# Detergents eight-0

## meeting the needs of the '80s

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## Session 2

# Current Future Fat-Based Raw Materials for Soap Manufacture

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### ABSTRACT

The traditional use of coconut and palm oils for soap manufacture can be expected to continue indefinately. Certain oils of the oleic/linoleic acid group are too unsaturated to yield soaps of the desired degree of hardness and stability. They may be hydrogenated to form suitable hard soap fats; a quantity of these oils is used regularly in the preparation of soft soaps and in blends with harder fats. The chief animal fat used in soapmaking is tallow. Other fats and oils less frequently used include babassu, palm kernel and olive oil. The ratio of tallow/coconut oil used for the manufacture of toilet soaps ranges from 85:15 to 75:25. A correlation of soap properties with the ratio of 95:5 to 75:25 of tallow and coconut oil demonstrates that properties such as cracking, swelling and hardness are not as sensitive to the changes in the blend ratios as are erosion characteristics, slushing and lather. Present production of Russian and Eastern European soap is from huge quantities of straight-chain, odd- and even-numbered, carbon saturated synthetic fatty acids (SFA). Future fat-based raw materials might include certain fractionated fatty acids, methyl ester intermediates, acidulated sunflower and/or safflower soapstocks. Jojoba wax might be a surprising new raw material.


### INTRODUCTION

When one considers the "old-fashioned" subject of soap, some get the mistaken impression of an obsolete product which is in the last stage of replacement with a new and improved synthetic detergent. What, then, could possibly be new and exciting in raw materials for soap? The statement, "Soap was made in the past from coconut oil and tallow, or both, is made from them now, and is likely to be made from them in the immediate and near future, albeit in ever decreasing volume," covers in a single sentence about 95% of all that could be legitimately said on the subject. Were that indeed the true situation, the soap future would be bleak. Nothing could be further from the true picture. It is predicted that soap will have somewhat of a renaissance in the next 10 years. Natural fats and oils, the basic soap raw materials, are animal- and vegetable-derived, and, as such, are replenishable, which is the chief long-range advantage for using them. Today, product development has demonstrated that several soap and "lime soap dispersant agent" combinations offer the hope of early circumvention of the environmental disadvantages of phosphate-built synthetic detergents. Some of these better lime soap dispersant agents also are made from natural source materials. In effect, what has almost been accomplished is that the main soap disadvantage—curding in hard water—may be at least partially eliminated. Because soap has always been relatively inexpensive, the possibility now exists that it will reenter some of the areas from which it was previously displaced. Also possible is that process development can achieve significant energy conservation in continuous soap manufacture, and other developments are underway. A "renaissance" is not unlikely.

### FATS AND OILS AS SOAP RAW MATERIALS

Fat-based raw materials comprise the primary feedstuff from which the soap part of the finished soap product is produced. This means that the fat or oil itself or the intermediate fatty acids (by splitting and fractional distillation) or, perhaps, the intermediate methyl esters (by alcoholysis and fractional distillation) furnish the anionic part of the soap molecule, irrespective of whether the cationic part is metallic, such as sodium or potassium, or organic, such as diethanolamine.

Toilet soap manufacture provides a perfect example. It is still made largely from tallow and coconut oil (and from similar composition fats and oils, i.e., palm kernel oil and certain high-grade fish oils). Consider just how much coconut oil and tallow are required for the optimization of toilet soap properties. Table I and Figure 1 show ranges of blends of tallow and coconut oil usually required for a satisfactory toilet soap. The first obvious conclusion that can be made is that the optimal ratio of tallow/coconut oil is in favor of the tallow. This is quite satisfactory, because the larger part is the cheaper priced animal fat. Thus, from these data, at least, it appears that the optimal ratio is ca. 67:33 to 85:15 tallow/coconut oil.

As soon as it became possible to determine the fatty acid distributions of both tallow and coconut oil, attempts were made to correlate finished soap bar properties with the tallow/coconut ratio based on the distributions of fatty acids in the raw materials. The correlation has always been difficult, and, over the years has become almost impossible. It is surprising that this unlikely and unsatisfactory approach to quality control persists.

In most tallow/coconut oil correlations, the laurate and myristate components originate from the coconut oil, but the stearate comes mostly from the tallow. It was soon recognized that palmitoleates, myristoleates and the C-18 oleates plus palmitates were contributed by both fats. The C-17 components, which are missing in coconut oil, come exclusively from the tallow; the C-6, 8 and 10 which are almost entirely absent. The elaidates and, presumably, the other *trans*-isomers of the "oleic" acids are derived from tallow, but are probably significant only in soaps produced by the fatty acid route, where they accumulate to a small extent as a result of the thermal conditions of fat splitting and fractional distillation. It wasn't until the early 1950s that fatty acid analysis exposed the severe limitations of the sweeping generalizations on correlation of soap bar properties with tallow/coconut oil ratios. However, certain observations on the effects of laurate and stearate were important and quite valid.

To illustrate the dangers and limitations involved in attempting to correlate soap properties with fatty acid composition of tallow and coconut oil, consider one recent example of fatty acid composition of binary tallow/coconut oil mixtures taken from 1968 literature (Fig. 1) (3) and notice the validity of the assumptions that were made. No significant conclusions were drawn.

The first assumption frequently made is that both the fat and the oil can be represented adequately by an average composition. This is not a reliable basis on which to start. Coconut oil fatty acid distribution varies from season to season, locality to locality, and in accord with climatic, genetic and other factors. The same situation prevails, possibly to a slightly lesser extent, with tallow. It is known that Indian tallow differs compositionally from Argentine tallow; North American tallows exhibit large fatty acid variations from such divergent factors as feeding, climatology, geographical location of the animals and the trimming practices of the slaughterhouses. Thus, conclusions are unsound that are based on the assumption that the feedstock is "fixed," even on an average one, when, it actually varies over a large range. Even if it were a reliable basis, an approach of this kind would require a huge background of performance information correlated with the level of occurrence of 17 different fatty acids in the two raw materials. Simply stated the latitude in raw material composition for both the fat and the oil is far too broad to be adequately represented by an average composition.

**TABLE I**

**Characteristics of Fats Used in Soapmaking (1,2)**

| Fat | Titer (C) | Iodine number | Saponification number |
|---|---|---|---|
| Coconut oil | 20-24 | 7-11 | 250-256 |
| Tallow | 40-48 | 40-48 | 195-205 |
| "Ideal" fat charge | 36-38 | 38-40 | 215-225 |

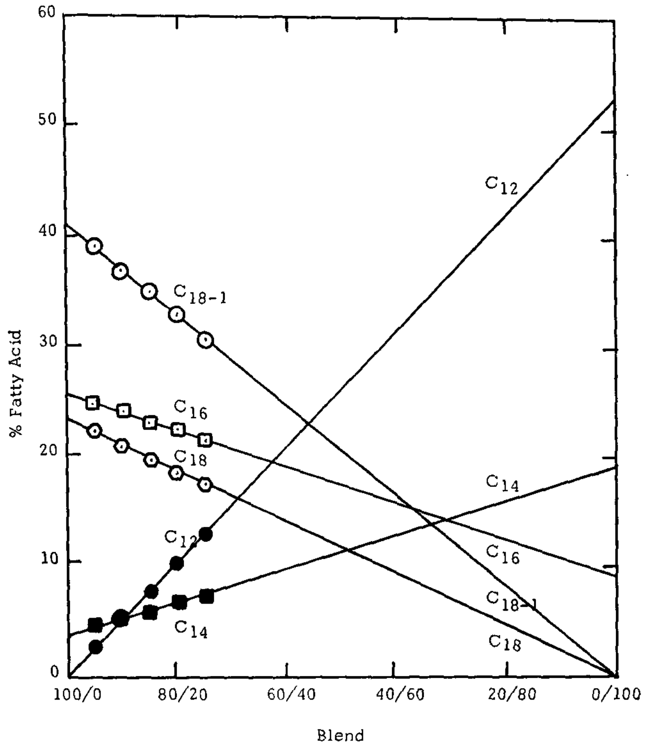


**FIG. 1. Variation of major fatty acids with tallow/coconut blends (3).**

Compositional data assume that coconut oil, usually with an IV of 10-12, contains no oleic acid (actually, it normally has 5-8%); linoleic acid is ignored (coconut oil has 1-2.5%); C-17 are mostly ignored (tallow has ∿2%), but sometimes are included with the C-18; palmitoleic and myristioleic are sometimes included with the common oleic, but frequently, the presence of these shorter chain unsaturated acids is ignored. Furthermore, it is assumed that coconut oil contains no stearate components (actually coconut oil of Philippine origin might have an average of ca. 2.2%). One can begin to appreciate that the broadness of the assumptions can invalidate many of the conclusions that could be drawn.

The situation relating to the correlation of toilet bar soap properties with tallow and coconut oil raw material composition probably is not so bleak as may have been implied. Some careful work from Armour-Dial in 1968 indicates that, with vigorous distinction between the definitive and nondefinitive soap properties, reasonable and worthwhile conclusions can still be made. This work relates to the effects of the binary blend ratios on certain finished bar toilet soap properties when the soap is produced through the distilled fatty acids by conventional methods.

It presupposes that some sodium stearate from the tallow is necessary for cleaning efficiency and that some sodium laurate from the coconut oil is required for solubility and foaming/sudsing properties.

The first property listed in Table II the "lather quickness," is a measure of the minimal mechanical energy that is expended to achieve lather in the shortest time. This is measured at 85 F in an apparatus described by Becher (4). The same results could be achieved by measuring the number of strokes necessary to generate a given foam height, or the concentration of soap required to produce a layer of foam just covering the surface of the liquid of specified area in a standard container. After measurement by any number of laboratory techniques, it is obvious that the 85:15 ratio was optimal. In an effort to relate hand lather preference (not performance) with lather quickness, it was apparent that other factors intervene, because the result for optimal lather quickness was an optimum of 85:15, whereas the "preference" data seemed to indicate a 75:25 ratio. Presumably, these other factors might be lather consistency, lather "feel and other subjective evaluations.

Mechanical erosion of soap bars is an important measure of the use-life of the soap product. Generally it is assumed today that extensive erosion of a soap bar is more indicative of wasted soap rather than of useful soap. That may be true, but not necessarily. Minimal loss in weight must be involved in any standard, useful cleaning operation; anything eroded beyond that figure fits the category of "wasted" soap.

If soap bar erosion were related to the solubility of the soap, one would expect a direct relationship with the sodium laurate content, the most soluble component. Although the erosion is higher in soap bars with higher amounts of sodium laurate, the relationship is not linear and the most rapid increase in erosion rate is observed between 95:5 and 90:10 compositions (entirely unexpected). Overall, the results suggest that 75:25 might be an optimum. The practical amount of erosion in these tests is of the order of 0.09 g/stroke for 95:5 and 0.12 g/stroke for a 75:25 composition, all at 85 F and with water of 127 ppm hardness. Note the apparent correlation of handwashing erosion with mechanical erosion: both tests gave apparent optima at 75:25.

Slushing is a soap bar property that relates to mechanical abrasion, in that the insoluble (but hydrated) material generated by use is measured in a standard test. A soap bar is shaved to uniform dimensions and placed on end in 200 ml of water in a 600-ml beaker for 16 hr. At the end of this time, the bar is removed from the solution and the resulting liquor (a suspension and a solution) is measured for solids content. The tendency to slush was found to vary linearly with the proportion of coconut fatty acids in the blend; presumably, this results from the presence of highly soluble laurate and lower soaps. It is assumed that high slushing is detrimental to economical soap use.

While there appears to be some influence of composition on soap bar softness, the effects are small, although titer, which is related indirectly to composition, is important. On the other hand, swelling and cracking properties show little or no dependence on the blend ratios.

Pioneering work on the importance and function of sodium stearate in toilet soap established the need for it as a cleaning agent. This was important with regard to soap raw materials, for it pinpointed the search for satisfactory raw materials to fats and oils containing or capable of generating by hydrogenation, optimal or near optimal quantities of stearate component. These stearate-containing fats or oils could then be blended with those of the laurate group, such as coconut, palm kernel or others, which have the required solubility and free-lather qualities not adequately present in the stearate-rich group, to give blends highly prized for soapmaking.

**TABLE II**

**Effect of Tallow/Coconut Fatty Acid Ratios on Properties of Bar Soaps (3)**

| Soap property | Optimal tallow/ coconut ratio |
|---|---|
| Lather quickness | 85/15 |
| Hand lather preference | 75/25 |
| Solubility mechanical erosion (85 F) | 75/25 |
| Solubility, erosion from handwashing | 75/25 |
| Slushing | 75/25 |
| Bar Softness | Little effects |
| Swelling | None |
| Cracking | None |

There is much published information which shows the properties and characteristics of sodium soaps of the common fats and oils. Information shown in Table III refers to the as-is sodium soaps formed directly from the listed fats and oils, i.e., without distillation and without partial or complete hydrogenation.

Marketing aspects of the raw materials are of interest. According to the U.S. International Trade Commission, formerly the Tariff Commission, the production of total salts of fatty acids, rosin and tall oil fatty acids for soap production was 821 million pounds in 1976. Statistics are similar for 1980. Breakdowns indicate that "coconut-oil-type" soaps, both sodium and potassium, amount to 160 million lb, tallow-derived soap was 353 million lb, and the mixed sodium and potassium soaps of various oleic acids was 2.8 million lb. It is believed that 65% of this soap was made from fats and oils by the conventional soapmaking method. Assuming that 100.2% of the coconut oil soap is equivalent to coconut oil raw material, one gets 104.2 million lb of coconut oil; assuming that 96.46% of the tallow soaps are equivalent tallow one gets 219.6 million lb of tallow used for soap production. Admittedly, all this is a good approximation.

## VEGETABLE OIL SOAPSTOCK RAW MATERIALS

There are a few raw materials that might be expected to be used for the soap production in the future, not as primary raw materials, but as indirect sources. These include safflower, sunflower and rapeseed oils. The individual who knows something about vegetable oils may wonder why safflower and sunflower oils are included. Both oils are members of the oleic/linoleic acid group of fats and oils and, like most of that group, are in too much demand as edible oils to be considered as primary raw materials for soap production. They are too expensive. No one today supposes that the soapmaking plant of 2000 A.D. will be based on either safflower or sunflower oils as raw materials. In natural form, neither oil has ideal fatty acid distribution, but this could be compensated through partial hydrogenation to increase the stearate primarily at the expense of linoleic, and partially of oleic acid content. The present production volume of both vegetable oils is quite low.

If either or both these vegetable oils achieve successful commercial-scale production, a significant quantity of soapstock will be available as a by-product from the refining operation, as with cottonseed and soybean oils. But, why should safflower and sunflower soapstock be considered for soap manufacture when cottonseed and soybean soapstock, which are already available in copious quantities, are not used?

Fat and oil soapstock generally contains 10-20% emulsified oil, mostly triglyceride. Included are substantial quantities of the color bodies (cottonseed soapstock is jet black in color from the gossypols concentrated in it), mainly vegetable pigments and their decomposition products, plus sterols, tocopherols and several other vegetable oil contaminants. The problem of upgrading inexpensive vegetable oil soapstock to a quality sufficient to permit toilet soap manufacture is largely economic, and the precise technology required to solve it not yet available. By conventional technology, it generally requires three redistillations of acidulated cottonseed soapstocks to achieve a reasonably satisfactory fatty acid color, but 20-25% of the material is lost to the still residues. Under these prohibitively poor overall economics, black cottonseed soapstocks find little or no use in toilet soap. Similarly, dark-brown-colored soapstocks from soybean oil, without the gossypol but with substantial linolenic acid component and other objectionable contaminants, is potentially able to afford a fatty acid of initial satisfactory color, but is unsatisfactory in color and odor stability when evaluated for soap production. Again, the loss of triglycerides in the redistillations is prohibitive. Do the amber-colored safflower and sunflower oil soapstock offer any real hope for future soapmaking?

If simultaneous or successive splitting can be incorporated into economic processing to permit the recovery of the fatty acids from the triglycerides (and give a mini-bonus in the form of glycerol credit), both safflower and sunflower soapstocks might, indeed, be utilized. Certainly, the initial color is infinitely superior to cottonseed and soybean, a minor advantage if other problems cannot be solved. Second, the impurities, at least superficially, appear to be more easily removed, but more development work is required before the final answer to that supposition is available. Choice of the preferred processing technology involves either splitting somewhat degraded residue from the distillation of acidulated soapstock, or splitting acidulated soapstocks first, followed by distillation of the combined fatty acids from the oil and acidulated soapstock.

Admittedly, the reference to possible use of these soapstocks is speculative and long-range, but not improbable or unlikely by any means. Will the ideal geographical location for the American soap plant of the future be right next door to a vegetable oil refinery somewhere in the safflower belt (Southwest USA), or sunflower belt (Texas, Minnesota or other places)? Assuming these "belts," will exist, remember that ca. one-fifth of the best toilet soap is from C-12-rich fatty acids, and that these will originate for the present, and apparently for a long time to come, from Philippine-imported coconut oil; thus, freight and transportation for this raw material definitely enter into the plant location picture.

## SYNTHETIC FATTY ACID RAW MATERIALS

Considering fatty acids as a direct raw material for soap manufacture is paradoxical, because all fatty acids are derived from fats and oils by splitting. The point is that most of the continuous soap production plants operate by splitting tallow or coconut oil, followed by fractional distillation of the liberated fatty acids and the blending of them, before or after, for the soap making charge. Thus, in most instances, the fatty acid is the raw material which goes directly into the soap making operation. But, from a different approach consider the use of synthetic fatty

TABLE III

Some Fats and Oils and Characteristics of Their Sodium Soaps (5)

| Soap | Color | Consistency | Odor | Foam | Detergent quality | Skin reaction | Uses |
|---|---|---|---|---|---|---|---|
| Coconut | White to yellowish | Very hard, brittle | Practically odorless | Quick, big bubbles short lasting | Good also in cold water | Rough | All kinds of soaps with tallow |
| Palm kernel | Yellowish | Very hard, brittle | Similar to oil, violet | Slow, small bubbles | Very good | Rough Ref. mild | Household and toilet, soap powder |
| Olive | Yellow to drab green | Hard | Weakly like oil | Fairly good | Good | Very mild | Household, textile and baby soap |
| Peanut | Light yellow | Hard (s.l.) Softer (n.) | Practically odorless | Fairly good | Very good | Mild | Similar to olive |
| Soybean | Light yellow to green | Hard | Practically odorless | Mediocre | Mediocre | Very mild | Similar to olive |
| Tallow | White to yellowish white | Very hard | Practically odorless | Very small bubbles, lasting | Good | Very mild | Household, textile toilet, shaving |
| Lard | White | Hard | Odorless | Quick, small bubbles, lasting | Good | Very mild | Household, toilet, flakes |
| Whale | Yellow-brown | Fairly soft | Fishy | Small bubbles, lasting | Fairly good | Mild | Soft soaps |
| Cottonseed | Gray white to dirty yellow | Fairly soft | Like the oil | Mediocre, lasting | Good | Mild | Household |

acids first.

There is no American synthetic fatty acid of satisfactory composition or quality available from which soap can be made. This is largely a matter of economics and conservation involving complex priority issues; soap could be made this way—the technology is available. The U.S. doesn't have to use all available vegetable or animal fats for food purposes, as does much of the rest of the world. It can afford the luxury of using our replenishable resources for industrial production, including soap manufacture. The U.S. is the only country in the world that can devote such a large part of its fat and oil resources, ordinarily highly suited for food purposes, to the manufacture of industrial materials. The figures reduce to a ratio of ca. 2:1, i.e., about twice as much is utilized for some kind of food production as for industrial applications, including soap; that is the highest proportion used for industrial production worldwide. Here is the first intensely important correlary of the fact: U.S. today is not in the unfortunate position of having to assign some significant proportion of its increasingly expensive, irreplaceable petroleum reserves to the manufacture of toilet soap.

Hunger is widespread in many other parts of the world, and petroleum hydrocarbons have to be used to supply industrial products, like soap, to permit fats and oils to be used for food. The animal and vegetable fats and oils that are produced in most of the other parts of the world simply are not sufficient to satisfy the minimal demand for food. As a consequence, there is a soap renaissance over 30 years old in Russia and several Eastern-European countries, except that the raw materials for it are exclusively synthetic acids derived from irreplaceable petroleum hydrocarbons and not from replenishable fats and oils. A brief, but illuminating, look at the nature, level of production and composition of some synthetic acids that are used in Eastern Europe today is worthwhile.

Russia and the near Eastern countries are estimated to produce ca. 1.1 billion lb of synthetic acids which are mixed odd- and even-numbered C-atom, straight-chain, saturated hydrocarbons. In comparison, the 1978 U.S. production of so-called "natural" fatty acids, as reported by the FAPC, was 956 million lb. This figure doesn't include tall oil fatty acids, which are largely inedible, amounting to 398.8 million lb, for a total U.S. production of 1.354 billion lb. The figures for 1979 are similar.

Table IV shows the general primary fractional distillation cuts of Russian SFA produced from straight-chain hydrocarbon feedstocks. These data were published in Russia during 1962-63 (6,7), and were taken as-is from a brief published (8) treatment of synthetic fatty acids. The Russian soap renaissance is not new at all; it's in its third decade.

The boiling points of the hydrocarbon feedstocks, in the far left column of Table IV, are for identification and characterization only; they obviously do not represent the boiling points used for separation. It is obvious from a look at these hydrocarbon feeds that the synthetic acids that are products of their oxidation, and any soaps made from the acids, do NOT contain any unsaturated, even-numbered fatty acids, but they DO contain substantial quantities of odd-numbered acids, e.g., 13, 15, 17 and 19. If is apparent why Russia doesn't try to utilize them in foodstuff production; the human digestion system is not conditioned to accept synthetic fats containing this many odd-numbered components. These are the primary SFA from the program; the particular fractionated acids that are used for Russian soap production are derived by further fractional distillation.

**TABLE IV**

**Variation in Composition of Synthetic Fatty Acids Produced from Different Raw Materials (6)**

| Boiling range of paraffin (C) | Composition (%) | | |
|---|---|---|---|
| | C5-9 | C10-20 | C21+ |
| 240-350 | 25.0 | 54.5 | 20.5 |
| 300-400 | 14.5 | 79.5 | 6.0 |
| 350-420 | 10.5 | 75.0 | 14.5 |
| 420-500 | 4.0 | 60.0 | 36.0 |

Two typical fractionated cuts that are used are $C_{10}$-$C_{16}$, used primarily for toilet soap, and $C_{17}$-$C_{20}$ for high-grade household soaps. Thus, assuming Russian toilet soap were to require an optimal of ca. 80% of C-18-rich acids and 20% C-12-rich acids, a distinct advantage is in having both cuts available. Contrast the potential economy of this situation with the basic American toilet soap raw material situation: coconut oil produced in the Philippine Islands and tallow from innumerable slaughterhouses in Kansas City, Omaha, Des Moines or, if cheap enough, from as far away as Argentina.

Reliable estimates of the quantity of Russian and Eastern European SFA that goes into soap production range from as little as 20% to as high as 35%, which translates to an amount between 240-420 million lb/year.

## FATTY ACIDS AS SECONDARY RAW MATERIALS

Consider the American use of high-quality fatty acids, both purchased and internally produced, for the manufacture of quality toilet soap. The workhorse in the field of purchased acids is the "slightly out of ordinary" triple-pressed stearic acid, which occurs in every fatty acid manufacturer's price list, but is not unfortunately, of the superlative quality that is required by every buyer. Fortunate indeed, is the manufacturer whose technology provides him with lily-white products of iodine value less than 0.2, peroxide value of nil or thereabouts, and storage stability to permit keeping the material on the consumer's shelf in cartons or bags for 12 months or more with no measurable deterioration in quality. Additionally, the market now demands an odor that in the past was always characterized as "bland," but which today requires conformity to increasingly stringent odor stability requirements. These quality requirements of the "Cadillac" triple-pressed stearic acid are attained only with scrupulous attention to securing clean raw materials, preliminary clean-up treatments of tallow, processing to remove nickel catalyst poisons, highly efficient fractional distillation technology and highly effective color bleaching methods. Furthermore, air leaks in fat splitters and in fractional distillation equipment, or any operating condition in which air is allowed to come onto contact with molten fat or fatty acid above 90 C, must be avoided.

In addition to stearic acid, the fractionated coconut and lauric acids and several grades of double-distilled white oleic acids are employed. The C-12 products are required in toilet soaps, and the unsaturated oleics mainly in textile soaps, household soaps and where a soft, gentle product is required (e.g., "Castille," baby soaps).

It has been estimated (9) that the total 1978 fatty acid market for soap production of all kinds was 70 million lb or 5.3% of the fatty acid total. It is also estimated that an additional 80 million lb of assorted fatty acids is used for the manufacture of household detergents, and 70 million lb is used for "cosmetics,"which soaps may or may not be included. A published citation (10) states "In 1964 the consumption of fatty acids for the production of soap is at least 25% of the fatty raw materials that are used (ca. 240 million pounds out of ca. 900 million pounds)." The volume of fatty acid used in continuous soap making operations from fats and oils as primary raw materials was undecided. Since the 1978 estimated figure is substantially lower, it is apparent that 1978 data represent only purchased fatty acids used for soap manufacture.

The undecylenic acid, from pyrolysis of castor oil is useful as a fungistat in the form of sodium or zinc soaps in medicinal soap products for the control of athlete's foot and similar infections.

## METHYL ESTERS AS RAW MATERIAL INTERMEDIATES

American soap has not been produced from intermediate methyl esters, which in certain other oleochemical production offers some quality and processing advantages (e.g., superamides, simple amides). Ever since the appearance in 1942 of a U.S. patent (11,12), the alcoholysis of various fats and oils to methyl esters has been known to be an efficient and relatively rapid reaction. Today, the alcoholysis of fats to methyl esters is practiced on a large scale in various segments of the industry. The patentees had intended that their fat alcoholysis technology be contemplated as a first step in the manufacture of anhydrous soap by a continuous process. The esters are easily saponified by caustic soda or caustic potash at a low temperature, and the methyl alcohol could be recovered for reuse.

Although there are several continuous soap manufacturers who use fatty acids as intermediates, no large-scale American continuous methyl ester technology soap plant has been built. Presumably, the advantages were not sufficient to economically justify this route. Actually, small quantities of soap have been produced this way; one example is potassium "cocoate" soaps from methyl "cocoate" made during the 1950s at the now defunct Eldorado Division of Foremost Food & Chemical Co., Oakland, California. Fractional distillation of C-12-rich and C-18-rich fatty acids from coconut oil and tallow, respectively, afforded sufficiently stable fatty acids for toilet soap manufacture. Possibly, if C-20, 22 and 24 fatty acids, mostly from hydrogenated fish oils, had been available earlier or found to offer some performance advantages, the use of methyl esters as intermediates might have been accepted. However, the necessity to handle and recover methanol in the methyl ester process was sufficient to prevent its selection despite the real advantage of offering less soap drying unit costs. However, for the rest of the world, the future situation does not necessarily paralled that in the USA. Israel, parts of Africa, India and other parts of the Orient can be expected to give much more attention to the methyl ester route for the new soap plants of the future. This trend already is underway, as evidenced by the choice of ethyl ester interchange technology for the proposed manufacture, not of soap, but of salad oil, in Israel (13). Soap manufacturing will not be far behind.

## RAW MATERIALS FOR COMBINATION SOAP DETERGENT BARS–THE PIONEERS

The major soap disadvantage compared to most synthetic detergents, and the principal reason that it has been displaced from the household laundry is the development of magnesium and calcium curd in hard water. Deposits of insoluble curdy soaps from hard water on fabrics that are to be cleaned posed a much more difficult removal problem than from human skin, on which curd substantially is not absorbed. Synthetic detergents never have achieved more than a 20% replacement of soap and this intrusion was in the form of "combo" toilet soap bars in which soap content averaged ca. 2:1 over detergents.

Table V lists specific examples of syndet use in soap through "combo" bars. These were the pioneer examples of combinations of soap and detergents that were introduced commercially in America. Listed are the detergent components, called "lime soap dispersant agents," LSDA. In group 1 are the alkali metal salts of isethionic acid, typified by Lever Brothers' Dove and Phase III (15). These bars were highly superfatted, containing 10-40% of stearic acid with soap and moisture. Group 2 represents the glyceryl ether sulfonates, used in Procter & Gamble's Zest, a hard-water bar (16,17). They are combined with fatty alcohol sulfates (group 3), sodium and magnesium soaps, and relatively high levels of salt (18-19). Group 4 LSDA, the sulfated monoglycerides, have been used in Colgate Palmolive's Vel Beauty Bar (20-26). Finally, group 5, the acyl methyltaurides, or Igepon T, believed to be used in a few Lever Brothers products (27-29).

Notice that some of the "detergent" components in these pioneer LSDA are naturally derived, the raw material in some cases being "fatty," mostly tallow (plus isethionic acid, glycerol, fatty alcohol methyltaurine). When the "tallowyl" derivative is specified in the patent literature, presumably the optimal fraction for overall performance is known but is not publicized, i.e., "tallowyl" derivatives ranging from 65-80% stearate components from hydrogenated tallow are useful.

All these combinations were able to eliminate the "bathtub ring." These are several reasons why they did not capture more than ca. 20% of the American toilet soap market. The major reason is economic; many of the detergent components used in these bars were relatively expensive. Also, the pioneer combo bars introduced entirely new problems into the applications area; some of these problems were not characteristic of soap. They imparted a different feel to the skin, a so-called "soft water feel" to which many consumers were not accustomed, and, therefore, rejected the soap. Another shortcoming was the tendency of the wet bars to smear.

## MODERN SOAP BAR RAW MATERIALS

For the past 10 years, a massive attack in research and development has been launched in an effort to find a cheaper, more efficient, combo bar–one that offers no

**TABLE V**

*Commercial Lime Soap Dispersant Agents, LSDA (14)*

| Group | Structure | Name | Reference |
|---|---|---|---|
| 1 | $RCOCH_2CH_2SO_3^-M^+$ | Fatty acid esters of isethionic acid (Igepon A) | 15 |
| 2 | $ROCH_2CHOHCH_2SO_3^-Na^+$ | Alkyl (fatty) glyceryl ether sulfonates | 16,17 |
| 3 | $ROSO_3^-Na^+$ | Alkyl (fatty) sulfates | 18-20 |
| 4 | $RCOOCH_2CHOHCH_2OSO_3^-Na^+$ | Glyceryl ester (fatty) sulfates | 21-26 |
| 5 | $RCON(CH_3)CH_2CH_2SO_3^-Na+$ | Acyl (fatty) N-methyltaurides (Igepon T) | 27-29 |

additional problems in toilet soap performance, and does the job started by the pioneer bars even better.

From among literally hundreds of LSDA developed by both government (30) and industry the following are suggested for improved soap combo bars. α-Sulfo fatty acids and esters are good to excellent LSDA and these solve the problem of "soft water skin feel" (31-34). A series of amphoteric sulfonates (35), sulfones (36) and sulfonamides (37) are worth watching. Also consider sulfonated phenyl sulfostearic acid (38). Japanese manufacturers may be farther along with this development than any U.S. counterpart: N-acyl (fatty) glutamic acids (39) and related aspartic acids (39). α-Olefin sulfonates, called AOS, will also perform well (40-49) if it is ever decided how much alkenesulfonate and how much hydroxylalkanesulfonate is optimal (45). On the fringe are the vicinal acylamidosulfonates (50) and organophosphorus compounds (51).

## JOJOBA WAX

The final raw material candidate to be considered to ensure a U.S. soap renaissance in the future is already in the "bandwagon" stage. It is not even fat-based and doesn't have a triglyceride structure.

Jojoba wax is a liquid ester composed primarily of C-20 and 22 monounsaturated fatty acids with C-20, 22 and 24 monounsaturated fatty alcohols (52-54). Proposed initially as a sperm oil substitute (55), or, perhaps as an industrial lubricant (56), it is being vigorously promoted (57) as a cosmetic base component, mainly for hair shampoos (58). Of course, it could potentially be used with certain synthetic detergents, but it appears to be suited for soap compatibility.

Jojoba wax originates from the jojoba bush, *Simmondsia chenensis*, a peculiar desert bush that can thrive in saline soil. Yields are ca. 350 lb of seed/acre; apparently, wax yield from the seed is over 50% (56).

Prices (ca. $50-55/gal) and availability for present jojoba wax (worldwide present production from Israel, Mexico and Southwest U.S. amounts to less than 200 million lb) do not justify immediate product development; however, improvements are occurring rapidly. While the early problems of uniformity of quality, quality control, product characterization and adulteration with cheaper materials loom large, perhaps the most significant progress for commercialization of this crop is the report (59) of the early success achieved in the development of a new strain of monoecious type, that is, each plant bears flowers that contain both male and female parts. Potentially, this development is capable of translation into a 100% increase in wax yield per acre.

## REFERENCES


1. Vallet Goytisolo, D.A., Seifen Oele Fette Wachse 95:690 (1969).
2. Jungermann, E., in "Bailey's Industrial Oil and Fat Products," 4th Edition, Vol. 1, edited by D. Swern, Wiley-Interscience, New York, 1979, p. 514.
3. Ginn, M.E., R.C. Steinhauer, I. Libeman and E. Jungermann, JAOCS 45:666 (1968).
4. Becher, P.J., and R.E. Compa, Ibid. 34:53 (1957).
5. Davidsohn, J., E.J. Better and A. Davidsohn, "Soap Manufacture," Vol. 1, Interscience, New York, 1953, p. 215.
6. Lubbe, E., Freiberg. Forschungsh. A221:7 (1962).
7. Krumstein, D.A., and V.L. Klimenko, Khim. Prom. (Moscow) No. 9:662 (1963).
8. Sonntag, N.O.V., and K.T. Zilch, in "Fatty Acids and Their Industrial Applications, edited by E.S. Pattison, M. Dekker, Inc., New York, 1968, pp. 353-368.
9. Ruach, J.A., JAOCS 56:779A (1979).
10. Sonntag, N.O.V., in "Fatty Acids," Part 4, edited by K.S. Markley, Interscience, New York, 1967, p. 2710.
11. Bradshaw, G.B., and W.C. Meuly, U.S. Patents 2,271,610 (1942); 2,360,844 (1944).
12. Bradshaw, G.B., Soap Sanit. Chem. 18:23, 69 (1942).
13. Koslowsky, L., Oleagineux 30:221 (1975).
14. Jungermann, E., in "Bailey's Industrial Oil and Fat Products," 4th Edition, Vol. 1, edited by D. Swern, Wiley-Interscience, New York, 1979, p. 575.
15. Geitz, R.C., U.S. Patent 2,894,912 (1959).
16. Mills, V. and E.O. Korpi, U.S. Patent 2,988,511 (1961).
17. Van Gaertner, R., U.S. Patent 3,082,249 (1963).
18. Shore, S., and D.R. Berger, in "Anionic Surfactants," Part 1, Chapter 5, edited by W.M. Linfield, M. Dekker, New York, 1976, pp. 162-163.
19. Chaffee, R.H., U.S. Patent 3,070,547 (1964).
20. Tuan, Tran Anh, Fr. Addn. 96.188 (1972) to Fr. Patent 1,582,765. See Helene Curtis Ind., British Patent 1,231,835 (1971).
21. Schmolka, I.R., U.S. Patent 2,945,816 (1960).
22. Dreger, E.E. and A.C. Bell, U.S. Patent 2,385,614 (1945).
23. Turck, J.A.V., Jr., U.S. Patent 3,030,310 (1962).
24. Anstett, R.M., U.S. Patent 3,076,766 (1963).
25. Anstett, R.M., U.S. Patent 3,226,330 (1965).
26. Farrar, R.E., and A.L. Schulerud, U.S. Patent 3,224,976 (1965).
27. Mayhew, R.L., and L. W. Burrette, Soap Chem. Spec. 38:55 (1962).
28. Kelley, W.A., U.S. Patent 3,043,778 (1962).
29. Ward, N.E., German Patent 1,144,428 (1963).
30. Linfield, W.M., JAOCS 55:87 (1978).
31. Stirton, A.J., R.G. Bistline, J.K. Weil and W.C. Ault, U.S. Patent 3,219,584 (1965).
32. Barnett, D.P., German Patent 2,140,789 (1972).
33. Hendricks, U.S. Patent 3,247,121 (1966).
34. Barnhurst, J.D., G.M. Leigh and J.A. Monick, U.S. Patent 3,442,812 (1969).
35. Hirst, D.G.S., U.S. Patent 3,660,470 (1972).
36. Lew, H.Y., U.S. Patent 3,232,879 (1966).
37. Hewitt, G.T., U.S. Patent 3,586,632 (1971).
38. Atherton, J.G., H.C. Nemeth and E.J. Miller, Jr., U.S. Patent 3,528,923 (1970).
39. Yoshida, R., M. Takehara, Kanagawaken, H. Akiba and Y. Usuba, U.S. Patent 3,663,459 (1972).
40. Groves, W., German Patent 1,949,107 (1970).
41. Woo, G.L., U.S. Patent 3,607,766 (1971).
42. Woo, G.L., U.S. Patent 3,673,122 (1972).
43. Sweeney, W.A., and G.L. Woo, U.S. Patent 3,652,662 (1972).
44. Woo, G.L., and R. House, U.S. Patent 3,867,317 (1975).
45. Sweeney, W.A., U.S. Patent 3,625,910 (1971).
46. Garrett, H.E., U.S. Patent 3,523,089 (1970).
47. Colgate-Palmolive Co., British Patent 1,194,861 (1970).
48. Werner, L., and W. Schneider, German Patent 1,949,562 (1971).
49. Barrett, D.P., British Patent 1,165,611 (1969).
50. Broussalian, G.L., U.S. Patents 3,325,412 (1967); 3,337,467 (1967).
51. Jungermann, E., in "Anionic Surfactants," Part II, Chapter 15, edited by W.M. Linfield, M. Dekker, New York, 1976, p. 548.
52. McKinney, R.S., and G.S. Jamieson, Oil Soap Chicago 13:289 (1936).
53. Miwa, T.K., JAOCS 48:259 (1971).
54. Duncan, C.G., D.M. Yermanos, J. Kumamoto and C.S. Levesque, Ibid. 51:534 (1974).
55. Crosswhite, F.S., "Studies of *Simmindsia chinensis* at the Boyce Thompson Southwestern Arboretum," University of Arizona, Boyce Thompson Southwestern Arboretum, Superior, Arizona, undated publication.
56. Yermanos, D.M., Calif, Agric., July-August (1979); see also JAOCS 57:Abstr. 479 (1980).
57. Miwa, T.K., Ibid. 57:Abstr. 210 (1980).
58. Skillern's Drugs, advertisement in Sunday Magazine, Dallas Times Herald, June 1, 1980, Dallas, Texas product: Queen Helene Jojoba Oil Shampoo.
59. Anonymous, Chem. Eng. News, August 18, 1980, pp. 28-29.