consists of a five-day test procedure. The exposure varies from 24 hours on the first day to 6 hours on days 2 to 5. The first application is four times longer than the others in order to induce damage on the skin barrier and allow the solution to start its irritating effect. The subsequent 6-hour applications are to allow the sites to develop scaling, flaking, and wrinkling. Evaluation of redness (erythema), scaling/flaking (dryness), and fissuring is carried out visually by a trained professional. Each of the parameters is given a score on a 0 to 4 (erythema) scale or a 0 to 3 scale (Table 7.5). The total score is determined by summing up the averages of the three parameters. If at any time a panelist experiences high irritation, the specific product is not reapplied.

The test is run in exaggerated nonrealistic conditions in order to ensure differentiation between products. The authors claim they can differentiate between two soaps with just 10 panelists. The big advantage is that multiple products (up to eight) can be evaluated at once, and it takes only eight days to complete the test.

(b) Patch Tests. There are a number of patch tests used to evaluate skin irritation. Table 7.6 lists the reaction and symptom rating scales for patch tests.

Twenty-four-hour occlusive test. This test is mainly used to screen potential compositions for a quick comparison [61,62]. A patch is used to keep the diluted product against the skin for 24 hours. The chambers are patched on the forearms

TABLE 7.5 Rating System for the Frosch–Kligman Soap Chamber Test

Erythema	Scaling	Fissures
1: slight redness, spotty or diffuse	1: fine	1: fine cracks
2: moderate, uniform redness	2: moderate	2: single or multiple broader fissures
3: intense redness	3: severe with large flakes	3: wide cracks with hemorrhage or exudation
4: fiery red with edema		

TABLE 7.6 Reaction Rating Scale and Symptom Ratings for Patch Test

Reaction	Rating	Symptom	Rating
No visible reaction	0	Vesicles	5
Reaction only just visible	1	Edema	4
Slight reaction	2	Redness	3
Moderate reaction	3	Flaking	2
Serious reaction	4	Dryness	1
		Wrinkles	1
		Semitransparency	1
		Glasslike	1

of volunteers. The arms are evaluated after 24 hours and in the case of a strong irritant response the product is likely to be irritating. If no irritation is observed then repeated exposures need to be performed before a safe conclusion on the irritation potential of the product is reached.

A variation of this test is that the arms are evaluated after another 24 hours without contact with the product have passed. Other variations include plastic or aluminum disks used for patching [63,64]. The overall rating is determined by multiplying the degree of reaction by the rating for the observed symptom.

Four-hour patch test. While the other patch tests include diluted products to simulate the most often encountered use conditions, in this test the product is used neat. As is known from Habits and Practices studies, a significant percentage of the population are neat product users. A procedure was developed by Dillarstone and Paye [65] where neat products are applied to the forearms of volunteers for a duration of 4 hours. The irritation potential of those products is compared to that of 10% SLS solution which is a "skin irritant." If a product is suspected to be an irritant, then several patches are performed and removed at 1, 2, 3, and 4 hours; if irritation occurs before 4 hours all patches are removed.

TABLE 7.7 Twenty-one Day Cumulative Patch Test Numeric Score Index

0	Negative reading (questionable erythema not covering entire patch area)
1	Definite erythema covering entire patch area
2	Erythema and induration
3	Vesiculation
4	Bullous reaction

Twenty-one-day cumulative patch test. This test [66] is designed to investigate the irritation potential of an LDLD that comes in contact with the skin for a prolonged period of time. Patches with diluted product (use conditions or slightly exaggerated) are applied on panelists for 21 days. The patches are removed every 24 hours, read 30 minutes after, and the new patch placed immediately after. At the end of the study, skin irritation in terms of erythema, dryness, and edema is visually evaluated based on a 0 to 4 scale (Table 7.7). This cumulative test has the advantage of detecting even weak irritants, so false negatives are extremely rare.

Human repeat insult patch test (HRIPT). This is the test usually used to determine an allergic reaction, and subsequently to make "hypoallergenic" claims. The product at 5% concentration is patched onto skin, 3 times a week for 3 weeks, followed by a rest period of 2 weeks without patching. The product is again patched on sites not previously patched, and the new sites are evaluated for erythema and edema after 2- and 3-day exposures, and are compared to the initial patching. If the levels of redness and swelling are higher than the original one, the panelist is considered to have an allergic reaction.

(c) Hand Soaking Tests. In these type of tests panelists soak their hands in LDLD solutions for 15 to 20 minutes, 2 or 3 times a day for 5 consecutive days; the conditions are defined in such a way that mimic realistic use conditions. After soaking, the hands are rinsed with tap water, and patted dry with a paper towel. The skin is assessed for erythema and dryness before and after soaking; instrumental measurements often accompany the visual assessments. Hard water and temperature are carefully monitored.

Patel *et al.* [67] used hand immersion testing to measure the skin-smoothing properties of a dishwashing detergent that incorporates a skin-smoothing compound. In this test panelists immersed their hands into a 1% solution of test composition at 41°C for 60 seconds, rinsed under tap water for 60 seconds, and towel dried. The panelists examined their hands as they dried them evaluating the smoothness. All panelists evaluated the test composition as making their hands smoother than the control without the skin-smoothing compound.

These tests discriminate very well, and have the added benefit of being run under normal usage conditions.

TABLE 7.8 Irritation Potential Based on Zein Value

Irritation classification	Zein value (mg N/100 ml)
Nonirritant	0–200
Slightly irritant	200–400
Severe irritant	>400

2. *In Vitro* Tests

In vitro tests are designed to allow screening of the irritation potential of LDLD products before conducting the more expensive *in vivo* tests. Most of these *in vitro* tests show a good correlation with the *in vivo* tests. They are rather simplified models that attempt to simulate what is really happening in the skin. The most often used tests address the denaturation of the skin surface proteins. A detailed list of the tests is offered by Paye [68].

(a) Zein Test. The procedure was originally developed by Gotte [69,70]. The Zein test determines the extent of denaturation of the Zein corn protein, which is insoluble in water, by surfactants. An amount of 0.5 g of Zein (Sigma, St. Louis, MO) is incubated with a solution of the test product at pH 7.0 for one hour, at constant temperature and with slight agitation. The solution is filtered and processed in a centrifuge. The zein value is calculated as:

$$\text{Zein value} = A - B \text{ mg/N}_2\text{/100 ml solution}$$

where A is the amount of nitrogen measured in the filtered solution using a micro-Kjeldahl method and B is the amount of nitrogen in the surfactant solution without Zein. The proposed irritation potential based on zein value is shown in Table 7.8. The more Zein that is solubilized, the more irritating the product.

A disadvantage of the test is that it does not work in the presence of magnesium, so all test formulas have to be made specifically for Zein testing.

(b) Collagen Swelling Test. This test [71] is used to determine the irritation potential of LDLD solutions containing anionic surfactants. It is based on the denaturation and swelling of the collagen protein (stratum corneum can also be used). The collagen sheets are incubated for 24 hours at 50°C in the presence of titrated water. After the 24-hour period, the sheets are rinsed, digested, treated, and analyzed for radioactivity. This measurement is used to calculate the water volume uptake by the dry collagen.

The swelling of collagen does not only occur because of denaturation, but also because of negatively charged surfactant binding to the protein. When cationic, amphoteric, or nonionic surfactants are present, swelling is minimal because of lack of adequate binding to the protein. Therefore, this method is valuable for

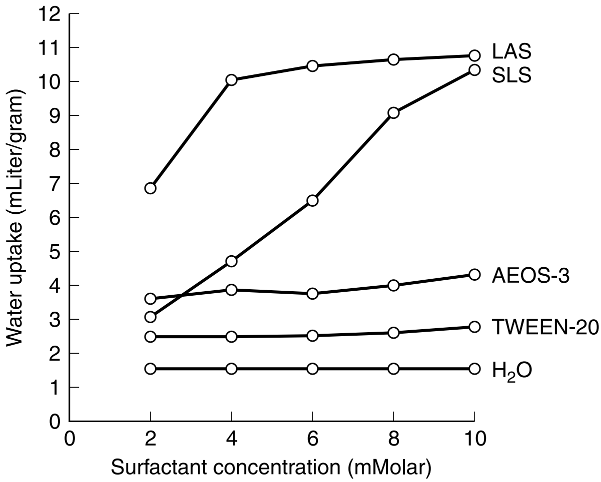


FIG. 7.1 Water uptake as a function of surfactant concentration using the collagen swelling test. (From Blake-Huskins, J.C., Scala, D., and Rhein, L.D., *J. Soc. Cosmet. Chem.*, 37, 199, 1986. Reproduced with permission.)

assessing the irritation potential of anionic surfactants and anionic-surfactant-containing LDLD products.

Figure 7.1 shows that LAS and SLS have a high irritation potential as compared to AEOS-3, Tween-20, and water, since they produce a high level of swelling. Similar results for LAS and SLS are reported by Putterman *et al*. [72] for isolated stratum corneum.

(c) Protein Denaturation. Protein denaturation by surfactants is considered to be one of the major causes of skin irritation and roughness induced by surfactants [73]. Consequently, simple and reproducible methods for evaluating protein denaturation by surfactants have been developed. These tests work by measuring the amount of protein that has been denatured after the protein and test composition have been in contact with each other for a given period of time. Prottey *et al*. [74] developed a method that can be used to predict the mildness of surfactants and thus dishwashing liquids. They found a correlation between the changes observed in the stratum corneum phosphatase specific activity during normal dishwashing conditions and dryness and flakiness. Figure 7.2 shows the correlation of hand dryness and acid phosphatase specific activity after hand immersion in various surfactants.

A commercial manufacturer of light-duty dishwashing liquids used this method to show a liquid detergent composition to have good mildness [75].

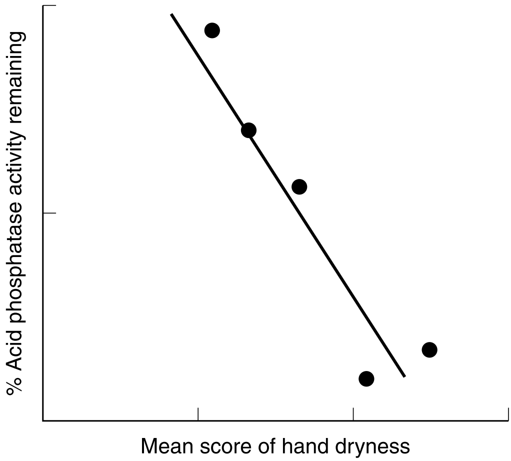


FIG. 7.2 Correlation of hand dryness and acid phosphatase activity. (From Prottey, C., Oliver, D., and Coxon, A.C., *Int. J. Cosmet. Sci.*, 6, 263, 1984. Reproduced with permission.)

In the protein denaturation test developed by Prottey *et al.* [74] the interaction of detergents with acid phosphatase enzyme is performed on skin. Others have developed a protein denaturation test that uses wheat germ [76]. Another protein denaturation method mixes an aqueous protein solution of egg yolk albumin and detergent composition [77]. The mixture is subjected to chromatography and compared to the results for only the egg yolk solution. Mildness is determined by the amount of denaturation, with the more mild the composition, the less the percent denaturation. Yet another method uses ovalbumin and human serum albumin and measures protein denaturation via gel permeation chromatography (GPC) [78]. Figure 7.3 shows an example of a chromatogram using this type of method. Percent denaturation is then calculated as:

$$\%\ \text{Denaturation} = \frac{H_\text{o} - H_\text{t}}{H_\text{o}} \times 100$$

(d) Corneosurfametry. This new test [68] combines protein denaturation and penetration through a barrier. Although it is an exaggerated test, it is useful to predict irritation by surfactant-based products. Superficial layers of the stratum corneum of human volunteers are collected by the use of an adhesive sheet; the diluted products are sprayed onto the skin samples, incubated, and rinsed off. The damage caused on the stratum corneum is determined by the degree of staining of the skin by a blue dye solution. With this method the direct interaction between

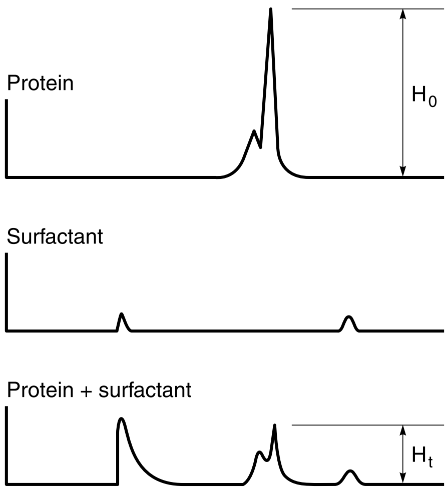


FIG. 7.3 GPC elution curves for protein, surfactant, and mixtures of protein and surfactant. (From Miyazawa, K., Ogawa, M., and Mitsui, T., *Int. J. Cosmet. Sci.*, 6, 33, 1984. Reproduced with permission.)

surfactant solutions and the skin is measured, and no artifacts are caused by the presence of magnesium.

D. Antibacterial Efficacy Evaluation

1. *In Vivo* Tests

These methods [79] help substantiate a claim of antibacterial activity on skin surfaces, where the efficacy of a product containing the active is compared to the efficacy of a placebo. Ideally, the test takes place once the formula is proven to be efficacious via *in vitro* testing.

(a) Agar Patch. The scope of the test is to assess the residual antibacterial activity of topical antibacterial products. Agar contact plates are inoculated with bacteria and are placed in contact with areas of the skin which have been washed with an antibacterial product. The surviving bacteria on the plate are enumerated and compared to the placebo. The objective is usually to achieve a 1 log reduction of organisms between the product containing the antibacterial ingredient and the placebo.

(b) Skin Occlusion and Bacteria Recovery Test or Cup Scrub Test. This test determines the immediate and/or residual antibacterial efficacy of topical preparations against a marker organism. The test is used for products which are applied

to skin and are either left on or rinsed from the skin. The antibacterial compounds are applied to the skin; the bacteria is applied to the treated area of the skin and occluded with a waterproof covering. After an appropriate period, the bacteria are harvested using a diluent, and the surviving bacteria are enumerated. The bacteria numbers from the sites treated with the placebo are compared to those treated with the active, and the difference determines the activity. At least 1 log reduction is desirable.

(c) Hand Imprint Test. This test is a qualitative test. It assesses the residual activity on hand products. The antibacterial and placebo products are applied to each hand, and the hands are washed individually, with product rinsed off as normal. The hands are placed on hand imprint seeded agar plates for a short contact time. After incubation, based on clearing (inhibition), a comparison is made between the residual activity of the active and the placebo. The objective is to observe a significant difference between the hand washed with the placebo product and the hand washed with the product containing the active.

(d) Health Care Personnel Hand Wash (HCPHW). This test measures the efficacy of antibacterial skin cleansing products to eliminate bacteria from the hands after a single contamination/wash cycle as compared to a baseline (untreated hand). The hands are artificially contaminated with a marker organism. The hands are prewashed with a nonantimicrobial soap, and bacteria are applied to hands and air-dried. Bacteria are then collected using the glove juice method to attain baseline counts. The hands are rewashed with a nonantimicrobial soap. Hands are recontaminated, air-dried, washed with the test product, and then rinsed off.

The objective of this test is to observe a significant difference between the baseline bacterial counts and the posttreatment bacterial counts. Counts are converted to log cfu (colony forming unit), and a t-test compares the mean log (baseline counts) to the mean log (posttreatment counts).

2. *In Vitro* Tests

These tests are used to test a new raw material or a complete formula. They are also used to support claim substantiation. They are easy, safe, and cheap tests and are designed to simulate actual use conditions. The first three of the tests discussed below can be used to screen products for either handwash products or for efficacy as surface disinfectants, as they test for bacteriocidal or bacteriostatic action without reference to a surface. The last two tests are specifically used to document surface disinfection claims.

(a) Minimum Inhibitory Concentration (MIC) Test. This test is used to screen possible antibacterial agents, or compare whole-formula inhibitory concentrations. Test tubes containing decreasing concentrations of the test agent are inoculated with the test organism, incubated, and examined for the presence or absence of growth. The MIC is determined from the last test tube in the dilution sequence where there

is no microbial growth. MIC is calculated based on the initial concentration of the active ingredient, and is given in ppm.

(b) Zone of Inhibition. The scope of the test is to determine the bacteriostatic activity of a compound against various organisms. Molten agar is inoculated with a pure culture and seed layer on the base agar. The compound is applied directly onto a disk or in a well to the seeded plates. After incubation the no-growth zones around the disks are measured. This is a qualitative test and is influenced by the diffusion rates of the actives. The results are given in millimeters, and they are comparable to the MIC values. The perimeter of the zone is where the diffusion has reduced that particular active ingredient to its MIC.

(c) Short Interval Kill Test (SIKT). The scope of the SIKT is to determine the bacteriocidal activity of compounds over a short period of exposure. Solutions are inoculated and neutralized at the end of a finite period. The surviving organisms are enumerated and compared to the control. The difference is expressed in log reduction.

(d) Use Dilution Test (UDT). The scope of the UDT [80] is to determine the germicidal efficacy of water-miscible disinfectants. Contaminated carriers are exposed to a diluted disinfectant solution. After a specific period of time, the carriers are transferred to a neutralizer broth (which stops the antibacterial action), incubated, and examined for growth. The test is usually given as 60 carriers or tubes, and growth must be absent from 59 to 60 of the tubes. Growth in two or more samples is failure in the test. This test is used for EPA registration of products as surface disinfectants. Depending on the organisms used, various levels of claim are recognized.

(e) European Requirements [81]. In European products the antibacterial efficacy claim is substantiated through the EN series of quantitative suspension tests where a 5 log microorganism kill needs to be achieved for bacteria, 4 log for fungi, and 4 log for viruses.

EN 1040: Bacteria. The test germs are *Pseudomonas aeruginosa* and *Staphylococcus aureus* and the test conditions include a temperature of 20°C and contact times of 1, 5, 15, 30, 45, and 60 minutes. This test evaluates the basic efficacy of the product.

EN 1279: Bacteria. This is the same as above, but two additional bacteria, *Escherichia coli* and *Enterococcus hirae*, are included. The temperature of the test remains at 20°C, while the contact time is 5 minutes. The test is performed with hard water, to better simulate household conditions.

EN 1275: Fungi. The test organisms are *Candida albicans* and *Aspergillus niger* (spores). The test is conducted at 20°C, and the contact times are 5, 15, 30, and 60 minutes.

EN 1650: Fungi. This is the same as EN 1275 but hard water is used.

DVV: Virus. This test is to satisfy the German regulatory requirements. It is conducted at 20°C and the contact time is adjustable up to 60 minutes.

E. Other Tests

Various other tests are used by formulators to aid formulation or to evaluate some specific benefits. Drainage and rinsing tests are among the examples.

1. Drainage Tests

The consumer benefits of liquid detergents that have good draining characteristics are faster and spot-free drying. A test method to measure the draining of light-duty liquids was described in U.S. Patent 5,154,850 [49]. In this test plates are immersed in a solution of product a fixed number of times, taken out, and air dried under ambient conditions. This cycle is repeated with the final dipping followed by rinsing. The plate is allowed to air dry and the water spots are counted. A product that provides good draining will give few to no spots on the plates.

In another drainage test [82] various regular kitchen utensils, such as drinking glasses, glass dinner plates, and ceramic dinner plates, are washed in test compositions under controlled conditions. The utensils are then rinsed and placed in a rack to dry. The time at which drainage begins and the percentage area dried by this drainage are recorded.

2. Rinsing Tests

Although copious and long-lasting foams are desirable for LDLDs, consumers also want the foam to be easily rinsed away from the dishes so as not to leave a residue that could appear as spots. A test method was disclosed in U.S. Patent 5,154,850 for the evaluation of the rinsability of foam generated for an LDLD [49]. This involves making a solution of product, charging it to a container, and stirring. The solution is discharged from bottom of the container leaving residual foam in the container. Tap water is added to the container with residual foam and stirred again. The stirring and draining steps are repeated until no foam remains in the container. The product that needs fewer additions of water has better rinsing properties.

3. Cloud/Clear Point Tests

It is important that a product does not turn cloudy either on the shelf at the point of sale or during the time of use or storage at home. To ensure this important product aesthetic, a cloud/clear point test is usually conducted. The product sample is put into a clear container and then immersed in some kind of cooling bath, such as a salt/ice bath. The turbidity of the sample is monitored as the temperature drops. The temperature at which the sample first becomes turbid is the cloud point. If the sample is removed from the cooling bath the temperature of the sample rises. The temperature increases slowly until the sample becomes clear again.

TABLE 7.9 Important Attributes of a Hand Dishwashing Liquid Detergent

Attribute
Effective cleaning
Copious and long-lasting foam
Mildness to hands
Pleasant fragrance
Convenient to use
Safe to humans
Safe to dishes and tableware
Storage stability
Economic to use

This temperature is the clear point. The acceptable cloud and clear temperatures are set based on the conditions to which the products may be subject.

V. FORMULATION TECHNOLOGY

A. Formulation

Formulating an LDLD is both a science and an art. It requires a good balance between product performance, aesthetics, safety, and cost. From the consumer point of view, the important attributes for a hand dishwashing liquid are listed in Table 7.9. Liquid dishwashing detergents are formulated to deliver against these consumer-relevant attributes.

Formulation of LDLDs typically involves (1) selecting appropriate raw materials for the desired performance, (2) developing formulas and optimizing for performance, (3) optimizing product aesthetics, (4) testing product safety, (5) optimizing product cost, (6) aging for product stability, (7) validating with consumers, and (8) documenting advertising claims. These steps are usually not sequential, but often take place in parallel.

The following sections present a review on formulation against these performance attributes with the intent of providing some guidelines.

B. Guidelines and Examples

1. Formulating for Effective Cleaning

The most important performance attribute of an LDLD is cleaning. As discussed in an earlier section, cleaning of dishes with an LDLD primarily relies on the interfacial properties provided by surfactants. Various surfactants exhibit different interfacial properties and thus have varying ability in removing different soils from various surfaces. In general, use of a combination of surfactants is necessary for an LDLD to be effective against a wide spectrum of soils encountered on a variety of surfaces in the real world.

A significant number of patents on LDLDs have been issued in the U.S., Europe, and Japan in recent years. Listed in Table 7.10 are examples of LDLD patents formulating for effective soil removal/cleaning. The technology utilized in these patents ranges from special surfactants, surfactant mixtures, salts, and microemulsion to the use of special additives such as lemon juice and abrasives.

2. Formulating for High and Long-Lasting Foam

It is well recognized that foam is the most important visual signal that consumers use to judge the performance of an LDLD. This is in spite of the lack of direct correlation between foaming and cleaning properties of an LDLD, as discussed earlier. Therefore, it is critically important that an LDLD is formulated with copious and long-lasting foam.

Copious foam usually requires the use of high-foaming surfactants, typically anionic or amphoteric surfactants or a mixture of surfactants. Long-lasting foam often requires the use of foam stabilizers in addition to surfactant mixtures.

Table 7.11 summarizes recent LDLD patents formulating for good foaming properties. The technologies involved either use novel surfactants/surfactant blends or use novel foam stabilizers.

3. Formulating for Mildness

For some consumers, mildness to skin is an important attribute of an LDLD, especially for those who have sensitive skins.

There are essentially two approaches to formulate an LDLD for mildness: (1) use mild surfactants such as nonionic surfactants, amphoteric surfactants, or a combination of such surfactants; (2) use additives that are anti-irritants such as modified protein or polymers. Examples of recent LDLD patents with mildness benefit are listed in Table 7.12.

4. Formulating for Desirable Aesthetics

The aesthetic attributes of LDLDs are just as important as their performance. This includes color, fragrance, cloud and clear points, viscosity, and product stability. Color, fragrance, and viscosity are usually chosen based on consumer preference. The cloud and clear points have to be adequate for the temperature to which the product is likely to be exposed.

(a) Cloud and Clear Points. The cloud point is the temperature at which the product begins to turn cloudy or hazy upon cooling. The clear point is the temperature at which the cloudy product turns clear again upon warming. In North America and Europe it is desirable that the cloud point be below 4°C and the clear point not exceed 10°C.

TABLE 7.10 Formulating LDLDs for Effective Cleaning: Patent Examples (1979–1995)

Patent (year)	Inventor(s) (company)	Technology	Claimed benefit
U.S. 5,378,409 (1995)	Ofosu-Asante (Procter & Gamble)	Alkylethoxy carboxylate mixture and Ca ions; pH 8–10	Good grease removal, mildness to skin, and good storage stability
U.S. 5,376,310 (1994)	Cripe *et al*. (Procter & Gamble)	Alkylethoxy carboxylate and Mg ions buffered at pH 8–10	Good grease removal, mildness to skin, and good storage stability
U.S. 5,298,195 (1994)	Brumbaugh (Amway)	Amido amine oxide or alkylethoxylated carboxylate	Improved detergency and foam stability over range of water hardness
U.S. 5,269,974 (1993)	Ofosu-Asante (Procter & Gamble)	Alkylamphocarboxylic acid and Mg or Ca ions at pH 7–10	Improved grease cleaning, sudsing, and stability
U.S. 5,230,823 (1993)	Wise *et al*. (Procter & Gamble)	Alkylethoxy carboxylate with minimal alcohol ethoxylate and soap byproducts; high pH and Mg ions	Good grease removal and mildness; high pH and Mg versions improve grease removal maintaining mildness
U.S. 5,236,612 (1993)	Rahman *et al*. (Lever Brothers)	Alkyl glycerates as coactive	Enhanced oil removal
U.S. 5,167,872 (1992)	Pancheri *et al*. (Procter & Gamble)	Polymeric and anionic surfactants forming complexes	High sudsing; improved grease efficacy
U.S. 5,096,621 (1992)	Tosaka *et al*. (Kao)	Dialkylamine oxides and anionics or nonionics	Permeability and efficacy
U.S. 4,992,212 (1991)	Corring *et al*. (Lever Brothers)	Organic base, zinc salt, and complexing agent	Superior cleaning without staining of aluminum utensils
U.S. 4,923,635 (1990)	Simion *et al*. (Colgate-Palmolive)	0.5–1.8% Mg; triethanolammonium	Improved oily soil removal
U.S. 4,904,359 (1990)	Pancheri *et al*. (Procter & Gamble)	Polymeric and anionic surfactants forming complexes	High sudsing; improved grease efficacy
U.S. 4,919,839 (1990)	Durbut *et al*. (Colgate-Palmolive)	Microemulsion	Superior grease removal
U.S. 4,834,903 (1989)	Roth *et al*. (Henkel)	Low DP long-chain polyglucoside alkylene oxide adducts	Improved detergency

(continued)

TABLE 7.10 (Contd.)

Patent (year)	Inventor(s) (company)	Technology	Claimed benefit
U.S. 4,797,231 (1989)	Schumann *et al*. (Henkel)	Abrasives	Neat — regular dishwashing; dilute – abrasive
U.S. 4,839,098 (1989)	Wisotzki *et al*. (Henkel)	Alkyl glucoside and dialkyl sulfosuccinate	Improved detergency and foam stability on proteinaceous soils
U.S. 4,853,147 (1989)	Choi (Colgate-Palmolive)	Cationic surfactant; C_{21}-dicarboxylic salt	Low-temperature detergency
U.S. 4,732,704 (1988)	Biermann *et al*. (Henkel)	Fatty alkyl C12–C14 monoglucosides	Enhanced foaming and detergency
U.S. 4,772,425 (1988)	Chirash *et al*. (Colgate-Palmolive)	Suspended low-density abrasives	Baked-on/dried-on food removal; improved stability with low viscosity
U.S. 4,772,423 (1988)	Pancheri *et al*. (Procter & Gamble)	Anionic-based with polymeric surfactant and betaine	Improved grease efficacy
U.S. 4,681,704 (1987)	Bernardino *et al*. (Procter & Gamble)	Mg alkylethoxy sulfate, C10–C14 alkyl amine oxide and amidoalkyl betaine	Greasy soil removal; good suds mileage
U.S. 4,614,612 (1986)	Reilly *et al*. (Lever Brothers)	Lemon juice	Effective against difficult soils
U.S. 4,492,646 (1985)	Welch (Procter & Gamble)	Highly ethoxylated drainage promoting nonionic surfactant	Complete drainage reducing spotting and filming on tableware
U.S. 4,430,237 (1984)	Pierce *et al*. (Colgate-Palmolive)	Nonionic mixture of alkyl glyceryl esters	Improved grease cleaning and foam stability
U.S. 4,368,146 (1983)	Aronson *et al*. (Lever Brothers)	Anionic/nonionic based plus polymers and alkali metal salt of casein	Rapid and uniform draining with no spotting or filming
U.S. 4,316,824 (1982)	Pancheri (Procter & Gamble)	Mg alkylethoxy sulfate and C10–C14 alkyl amine oxide	High sudsing; more effective detergency
U.S. 4,268,406 (1981)	O'Brien *et al*. (Procter & Gamble)	Reducing agent and nitrogen-containing protein denaturant	Superior cleaning of protein and carbohydrate soils
U.S. 4,133,779 (1979)	Hellyer *et al*. (Procter & Gamble)	Mg alkyl polyethoxy sulfate and C8–C16 alkyl amine oxide	Removal of greasy soils

TABLE 7.11 Formulating LDLDs for High and Long-Lasting Foam: Patent Examples (1981–1995)

Patent (year)	Inventor(s) (company)	Technology	Claimed benefit
U.S. 5,352,387 (1994)	Rahman *et al*. (Lever Brothers)	Novel *N*-alkylglyceramide surfactants	Enhanced foam stability
U.S. 5,338,491 (1994)	Connor *et al*. (Procter & Gamble)	Glycerol amides [*N*-(1,2-propanediol) fatty acid amide]	Foaming and solubility benefits to comparable ethanolamides
U.S. 4,877,546 (1989)	Lai (Colgate-Palmolive)	Nonionic hydroxypropyl guar gum derivative	Enhanced foaming
U.S. 4,732,707 (1988)	Naik *et al*. (Lever Brothers)	Alkyl ether sulfates based on specific aliphatic carbon chain	Excellent foaming and detergency
U.S. 4,663,069 (1987)	Llenado (Procter & Gamble)	Alkyl polysaccharide-based surfactant composition	Stable foam, easily rinsed
U.S. 4,680,143 (1987)	Edge *et al*. (Lever Brothers)	Ternary system: dialkyl sulfosuccinate, LAS and/or SAS and alkyl ether sulfate	Improved performance and physical characteristics
U.S. 4,596,672 (1986)	MacDuff *et al*. (Lever Brothers)	Dialkyl sulfosuccinate and fatty acid dialkanolamide	Enhanced performance and physical characteristics
U.S. 4,599,188 (1986)	Llenado *et al*. (Procter & Gamble)	Alkyl polysaccharides and anionic surfactant blends	Stable foam, readily rinsed
U.S. 4,576,744 (1986)	Edwards *et al*. (Lever Brothers)	Polymers	Enhanced foam stability and increased viscosity
U.S. 4,528,128 (1985)	Naik (Lever Brothers)	Dialkyl sulfosuccinates of particular chain lengths	Enhanced foam stability in both soft and hard water
U.S. 4,537,709 (1985)	Edge *et al*. (Lever Brothers)	Particular chain length LAS and alkyl ether sulfates	Improved foaming performance
U.S. 4,556,509 (1985)	Demangeon *et al*. (Colgate-Palmolive)	Low-molecular-weight organic diamine diacid salt	Improved foam stability and degreasing activity in soft water

(continued)

TABLE 7.11 (Contd.)

Patent (year)	Inventor(s) (company)	Technology	Claimed benefit
U.S. 4,536,318 (1984)	Cook *et al*. (Procter & Gamble)	Alkyl polysaccharide with anionic cosurfactants	Stable foam, readily rinsed
U.S. 4,434,087 (1984)	Hampson *et al*. (Lever Brothers)	Dialkyl sulfosuccinate (C6 and C8 alkyl)	Good foaming and cleaning
U.S. 4,434,089 (1984)	Billington *et al*. (Lever Brothers)	Dialkyl sulfosuccinate with protein	Enhanced foaming and cleaning in hard water
U.S. 4,434,090 (1984)	Hampson *et al*. (Lever Brothers)	Unsymmetrical dialkyl sulfosuccinate and dialkyl sulfosuccinate	Enhanced foaming and cleaning
U.S. 4,434,091 (1984)	Cox *et al*. (Lever Brothers)	Unsymmetrical dialkyl sulfosuccinate	Enhanced foaming and cleaning
U.S. 4,454,060 (1984)	Lai *et al*. (Colgate-Palmolive)	Novel cationic copolymer	Improved foam stability
U.S. 4,435,317 (1984)	Gerritsen *et al*. (Procter & Gamble)	Tertiary anionic surfactant mixture; Mg level corresponds to alkyl sulfate level	Maximum foam stability
U.S. 4,486,338 (1984)	Ootani *et al*. (Kao)	Succinic acid derivative with anionic and tertiary amine oxide	Superior foaming, detergency, and stability
U.S. 4,490,279 (1983)	Schmolka (BASF)	Nonionic block polymer surfactant with an amine oxide	High foaming and good foam stability
U.S. 4,277,378 (1981)	Tsujii *et al*. (Kao)	Partially neutralized succinic acid derivative	Good detergency and foaming; mild to skin
U.S. 4,235,752 (1980)	Rossall *et al*. (Lever Brothers)	Effective secondary alkyl sulfate isomers	Improved foam stability

TABLE 7.12 Formulating LDLDs for Mildness: Patent Examples (1980–1995)

Patent (year)	Inventor(s) (company)	Technology	Claimed benefit
U.S. 5,387,373 (1995)	Naik (Unilever)	C10–C11 primary alkyl sulfate	Enhanced mildness
U.S. 5,284,603 (1994)	Repinec *et al*. (Colgate-Palmolive)	Nonionic-based surfactant system	Mildness
U.S. 5,340,502 (1994)	Palicka (Berol Novel AB)	Anionic surfactant; combination of three amphoteric compounds	Mildness maintaining good cleaning
U.S. 5,230,835 (1993)	Deguchi *et al*. (Kao)	Alkyl polyglucoside with polymers	Reduced irritation, increased foaming and detergency; rinsing and feel to hands
U.S. 5,084,212 (1992)	Farris *et al*. (Procter & Gamble)	C8 alkyl glyceryl ether sulfonate; foam enhancers	Ultramild surfactant
U.S. 5,139,705 (1992)	Wittpenn *et al*.	Blend of nonionics with low and high melting points	Mild, nonirritating composition
U.S. 5,154,850 (1992)	Deguchi *et al*. (Kao)	Alkyl glucoside	Reduced irritation and damage to hair and skin
U.S. 5,075,042 (1991)	Allison *et al*. (PPG Industries)	Alkyl polyethyleneoxy sulfonate; anionic/nonionic	Reduced primary skin irritation potential
U.S. 5,025,069 (1991)	Deguchi *et al*. (Kao)	Alkyl glucoside-based compositions; terpene and isothiazolone derivatives	Reduced irritation and damage to hair and skin; color and odor stability
U.S. 5,073,293 (1991)	Deguchi *et al*. (Kao)	Alkyl glucoside and dicarboxylic acid surfactant	Mild, pleasant feel to hands
U.S. 4,595,526 (1986)	Lai (Colgate-Palmolive)	Novel high-foaming nonionic surfactant-based composition	Superior skin mildness

(continued)

TABLE 7.12 (Contd.)

Patent (year)	Inventor(s) (company)	Technology	Claimed benefit
U.S. 4,555,360 (1985)	Bissett (Procter & Gamble)	Anionic surfactants with betaine and amine oxide	Improved mildness
U.S. 4,554,098 (1985)	Klisch *et al.* (Colgate-Palmolive)	Alkyl ether sulfate, nonsoap anonionic, zwitterionic, and alkanoic acid alkanolamide	Reduced skin irritation; good cleaning and foaming
U.S. 4,526,710 (1985)	Fujisawa *et al.* (Kao)	Anionic phosphate surfactants in combination with amides and amine oxide	Mild to hands
U.S. 4,37,146 (1983)	Jones *et al.* (Procter & Gamble)	Surfactant with tertiary alcohol	Mild to skin
U.S. 4,247,425 (1981)	Egan *et al.* (Sherex Chemical)	Nonionic with polyoxyalkylene chain composed of randomly distributed oxyethylene and oxypropylene residues	Low eye and skin irritation
U.S. 4,256,611 (1981)	Egan *et al.* (Sherex Chemical)	Ethylene oxide adduct of partial glycerol esters of detergent-grade fatty acid and certain anionic surfactants	Low eye and skin irritation; adjust viscosity of aqueous solutions
U.S. 4,287,102 (1981)	Miyajima *et al.* (Lion)	Salt of olefin sulfonic acid (C12–C16) and tertiary amine oxide	Good detergency and little and roughening
U.S. 4,259,216 (1981)	Miyajima *et al.* (Lion)	α-Olefin sulfonate, alkylethoxy sulfate, and alkyl amine oxide with aryl sulfonate	No hand roughening and good for vegetables
U.S. 4,235,759 (1980)	Ohbu *et al.* (Lion)	Polyoxyalkylene alkyl ether sulfate and cationic surfactant	Mild to skin and good detergency
U.S. 4,195,077 (1980)	Marsh *et al.* (Procter & Gamble)	Modified protein	Protect keratinous material

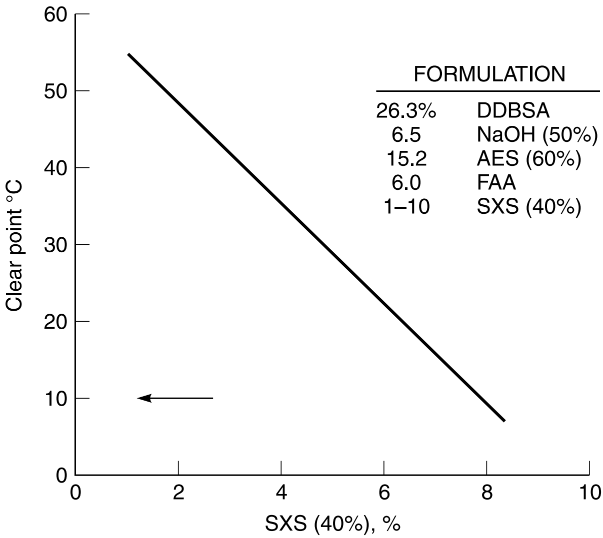


FIG. 7.4 Effect of sodium xylene sulfonate on the clear point of a premium LDLD blend. (From Drozd, J.C., *Chemical Times & Trends*, 8, 49, 1985. Reproduced with permission.)

The cloud and clear points of an LDLD can be adjusted using hydrotropes [83,84] such as sodium xylene sulfonate (SXS), sodium cumene sulfonate (SCS), alcohols, or urea. Figure 7.4 illustrates the significant effect of SXS on the clear point of an LDLD formulation.

(b) Viscosity. The viscosity of an LDLD is very important for its consumer acceptability and its dispersibility on dilution [85]. The viscosity of an LDLD is typically in the range 100 to 500 cP. In some markets such as Malaysia, Singapore, and Hong Kong, consumers prefer a much thicker product with viscosity in the range 2000 to 3000 cP. Consumers generally associate a thicker product with more "ingredients" in the product. However, technically, the viscosity of an LDLD is a strong function of not only its active ingredient level but also the isomer distribution in the surfactant, the relative amount of different surfactants, and the salt levels. Salt can be both a viscosity builder and a viscosity reducer, depending on where the formulation is on its salt curve, as mentioned above. An example of a simple system is sodium dodecylether sulfate (2.8EO) at 15% concentration. The viscosity first increases with the addition of NaCl and then decreases with further increase of the amount of NaCl [86]. AEOS with a narrow EO distribution thickens much more than AEOS with a conventional, broad EO distribution. Other factors that affect salt thickening are carbon chain length and carbon chain distribution [86].

Salt also has a significant effect on LAS. Depending on the cation of the LAS, salt in the range 0 to 2% can have a modest or large effect on the viscosity.

Fatty alkanolamides are mainly used as foam stabilizers, but they can also have a large effect on the viscosity of an LDLD formulation, usually increasing it. Other viscosity modifiers include hydrotropes such as alcohol, SXS, SCS, urea, and water-soluble polymers. However, not all of these have the same magnitude of effect, which depends on the surfactant system in the product.

(c) Physical Stability. Physical stability is another important product attribute that cannot be overlooked. Consumers would not want to purchase a product that changes physically over time. This may include precipitation, phase separation, or microbial contamination.

Aging studies are typically conducted to ensure physical stability of products at market age. Various aging conditions are necessary to simulate the conditions the product may encounter from warehousing, transportation, and storage in stores and at home. These conditions include elevated temperature such as 50°C and low temperature just above freezing point.

The other standard aging study normally conducted is to expose the product to sunlight to simulate storage of the product at home near a kitchen window to test for color and phase stability.

During aging, periodic examinations of products are made to check for effects to the key product characteristics such as pH, color, fragrance, product appearance; packaging is checked for any changes and deviations from room temperature samples. Any unacceptable changes and deviations need to be investigated to identify the cause and to determine the corrective measures. The entire series of aging studies need to be repeated when corrections are made to the formula.

To ensure a product's ability to withstand microbial contamination, adequacy of preservation studies need to be conducted. Consumers can contaminate products during use in the home. If the product is not able to control the growth of microorganisms, unsightly growth could result in the product affecting its quality. If the formulation is not self-preserving then the incorporation of a suitable preservative would be necessary.

C. Factors Affecting Performance

1. Effect of Surfactant Type

Detergents in general do a better job of cleaning if they contain a mixture of surfactants. It is best if the mixture includes a variety of types of surfactants as well as a variety of carbon chain lengths. As discussed earlier, it is an advantage to mix anionic with nonionic or amphoteric surfactants. These mixtures can show a reduction in CMC and improvement in grease cleaning and foaming compared with individual surfactants due to the favorable interaction of head groups.

TABLE 7.13 Optimum Chain Length of LAS as a Function of Hardness

Hardness (ppm)	Optimum foam stability[a]
0	C13
50–150	C11–C12
>150	C10–C11–C12

[a]Product formulation: 24% LAS, 6% AEOS, and 2% LMMEA.

2. Effect of Carbon Chain Distribution

Several authors have described the effect of alkyl chain length on performance. For LAS, a widely used surfactant in LDLDs, the most important factor in the performance is the carbon chain distribution [87]. The optimum chain length of LAS for foam stability in a typical LDLD formulation varies depending on water hardness. This is illustrated in Table 7.13 for a formulated product of 24% LAS, 6% AEOS, and 2% LMMEA.

The location of the phenyl group on the alkyl chain (within the limits of commercially available LAS) has little effect on the performance [87]. For SAS, an anionic surfactant widely used in European LDLDs, more plates are cleaned in the C14–C15 range than at longer or shorter lengths. This is true for SAS alone and for SAS/AEOS mixtures (see Figure 7.5) [88].

3. Effect of pH

The pH can do more than giving a stable formulation. Acidic pH can act as an antibacterial condition. Slightly acidic pH (around 5.5) is matched to the physiologic pH of skin. Alkaline pH can help clean greasy soils, although it is irritating to skin. Shifts in pH can improve preservation of the product improving the efficacy of preservatives or shifting the formulation to pH values more hostile to microbes. As a balance to give maximum grease cleaning while maintaining skin mildness, most commercial products have a pH close to neutral. Most surfactants are also most stable under neutral pH.

4. Effect of Inorganic Ions

An important factor in the formulation of dishwashing liquids is the presence of inorganic ions. These can be present as impurities in all commercial surfactants. They are also present as calcium and magnesium carbonates, sulfates, and chlorides in hard water. They are deliberately added to products by some manufacturers as important performance boosters and viscosity modifiers. As performance boosters, divalent ions have a special function and are added as an inorganic salt, such as $MgSO_4$, or as the counterion of an anionic surfactant, such as $Mg(LAS)_2$.

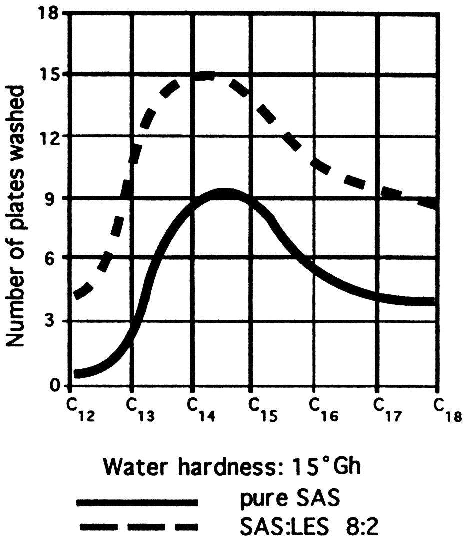


FIG. 7.5 Miniplate test of SAS (and mixtures) as a function of the C chain length. Concentration: 0.3 g/L of active substance. (*Source*: From Ref. 88. Reproduced with permission.)

One of the effects of increased electrolyte concentration is lowering of the CMC. This has direct implications for detergency. Electrolytes do this for ionic surfactants by screening the ionic head groups in a micelle from each other. Adding salts decreases the CMC in the following order for lauryl sufate: Ca^{2+}, Mg^{2+} < $N(C_2H_5)_4^+$ < $N(CH_3)_4^+$ < Cs^+ < K^+ < Na^+ < Li^+. The larger the polarizability of the ion and the larger the valence, the greater is the decrease in the CMC. The smaller the radius of the hydrated ion, the greater is the decrease in the CMC [34].

A similar effect occurs in the electrical double layer that surrounds the surface of an object to be cleaned. Items with a relatively highly charged surface, such as glass, ceramics, and metals with oxide coatings, first repel surfactants with a like charge and attract surfactants with an opposite charge. Adding salts causes a decrease in the adsorption of the like-charged surfactant. In dishwashing liquids, many of the surfaces to be cleaned are negatively charged. Because the principal surfactants used in dishwashing detergents are anionic, adding salts increases the adsorption of anionics onto a negatively charged surface. For nonpolar items, such as many plastics, electrolytes also increase the adsorption of ionic surfactants because the mutual repulsion between the head groups is decreased.

Ionic strength also affects the stability of the emulsions that are formed as the dishes are cleaned. Emulsions in general decrease in stability with increasing electrolyte concentration. In the presence of electrolyte, the thickness of the electrical double layer is decreased. This decreases the stability of the emulsion. If the stability of the emulsion is too low, redeposition of soil can be a problem. Fortunately, the emulsion formed in dishwashing need not last very long. Also, many modern dishwashing formulations include substantial amounts of both anionic and nonionic surfactants. Nonionic emulsions are much less affected by ionic strength.

The most important effect of electrolytes is the effect of Ca^{2+} and Mg^{2+} ions on dishwashing performance. Numerous patents deal with the beneficial effects of both ions on dishwashing performance. It is thought that these divalent ions form a complex with anionic surfactants. This complex allows the anionic surfactant to adsorb more readily on surfaces with a negative surface charge.

A preferred mode of adding magnesium to a dishwashing liquid is to use the MgO or $Mg(OH)_2$ to neutralize the surfactants after they are formed by sulfonation or sulfation [89]. This method is preferred because adding magnesium from salt generally requires additional hydrotrope. Magnesium is typically preferred for use over calcium, since calcium surfactant salts are much less soluble. However, one series of patents discloses the use of calcium added to the formulation in the form of calcium xylene sulfonate for improved stability [90].

Recent patents describe the use of low-molecular-weight organic diamines in place of the Ca or Mg divalent ions [91,92]. The inventors claim that the diamines in hand dishwashing detergents are most effective when the pH is in the range 8 to 12. The diamines provide the same function as the divalent ions but with additional benefits. The reduction or elimination of the divalent ions leads to improved benefits in dissolution, rinsing, and low-temperature product stability, according to the patents.

5. Effect of Raw Material Variations

Some LAS mixtures appear to be self-hydrotroping; others need extra hydrotrope [93]. Commercial LAS contains various amounts of the 2-phenyl isomer and dialkyltetralin sulfonates. The 2-phenyl content significantly affects the solubility, and the tetralins considerably reduce the viscosity. This variation in 2-phenyl isomer and tetralin content is a result of the industrial process used to make the linear alkylbenzene. LAS is made from three primary processes that use different catalysts, $AlCl_3$, HF, and DETAL, resulting in different amounts of 2-phenylalkanes and dialkyltetralins. Material from the $AlCl_3$ process is considered high in 2-phenyl content and high in dialkyltetralins, material from the HF process is considered low in 2-phenyl content and low in dialkyltetralins, and material from the DETAL process is considered high in 2-phenyl content and low in dialkyltetralins.

Another consideration is the source of the hydrophobic end of the surfactant. It is well known that oleochemical fatty alcohols have even numbers of carbons and petrochemicals fatty alcohols have odd and even numbers. As discussed earlier, carbon chain length has an effect on dishwashing performance. However, when dishwashing compositions were made out of lauryl range (C12) hydrophobes, there was no difference in performance or physical properties between those from oleochemical and petrochemical sources [94].

D. Recent Patent Trends (1996–2003)

Over 160 U.S. patents were granted between 1996 and 2003 in the area of LDLDs or hand dishwashing liquids. Many of these can be classified as general composition of matter patents often utilizing mixed surfactant systems for beneficial overall performance. Some patents describe the use of microemulsion technology for improved grease removal. Many patents describe the use of novel surfactants or the use of nontraditional surfactants formulated in LDLDs, described in more detail below. There are a significant number of patents describing use of various polymers in LDLDs. An interesting new development is the use of enzymes in LDLDs. Several recent patents relate to enzymes in hand dishwashing. Disinfectant-type applications or formulations are also described. A few patents describe cleaning extra tough soils and other unique applications. All of these recent patent trends are described in more detail below.

1. Novel Surfactants

Patent examples utilizing new or atypical surfactants are summarized in Table 7.14. The types of surfactants used in the examples are anionic, nonionic, amphoteric, and one cationic. Examples of novel anionic surfactants are mid-chain branched ethoxy sulfates. These surfactants are claimed to prove useful in the cleaning of heavily soiled dishware. The chelating surfactant ethylene diaminetriacetate is claimed to provide good foaming and grease cutting properties, particularly in hard water. Some novel nonionic surfactants include an ethoxylated/propoxylated nonionic surfactant, a gemini surfactant, and a bridged polyhydroxy fatty acid amide. A few patents list use of the amphoteric surfactant sultaine, which is new for use in LDLDs but has found previous use in personal care products.

2. Polymers in LDLDs

Several recent patents describe the benefits of polymers in LDLDs (Table 7.15). Polymers are well known to interact with surfactants and provide many interesting properties. Some of the benefits claimed in the patents summarized in Table 7.15 are soil resistance due to amino acid copolymers, polyethylene glycol as a grease release agent, increased grease removal from polyoxyethylene diamine, enhanced foam volume and duration, increased solubility, and enhanced mildness by ethylene oxide–propylene oxide copolymers. As described in these various patents, the addition of polymers to LDLDs can aid performance in many important attributes of the product.

TABLE 7.14 Formulating LDLDs with Novel Surfactants: U.S. Patent Examples (1996–2003)

Number	Year	Inventors	Company	Title	Benefit
6,617,303	2003	Smith, Smadi	Huntsman	Surfactant compositions containing alkoxylated amines	Contains alkoxylated amines
6,602,838	2003	Koester, Behler, Neuss, Schmid, Elsner	Cognis	Hand dishwashing liquid comprising an alkoxylated carboxylic acid ester	Contains an alkoxylated carboxylic acid ester
6,495,507	2002	Arvanitidou	Colgate	High-foaming, grease-cutting light-duty liquid detergent	Contains an amphoacetate
6,492,314	2002	Jakubicki, Szewczyk	Colgate	High-foaming, grease-cutting composition containing a C12/C14 alkylamidopropyldimethyl amine oxide	Contains a C12/C14 alkylamidopropyldimethyl amine oxide
6,423,678	2002	Brumbaugh, Faber, Berube	Amway	Alcohol ethoxylate–PEG ether of glycerin	Hydrotrope provides increased foam generation
6,281,181	2001	Vinson, Cripe, Scheper, Stidham, Connor	Procter & Gamble	Light-duty liquid or gel dishwashing detergent compositions comprising mid-chain branched surfactants	Contain mid-chain branched ethoxy sulfates; useful for heavily soiled dishware at low temperature and high hardness
6,268,331	2001	D'Ambrogio, Connors	Colgate-Palmolive	Grease-cutting light-duty liquid detergent comprising lauryol ethylene diaminetriacetate	Contains ethylene diaminetriacetate — a chelating surfactant; good foaming and grease-cutting properties
6,187,734	2001	Erilli, Gallant	Colgate-Palmolive	High-foaming, grease-cutting light-duty liquid detergent comprising dialko sulfo succinates and zwitterionic surfactants	High-foaming, good grease-cutting properties

(continued)

TABLE 7.14 (Contd.)

Number	Year	Inventors	Company	Title	Benefit
6,187,733	2001	Fabry, Weuthen	Henkel	Aqueous manual dishwashing composition containing a monoglyceride sulfate and at least two other surfactants	Contains monoglyceride sulfate
6,127,328	2000	D'Ambrogio, Jakubicki, Arvanitidou, Gambogi	Colgate-Palmolive	High-foaming grease-cutting light-duty liquid composition containing a C12 alkyl amido propyl dimethyl amine oxide	Contains a C12 alkylamidopropyldimethyl amine oxide for superior grease cutting
6,066,755	2000	Koch, Kwetkat	Huels	Amphiphilic compounds with a plurality of hydrophilic and hydrophobic groups based on carbonic acid derivatives	Amphiphilic compounds which have at least two hydrophilic and two hydrophobic groups
6,022,844	2000	Baillely, Perkins	Procter & Gamble	Cationic detergent compositions	Cationic esters to facilitate removal of greasy soils
5,932,534	1999	Gorlin, Gambogi, D'Ambrogio, Jakubick, Zyzyck	Colgate-Palmolive	Light-duty liqiuid containing sultaine surfactants for cleaning dishware and leaving a shiny appearance	Contains sultaine surfactants
5,922,662	1999	Thomas	Colgate-Palmolive	High foaming mild nonionic surfactant-based liquid detergents	Contains an alkyl succinamate
5,888,955	1999	Foley, Clarke, Yi-Change, Vinson	Procter & Gamble	Liquid dishwashing detergent compositions	Contains a bridged polyhydroxy fatty acid amide for improved sudsing
5,872,111	1999	Au, Harichian, Hung, Vermeer	Lever Brothers	Compositions comprising glycosylamide surfactants	Contain environmentally friendly carbohydrate surfactants

5,811,384	1998	Tracy, Li, Dahanayake, Yang	Rhodia	Compositions comprising at least one nonionic gemini surfactant – is useful, e.g., in personal care compositions, household cleaning products and industrial cleaners	Contain at least one nonionic gemini surfactant and are extremely effective emulsifiers and provide improved detergency
5,780,417	1998	Gorlin	Colgate-Palmolive	Light-duty liquid cleaning compositions	Contains ethoyxlated/propoxylated nonionic surfactant
5,739,092	1998	Ofosu-Asante	Procter & Gamble	Liquid or gel dishwashing detergent containing alkyl ethoxy carboxylate divalent ok ions and alkylpolyethoxypolycarboxylate	Certain alkylpolyethoxypolycarboxylate surfactants prevent insoluble salt precipitation
5,736,503	1998	Vinson	Procter & Gamble	High-sudsing detergent compositions with specially selected soaps	Contain specially selected soap such as sodium 2-butyl-1-octanoate; provide spontaneous emulsification of grease
5,489,393	1996	Connor, Scheibel, Fu	Procter & Gamble	High-sudsing detergent with *n*-alkoxy polyhydroxy fatty acid amide and secondary carboxylate surfactants	Use of secondary carboxylate surfactants
5,480,586	1996	Jakubicki, McCandlish	Colgate-Palmolive	Light-duty liquid detergent composition containing a sulfosuccinamate-containing surfactant blend	Use of sulfosuccinamate
5,393,466	1995	Ilardi, Massaro, Rerek, Wenzel	Lever Brothers	New fatty acid ester compounds of polyoxyalkylene isethionate salts — are mild surfactants with good calcium tolerance for use in liquid and solid detergent compositions and personal care products	Superior to nonalkoxylated isethionates in mildness, performance, and calcium tolerance

TABLE 7.15 LDLDs Containing Polymers: U.S. Patent Examples (1996–2003)

Number	Year	Inventors	Company	Title	Benefit
6,645,925	2003	Sivik, Bodet, Kluesener, Scheper, Yeung, Bergeron	Procter & Gamble	Liquid detergent compositions comprising quaternary nitrogen containing and/or zwitterionic polymeric suds enhancers	Contains a polymer claimed to be a suds enhancer, suds volume extender, and effective in preventing redeposition of grease
6,509,306	2003	Wisniewski, Thomas, Paye	Colgate	Light-duty liquid cleaning composition	Contains a silicon polymer; demonstrates improved sensory attributes and foam
6,455,482	2002	D'Ambrogio, Hassan, Dixit	Colgate	Light-duty liquid cleaning compositions comprising a crosslinked polymer	Contains a crosslinked polymer
6,380,150	2002	Toussaint, Oldenhove, Broze	Colgate	Light-duty liquid composition containing gelatin beads and polyacrylate thickener	Stably suspended oil containing gelatin beads with a polyacrylate polymeric thickener
6,172,024	2001	Arvanitidou	Colgate-Palmolive	High-foaming and grease-cutting light-duty liquid detergents comprising a polyoxyethylene diamine	Contain positively charged polymer to provide increased grease removal in compositions already exhibiting excellent disinfectant properties on hard surfaces
6,172,023	2001	Arvanitidou	Colgate-Palmolive	High-foaming grease-cutting light-duty detergent	Addition of polymers to high disinfectant acidic compositions to improve grease cutting
6,172,022	2001	Arvanitidou	Colgate-Palmolive	High foaming and grease cutting light-duty liquid detergents comprising a polyoxyethylene diamine	Contain positively charged polymer such as a poly(oxyethylene diamine) to provide increased grease removal
6,160,110	2000	Thomaides, Rodriques, Peterson	National Starch	Amino acid copolymers having pendant polysaccharide moieties and uses thereof	Copolymers assist in providing soil resistance

6,133,217	2000	Lewis, Lewis	Huntsman	Solubilization of low 2-phenyl alkyl benzene sulfonates	Addition of EO–PO block copolymers to detergents to increase solubility
6,083,897	2000	Lewis, Lewis	Huntsman	Solubilization of low 2-phenyl alkyl benzene sulfonates	Addition of polyethylene glycols to detergents to increase solubility
5,985,813	1999	Arvanitidou	Colgate-Palmolive	Liquid cleaning compositions based on cationic surfactant, nonionic surfactant and nonionic polymer	Addition of EO–PO block copolymers to cationic-based detergents to increase grease cutting
5,977,275	1999	Rodriques, Carrier, Furr	National Starch	Polymers having pendant polysaccharide and uses thereof	Polymer provides soil resistance to an article
5,756,439	1998	He, Fair, Massaro	Lever Brothers	Liquid compositions comprising copolymer mildness actives	Enhanced mildness by addition of EO–PO copolymers
5,604,195	1997	Misselyn, Erilli, Broze	Colgate-Palmolive	Liquid cleaning compositions with polyethylene glycol grease release agent	Contains a grease release agent
5,552,089	1996	Erilli, Mahieu, Misselyn, Yianakopoulos	Colgate-Palmolive	Aqueous light-duty liquid detergent compositions preventing grease buildup — comprising surfactants, solubilizing agent and grease release agent	Exhibits grease release effect, grease buildup prevented
5,486,307	1996	Misselyn, Mahieu, Erilli	Colgate-Palmolive	Liquid cleaning compositions with grease release agent and perfume	Contains grease release polymer
6,207,631	2001	Kasturi, Schafer, Sivik, Kluesener, Scheper	Procter & Gamble	Detergent compositions comprising polymeric suds volume and suds duration enhancers and methods for washing with same	Polymeric materials provide enhanced foam volume and duration

3. Use of Enzymes in LDLDs

Enzymes have been used widely in laundry detergents and automatic dishwashing detergents, but not previously in applications involving contact with the skin. Table 7.16 summarizes some recent patents describing the use of enzymes in hand dishwashing detergents. The enzyme supplier Novo Nordisk has patented modified polypeptides that have reduced allergenicity for use in hand dishwashing and personal care products [95]. Several formulations containing enzymes are patented by Procter & Gamble. The enzymes are added for skin conditioning, removing protein soils (protease), removing juice soils (pectinesterase), removing starch-based soils (amylase), and fat degrading (lipase).

4. Disinfectants

The series of patents listed in Table 7.17 describe LDLD formulations that are disinfecting to hard surfaces. One technology used to obtain disinfectant properties is the use of acids such as salicyclic acid or alpha-hydroxy acids. The pH of these formulations are claimed to be between 3 and 6. The second type of disinfecting formulation utilizes quaternary ammonium compounds as the active antimicrobial agent. However, these formulations will need to avoid using common anionic surfactants so as not to form the inactive anionic–cationic complex. Also claimed as active ingredients are Zn salts, terpene alcohols, trichlorocarbanilide, hydrogen peroxide, and an iodophor.

5. Enhanced Mildness and Skin Feel

Several patents listed in Table 7.18 describe the use of high levels of nonionic surfactants formulated with the specific purpose of increased mildness. As discussed earlier, this is one approach to formulating mild LDLDs. The remainder of the patents listed in Table 7.18 describe the addition of an ingredient to enhance mildness or improve the skin feel of the hands of the person doing the dishwashing. The ingredients claimed to benefit the skin feel attributes of the hands are an organosilane, monoalkyl phosphate ester, succinamate, and sucroglyceride surfactant.

6. Heavy-Duty Cleaning

A few recent patents are listed in Table 7.19 that describe the cleaning of really tough, burnt-on soiled dishware. In general these products are alkaline ($pH > 8$), might be thickened with a polymer thickener, and may contain a soluble abrasive. In one case, the use of branched ethoxy sulfate surfactants proves useful in cleaning heavily soiled dishware.

VI. NEW PRODUCTS

Since 1993 an incredible wave of evolution has taken place in the hand dishwashing liquid market. New products not only include "smarter" surfactants

TABLE 7.16 LDLDs Containing Enzymes: U.S. Patent Examples (1996–2003)

Number	Year	Inventors	Company	Title	Benefit
6,544,941	2003	Lee, Ghatlia	Unilever	Dishwashing composition	Contains serine protease and a metalloprotease and shows protein soil removal
6,201,110	2001	Olsen, Hansen, Beck	Novo Nordisk A/S	Polypeptide with reduced respiratory allergenicity	Modified polypeptides with reduced allergencicity for use in dishwashing, personal care products, etc.
6,162,778	2000	McKillop, Foley, Crabtree, Burckett-St. Laurent, Clarke, Patil	Procter & Gamble	Light-duty liquid or gel dishwashing detergent compositions having beneficial skin conditioning, skin feel and rinsability aesthetics	Nonionic surfactant- and hydrotrope-containing skin feel/rinsability enhancing system and skin conditioning protease enzymes
6,136,778	2000	Kamiya	—	Environment safeguarding aqueous detergent composition comprising essential oils	Composition maximizes the decomposing action of an enzyme and minimizes the use of surfactant
6,113,655	2000	Tsunetsugu, Moese, Baeck, Herbots	Procter & Gamble	Detergent compositions comprising a pectinesterase enzyme	Contains a pectinesterase; useful for removal of body, plant, fruit, and vegetable juice soils
5,952,278	1999	Mao, Marshall, Visscher	Procter & Gamble	Light-duty liquid or gel dishwashing detergent compositions containing protease	Small amounts of protease
5,851,973	1998	Foley	Procter & Gamble	Manual dishwashing composition comprising amylase and lipase enzymes	Comprises surfactants, calcium or magnesium ions, enzymes, and polymer thickeners
5,830,837	1998	Bisgard-Frantzen, Borchert, Svendsen, Thellersen, Van der Zee	Novo Nordisk A/S	Amylase variants	Variant of the parent alpha-amylase enzyme having improved dishwashing performance
5,786,316	1998	Baeck, Busch, Verschuere, Katrien	Procter & Gamble	Cleaning compositions comprising xylanolytic enzymes	Compositions have xylanase activity; show an excellent boost in cleaning performance on fruit, vegetables, and mud or clay soils

TABLE 7.17 Disinfectant LDLD Formulations: U.S. Patent Examples (1996–2003)

Number	Year	Inventors	Company	Title	Benefit
6,617,296	2003	Connors, D'Ambrogio, Nascimbeni	Colgate-Palmolive	Antibacterial light-duty liquid detergent	Contains a stable zinc inorganic salt which provides antibacterial benefits
6,258,763	2001	Arvanitidou, Sandhu	Colgate-Palmolive	Light-duty liquid composition containing an acid	High-foaming liquid-disinfecting composition which has good grease-cutting properties; has a pH of 3–6
6,187,735	2001	Gambogi, Durbut, Broze, Zyzyck	Colgate-Palmolive	Light-duty liquid detergent	High level of disinfectant properties, based on cationic and nonionic surfactants
6,184,194	2001	Arvanitidou, Suriano, Engels, Jakubicki	Colgate-Palmolive	High-foaming, grease-cutting light-duty liquid detergent having antibacterial properties comprising proton donating agent	High foaming and good grease-cutting properties, good mildness, as well as excellent disinfecting properties on hard surfaces
6,152,152	2000	Reynen, Aryana	Procter & Gamble	Antibacterial liquid dishwashing detergent compositions	Comprise surfactant, hydrotrope, and unsaturated terpene alcohol; disinfect dishware cleaning implements
6,140,290	2000	Gorlin	Colgate-Palmolive	High foaming nonionic surfactant-based liquid detergent	Contains an antibacterial agent (trichlorocarbanilide) which is soluble in polyethylene glycol
6,140,289	2000	Frank, McCandlish	Colgate-Palmolive	Cleaning composition for manual dishwashing comprises cationic, ethoxylated nonionic, amine oxide, and alkyl polyglucoside surfactants	High level of disinfectant properties, based on cationic and nonionic surfactants

6,113,933	2000	Beerse, Morgan, Baier, Bartolo, Bakken Schuette	Procter & Gamble	Mild, rinse-off antimicrobial liquid cleansing compositions containing acidic surfactants	Antimicrobial cleansing compositions based on anionic and nonionic surfactants and a pH of 3.0–5.5
6,106,851	2000	Beerse, Morgan, Baier, Bartolo, Bakken Schuette	Procter & Gamble	Mild, rinse-off antimicrobial liquid cleansing compositions containing salicyclic acid	Antimicrobial cleansing compositions based on 0.15–2% salicylic acid
6,103,683	2000	Romano, Trani, Minervini, Brown	Procter & Gamble	Disinfecting compositions and processes for disinfecting surfaces	Disinfecting of surfaces with 0.1–15% hydrogen peroxide, antimicrobial essential oil or mixture
5,968,539	1999	Beerse, Morgan, Baier, Chen, Bakken	Procter & Gamble	Mild rinse-off antimicrobial liquid cleansing compositions which provide residual benefit versus gram-negative bacteria	Antimicrobial compositions based on organic acids and antibacterial ingredients
5,728,667	1998	Richter	Reckitt & Colman	Compositions containing organic compounds	Anionic formulation containing quaternary ammonium germicidal compound
5,707,955	1998	Gomes, McCandlish, Fischler	Colgate-Palmolive	High-foaming liquid detergents containing a nonionic surfactant and three anionic surfactants	Contains disinfecting agent (iodophor) complexed with nonionic

TABLE 7.18 Formulating LDLDs for Enhanced Mildness or Skin Feel: U.S. Patent Examples (1996–2003)

Number	Year	Inventors	Company	Title	Benefit
6,509,306	2003	Wisniewski, Thomas, Paye	Colgate	Light-duty liquid cleaning composition	Contains a silicon polymer; demonstrates improved sensory attributes and foam
6,214,781	2001	Gambogi, Dalimier, Paye, Zocchi	Colgate-Palmolive	Light-duty liquid cleaning compositions comprising an organosilane	Improved sensory attributes for the hands
6,013,611	2000	Thomas, Gomes, Drapier, Church	Colgate-Palmolive	Light-duty liquid cleaning compositions especially for dishwashing	Contains a water-soluble nonionic surfactant
5,874,394	1999	Thomas, Gomes	Colgate-Palmolive	Light-duty liquid cleaning compositions containing monoalkyl phosphate ester	Enhanced mildness to the human skin
5,869,439	1999	Thomas, Gomes	Colgate-Palmolive	High-foaming nonionic surfactant-based liquid detergent	Contains alkyl succinamate; improved skin feel attributes
5,856,291	1999	Thomas, Gomes	Colgate-Palmolive	Light-duty liquid cleaning compositions containing alkyl sucroglyceride	Contains a sucroglyceride surfactant
5,629,279	1997	Erille, Repinec, Gomes	Colgate-Palmolive	High-foaming nonionic surfactant-based liquid detergent	High foaming nonionic based

TABLE 7.19 Formulating LDLDs for Tough Soils or Other Specialty Products: U.S. Patent Examples (1996–2003)

Number	Year	Inventors	Company	Title	Benefit
6,589,926	2003	Vinson, Oglesby, Scheper, Kasturi, Ofosu-Asante, Clarke, Owens, Castro, Embleton	Procter & Gamble	Dishwashing detergent compositions containing organic diamines	Low-molecular-weight diamine-containing compositions have improved grease removal, sudsing, low-temperature stability and improved dissolution properties
6,362,155	2002	Kinscherf	Colgate-Palmolive	Thickened microemulsion cleaning compositions comprising xanthum gum	Superior cling to a vertical surface and effective in the removal of oily and greasy soil
6,337,312	2002	Kinscherf, Aszman, Thomas	Colgate-Palmolive	Liquid crystal compositions comprising an abrasive and magnesium sulfate heptahydrate	Effective as prespotting agent and for removing hard-to-remove soils from substrates
6,281,181	2001	Vinson, Cripe, Scheper, Stidham, Connor	Procter & Gamble	Light-duty liquid or gel dishwashing detergent compositions comprising mid chain branched surfactants	Contain branched ethoxy sulfate surfactants found especially useful for cleaning heavily soiled dishware
6,274,539	2001	Kacher, Wallace, Allouch	Procter & Gamble	Light-duty liquid or gel dishwashing detergent compositions having controlled pH and desirable food soil removal, rheological, and sudsing characteristics	Alkaline product thickened with acrylic copolymer useful for heavily soiled dishware
6,228,832	2001	Kinscherf, Thomas, Slezak, Psihoules	Colgate-Palmolive	Microemulsion cleaning composition	Alkaline, microemulsion composition effective in cleaning burnt-on greasy soils

(continued)

TABLE 7.19 (Contd.)

Number	Year	Inventors	Company	Title	Benefit
6,225,272	2001	Giesen, Zaika, Middelhauve, Hofmann, Legel	Henkel	Dishwashing detergent with enhanced cleaning effect	Contains soluble abrasive component for excellent cleaning against dried-on and burnt-on food soils
6,165,958	2000	Arvanitidou	Colgate-Palmolive	High-foaming, grease-cutting light-duty liquid detergent comprising vinylidene olefin sulfonate	Addition of vinylidene olefin sulfonate to α-olefin sulfonate to improve rheology of AOS and increase detergent performance in hard water
6,051,542	2000	Pollack, Gomes	Colgate-Palmolive	Post foaming cleaning compositions comprising isopentane	Compositions sprayed on surface and then composition foams
5,919,312	1999	Wierenga, Weikel, Underwood	Procter & Gamble	Compositions and methods for removing oily or greasy soils	Composition for cleaning cooking surfaces has a pH no less than 8
5,891,836	1999	Kacher	Procter & Gamble	Light-duty liquid or gel dishwashing detergent compositions which are microemulsions and which have desirable greasy food soil removal and sudsing characteristics	Microemulsion compositions for heavily soiled dishware

and surfactant mixtures, but also address multiple consumer needs offering multidimensional benefits.

A. Antibacterial Products

The first liquid hand soap and hand dishwashing liquid product that offered long-lasting antibacterial protection on hands was introduced in 1994 by Colgate-Palmolive. The antibacterial ingredient was triclosan, and the product delivered the advertised efficacy as documented in clinical and laboratory testing. The color of the product was chosen carefully through extensive market research to be orange, conveying a strong antibacterial benefit. In addition, the fragrance had no strong "medicinal" connotation. A trend was established, and followed by other LDLD manufacturers in North America, Europe, and the rest of the world. In Europe, however, these products have not enjoyed the tremendous success they found in the U.S. The choice of triclosan as the antibacterial ingredient was unanimous in the U.S., while European countries chose either essential oils such as geraniol or *d*-limonene or used until recently buffering organic acids that impart a low pH to the system. The local regulatory requirements are always the driving force for the choice of the active ingredient.

1. Typical Antibacterial Actives

Triclosan (2,4,4′-trichloro-2′-hydroxydiphenyl ether) is used in most antibacterial LDLD products in the U.S. It is usually known as Irgasan or Irgacare or DP300, and its major supplier is Ciba Geigy. It is almost insoluble in water (0.004%), and soluble in ethanol and Tween 20 or 80. Triclosan's thermal, hydrolytic, and light stability is very high. Triclosan has a broad spectrum of antimicrobial activity against gram-positive and gram-negative bacteria, as well as fungi. Depending upon the concentration, it exhibits both bacteriostatic and bactericidal activity. Studies indicate that the mode of action is nonspecific and the primary site of the antimicrobial activity of triclosan is the cytoplasmic membrane. At low bacteriostatic concentrations, triclosan interferes with the uptake of essential nutrients such as amino acids from the medium needed for biological activity. At bactericidal concentrations, triclosan disorganizes the cytoplasmic membrane causing leakage of low-molecular-weight compounds and other vital cellular constituents such as nucleic acids leading to the death of the cell. More details on the mode of action of triclosan were offered by Regos and Hitz [96].

Triclosan is highly substantive to many surfaces including skin, fabric, and hair, and can provide residual bacteriostatic activity. The residual antibacterial activity is summarized in Table 7.20 and Table 7.21.

Triclorocarban (3,4,4′-triclorocarbanilide or TCC) is an odorless solid compound that is sparingly soluble in water (50 to 100 ppb at room temperature) and

TABLE 7.20 Agar Patch Test Results on Skin for an LDLD Containing Triclosan

Organism/bacteria count (log)	Placebo	LDLD with triclosan	Log reduction
Staphylococcus aureus	1.59	0.05	1.53
Escherichia coli	1.70	0.00	1.70

TABLE 7.21 Zone of Inhibition Test Results on Cotton Fabric for a Fabric Softener Containing Triclosan

Organism/bacteria count (log)	Control	Fabric softener with triclosan
Staphylococcus aureus	0/20	20/20
Escherichia coli	0/20	20/20

fairly soluble in organic solvents and surfactants. It is highly stable in acidic pH and hydrolyzes under alkaline conditions and high temperature resulting in dichloro- and *para*-chloroanilines.

TCC is highly effective against gram-positive bacteria but not against gram-negative bacteria. Its mode of action is based on destabilization of the integrity of the cytoplasmic membrane through destruction of the semipermeability of the membrane, uncoupling of oxidative phosphorylation, and inhibition of transportation of the essential substances through the membrane [97,98]. TCC is mostly used today in personal care products, e.g., soap bars, liquid hand soap formulations, and shower gels, and it is not found in LDLD formulations in the U.S., probably because of its limited antibacterial activity. It could become a viable alternative for triclosan.

Para-chloro-*meta*-xylenol, or PCMX, is a phenolic antimicrobial agent. It is a white to off-white crystalline powder with a faint phenol odor. It is sparingly soluble in water, and soluble in alcohol.

PCMX acts by destroying the cell wall and by inactivating enzymes. It is highly effective against gram-positive bacteria but less effective against gram-negative bacteria, mycobacteria, fungi, and viruses. The pseudomonas species are resistant to PCMX. Its antibacterial activity is also reduced by nonionic surfactants due to incorporation into the micelles. Compared to triclosan it is less effective as an antimicrobial agent, but it is more effective than TCC against gram-negative bacteria. PCMX is currently used in private label LDLD formulations. The effectiveness (MIC values) of the previously discussed antibacterial ingredients is listed in Table 7.22. The regulatory status of these ingredients is summarized in Table 7.23.

TABLE 7.22 Effectiveness of Three Antibacterial Agents as Shown by their Minimum Inhibitory Concentration (MIC)

Organism	MIC (ppm) of triclosan	MIC (ppm) of PCMX	MIC of TCC
Staphylococcus aureus	0.01	20	0.1
Streptococcus pyogenes	3.0	—	<0.05
Escherichia coli	0.3	75	>10,000
Pseudomonas aeruginosa	>1000	—	~10,000
Serratia marces	>100	—	~10,000
Klebsiella pneumoniae	0.3	125	—
Staphylococcus epidermis	0.01	30	0.5
Candida albicans	3	—	—
Aspergillus niger	30	—	—

2. Food and Drug Administration

Antibacterial LDLD compositions are regulated by the FDA in the U.S. The reason is because they are positioned as "antibacterial liquid hand soaps."

The proposed OTC Monograph in 1974 established seven categories for topical antimicrobial preparations, which are: antimicrobial soap, health care personnel hand wash, patient preoperative skin preparation, skin antiseptic, skin wound cleanser, skin wound protectant, and surgical hand soap. The reason for establishing seven categories was because not all antimicrobial products are used for the same purpose; therefore, the requirements for effectiveness should not be the same. By 1994 the tentative Monograph had eliminated antimicrobial soaps from being a separate category. Since that time, antimicrobial soaps must meet the efficacy requirements that equate to healthcare products. Antimicrobial body wash, hand wash, and food handling hand wash products are all treated "equally." The test method requirements are as follows:

- *In vitro:*

  MIC and SIKT (no criteria listed by FDA)

  Ingredient, product, and vehicle (product without active)

- *In vivo:*

  HCPHW test (2 log reduction after first wash, 3 log reduction after tenth wash)

  Patient preoperative test

  Surgical hand scrub test

TABLE 7.23 Regulatory Status of Three Antibacterial Agents in the U.S., Europe, and Japan

	Triclosan	TCC	PCMX — chloroxylenol
U.S. (FDA)	Category III for Safety and effectiveness	Category I for safety, Category III for effectiveness	Short-term use (0.24–3.75%): Category I for safety, Category III for effectiveness; Long-term use: Category III for safety and effectiveness
Europe	EU directive on cosmetics: preservative for cosmetics up to 0.3%; higher level allowed as antibacterial agent CAS: 3380-34-5. Dangerous substance directive: classified in Annex I (29th atp) as: Xi, R36/38; N, R50/53; with specific concentration limits: 0.0025–0.025: R52-53; 0.025–0.25: R51-53; ≥0.25%: R50-53; ≥ 20%: R36/38, R50/53	EU directive on cosmetics: preservative for cosmetics up to 0.2%; higher level allowed as antibacterial agent CAS: 101-20-2. Dangerous substance directive: *not* classified in Annex I; supplier classification: N, R50/53	EU directive on cosmetics: preservative for cosmetics up to 0.5% CAS: 88-04-0. Dangerous substance directive: classified in Annex I as: Xn, R22; Xi, R36/38; Xi, R43; without specific concentration limits
Japan	Japanese standard on cosmetics, preservative for all cosmetics up to 0.1%. Japanese standard on quasi-drugs, active ingredient for toothpaste up to 0.02%	Japanese standard on cosmetics, preservative for cosmetics on use to mucous membrane and cosmetics on use without rinse up to 0.3%	This ingredient is not found in Japanese standard. It is necessary to register as new ingredient to MOH for new preservative for cosmetics with data on safety or for new active ingredient for quasi-drug (toothpaste) with data on safety and effectiveness

Note: Category III means that insufficient data exist.

The industry has been active since 1997 (HealthCare Continuum Model) organizing meetings, gathering data, and discussing test methodologies in order to guide future FDA rulings.

The current expectation is that the Antimicrobial Handwash Monograph will be split into two sections. One section will be for professional hand wash (hospitals, food handlers, etc.) and the second will deal with consumer products. The best estimate for the FDA to take action on the consumer product section is around 2006.

3. Current Antibacterial Dish Liquid Products

A list of some antibacterial products marketed in North America and Europe is given in Table 7.24 and Table 7.25.

B. Concentrated Products

Up to 1995 the highest surfactant level at which an LDLD was formulated was 32 to 34% worldwide. Procter & Gamble in 1995 introduced in the U.S. for the first time a more concentrated "ultra" LDLD that the consumer can use at a dose that is 2/3 of the previous dose. The products are formulated at higher surfactant level (about 48%) to provide the same performance, and the package has also shrunk from 22 oz to 14.7 oz to flag the latest change. Most manufacturers in the U.S.

TABLE 7.24 Antibacterial LDLD Products Marketed in North America

LDLD product	Active	Company
U.S.		
Ajax Antibacterial	Triclosan	Colgate-Palmolive
Ajax Fiesta	Triclosan	Colgate-Palmolive
Dawn Antibacterial	Triclosan	Procter & Gamble
Dawn Power Plus	Triclosan	Procter & Gamble
Dawn Fresh Escapes	Triclosan	Procter & Gamble
Joy Antibacterial	Triclosan	Procter & Gamble
Joy Escapes	Triclosan	Procter & Gamble
Palmolive Antibacterial	Triclosan	Colgate-Palmolive
Palmolive Original Antibacterial	Triclosan	Colgate-Palmolive
Palmolive Lemon Antibacterial	Triclosan	Colgate-Palmolive
Palmolive Spring Sensations Ocean Breeze	Triclosan	Colgate-Palmolive
Sunlight Antibacterial	Triclosan	Unilever
Canada		
Ivory Antibacterial Orange	Triclosan	Procter & Gamble
Palmolive Antibacterial Orange	Triclosan	Colgate-Palmolive
Palmolive Lemon Antibacterial	Triclosan	Colgate-Palmolive
Spring Sensations Ocean Breeze	Triclosan	Colgate-Palmolive
Sunlight Antibacterial Orange	Triclosan	Unilever

TABLE 7.25 Antibacterial LDLD Products Marketed in Europe

LDLD product	Company	Country
Dawn von Fairy	Procter & Gamble	Germany, Benelux
Dreft	Procter & Gamble	Sweden, Finland
Fairy	Procter & Gamble	U.K., Greece, Portugal, Spain
Yes	Procter & Gamble	
Mir	Henkel	France
Nelsen	Procter & Gamble	Italy
Paic XL Antibacterial	Colgate-Palmolive	France
Palmolive Antibacterial	Colgate-Palmolive	France, Germany, Austria, Switzerland, Greece
Palmolive Spring Sensations Antibacterial Ocean Breeze	Colgate-Palmolive	France, Germany, Austria, Switzerland, Greece
Persil	Unilever	U.K.
Pril	Henkel	Germany
Pril 2-in-1	Henkel	Germany
Super Pop antibacterial	Colgate-Palmolive	Portugal
Super Pop Spring Sensations Antibacterial — Ocean Breeze	Colgate-Palmolive	Portugal
Svelto	Unilever	Italy, Greece
Vel	Colgate-Palmolive	Denmark

followed this trend, which became a major success with increased sales volumes. At the same time, they kept producing the regular sizes. This trend certainly was tested in Canada and later in Europe. The bulk of sales in these regions remain in the regular strength products.

C. Hand Care Products

The consumer need for a milder dishwashing liquid was met in the early 1990s with the successful introduction of Palmolive Sensitive Skin and the milder positioning of Ivory LDLD. The use of nonionic and amphoteric surfactants resulted in clinically milder and less irritating products. In the last decade, however, further improving mildness was a significant objective for the major players in the LDLD market. Dawn Hand Care was the first to introduce protease, an enzyme that is claimed to soften skin by exfoliation of the top layer.

D. High-Efficacy Products

These products are designed to offer an advantage on tough soils such as greasy, starchy, or cooked-on/burnt soils. The formulation of these products is based on a high anionic surfactant mix, an abrasive, polymers, and enzymes specific to target starch or grease. Examples of such products include Palmolive Pots & Pans, Dawn Power Plus, and Palmolive Max Power. In the high-pace environment of the developed world, consumers demand speed and high efficacy. Nonetheless, baked-on food and grease removal with manual dishwashing liquids still remains a challenge.

E. Sensorial Products

Efficacy, hand care, and added benefits have been the fundamental elements of every LDLD product since the second half of the 1990s. With the dawn of the new millennium dishwashing moved into a new dimension: the experiential dimension, with different colors and fragrances introduced to add more fun to a cleaning task. Colgate-Palmolive introduced the Spring Sensations line in the spring of 2000. The line has not stayed stagnant but is constantly "rejuvenating" itself with new introductions such as Orchard Fresh and Green Apple. Procter & Gamble followed with Joy Invigorating Splash and Tropical Calm, and more recently in the spring of 2001 with Dawn Fresh Escapes featuring Citrus Burst Apple Blossom and Wildflower Medley. In the summer of 2001 Colgate-Palmolive also launched Ajax Fiesta, taking the nonpremium LDLD segment to the experiential dimension as well. The sensorial trend has already moved to Canada, Europe, Asia, and Latin America. The fragrance experience was taken a step further with the launch of Colgate-Palmolive's Aromatherapy variants in 2002, an extension of a trend that was gaining momentum in personal care products.

VII. FUTURE TRENDS

Some consumers feel unsafe [99] because kitchen sites are contaminated and cross-contaminated through the use of sponges, dishcloths, cutting boards, and other cleaning or food preparation implements [100,101]. This cross-contamination is responsible for food poisoning incidents with salmonella and *Escherichia coli*, which are on the increase. Consumers remain germ-phobic, and guarding the family is their primary objective [102]. Therefore, the demand for antibacterial products will not only remain in the future, but the need for more effective ones will dominate. Efficacy is geared toward a broader range of microorganisms, and ideally with antibacterial actives that are naturally derived.

Washing the dishes is undoubtedly a chore and it is very difficult to make it sound appealing. Consumer product companies, however, have found a way to make it more fun by introducing pleasing and nontraditional fragrances. Experiential fragrance notes and appealing perfumes are here to stay.

These new fragrance trends came to complement the more traditional fragrances which are more associated with cleanliness and germ killing, such as lemon, lime, citrus bouquets, and mandarin orange accords [103].

In Japan, Family Pure dishwashing liquid by Kao is positioned as having a new deodorizing effect. Containing a new deodorizing agent "ASA" and herbal extract, it removes stubborn odors while cleaning the dishes. More deodorizing and air freshening benefits are expected to be added to the current experiential variants.

The experiential dimension does not have to stay in the fragrance or color arena. It is expanding to the beads, pearls, and other attractive elements seen in personal care products. A recent example is the Rainett aux Algues Marines LDLD introduced in France by Werner & Mertz. This product contains natural marine algae extracts encapsulated in beads. The extracts offer hand care benefits. Pearls or beads can be used as carriers of actives to enhance efficacy or mildness perceptions.

Aromatherapy has had an impact on the air care and candle segments of the household market, where products are often positioned as "soothing" and "relaxing." This trend is currently expanding with tremendous speed in body care products such as shower gels (Bed & Body Works, Bed & Bath stores) and soon in fabric care products such as fabric conditioners. With the recent launch of Ultra Palmolive Anti-Stress Aromatherapy Dish Liquid, Colgate-Palmolive has led the way of taking dishwashing to "a whole new sensation."

The trend toward natural products that use "natural" ingredients and "natural" fragrances are also growing. Natural and clean go together. This trend originated in Europe where consumers are more aware and passionate about environmental issues; soon the trend is expected to cross the Atlantic to North America. Garden Fresh and Fresh Rain are some examples [103].

Cleaning implements are also expected to enter the dish liquid market shortly. These implements could be either in the form of a wipe or dish tools like sponges/scourers recently introduced by Procter & Gamble in the UK. Wipes are now expanding from personal care applications to cleaning (floor or furniture wipes). The major advantage they offer is convenience for today's busy consumer. Dish tools can add speed to traditional dishwashing.

Can LDLD products be upscaled? There are already some manifestations of this trend; it remains to be seen if it will stay for a long time. Stores like the Good Home Company, The Thymes, Vermont Soapworks, Restoration Hardware, and Williams Sonoma include dish liquid in a series of home cleaning products, inspired by memories and nostalgia, designed to enhance life's daily duties and the overall kitchen experience. (According to the National Association of Professional Organizers a woman spends nearly 1100 hours a year in the kitchen!)

Enzymes made a splash in the automatic dishwashing detergents market first, and recently have been introduced in LDLDs for manual washing (e.g., Dawn Hand Care and Power Plus). The intention is to increase the cleaning power by introducing an ingredient like amylase that will break starchy food, or improve hand appearance by introducing enzymes such as protease. Kao also developed a genetically engineered amylase and expected to introduce it in its LDLD products.

Nowadays consumers are more sophisticated than they were 10 years ago, when they bought what was offered. Today, they demand choice. And choice can also be manifested through packaging and labels. This was especially evident in the original offering of the Method line of dishwashing products [104]. The bottles were designed in unusual shapes, and were intended to be stored upside down because they incorporated squeeze-activated valve to dispense the product. These products have gained significant market share in some large discount stores. Beautiful scenes and decorative bottles can definitely complement an efficacious product with a pleasing and appealing scent.

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