Heavy-Duty Laundry Detergents

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ABSTRACT

Current powder and liquid household laundry detergent formulations are reviewed. Methods for quantifying the important performance and physical properties of these formulations are described. Optimization of ingredients and manufacturing methods are included.

INTRODUCTION

A heavy-duty laundry detergent is, very simply, a powder or liquid product which is added to a washing machine to help get clothes clean. Beneath this simplicity lies a multitude of technologies which have been assimilated over the years to produce $1.5 billion of product in 1979. This presentation provides a concise overview of the technologies used to formulate household detergent products. Specifically, an outline of the components used to formulate detergents, typical formulations, test methods and manufacturing processes will be provided. Within this framework, some of the more current technical achievements are discussed.

COMPONENTS

Surfactants

Perhaps the single most important ingredient in laundry detergents is the surfactant. A surfactant is composed of both a hydrophilic group and an oleophilic group, and thus is "active" at air/water, fabric/water and soil/water interfaces. In lowering these boundary tensions, the surfactant improves fabric wetting by water, so that soil may be more readily removed by mechanical action. A surfactant functions to remove soil by a solubilization process and also assists in soil suspension, thereby preventing the redeposition of removed soil onto laundered fabrics. By lowering oil/water interfacial tension, a surfactant promotes the roll-up and emulsification of oily soils.

Most surfactants used in laundry products are either nonionic (unionized head group) or anionic (negatively charged head group). Each of these classes is characterized by distinct performance and physical properties.

Nonionic surfactants are prepared by adding ethylene oxide onto alkylphenols, or primary or secondary alcohols of varying chain length. The performance and physical properties of the surfactant are related to the hydrophobe type, and the degree of ethylene oxide substitution in the hydrophile.

Alkylphenol ethoxylates usually are liquids at ambient temperature and do not require heated storage facilities. The alkylphenol ethoxylates exhibit somewhat lower biodegradation rates relative to alcohol ethoxylates, but results of recent studies indicate that, with time, these materials undergo virtually total primary biodegradation in natural and simulated systems (1). Alkylphenol ethoxylates are extremely effective in lowering oil/water interfacial tension (2) which, in part, accounts for their excellent laundering performance on oily soils.

Ethoxylates prepared from primary alcohols are widespread in the marketplace, and generally exhibit excellent biodegradation characteristics. Detergent-range primary alcohol ethoxylates (12-15 carbon chain, 7-9 mol ethylene oxide) require heated storage facilities. Ethoxylates based on lower molecular weight primary alcohols (9-11 carbon chain) are liquids at ambient temperature, but these have been shown to exhibit somewhat poorer laundering performance in direct comparison to detergent range alcohol ethoxylates (3). Ethoxylates based on secondary alcohols are liquids at ambient temperature, are known to be excellent wetting agents and also exhibit good biodegradation characteristics.

The degree of ethylene oxide substitution governs the hydrophilicity, and the hydrophile/lipophile balance (HLB) of the surfactant. Removal of certain soils often can be optimized by selecting nonionic surfactants of specific hydrophobe and ethylene oxide chain lengths (4). Further improvement in laundering performance often can be achieved by blending surfactants with different HLB values (5).

Nonionic surfactants are becoming more popular because of their ability to remove oily soils from synthetic fabrics. Nonionic surfactants exhibit good cool-water solubility, are low foaming and are less sensitive to water hardness than are anionics. Nonionic surfactants also exhibit good solubility characteristics in unbuilt heavy-duty laundry detergents. Because of their low critical micelle concentration (cmc), nonionic surfactants are more effective at lower dosage levels than are most anionic surfactants. Many nonionic surfactants are difficult to incorporate into powder detergents because of their liquid or semiliquid state, and because they are oxidatively sensitive to the heat and large volumes of air used in a spray drying process.

Anionic surfactants are the most widely used in household detergent products. These surfactants are prepared from hydrocarbons or alcohols by processes which mostly use oleum or air/SO_3 as sulfating or sulfonating agents. Considerable unreacted sulfuric acid is present in the finished product, leading to sulfate salts after the neutralization step. The sulfonic acids or sulfuric acid esters produced by the sulfonation or sulfation process are neutralized to their respective sodium, potassium, ethanolamine or ammonium salts prior to, or as part of, detergent manufacturing. The performance and physical properties of anionic surfactants are governed by the type of starting hydrocarbon or alcohol, the type and level of by-products, and by the associated cation.

Linear alkylbenzene sulfonate (LAS) usage far exceeds that of any other surfactant because of its good performance, competitive cost, high quality and history of safety (6). Other anionic surfactants widely used in household detergent products include the alcohol sulfates and alcohol ethoxysulfates.

Anionic surfactants are particularly effective in removing particulate soils from natural fabrics. Performance of these materials is enhanced by increased temperature and by the presence of certain builders. Anionic surfactants provide foam which consumers perceive as an indicator of good laundering performance. Anionic surfactants are easily spray-dried, and, therefore, are favored in powder production. Anionic surfactants are more sensitive to water hardness, although the alcohol ethoxysulfates are somewhat less sensitive.

Auxiliary Components

Of all the auxiliary components included in laundry products, builders rank first in importance. These are described in detail by Schweiker in another issue of *JAOCS* (58:170A).

Fillers are used in detergent products to control density and to improve flow properties. Sodium sulfate, which is used in detergent powders, also increases ionic strength which aids in the removal of fatty acid soils. Sodium carbonate, sodium chloride and calcium silicate also have been described as powder detergent fillers. Ionic fillers are expected to promote the surface activity of surfactants, especially ionic surfactants.

Water is used as the filler in liquid detergent products. Urea also may be used as a filler, primarily to increase the solids level and alkalinity of liquid detergents.

Fluorescent whitening agents and perfumes are described by Neiditch in another issue of *JAOCS* (58:162A).

The preceding ingredients constitute the basic construction of most detergent products. Other special pupose additives also may be incorporated.

A small amount of fatty acid soap may be incorporated into laundry detergents to improve detergency and to provide a measure of foam control. Soaps also can help suspend soil to prevent soil redeposition (7). Fatty acid soaps, however, can react with hard water cations to form insoluble deposits which are difficult to remove from fabrics and machine surfaces.

Foam control agents may be used in anionic surfactant-based formulations. Nonionic surfactants and soaps provide a measure of foam control, as previously noted. Certain silicones (8), microcrystalline waxes (9), and melamine derivatives (10), for example, have been described as foam control agents in the patent literature.

Hydrotropes, such as sodium xylene sulfonate or sodium toluene sulfonate, are effective coupling agents for anionic surfactants in liquid detergent systems. The inclusion of a hydrotrope reduces viscosity and improves compatibility and low temperature storage stability. These particular hydrotropes allow the inclusion of high levels of active ingredients and supplement the solids level of the product. Hydrotropes are also beneficial in powder processing. A hydrotrope can reduce slurry viscosity, which, in turn, reduces the total water requirement and improves energy efficiency. The physical properties of the finished product also are improved because these materials improve powder pouring ability and reduce caking tendencies, as well as help control bulk density. Powder detergents formulated with nonionic surfactants normally are very high in bulk density, whereas systems containing sodium toluene sulfonate are much lower in bulk density (U.S. patent pending).

Bleaches such as sodium perborate provide free oxygen to oxidize nonpolar soils to polar soils which are more easily removed. Oxygen bleaches are not very effective under the household laundering conditions commonly used in the U.S. A host of oxygen bleach activators has been described in the patent literature (11) for improving the effectiveness of bleach-containing powders. Oxygen bleaches are sensitive to prolonged storage, especially in the presence of certain detergent components under conditions of high heat and humidity. Bleaching performance can be improved with the inclusion of chelating agents (12) or stabilizing agents (13) in the formulation. Oxygen bleaches normally are not incorporated into liquid products.

An anticaking agent may be added to a powder detergent to improve the physical properties of the finished product. Anticaking agents usually are high melting, non-hygroscopic powders. The action of these materials is primarily mechanical, in that they tend to coat the detergent granules to prevent them from coming into contact and sticking together. Materials such as calcium sulfite (14), high molecular weight ethylene oxide derivatives (15 and U.S. patent pending), magnesium sulfate (U.S. patent pending) and aluminum borates (16) have been reported to be effective as anticaking agents for powder detergents.

Clay minerals, particularly smectite clays, recently have been discussed in the patent literature as additives to detergent powders. Certain clay minerals provide a degree of ion-exchange capacity, and thus, they can improve detergency in water of low dissolved solids content. Bentonite acts as a builder in soap and synthetic detergent compositions (17). Sodium bentonite also is a good emulsifying and soil suspending agent. Smectite (18) and metakaolin (19) clay minerals also have been cited for textile softening effects. Clays may deposit on the textile surfaces to yield a better fabric hand. Removal of calcium and magnesium from the wash water also prevents the precipitation of their salts onto fabric surfaces, which helps maintain fabric hand. Textile softening effects of smectite clays are reported to be improved by replacing the exchangeable metal ions with alkyl-substituted quaternary ammonium ions (20). Conventional fatty and imidazolinium quaternaries also can be used as softeners in detergent systems.

Ethanolamines, particularly triethanolamine (TEA), are included in liquid laundry detergents primarily as a source of alkalinity. Through an ionization process, TEA can aid in the dispersal of metal oxides and insoluble calcium and magnesium salts, as well as aid in soil suspension. TEA and TEA salts of anionic surfactants exhibit good solubility characteristics in liquid products. TEA also improves the physical properties of the finished product by assisting in FWA solubilization, by reducing viscosity and low temperature haze points and by improving low temperature storage stability.

Lower monohydric alcohols such as isopropanol, and particularly ethanol, act as nonionic surfactant coupling agents in liquid detergents. The coupling activity reduces viscosity for improved handling in the plant and in use, and improves solubility and low temperature storage stability. The cost of adding ethanol to improve physical properties sometimes is questioned, because unlike TEA, ethanol does not improve laundering performance or increase solids level.

Built liquid laundry detergents may contain polymeric stabilizers to improve long-term storage stability. Unbuilt liquid detergents also may contain an opacifier for esthetic purposes. That is, the opacified formulation has the appearance of a built product, and may be perceived as a "richer" formulation.

FORMULATIONS

Liquids

Typical ranges of components used in unbuilt liquid laundry detergents are shown in Table I. Detergency is provided by a mixture of nonionic and anionic surfactants, usually at a 3:1 ratio. In most cases, the nonionic surfactant is a 7- or 9-mol ethoxylate of a linear primary alcohol. Nine-mol ethoxylates of alkylphenols also are used because these surfactants presently are lower cost relative to alcohol-based nonionics. In some cases, the cost savings may be mitigated by density differences. Liquid systems formulated with alkylphenol ethoxylates require more material by weight to achieve the necessary solids level and filling volume. Secondary alcohol ethoxylates also are appropriate choices for liquid detergents because they impart low viscosity which reduces hydrotrope requirements. Secondary alcohol ethoxylates normally are used in specialty applications because of their current high price relative to other nonionics.

Most systems contain the sodium or triethanolamine salt of LAS, though the magnesium salt is also used. Recently, alkaline earth metal salts of anionic surfactants have been described as being particularly effective in removing oily soils (21). Liquid systems containing magnesium salts of anionic surfactants are somewhat difficult to prepare, but the presence of other surfactants during the neutralization step improves clarity of the resultant product (22). The use of alkaline earth salts of anionic surfactants may also be effective in preventing precipitation of certain FWA (23).

Free TEA may be present to improve detergency and physical properties of the system. Because systems formulated with high levels of TEA have the potential to cause skin irritation, TEA usually is present up to a maximum of 8%.

Some systems contain ethanol, usually up to a maximum of 7%. Small amounts of fluorescent whitening agents, perfume and dye normally are present, and the balance is water. The primary deficiency of these products is that they do not contain a builder to counteract the deleterious effects of water hardness. However, being highly concentrated in nonionic surfactants, these products are particularly effective in removing oily soils from synthetic fabrics.

Typical ranges of components used in built liquid laundry detergents are shown in Table II. The products contain nonionic and/or anionic surfactants, usually at a maximal concentration of 15%. Phosphate-based systems usually contain TKPP because it is more stable than STPP in aqueous systems. STPP can be used in certain formulations while detergency and stability (24) are maintained, particularly when STPP is combined with TKPP (25) or orthophosphate (British patent pending). No-phosphate formulations may contain sodium citrate. Most built liquids contain sodium silicate. The mutual incompatibility of the surfactants and builder salts used in liquid detergents requires the use of hydrotropes, polymeric suspending agents and/or emulsifying agents. The hydrotropes previously described are applicable to these formulations, as are certain phosphonic acid salts described in the patent literature (26). Polymeric suspending agents, such as acrylic anhydride/vinyl methyl ether copolymers, can be used to prepare stable suspensions of the builder salt in aqueous medium. Emulsifying agents such as alkanolamides (27) are appropriate, and sodium sulfate also has been described as a stabilizing agent for emulsions and suspensions (28). Potassium salts can lend further stability to these products. Sodium CMC can be incorporated into stabilized products. Small amounts of FWA, perfume and dye are included, and water comprises the balance.

Powders

The typical range of components used in powder detergents, based on non-zeolite builders, is shown in Table III. These products normally contain anionic surfactants, but certain processing methods allow the inclusion of nonionic surfactants. The type and level of builder salts vary widely, but, in general, are composed of either STPP, carbonate, or a mixture of both. Sodium silicate and sodium CMC are used in most products at the ranges indicated. Small amounts of perfume, dye and FWA are used, and sodium sulfate comprises the balance.

A typical zeolite-based formulation is shown in Table IV. The formulation can contain either phosphate or carbonate as the auxiliary builder. TKPP may be used for magnesium control, in which Type A zeolites are deficient (29). Other builders such as sodium citrate have been described as appropriate for correcting the magnesium sequestration deficiency (30). Also, the level of silicate normally is low, partially to improve the dissolution of the spray-dried bead, and to reduce the formation of zeolite-silicate aggregates which can deposit on laundered garments (31).

Laundry detergents containing fabric softeners recently were introduced into test markets by a variety of manufac-

TABLE I

Unbuilt Liquid Laundry Detergent

Component	Weight (%)
Nonionic surfactant	20-40
Anionic surfactant	10-30
Triethanolamine	0-8
Ethanol	0-7
Fluorescent whitening agent	0.2-0.4
Perfume	0.05-0.1
Dye	q.s.
Water	to 100

TABLE II

Built Liquid Laundry Detergent

Component	Weight (%)
Nonionic surfactant and/or anionic surfactant	5-15
Builder (tetrapotassium pyrophosphate or sodium citrate)	20-30
Sodium silicate	2-5
Polymeric stabilizers	0-2
Sodium xylene sulfonate	0-5
Emulsifying agents	0-2
Sodium carboxymethylcellulose	0-2
Fluorescent whitening agent	0.2-0.4
Perfume	0.05-0.1
Dye	q.s.
Water	to 100

TABLE III

Powder Detergent

Component	Weight (%)
Anionic surfactant and/or nonionic surfactant	5-30
Builder (sodium tripolyphosphate or sodium carbonate)	20-60
Sodium silicate	5-15
Sodium carboxymethylcellulose	0-2
Fluorescent whitening agent	0.05-0.1
Perfume	q.s.
Dye	q.s.
Sodium sulfate	to 100

TABLE IV

Zeolite-Based Powder

Component	Weight (%)
Linear alkylbenzene sulfonate	8-12
Fatty alcohol ethoxysulfate	4-8
Sodium tallow alcohol sulfate	2-5
Sodium aluminosilicate	15-25
Sodium tripolyphosphate	0-24
Sodium carbonate	0-24
Sodium silicate	1-3
Fluorescent whitening agent	0.05-0.1
Perfume	q.s.
Dye	q.s.
Sodium sulfate	to 100

turers. A detergent powder which contains a fabric softener is now being distributed nationally. In a related area, certain fabric-care benefits, such as ease of ironing, are said to be imparted by detergent products which contain starch (32), or starch particles which contain water-insoluble liquids such as mineral oil (33).

Liquid laundry detergents with added fabric softeners may contain fatty quaternaries (34), imidazolinium quaternaries (35) or certain dicarboxylic acids (36). Most of these products do not contain anionic surfactants because of the adverse interaction between anionic and cationic materials. Although most of the anionic-cationic complexes are effective fabric softeners, most are not very soluble in liquid products. These products formulated with anionic surfactants contain only a low level of cationic softener. The selection of components, particularly the FWA and hydrotrope system, is especially important to the stability of these products.

DETERGENT PRODUCT TESTING

The commerical success of a detergent product is determined by a variety of properties which are judged objectively and subjectively by the consumer. Tests have been designed to quantify physical properties, storage stability and laundering performance, which are integral parts of the package that determines consumer acceptance. This paper includes only the key elements of detergent product testing. Methods other than those listed are available, and certain detergent manufacturers may wish to quantify properties other than those included here.

Physical Properties

The key physical properties of powder detergents include bulk density, caking tendencies, free-flow, dusting and solubility. Tight control over bulk density is necessary to ensure that the appropriate filling volume is attained in standard package sizes, and to ensure that sufficient active matter is delivered to the washing machine by a standard volume dosage level. Bulk density normally is measured by determining the weight of a known volume of detergent. Ideally, a powder should remain free of lumps, even under the most adverse temperature and humidity conditions. Caking tendencies can be measured by subjecting a sample of the powder to pressure, and then quantifying the force needed to break the briquette so formed. The free-flow properties and dusting propensity also are important for efficient delivery of the detergent to the measuring vessel. A common test of flow properties consists of merely measuring the time required for a given volume of powder to flow through a funnel. Dusting tendencies can be estimated by determining the particle size distribution of the detergent with screens of varying mesh size. Good solubility is important for laundering efficiency and for avoiding detergent deposits on laundered fabrics. Residual, undissolved matter can be filtered and weighed upon completion of a wash cycle, e.g., in a Terg-O-Tometer.

The key physical properties of liquid detergents include viscosity and clarity. The viscosity of the product must be low enough to permit efficient delivery from the bottle to the measuring vessel, and then to the washing machine. The viscosity of the product must be high enough to create the appearance of sufficient active matter. Viscosity can be conveniently measured by the Brookfield or Cannon-Fenske methods. The clarity of a transparent liquid is largely a function of compatibility. It usually suffices to assess clarity by eye, but as a refinement, it can be measured by light scattering techniques.

Storage Stability

Through prolonged storage, especially under high temperature or humidity conditions, liquid components can separate from detergent powders, or the particles themselves can segregate on a size basis. The separation of liquid components can be measured by placing the powder on absorbent paper and storing under a given set of constant or cycling temperature/humidity conditions. The separation of liquid components can be quantified by determining the increase in the weight of the absorbent paper. Particle segregation can be determined by inspecting the particle size distribution at various locations within the container.

The potential incompatibilities of liquid detergents may be established through prolonged storage testing at high or low temperatures. The low temperature haze (cloud, or separation) point provides a measure of the mininum safe storage temperature. Liquid detergents should remain stable through at least three freeze/thaw cycles, and after storage for 24 hr at 120 F.

Laundering Performance

Acceptable physical properties and storage stability are necessary, but insufficient, conditions for the commercial success of detergent products. The type and level of components used in a detergent are selected primarily to clean clothes. Products which exhibit good laundering performance are developed by integrating results obtained in both theoretical and practical tests of detergency.

Today's detergent formulations are based, in part, on the results of extensive studies of fundamental detergency mechanisms. Several model detergency systems and methods for measuring pertinent surface-chemical parameters have been devised to enable workers to increase their understanding of the detergency process. One area of importance centered on the early work of Adam (37) who derived expressions relating the contact angles of oily soils on a fabric substrate to the surface and interfacial energies in an aqueous detergent system. Subsequently, many workers have devised improved methods for observing the "roll-up" of oily soils and, thereby, have demonstrated the practical importance of surface tension, oil/water interfacial tension and contact angle in the overall detergency process (2,38-42). Methods for studying the penetration of surfactant molecules into oily soils were established (43-47), and ternary phase diagrams were produced to represent these systems. McBain's classical work on solubilization (48) prompted other investigations (49-55) and experimental techniques were further improved. Methods for studying emulsification also were developed (56-61), and the importance of attaining a low oil/water interfacial tension was proposed and demonstrated. Still other techniques were developed (62), and together they constitute a variety of valuable experimental techniques for studying fundamental detergency processes.

Today's detergent formulations also are based on results of simulated in-use tests. These tests normally are conducted in a Terg-O-Tometer, which is a battery of small scale washing machines, although a full-scale washing machine also can be used. In Terg-O-Tometer experimentation, one can control the key variables of the laundering process, e.g., water temperature, rate of agitation, detergent concentration, water hardness and cloth/liquid ratio. One Terg-O-Tometer test constitutes only one specific combination of end-use conditions.

Soiled and clean test swatches constitute the laundry load. These swatches can be cellulosics, polyamides, polyesters, or blends thereof. In anticipation of the variety of laundry problems which may be encountered, the test swatches may be soiled with any one, or a combination, of the following: clays, vacuum cleaner dust, airborne-particulate, carbon black, synthetic sebum, mineral oil, triglycerides, natural soil, food stains (gravy, vegetable oil, spaghetti sauce), cosmetics (lipstick, mascara, other make-up), and stains such as grass or ball point ink. Tests which use any of these soils can help to predict the performance of a product in use when that specific soil or soil combination is predominant. However, the wide variety of laundering conditions, fabrics and soils that can be encountered dictates that Terg-O-Tometer experiments be replicated many times in order to assess the performance of a product under a wide range of conditions.

Most artificial soils include some type of pigmented material, so that the removal of the soil can be monitored by quantifying the light reflected from the fabric before and after laundering. Alternatively, a test panel can evaluate the cleanliness of a swatch after laundering by comparing it to graded standards. The removal of colorless soils also can be monitored by using radioactively tagged components, and counting the activity before and after laundering (63). Particulate soil removal also can be monitored by radiotracer techniques (64).

The next stage of laundering performance evaluation involves the comparison of an experimental product to a standard control product. Two matched bundles of laundry are worn or used in the normal way by two families. Each bundle is laundered separately, in the laboratory, using either the experimental or the control product. This cycle continues for an extended period, typically 10 weeks, with the same detergent used for the same bundle each time. Although this test more closely resembles actual in-use conditions, it is very expensive to run, and the comparison can be influenced by interfamily differences and by the different soil types encountered.

Prior to test market introduction, a detergent often is field tested. Samples of the experimental and control detergent are supplied, and consumer preferences are determined. These responses can affect the final formulation selected for the product ultimately introduced.

PROCESSING

Liquids

Manufacturing unbuilt liquid detergents is relatively simple and can be conducted in a stainless steel vessel equipped with a stirring device. In some cases, heating or cooling may be necessary. A few precautions should be taken to maximize efficiency and product stability. The nonionic surfactant should be added after addition of most of the water to completely hydrate the surfactant in order to avoid the formation of nonionic surfactant aqueous gel which is difficult to dissolve. The FWA should be predissolved in the nonionic surfactant, in the water, or preferably in a mixture of water and ethanol. Mixing should be conducted at a slow enough speed to avoid the formation of a vortex, which may cause air to whip into the mixing system. The resultant foam may be difficult to break. Most salts, such as sodium LAS, urea or SXS should be added last, to avoid nonionic surfactant gel formation.

In the preparation of built liquids, an excess of potassium ions (in the form of KOH) first is added to the requisite water, followed by the silicate and polymeric stabilizer. The TKPP and surfactant are normally added last.

Powders

Because of the highly desirable properties of spray-dried powders, nearly 75% of all laundry detergents are manufactured by this process. Some of the characteristic features of such products include (65): (a) relatively high amounts of active matter that can be incorporated into a dustless, free-flowing powder; (b) powders that have a low bulk density and a pleasing appearance; (c) dissolution rates that are relatively fast. Thus, although operating costs and the initial capital investment of a spray drying tower are quite substantial, a very high quality product with all the properties just listed is obtained reproducibly with good control.

The first step in a spray drying process is production of the slurry, which can be done either continuously or in batch mixers (crutchers). Although the batch process allows for easy control of constituent concentrations and mixing, on the whole, the advantages of continous feeding, viz., easy and efficient heat control, short residence time, improved slurry homgeneity and a high solids content, greatly outweigh the advantages and lower investment costs of batch preparations. In a continuous process, solids are premixed on a screw conveyor and this blend, in turn, is transferred along with the liquids and/or pastes into the slurry mixer, which is a small, high-speed crutcher designed to break agglomerates. In the batch process, the slurry usually contains ca. 40% water; thus the crutcher acts like a "doughmaker," operating on each batch for 10-15 min. At least two crutchers are needed, so that, while one slurry is being pumped into the booster tank, the other can be used to prepare a fresh batch.

To demonstrate the role of the various ingredients in the spray drying process, a typical batch preparation may be considered. A 40% silicate solution is usually added first, such that the amount of silicate in the final product is set at around 6%. The silicate serves as a neutralizing base for the subsequent sulfonic acid addition, introduces a controlled amount of water in the slurry, and keeps sodium tripolyphosphate, if used, from "setting-up." Sulfonic acid is usually added next, along with sufficient 50% sodium hydroxide solution to complete neutralization of the acid. Sodium tripolyphosphate, usually in its Type II (slow hydrating) crystalline form, is then added. Sodium sulfate is included as a processing aid to prevent the sodium tripolyphosphate from going into solution and, consequently, degrading. Any ancillary ingredients are added as the final step.

From the crutchers, the slurry is pumped into a booster tank, which serves mainly to ensure a uniform and constant feed to the tower. The slurry is pumped from the booster tank to the spray tower by a high-pressure pump to allow easy and uniform atomization at the entry point in the tower. A two-fluid nozzle generally is used in the tower, wherein the second fluid is air.

There are two basic tower designs in use today, i.e., the concurrent an the countercurrent. The concurrent type has the hot drying air coming in at the top of the tower so that the air is hottest when the powder is wettest. A swirling pattern is generated to avoid rapid dehydration and incipient dust formation. The exhaust air leaves the bottom of the tower at a temperature 10-26 C above the powder temperature. This design yields a very high quality product. The countercurrent process uses hot air coming in the bottom of the tower and striking the powder when it is driest. This method is cheaper, gives good control over moisture content, and the powder is easier to swirl. However, the general product quality is inferior to that of the concurrent process, and the powder tends to have a very hard, dry surface.

After the spray tower, many manufacturers incorporate a fluidized bed treatment to reestablish the desired moisture content and help break-up agglomerates. The powder then passes onto a continuous belt where it receives various minor ingredients, i.e., perfumes, anticaking agents and dyes. After thorough mixing, the finished product passes to a conveyor belt for packaging.

Within the spray drying system, there are recycling stages for particles too large or small to be acceptable. The heavy particles are removed from the bottom of the tower and placed back into the crutcher for respraying, whereas the fines are generally removed from the top of the tower, collected in bag houses via cyclones, and reintroduced into the top of the tower such that they come into intimate content with the still-wet spray of the slurry falling down from the nozzles.

Nonionic surfactants are difficult to incorporate into spray-dried products because they can decompose when exposed to the heat in the tower. To avoid spray tower "pluming," which results from the degradation of the surfactant, a lower temperature may be used in the tower or a higher molecular weight surfactant which is more heat-stable may be used, followed by the post-addition of a lower ethoxylate to improve detergency (66). The patent literature also shows that certain alkaline components (67) and nitrogen compounds (68) inhibit the autoxidation of nonionic surfactants in the spray tower. Processing the slurry also can be difficult because the nonionic tends to separate. One approach is to pre-absorb the nonionic onto calcium carbonate (69) to facilitate processing, or clay (70) to ensure slurry stability.

Other less widely acclaimed powdered-detergent manufacturing techniques include agglomeration and dry blending. In agglomeration, a container fixed with a rotary mixing screw is loaded with the wet ingredients, e.g., sodium silicate, sodium tripolyphosphate and surfactant, and the material is mixed and allowed to solidify. The sodium tripolyphosphate picks up water and readily forms cohydrates with nonionic surfactants. The solid mass is then broken up and dropped onto a two-roll mill for final processing. When dry blending an ingredient, the inorganic ingredients are charged to a conventional batch or continuous blender and the liquid components, i.e., water, nonionic surfactants and perfumes, are absorbed onto the dry powder by pumping the liquid through a jet and onto the powder. The finished product is either placed in storage to await packaging or, in some cases, discharged onto a concrete floor and aged. Both dry blending and agglomeration methods suffer from the same major drawbacks, i.e., relatively low surfactant "active" levels are obtained and the finished products generally exhibit relatively poor physical properties. The use of calcium salts of anionic surfactants is said to improve the efficiency of the mixing operations as well as the storage stability of the finished product (71,72).

Recent powder processing achievements combine the advantages of spray drying and mechanical mixing techniques. A spray-dried support bead composed of phosphates, carbonates or zeolites is coated with nonionic surfactants to produce a detergent powder with excellent free-flow properties (U.S. patents pending). The support bead may contain other ingredients and optionally may be "sealed" with zeolite (U.S. patent pending). In this way, a high level of nonionic surfactant may be incorporated into a detergent powder while very desirable physical properties are maintained.

For energy conservation, a processing technique frequently cited in the patent literature is notable. Certain ingredients are amenable to comixing at the melt. When the mixture solidifies, it can be granulated, then post-added to a spray-dried detergent powder. In this way, a portion of the powder is produced by a less energy-intensive route. This technique is most appropriate for components which are sensitive to the heat of the spray tower. For example, "agglomerates" of quaternary ammonium compounds with water-soluble salts (73,74) or fatty alcohols (75), agglomerates of starch with polyethylene glycol (76) and agglomerates of nonionic surfactants with soap (77) or zeolites (78) have been described for post-addition to detergent powders. This technique also is appropriate for components which are sensitive to alkaline components or moisture in the powder, such as bleaches (79,80) or enzymes. Thus, components which are difficult to dry, or components which perform better when not an integral part of the spray-dried bead, can successfully be added to detergent powders.

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Liquid Light-Duty Detergents

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ABSTRACT

Technical development of a light-duty liquid detergent requires a knowledge of the kinds of ingredients that may be used and their functions, and an understanding of the techniques used for evaluating performance characteristics. It involves selection or optimization of an active ingredient system, adjustment of product physical properties, incorporation of suitable colorant and perfume, conduction of appropriate aging studies and testing of resistance to microbiological contamination to ensure proper quality at time of purchase, and assessment of safety to humans.

INTRODUCTION

Liquid light-duty detergents were first introduced in the late 1940s. Except for one or two of the earliest entries, they were formulated to provide the generous suds desired by consumers for hand dishwashing and all seemed to offer excellent detergency. Their convenience of use, rapid dissolution in water and pleasant fragrances soon caught the attention of the consumers, who had been accustomed to conventional, somewhat dusty, granule-form powder products. Acceptance and popularity grew rapidly, and so the liquids began their displacement of powders, a trend that in another decade would result in complete dominance of the category. Relative to the rate of displacement, the actual consumption of liquids increased at a faster pace as the size of the category continued to expand in proportion to population growth.

In 1980, the light-duty detergent category represents sales of over 60,000,000 cases valued at about $650,000,000 with almost all accruing from liquid hand-dishwashing products. Recent estimates indicate volume may have leveled off despite year-to-year increases in the number of households, but sales will continue to reflect inflation-related trends.

Light-duty liquids are used in over 90% of all households. It is notable that their incidence has not been diminished by the increase in automatic dishwashers; they still find application in the washing of pots and pans, as fine fabric detergents, and for light cleaning chores. Such broad use and appeal is a result of product development and marketing efforts that have effectively satisfied consumers' diverse wishes and requirements. There are brands that promise mildness, efficacy, economy and combinations of attributes; their positionings are highlighted by individualistic store shelf images.

The design and formulation of a product for this strongly competitive environment encompass many technical considerations and concerns—selection of ingredients to provide performance, esthetic and physical properties; performance evaluation to define the product's competitive stance and to try to predict its acceptability as judged by the consumer; physical testing to ensure maintenance of quality during shipment and storage; safety testing for compliance with federal regulations; and examination of other factors that could influence profitability and consumer satisfaction. A description and discussion of each of these follow.

INGREDIENTS

Light-duty liquids are designed for the hand washing of dishes. They are purchased for this operation to provide aid in the removal of food residues and other soils from utensils, glassware, dishes, pots and pans. Cleaning efficacy, however, appears equated with foaming ability by users who seemingly consider both the quantity of suds generated and their persistence as the major criteria for judging the acceptability of a product for this purpose. Further, adequate foam stability is essential for ensuring presence of a suds blanket over the washing solution to hide the dirty wash water.

The most important components, therefore, of any light-duty liquid are, or should be, the surfactants that make up the so-called "active ingredients" or AI system responsible for a product's foaming and cleaning performance. Any such AI system conventionally includes one or two primary surfactants and a foam promoter/stabilizer. Currently marketed products are based on combinations of either (a) linear alkylbenzene sulfonate/alcohol ethoxy-