The New Toilet Soaps

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Abstract

Toilet soap bars have undergone few major technical changes in the last century. Noteworthy improvements were floating soap, the development of effective deodorant and antibacterial soaps, the so-called "hard water" bars, and advances in packaging technology. The trends in these areas toward product and process improvement will accelerate in the 1970's. New raw materials are becoming available which will give greater formulation flexibility, with emphasis towards greater mildness and effectiveness. Among these products are the synthetic fatty acids which could partially replace coconut acids, more effective broad spectrum antibacterial agents for better control of skin microorganisms, and mild detergent additives with good physical properties and less defatting tendency. In processing, the move is toward continuous soapmaking equipment in place of the old kettle processes which are still widely used. More powerful and specialized plodders are available; these will facilitate the development of new product types.

Introduction

Toilet soaps have been a commonly used aid to personal cleanliness since Roman times. In the last hundred years changes in soap composition and performance have been gradual, but a marked overall quality improvement has been achieved. Six major technical advances have accounted for nearly all of this improvement: (a) incorporation of synthetic detergents in toilet bar compositions, (b) evolution of deodorant soaps based on antibacterial agents, (c) development of floating soap bars, (d) development of continuous processing techniques to replace the batch kettle boiling processes for soap manufacture, (e) mechanization of soap-finishing operations, and (f) adaptation of protective packaging systems. Many of these developments will continue to influence the toilet bars of the 1970's.

Discussion

Detergent Bars and Combination Soap-Detergent Bars

Since World War II synthetic detergents have made tremendous inroads into markets which were previously dominated by soap. In compositions for washing clothes and dishes, detergents have completely replaced soaps; in shampoos the changeover has been nearly complete. The only product category where soap has retained the lead over detergents is toilet bars.

Toilet bars containing surfactants in place of or in addition to soap have been available for 20 years. However, they did not achieve an appreciable penetration of the toilet bar market until the late 1950's (1). The inclusion of detergents in toilet bars was undertaken for the purpose of dispersing or preventing the formation of the lime soap curds which cause bath tub ring. These curds are formed when sodium soaps react with the calcium and magnesium salts in hard water. Many detergents have been screened for use in toilet bars but relatively few are in actual use in such bars at present. Criteria for detergent-containing toilet bars were reported by Verheggen (2). Detergent bars should demonstrate soap-like properties to a large extent. Some of the more important properties are soap-like appearance, plasticity, lubricity, resistance to disintegration when immersed in water, solubility, resistance to cracking, and bland odor. Surfactants which have met these requirements sufficiently well to merit use in synthetic detergent and combination bars include: acyl isethionates, acyl N-methyltaurides, alkyl glyceryl ethersulfonates, acyl glyceryl sulfates, and alkyl sulfates. All of these detergents possess long chain alkyl or acyl groups of the type found in natural fats and oils. Most soap-detergent formulations contain 15–20% of synthetic detergent. The greatest shortcoming of synthetic detergent-containing bars (3) is that they still do not completely overcome the tendency of the wet bar to smear. Combinations of synthetic detergents with soaps, plasticizers, salts, chelating agents and foam boosters have been recommended to obtain the balance of characteristics required to compete with all-soap toilet bars.

Synthetic detergents employed as lime soap dispersants have been divided into two distinct categories. Schonfeldt (4) has reported that most anionic surfactants must be present in relatively large amounts (10–20%) before their effectiveness is apparent, while nonionic surfactants demonstrate incremental effectiveness which is observable at low levels. Examples of both types have been recommended for toilet bar use in recent literature: sodium methyl alpha-sulfopalmitate; ethoxylated oleyl alcohol; phosphorylated ethoxylated fatty alcohols; alkyl sulfonates; alkylbenzene sulfonates; alkylphenoxy polyoxyethylene ethanol; propylene oxide-ethylenediamine-ethyleneoxide condensates (Tetronic polyols, Wyandotte Chemical Company); propylene oxide-propylene glycol-ethyleneoxide condensates (Pluronic polyols, Wyandotte Chemical Company); N-lauryl β-alanine; and N-alkyl alkylolamines.

Lime soap dispersants which are not conventional synthetic detergents have also been recommended. Thiodisuccinate salts (5), β-hydroxy alkyl sulfoxides (6), sodium polyacrylate (7), and polyitaconates (8) were reported to be effective lime soap dispersants. Detergent bar formulations described in the patent literature often contain fillers to lower the cost. Such materials as wheat flour, starch in an alkali-stable form, and amylopectin are recommended.

In view of the research effort expended by the soap and detergent industry on detergent containing toilet bars, it is probable that this portion of the toilet bar market will continue to expand at a slow rate in the 1970's. The synthesis of a more soap-like surfactant could accelerate this growth.

Deodorant and Antibacterial Soaps

Soaps containing effective levels of antibacterial agents have been manufactured for 20 years. Toilet bars marketed domestically in 1968 which make deodorant claims include bars based on soap, synthetic detergent or soap-synthetic detergent combinations containing one or more active antibacterial agents. Deodorant bars represent the most rapidly

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growing segment of the toilet bar market, accounting for more than 50% of the soap bars sold.

The number of antibacterial agents available for use in deodorant bars is limited because of the stringent technical, esthetic and safety criteria they must satisfy: Activity against a broad spectrum of bacteria in the presence of large quantities of soap; effective deodorancy; skin substantivity; dispersibility in soap without adverse effect on color, odor or shelf stability; non-reactivity with other soap components, i.e., perfumes, antioxidants, etc.; skin degerming; low toxicity and skin irritancy; and efficacy in control of bacterially caused skin conditions, such as diaper rash, erythrasma and secondary infections. The soap bacteriostats which are currently used in domestic toilet bars are hexachlorophene, 3,4,4′-trichlorocarbanilide (TCC), 3,4′,5-tribromosalicylanilide (TBS), and 4,4′-dichloro-3′-(trifluoromethyl) carbanilide. These antibacterial agents meet most of the specifications listed above but have some deficiencies which make them less than ideal. The phenolic germicides cause some discoloration when the soap is exposed to light, and the substituted ureas are not completely resistant to alkaline hydrolysis. Many other compounds proposed for soap use have failed in one or more important performance characteristics. Bithionol [2,2′-thiobis (4,5-dichlorophenol)] and 3,3′,4′,5-tetrachlorosalicylanilide have been identified as skin photosensitizing agents (9,10). Other bacteriostats which have been recommended for use in antibacterial soaps but which are not presently employed in these products are tetramethyl thiuram disulfide (TMTD), 3,5-dibromo-3′-trifluoromethyl salicylanilide and zinc-2-mercaptopyridine-1-oxide. Synergistic mixtures of two or more bacteriostats, first suggested by Casely and Noel (11), are employed in some products to provide a higher order of antibacterial activity than individual bacteriostatic agents can provide when employed in equal concentration.

The popularity of deodorant and antibacterial soaps is reflected by the number of patents which indicate the extensive research programs directed toward the development of potent new antibacterial agents. For the next decade it is anticipated that particular emphasis will be placed on developing compounds with greater activity against gram negative bacteria, molds and fungi than the current antibacterial agents. Antibacterial agents with more effectiveness per dollar of cost will also be sought, in order to allow greater effectiveness within economic limits. Extremely mild, non-toxic antibacterial agents will also be the object of research because of the increasing interest of regulatory agencies in the safety aspects of consumer products.

Synthetic Fatty Acids

The use of synthetic fatty acid as a partial replacement for the naturally-derived acids can be anticipated during the next decade. The high price level of coconut oil and the fluctuations in this level create a favorable economic situation for synthetic acids in the coconut acid range, i.e., the 11 to 15 carbon acids. In addition to economics, improvements in specific bar properties are possible with synthetic acids. Moffett and deAcetis (12) have reported that ordered and homologous nature of natural fatty acids imposes limitations to their utility, and inferred that synthetic acids prepared by the oxo-process could overcome some of these restrictions. The acids described by these authors contain odd and even numbers of carbon atoms, and a small percentage of branched acids.

Synthetic acids as a potential threat to the fatty acid chemical industry were the subject of a symposium (13) two years ago. The participants concluded that petrochemical based fatty acid substitutes would make some inroads in business areas where the short supply and high price of natural acids was restricting growth. Synthetic routes to carboxylic acids suitable for use in soap include air oxidation of paraffins to a mixture of C10–C20 straight chain acids; oxo-process synthesis of mixed straight and branched chain acids; and conversion of Ziegler process intermediates to straight chain acids.

In addition to providing a potentially economical replacement for coconut fatty acids in soap, synthetic acids have two other possible uses in toilet bars, namely that individual synthetic acids can be employed as additives to soap formulations to modify some physical or performance attribute, and the manufacture of the fatty based surfactants used in detergent bars can also be performed with synthetic acids.

Floating Soaps

Floating soap bars have played a prominent role in the toilet bar market for about 50 years. Until recently, equipment for the high speed manufacture of floating bars was very specialized and not versatile enough for use in the general purpose soap plant. Plodders for the manufacture of floating soap have been developed which permit the use of standard soap drying and handling equipment in the preparation of soap for aeration (14). This equipment may encourage the development of floating toilet bars in the 1970's, including floating detergent bars.

Soap Processing

The soap industry is gradually converting from the slow kettle process of saponification to continuous high speed techniques. Although most soap plants constructed in the last decade employ continuous processes, the kettle processes probably are still predominant. The excess kettle capacity created when detergents replaced soaps in most washing compositions in the early 1950's left soapmakers with ample equipment for bar soap manufacture. Modern processes employ either direct saponification of fats and oils in efficient reactors, using centrifuges to hasten washing stages, or high temperature hydrolysis of triglycerides followed by distillation of the resulting fatty acids and neutralization. It is anticipated that soap plant construction in the 1970's will employ the continuous processes.

Other changes have occurred in toilet bar finishing equipment, largely as a result of the development of synthetic detergent-containing bars. The traditional soap mills and plodders were found to be inadequate to process synthetic detergent formulations, which tend to be sticky. The problems encountered in attempting high speed production of detergent-containing bars may have been partly responsible for the failure of detergents to displace soaps from the toilet bar market. The design of versatile equipment suitable for the finishing of toilet soaps, synthetic bars and floating soaps has been a relatively recent achievement, and should have a marked impact on the types of toilet bars available in the 1970's. This need for special equipment for detergent bar manufacture was recognized in the 1950's (15).

Packaging

The packaging developments of the past two decades have been directed toward providing protective covering for toilet bars. Foil wrappers and plastic film overwrappers for cardboard cartons provide complete protection from light exposure and a degree of protection against moisture loss. Packaging innovations in the 1970's will include the use of transparent plastic film laminates as a wrapping material, or rigid transparent plastic boxes to provide both protective and display properties. Very high speed packaging equipment is also a probability.

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