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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 ethoxysulfate/amide or (b) alcohol ethoxysulfate (alone or with alcohol sulfate)/amine oxide. Further definition of these ingredients and alternates, and of various others necessary in achieving a marketable product, follows.

Primary Surfactants

These are the workhorse ingredients that form the backbone of dishwashing products; all are anionic detergents. Selected for their ability to provide high volumes of suds for hand dishwashing operations, they also function as cleaning agents by working to emulsify/disperse grease and oil and aiding in the removal of other food residues from the various items washed. Typical surfactants used or considered workable options are linear alkylbenzene sulfonate (LAS), α-olefin sulfonate (AOS), secondary alkane sulfonate or paraffin sulfonate (SAS), alcohol ethoxysulfates (AEOS), and fatty alcohol sulfate. The sulfonates, in general, are most effectively used in combination with AEOS in proportions reflecting cost/performance guidelines set by the marketer of the finished product.

Presently, LAS is used in all sulfonate-containing dishwashing liquids and, as previously indicated, is combined with AEOS and amide. Of the two molecular weight versions commercially available, only the one based on dodecylbenzene finds application; the tridecylbenzene type has poorer solubility, necessitating use of additional solubilizer, a cost penalty, for acceptable product physical properties. AOS and SAS appear to be suitable alternatives for LAS on a direct replacement basis from a performance standpoint. AOS is close in price to LAS whereas SAS is more expensive, being available only via import from Europe where it is a major ingredient in several light-duty liquids. Use of either to replace LAS in a given formulation can cause product viscosity shifts which may require corrective measures.

AEOS is used in all dishwashing liquids—both in those that contain a sulfonate and in those that do not. Conventionally, this ingredient has been a C_{12-13} to C_{12-15} primary alcohol ethoxysulfate containing an average of 3 mol ethylene oxide/mol alcohol. This degree of ethoxylation is believed optimum from a mildness/performance standpoint on the basis that higher ethoxylation results in a directionally milder surfactant, but with somewhat poorer foaming ability and greasy soil dispersion ability; lower ethoxylation gives surfactants with increased irritation potential and poorer solubility characteristics. However, there is limited use of a combination of fatty alcohol sulfate and an alcohol ethoxysulfate averaging 9-12 mol ethylene oxide/mol alcohol.

Foam Promoters/Stabilizers

Although the primary surfactants alone or in combinations are high foamers, the stability of their foam is adversely influenced to various degrees by food soils removed from items being washed. Fats, in general, and excesses of certain protein and carbohydrate food residues provide "foamicidal" effects that could readily be perceived by consumers as reflective of the inadequacies of any unsupported detergent system. Most troublesome are fats, especially those that are easily emulsified.

Consequently, foam promoters or stabilizers are widely used to slow collapse of foam generated for dishwashing purposes and are particularly helpful in the presence of fatty soils. These additives also can contribute to fatty soil removal and dispersion. Typical of the types used are fatty acid monoethanolamide and diethanolamide and alkyl dimethylamine oxide.The amides work best with primary surfactants that are sulfonates whereas amine oxide is the preferred foam promoter for sulfates. In combination sulfonate/sulfate active ingredient systems, amides appear to offer advantages over amine oxide from a cost/performance standpoint and thus are used exclusively.

Both fatty acid monoethanolamide and diethanolamide are currently used in sulfonate-containing products. Diethanolamide is slightly lower in cost, substantially more soluble in formulated compositions, and easier to handle and store due to its lower melting point; however, hand dishwashing tests can demonstrate that a diethanolamide is not quite as effective, under some conditions, as a monoethanolamide when evaluated on a direct substitution basis. The selection of one form over the other usually entails substantial laboratory cost/performance optimization studies, can be influenced by the performance criteria set for judging efficacy, and is best decided by appropriate consumer testing of formula options.

Highest quality amides are preferred which are based on lauric acid or a lauric/myristic acid blend. Amides based on broad fatty acid mixtures, although lower in cost, are poorer from boosters and contain higher levels of nonfunctional components or impurities that may have an adverse influence on product properties. Ethoxylated monoethanolamides are available, but they, too, offer somewhat decreased functionality.

Amine oxide is currently used with primary surfactant sulfates in sulfonate-free products. The conventional type is lauryl dimethylamine oxide, because the indicated long alkyl group provides optimal suds support whereas the indicated short alkyl groups give best solubility in water.

Solubilizers/Viscosity Modifiers

When appropriate proportions of primary surfactants and foam promoters/stabilizers are combined with the intention of producing an aqueous solution representative of the composition to be marketed, it is necessary to incorporate special additives to ensure that the product has satisfactory physical properties—adequate physical stability, optimal viscosity, ease of dissolution, and resistance to "skinning" on exposure to air.

Adequate physical stability is a particularly important feature of any liquid because it is unlikely that consumers will want to purchase a product that exhibits a precipitate or a more severe phase separation. Any such incompatibility is evidence that one of the components of the active ingredient system, or a complex mixture of several, has exceeded its solubility limit at some temperature and has not yet redissolved. Invariably, this limit is reached when a product is cooled sufficiently to cause a haze or cloud to first appear. Storage below this temperature (normally called the cloud point) will result in increased formation of the secondary phase; eventually, stratification will occur if the viscosity of the continuous phase has not risen so much as to hinder movement of particles. Upon rewarming, the product will return to a homogeneous state at a temperature normally called the clear point, and the rate of recovery depends on the nature of the secondary phase and the degree of agitation provided.

This is not an uncommon course of events for products exposed to cold weather during shipment or warehouse storage. To minimize the possibility that any not fully recovered will reach a store shelf, it is desirable that cloud points be below 40 F and clear points not exceed 50 F (10 C). If the product under consideration is opacified, cloud/clear points of the clear base usually are measured to judge potential tolerance of low temperatures. Control of cloud/clear points is achieved through use of one or more hydrotropes or solubilizers such as ammonium or sodium xylene sulfonate, sodium or potassium toluene sulfonate, ethyl alcohol, or urea.

The xylene sulfonates are preferentially used in conjunction with LAS/AEOS/amide active ingredient systems whereas toluene sulfonates have appeared in AEOS/amine oxide-based products. Ethyl alcohol, a very effective solubilizer, is present in essentially all products because it also provides other functional benefits–modifies viscosity more readily than the aforementioned hydrotropes, lowers specific gravity, helps control microbiological contaminants and lifts fragrance. However, it can also undesirably lower flash point. Urea has limited usage; it seems most functional when levels of ethoxysulfate and amide are quite low, but has a drawback in that it tends to hydrolyze, causing troublesome upward shifts in product pH.

Optimal viscosity can be described as that product fluidity which is sufficiently high to create esthetic appeal and connote richness or efficacy, but is low enough to permit efficient high speed filling of bottles during manufacture and convenient dispensing in use. Ease of dissolution refers to a product's ability to quickly disperse and dissolve in the warm tap water used to prepare a dishwashing solution without the use of externally applied assistance. Any tendency to resist dissolution would slow release of foaming agents and concomitant generation of suds. Resistance to "skinning" implies the ability to avoid formation of a viscous or gelatinous film at any liquid surface exposed to air for an extended period of time. "Skinning" can speed clogging of the external orifice of a dispensing cap by interfering with drainage of residual liquid back into the bottle. These properties can be controlled with judicious combinations of hydrotropes, ethyl alcohol and inorganic salts.

Hydrotropes such as xylene and toluene sulfonates and ethyl alcohol lower viscosity whereas inorganic salts can either raise or lower viscosity. The most effective inorganic salts are chlorides such as NaCl, KCl, or $MgCl_2$, but their use requires that manufacturing equipment be adequately corrosion resistant. Inorganic salts are probably best for antigelling effects but, compared to ethyl alcohol, they have the disadvantage of raising the specific gravity of the product. Higher specific gravity results in increased weight of product in a bottle and therefore in a case. This introduces a cost penalty based on the extra product which could be substantial for a large volume major brand.

Opacifiers

These materials are used at times to try to provide a product with improved esthetic appeal. Typical examples are glycol distearates or emulsions of styrene-based copolymers, which produce a uniform dispersion of very fine particles. Care should be taken in adequately evaluating their compatibility with the base into which they are incorporated, because many factors can adversely affect the physical stability of the opacifying dispersion.

Colorants

A wide variety of product color options is available through the careful selection of one or more water-soluble dyes. In working to finalize a system, adequate stability in the product under various storage conditions and the absence of any tendency to permanently stain fabrics or dishwashing aids should be demonstrated.

Perfumes

In general, perfumes are selected to provide a pleasant fragrance during use of a product. Their complex composition and diverse properties of components necessitate that appropriate tests be run to assess compatibility of a candidate with the product and the package to be marketed. Some components can cause progressive product color change upon exposure to elevated temperatures and/or sunlight; others can diffuse through the wall of a plastic container; still others seem to lose their character during storage. Appropriate attention to these possibilities can help ensure a consumer-acceptable product.

Preservatives

Microbiological contamination of a product with uninhibited growth of the organism(s) can cause a number of problems–change in clarity and/or color, destabilization of an opacifier dispersion, development of a disagreeable odor, or formation of an unpleasant-looking, slimy aggregate that might become large enough to clog a dispensing cap's orifice. Any product being considered for manufacture and sale should be checked via standard techniques to determine whether it can withstand contamination by bacteria, mold, or other species that may be of concern to the microbiological laboratory. If failure occurs in such tests, an appropriate preservative should be incorporated. Its presence, however, will not necessarily guarantee absence of any problem, as unusual or resistant strains can be present in the plant environment. To prevent or reduce the magnitude of contamination with such a microorganism, good housekeeping should be practiced in the manufacturing area and equipment must be thoroughly cleaned on a periodic basis.

pH Control Agents

Most light-duty liquids have a pH between 6.5 and 7.5. If the mixture of formula components does not give a pH directly meeting a manufacturer's specification, adjustment of pH is achieved by addition of organic or inorganic acid, or of alkali. A pH that is too low can result in the hydrolysis of some surfactants whereas a pH that is too high can cause generation of ammonia from the ammonium ions present in many products due to the use of the ammonium salt of a surfactant.

Floc Control Agents

Some raw materials contain water-insoluble impurities that can be characterized as, e.g., heavy metal silicates, oxides or hydroxides. In the finished product, these particles flocculate and slowly settle to the bottom of the bottle to produce a somewhat fluffy, but very visible, sediment that could impact quite negatively on a consumer if a translucent or clear bottle is the package form. Sequestrants may be tried to hinder its appearance, but effective filtration can provide the best ensurance of floc control.

Special Ingredients

At times, a marketer may utilize a special ingredient to provide support for an advertising claim. Usually, such an ingredient is promoted for being mild/beneficial to the skin of the hands or for improving the efficacy of the product. Patent protection is desirable so that a competitor cannot readily simulate the improvement and take advantage of the positioning.

PERFORMANCE EVALUATION

The design of an entirely new, light-duty liquid product or modification of an existing one usually involves efforts first directed at achieving performance goals and then working to develop desired esthetic and physical properties while giving due consideration to the impact of ingredient decisions on finished product cost. Performance goals usually are established by selecting one's own or a competitive product as a target to be matched or surpassed. Once such guidelines are set, the most challenging, though tedious, part of the product development effort begins—the laboratory evaluation of performance characteristics aimed at finalizing an active ingredient system and predicting acceptability under home-use conditions.

Foam Characteristics

As previously indicated, light-duty liquids are purchased to provide aid in cleaning the various items encountered in hand dishwashing operations. Consumers, however, equate cleaning efficacy with foaming ability and therefore judge the quality of a product by the amount of suds generated and their persistence during a soaking or dishwashing procedure. Further, suds provide the additional benefit of hiding the dirty dishwater. Consequently, the assessment of performance of any composition centers on efforts to describe the properties of the foam it produces. Obviously, the most reliable and meaningful way of accomplishing such an assignment would be to have consumers conduct the evaluations under home-use conditions. Although this may be done with a finalized product ready for marketing, it would be much too slow and expensive a procedure to use in formula development studies.

As a result, many different techniques have been developed and used for predicting how a product will behave in the hands of a consumer. All are designed to provide an increasing food soil load in a dishwashing detergent solution after an initial foam height or volume has been generated; the number of units of food soil charged to cause complete foam breakdown are used to judge the product's performance level. Solid fatty materials such as animal fats or shortenings generally are used as the "foamicidal" agents, for they are the most effective in this respect; however, proteinaceous materials such as egg or flour are incorporated into the fat used by some investigators to highlight differences among certain types of surfactants.

Mechanical devices can permit rapid evaluation of formulations and avoid variables introduced in manual operations. One example is the Terg-o-Tometer; it readily generates a head of foam and speeds emulsification of unit charges of soil. The number of soil charges causing complete foam collapse is used as a relative measure of product performance. A manual operation that can also permit rapid evaluation of formulations is a so-called miniplate dishwashing procedure. Soiled watchglasses are washed with a small, soft brush in a miniature dishpan. The number of watchglasses needed to cause foam collapse are viewed as representative of the number of soiled, standard-sized plates that would produce the same endpoint in a conventional dishpan.

Some investigators feel that these techniques do not adequately predict the relative performance of products because they do not simulate the kind of interactions among hand, plate, soil, detergent solution, and foam layer that occur in the kitchen sink. They resort to manual hand washing of dinner plates under controlled laboratory conditions. The plates are usually presoiled with some selected reproducible soil or, if appropriate facilities are available, soiled dishes from a cafeteria may be used. As expected, these procedures are quite time-consuming and therefore greatly slow investigative studies.

With any of these methods, binary and ternary diagrams can be developed relating foam stability to surfactant system composition, or direct product comparisons can be made. In conducting such studies, the influence of water hardness elements on performance must be examined. Further, if naturally soiled dishes are not used, it is prudent to use more than one type of standard or artificial (mixed) soil to increase confidence in ranking of products.

Cleaning Efficacy

In a hand dishwashing operation, the manual energy that is provided in washing dishes and other table items or pots and pans readily removes all soils that are not firmly attached via adhesive forces to the substrate being cleaned. Cleaning efficacy primarily reflects the dishpan solution's ability to emulsify and disperse fatty material. If items soiled with fatty or greasy material are first soaked at the disgression of the dishwasher, the rate and degree to which such soil is lifted off a substrate may be observed and perceived as some indication of the merits of the light-duty liquid being used. Consequently, laboratory soak tests utilizing presoiled dishes or other suitable substrates, such as metallic discs, may be used to assess relative capabilities of preliminary compositions or finished products, or to evaluate the functionality of special surfactants or additives in a search for a competitive superiority.

When dried, baked-on, or burnt food residues are present, soaking in dishwashing solution for some extended period of time is necessary to permit their rehydration, softening, and disintegration so that removal can be accomplished with minimal use of scouring aids. Great success has not yet been achieved in substantially reducing the soak time needed for most stubborn residues. A few additives have been reported to be effective in easing the removal of some rather specific baked-on food remnants. In general, however, work on this problem is a challenging assignment.

PRODUCT QUALITY ASSURANCE

Assuming that a selection of a new active ingredient system or modification of an existing one is made based on performance considerations, the development program usually next involves adjustment of the physical properties of the contemplated product with suitable additives to meet pH, viscosity and cloud/clear point specifications. Colorants, perhaps opacifier, and perfume are incorporated to give a desired esthetic effect or impact. A final adjustment of physical properties is then made if necessary. Before this finished composition can be viewed as ready for preliminary evaluation by consumers or for actual sale, several key tests must be conducted to provide ensurance that the packaged product, after exposure to various ambient conditions and stored for an extended period of time, will reach the consumer in essentially the same condition as when it was first manufactured.

Aging Studies

These are conducted to try to predict the product's tolerance to exposure to various temperatures it may encounter during transportation and warehousing. Some samples are stored in both glass bottles and in the intended package at an elevated temperature such as 50 C for a minimum of one month to accelerate degradative chemical reactions. Periodic examinations are made to check for pH, color and fragrance changes, appearance of sediment, destabilization of opacifier if used, and shape distortion of plastic bottles. If substantial deviations from room temperature samples (controls) are noted, the cause must be determined and corrective measures taken.

Other samples are stored at low temperatures, preferably just above freezing, as well as below freezing. When phase separation occurs, samples are allowed to slowly return to room temperature without agitation and observations are made of the rate and extent of recovery. Depending on the results, a judgment is made as to whether any corrective measures are necessary.

Still other samples are exposed to sunlight to simulate storage of a non-opaque plastic bottle near a kitchen window and to investigate sensitivity to artificial light. Fading of color or darkening of product requires that the troublesome components be identified and corrective measures taken.

Whenever any formula corrections are made, the entire series of aging studies should be repeated. It is obvious that unexpected difficulties can easily upset marketing timetables.

Adequacy of Preservation Studies

These are conducted to assess the product's ability to withstand microbiological contamination. Inability to control the growth of key species usually demands incorporation of a suitable preservative.

PRODUCT SAFETY ASSESSMENT

The most important tests run on a finalized product are those that permit assessment of its medical safety. These include animal tests specified by the Federal Hazardous Substances Law, human skin irritation tests, and analyses for presence of contaminants or impurities of concern to government regulatory bodies.

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Formulation of Household Automatic Dishwasher Detergents

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ABSTRACT

The growth of the household automatic dishwasher detergent market and factors affecting future growth is reviewed. Major formulation changes that have occurred during the years are discussed, with emphasis on those contributions which resulted in significant improvement in performance. Present day formulations are classified according to types of ingredients and method of manufacture. Formulation options, types of equipment that can be used and factors which affect product performance are discussed, and performance test methods are described.

INTRODUCTION

Mechanical dishwashers were in use before the turn of the century, but an effective detergent product did not reach the market until the mid-1930s. The early products were soaps or simple mixtures of alkalies which softened water by precipitation. Gross food deposits were flushed away but were replaced by a film of insoluble calcium and magnesium salts.

Several major formulation improvements have occurred during the years to provide the high performance formulations available today (1).

DEVELOPMENT OF HOUSEHOLD FORMULATIONS

The first major improvement in dishwasher detergent occurred in the mid-1930s with the discovery that polyphosphates could be used to complex calcium and magnesium ions and prevent the formation of insoluble films (2,3). A sodium polyphosphate glass (Graham's salt) was used in the first of these products, but eventually was replaced by sodium tripolyphosphate because of its better performance and handling properties.

In addition to its ability to soften hard water, sodium tripolyphosphate is an excellent emulsifier and dispersing agent for soils, and helps hold the soils in suspension so that they can be rinsed freely from the dish surfaces (4).

The next major improvement was the discovery that an available chlorine compound in the formulation could promote free-rinsing and help to eliminate water spotting (5-7). Chlorine is particularly effective in breaking down protein-type soil to soluble amino acids which are more easily removed by the detergent. Without the chlorine, minute particles of residual soil remain on the dishes and glassware and allow droplets of water to remain through the rinse cycle. Upon drying, these droplets leave behind dissolved solids which cause unsightly spots. In addition to elimination of water spotting, the available chlorine compound also provides improved removal of stains and contributes to sanitizing (5).

The first source of available dry chlorine found to give good performance in automatic dishwashing was chlorinated trisodium phosphate. More recently, chlorinated isocyanurates have been used as the source of available chlorine (8). These compounds provide better stability at elevated storage temperatures, less caking tendency and lower formulation cost than chlorinated trisodium phos-