

Advances in Bar Soap Technology¹

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ABSTRACT

This paper reviews recent trends in bar soap technology. Toilet soap markets are highly competitive and the supporting technology is changing rapidly. New equipment and processing techniques have been developed, such as high caustic-high solids saponification, high speed finishing equipment, and more efficient dryers with better pollution controls. Multicolored, marbled soaps have become important in the marketplace and new plodder designs have been developed for their manufacture. A large number of new ingredients for use in soap-synthetic combination bars have been reported. Also, the antimicrobial/deodorant soap segment, representing over 50% of U.S. market, has undergone considerable shifts due to governmental actions which has resulted in restrictions on hexachlorophene. Future regulatory actions on other antimicrobial agents are probable.

INTRODUCTION

Over 80% of the toilet soaps sold in the U.S. essentially are based upon soaps prepared from a mixture of tallow and coconut oil fat stock. The balance is held by so-called "combars" which are mixtures of soaps, synthetic detergents, and other builders.

Consumption of toilet soaps in the U.S. has continued to grow faster than population (Table I). This 500 million lb/year market is made up of the following segments: deodorant soaps, 51%; complexion soaps, 20%; floating soaps, 16%; and miscellaneous soaps, 13%.

In recent years there has been a number of technical and legislative developments which has altered greatly the manufacturing practices and formulations of toilet soaps. This paper will review several aspects of bar soap technology.

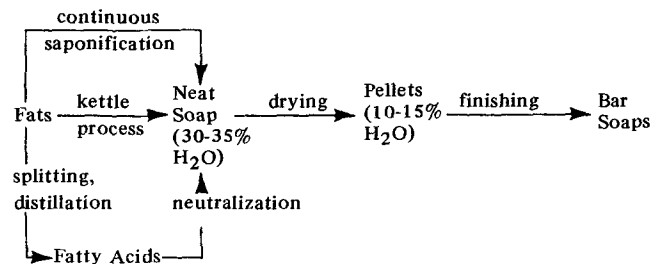
PROCESSING TECHNIQUES

The manufacture of toilet soaps comprises several steps. It starts with the conversion of fats into soap concentrate (neat soap). This is carried out either by direct saponification with caustic soda, using the old-fashioned kettle soap process, or by continuous neutral fat saponification processes. Alternatively fats first are converted into fatty

acids and glycerol by a high pressure continuous fat splitting process (1). The crude fatty acids then are distilled and neutralized using either pH or viscosity controls resulting in neat soap. Neat soap contains ca. 65-70% anhydrous soap.

Drying is the next key step in soap manufacture. The neat soap is converted to soap pellets containing 10-15% moisture.

The final step in bar soap processing is the "finishing" operation, that is the physical "working" and mixing of the soap pellets. This includes milling, plodding, and the addition of additives, such as perfumes, colors, antioxidants, or germicides. The various processing steps are summarized below.



Two developments have become important to soap manufacturing in recent years: (a) high caustic-high solids saponification techniques which eliminate the drying step, and (b) manufacture of marbled soaps.

Direct Saponification

Continuous processes have been developed by Sharples, Alfa-Laval, Meccaniche Moderne, and Mazzoni (2-5). The Sharples and Alfa-Laval processes use centrifuges for continuous phase separations, while Meccaniche Moderne and Mazzoni use heat exchangers and continuous settlers. The final choice of process, as well as a consideration of the alternate fatty acid approach, depends upon raw material availability, size of plant, and overall economic considerations.

Fat Splitting and Fatty Acid Distillation

No important developments have occurred in the last 5 years in fat splitting and fatty acid distillation, except for greater attention to air pollution problems associated with these processes. Catalytic oxidation of odorous gases from splitting and distillation is now practiced by several companies in Europe (6).

High Caustic-High Solids Saponification

High caustic-high solids saponification is a new approach to soap processing. The objective is to carry out the neutralization with minimum amounts of water by using high concentration caustic soda solution (50%) and finishing with 86% anhydrous soap, thus eliminating the drying step. A design incorporating this principle has been developed by Alfa-Laval and has been installed in the

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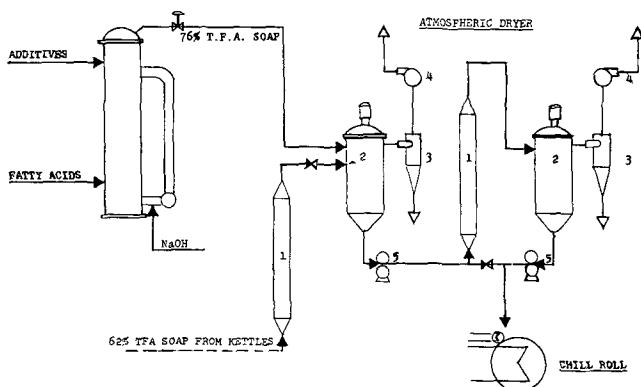


FIG. 1. Flow diagram, Dynamit Nobel AG Plant, Witten, West Germany. 1. Heat exchanger; 2. expansion chamber-mixer; 3. cyclone; 4. exhaust fan; 5. pump.

TABLE I

U.S. Toilet Soap Market
(\$ Volume [000,000])

1970	1971	1972
295	310	324

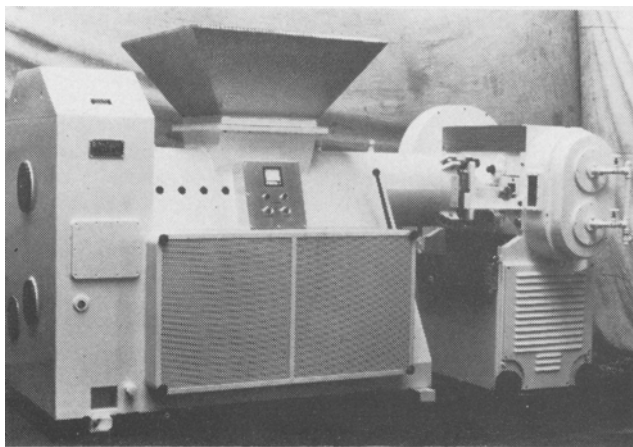


FIG. 2. Mazzoni plodder mill.

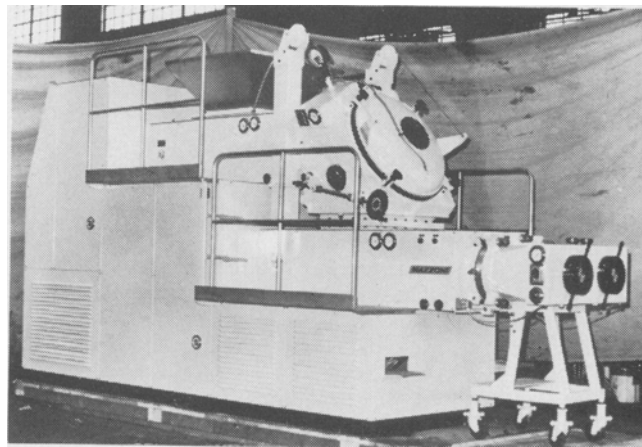


FIG. 4. Twin worm duplex vacuum plodder (Mazzoni).

Dynamit Nobel AG plant at Witten, West Germany (described by Osteroth [7]). The key points of this process are illustrated in Figure 1.

The Alfa-Laval saponification column on the left hand side of Figure 1 is capable of producing 86% anhydrous soap. The degree of neutralization is controlled by viscosity measurements. This soap can be moved directly to the chill roll (lower right hand side) and a pelletizing plodder resulting in regular soap pellets. The Alfa-Laval neutralizing column usually is operated to yield 82% anhydrous soap. The plant also generates 72% anhydrous soap (62% total fatty acids [TFA]) from normal kettle processes. Both soap streams are brought to the desired concentration using a Weber and Seelander 2 stage flash dryer (unit 2). There are probably 2 reasons why this intermediate drying step has been installed. First, the dryer acts as a buffer vessel when operating the high concentrated Alfa-Laval unit, and secondly, drying is associated with deodorization, and hence this step also has quality implications.

It is believed that a unit incorporating similar principles, but utilizing a pH control system instead of a viscosity control system, is being developed by the Mazzoni Corporation. The high caustic-high solids approach to soap making, with potential for eliminating the drying step, is a major step forward in the area of soap manufacture, promising better economics and less pollution problems.

Drying

There have been some important technical improvements recently in soap dryers. Alfa-Laval has designed dryers utilizing plate heat exchangers instead of the more conventional tubular heat exchangers. One unit has been

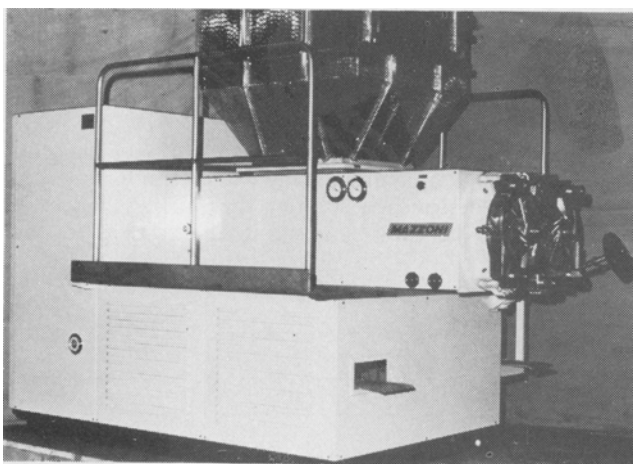


FIG. 3. Twin worm modular simplex plodder (Mazzoni).

tested at Kappus, Offenbach, Germany, though it has not yet found commercial application.

The Mazzoni C dryer has been available for some time in either single vacuum or in a combination atmospheric flash plus vacuum multistage system. This dryer has been changed in 2 respects: there is a greatly improved dust return system, utilizing multicyclones, and surface condensers which replaced barometric condensers.

Bar Soap Finishing

Important advances have been made in developing new soap finishing equipment: these include mills, amalgamators, plidders, and combinations of these units. These units have the following functions: blending various active ingredients, such as perfumes, germicides, color, etc., into the soap pellets and then physically "working" the soap pellets and extruding the soap as a continuous rod. This action affects the degree of compaction of the soap, the operating temperatures, and the crystallinity of the soap. The extruded soap rod then is cut into soap slugs, stamped, and wrapped. Improvements fall into several categories: greater efficiencies, the ability to use soap and soap synthetic combinations, the development of attachments for production of multicolored or marbled soap, and increased speed and output. Finishing equipment can now operate at the rate of 300 to 400 bars/min, and these rates are presently ahead of the capabilities of packaging equipment.

Examples of recent developments are the plodder mill

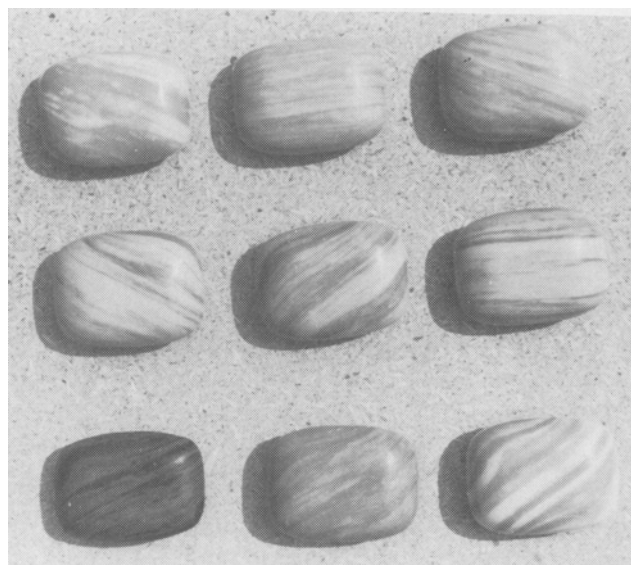
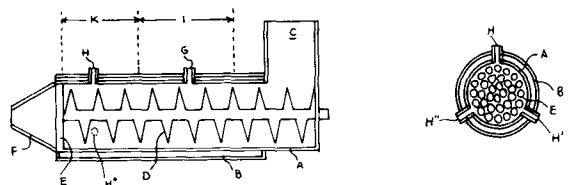


FIG. 5. Marbled soaps.



U. S. PATENT № 3,663,671

FIG. 6. Liquid injection method for marbleizing soap.

shown in Figure 2 and the modular twin worm plidders shown in Figures 3 and 4.

The Mazzoni plodder mill, shown in Figure 2, combines vacuum plodding and milling. It is a simplex refiner with 2 rolls, conceived to satisfy an industry still engaged in debating the relative merits of vacuum plodding and milling.

Tests on soap bars made with the Mazzoni plodder mill compared to a line utilizing a triplex vacuum plodder showed that the bars produced on the plodder mill line had better washdown temperature characteristics. This is a measure indicating when roughness in a bar is first detected as the water temperature is dropped at a rate of 1-2 C/min, while continually manipulating the bar underwater. The lower the temperature, the better the bar.

Modular twin worm plidders have affected line speeds and efficiencies. These units can be used for synthetic products and for large capacity lines. A twin worm modular simplex refiner is shown in Figure 3 and a twin worm duplex vacuum plodder in Figure 4.

MARBLEIZED SOAPS

The appearance of mass produced multicolored or marbled soaps in the U.S., Europe, and in Australia has required the development of new equipment and techniques. Figure 5 shows some examples of marbled soaps.

Two techniques are used to produce these effects: the first employs a liquid-solid mixing system (8,9); the second system (solid-solid) utilizes different colored solid soaps which are mixed within the plodder (10,11).

An approach using the principle of liquid-solid mixing and designed for the continuous manufacture of marbled soap is illustrated in Figure 6. The process utilizes a soap plodder provided with a conical nozzle. The soap mass at a temperature not exceeding 60 C is moved through the plodder by means of a screw thread, and dye solution is introduced into the soap through at least 2 inlets arranged in the jacketing for the plodder. The position of the inlet tubes is claimed to be critical (8). In a second method of liquid-solid mixing, color is injected into the vacuum chamber of a duplex vacuum plodder (9).

The second principle for marking marbled soap utilizes solid-solid systems. The first system is designed for the production of soap with 2 or 3 color combinations in a wide variety of designs (10). A drawing of this system is shown in Figure 7.

The main element in Figure 7 is the colored base forming plodder (MBP). This is a twin worm pelletizing plodder which receives all the scrap, as well as uncolored pellets. The second unit is a marbleizing plodder which is a single worm plodder (MR) with a variable speed motor which receives the color pellets from the colored base forming plodder (MBP) and introduces it into the marbleizing extruder head (ESM) which is mounted on the final plodder of the finishing line. Colored and uncolored pellets are mixed in this marbleizing extruder head.

An alternate approach to a solid-solid mixing process (11) is illustrated in Figure 8. In this process, 2 or more differently colored batches of soap with ca. the same viscosity and plasticity are prepared. Appropriate proportions of pellets then are charged into a vacuum chamber,

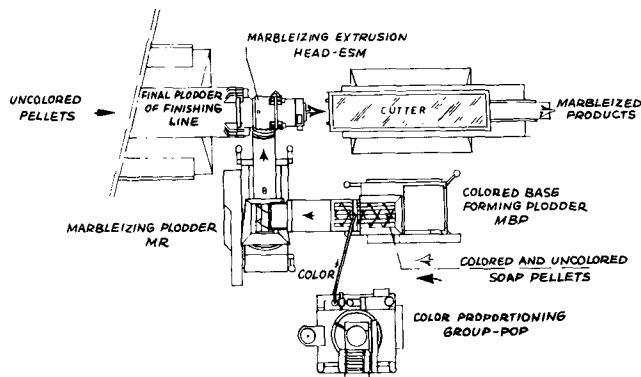


FIG. 7. Solid-solid method for marbling soap by Mazzoni.

extruded, cut, and stamped in the usual way.

Another technique for manufacturing multicolored soap has been reported based upon effecting color changes in a bar soap by irradiating a portion of the bar with high energy electrons (12).

NEW SOAP-SYNTHETIC COMBINATIONS

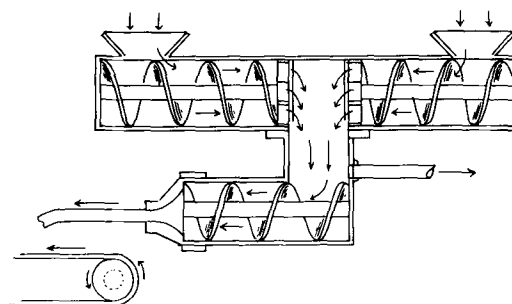
The most active formulation programs in the toilet soap area appear to be the search for lime soap dispersants for incorporation into hard water bars. These products are either a combination of soap and synthetic lime soap dispersants or are purely synthetic bars. Some of the lime soap dispersants historically used in these hard water bars are sulfated fatty monoglycerides (13,14), fatty alcohol sulfates (15-20), sulfosuccinate half esters (21,22), and sulfonates (23-25), such as Igepon A (fatty acid ester of sodium isothionate) and Igepon T (oleyl methyl tauride).

There has been considerable activity in recent years aimed at developing new lime soap dispersants for use with soap. This has resulted in the discovery of a number of novel and potentially useful new materials, including amphoteric sulfonates (26), sulfons (27), sulfonamides (28), sulfonated phenyl sulfostearic acid derivatives (29), alpha-sulfo fatty acids and esters (30,31), magnesium thiodisuccinic acid (32), vicinal acylamido sulfonates (33,34), hydrogenated olefin sulfonates (35-37), and alpha olefin sulfonates (38-46). There also have been a series of papers by Linfield et al., describing lime soap dispersants derived from tallow, including sulfated alcohols, sulfated hydroxyethyl amides, alkylaryl sulfopropionates, oxyethylated diethanolamides, and sulfopropyl esters (47-53).

The lime soap dispersants which are most likely to make an impact in the next few years include the hydrogenated olefin sulfonates, the alpha olefin sulfonates, and the alpha sulfo fatty acid derivatives when these products are used either alone or in combinations with older established surfactants.

ANTIMICROBIAL/DEODORANT SOAPS

Deodorant and antimicrobial soaps represent the largest



U. S. PATENT № 3,673,294

FIG. 8. Solid-solid method for marbling soap by Lever Brothers.

segment of the U.S. toilet soap market: over one-quarter billion lb of deodorant soaps are sold annually. These products have found great acceptance by the public, because they provide definite deodorant protection and some protection against minor skin infections (54-59). Several critical reviews on the use of bacteriostats in soaps have been published (60-63).

The chief antimicrobial agents used by the soap industry include hexachlorophene (2,2'-methylenebis-3,4,6-trichlorophenol); 3,4,4'-trichlorocarbanilide (TCC); 3,4',5-tribromosalicylanide (TBS); 4,4'-dichloro 3'-(trifluoromethyl) carbanilide (Irgasan CF₃ [trademark, Ciba-Geigy]); and 2-hydroxy-2',4,4'-trichlorodiphenyl ether (Irgasan DP300 [trademark, Ciba-Geigy]). Some of these compounds, particularly hexachlorophene, recently have had considerable adverse publicity, followed by FDA regulatory action (64).

While there was no evidence that toilet soaps containing reasonable amounts of hexachlorophene (up to 1%) had ever had harmful effects on adults or babies, FDA proposed regulations in early 1972 (65) limiting the use of hexachlorophene to a maximum level of 0.75% and required a cautionary label and an approved new drug application. This recommendation was based upon a series of animal toxicity and human absorption studies published by Kimbrough and Gaines (66) and Curley and Hawk (67,68), and this recommendation was discussed in detail by Lockhart (69).

In September 1972, FDA abandoned the previous recommendation and essentially banned the use of hexachlorophene in toilet soaps. The key evidence on which FDA based its ban of hexachlorophene was a case of gross misuse in France when a manufacturer inadvertently added 6% hexachlorophene to a baby powder, resulting in over 30 deaths and alarming headlines. There was also a study reported by workers at the University of Washington Medical School (presently unpublished) which evaluated the amount of formations of brain stem lesions on premature babies who were anointed with an undiluted preparation of a detergent liquid containing 3% hexachlorophene. This was done to the whole body of newborn babies who were then rinsed.

Another widely used material, 3,4',5-tribromosalicylanide, is also presently under review by the FDA-OTC Review Panel, and its future is not at all clear. It already has been withdrawn voluntarily from several nationally distributed brands of toilet soap.

The high level of governmental activity and the resultant uncertainties have affected the deodorant soap business. The industry uses several million lb of bacteriostats annually, and the sudden banning of a product could result in quick shifts in the supply and demand situation and requires the development of new formulations which have been fully tested and proven efficacious and safe. Several major formulation changes already have taken place in the industry in recent months and others may yet be coming.

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