Soap and Lime Soap Dispersants

W.M. LINFIELD, Eastern Regional Reasearch Center
ARS, USDA, Philadelphia, Pennsylvania, USA

ABSTRACT

In recent decades, soap has largely been replaced by petrochemicals and polyphosphates as the major components of laundry detergents in the U.S. Currently, the use of soap is primarily confined to the toilet soap bar field, and technological advances here have been mainly in processing. In view of the rising costs and increasing scarcity of petrochemicals and polyphosphates, tallow, a replenishable, inexpensive agricultural by-product, was examined as an alternate raw material. Tallow soap has a long history of efficacy and safety but suffers from poor performance in hard water and insolubility in cold water. It has now been shown that the performance of soaps can be drastically improved in cold water solubility and in hard water detergency by the addition to the soap of lime soap dispersing agents (LSDA). These are anionic or amphoteric surfactants possessing one or more bulky polar groups. These soap-LSDA combinations form mixed micelles in water and essentially take on the surface active characteristics of a single anionic surfactant. Soap-LSDA combinations wash well in hard water without curd formation; they can be "built" with various materials such as phosphates and trisodium nitrilotriacetate (NTA) to enhance detergency. Soap-LSDA combinations equal the conventional detergents in every performance respect and undergo biodegradation more readily and completely.

INTRODUCTION

Although soap is the world's oldest and probably safest surfactant, its use dwindled rapidly in most developed countries after World War II. The major reasons for this decline were the rapid advances in surfactant technology, the relative abundance and low cost of petrochemicals, and the unpredictable price fluctuation of natural fats and oils. The increasing cost, scarcity, and price fluctuation of petrochemicals coupled with recent advances in soap technology and relative abundance and low cost of fats and oils, such as tallow and palm oil, now make soap look more attractive. Soap, i.e., the alkali metal salts of fatty acids, has retained its position as the major component of toilet bars, although soap-syndet combination bars have made some inroads, particularly in the U.S. On the other hand, soap has all but disappeared as a component of detergent products. This presentation is a summary of recent developments in soap technology as applied to the toilet bar and detergent fields.

TOILET BARS

The technological advances in the toilet bar field as summarized by Jungermann (1) have been largely in the mechanical and engineering fields. Although there has been some research activity in soap germicides and lime soap dispersants, the chemical nature of these additives to bar soaps has not been changed greatly during the past 20 years. However, during that period the popularity of bars containing deodorants and those containing surfactants has greatly increased.

In the engineering area substantial advances have been made in continuous saponification or continuous fat splitting followed by neutralization. Vacuum drying and plodding have largely replaced mills for the finishing of toilet bars. Striated or marbleized bars have achieved some popularity in the U.S. and elsewhere and are an example of what effects can be achieved with modern soapmaking equipment.

DETERGENTS FROM SOAP

During the past 7 years a substantial amount of research has been carried out at the Eastern Regional Research Center of the U.S. Department of Agriculture on the use of soap as the major ingredient in laundry detergents. Factors leading to the initiation of this research included water pollution due to phosphate builders, dwindling petroleum resources, and the abundance of inedible tallow, a replenishable agricultural by-product.

The basic concept of soap modification is the addition of a lime soap dispersant to tallow soap. This enables the soap to act as an efficient detergent in hard or soft water without deposition of soap scum during the wash cycle or during rinsing. About 20 different classes of surfactants were synthesized and evaluated for their lime soap dispersing ability at ERRC. It was found that anionic or amphoteric surfactants could be lime soap dispersants. Nonionics, although effective dispersants, were not usable. For reasons not clearly understood, nonionic surfactants are antagonistic to the washing action of soap. Cationic surfactants, of course, are not suitable since they form precipitates with soap.

For a surfactant molecule to function as a lime soap dispersing agent (LSDA), it must possess a bulky polar group. It is visualized that soap and the LSDA form a mixed micelle in which the LSDA, due to its bulky nature, acts as a wedge. In hard water the LSDA wedge forces the particle to retain its curvature with the polar groups on the periphery, whereas soap micelles by themselves invert in hard water with the nonpolar long alkyl chains turned outward, thus producing the familiar lime soap curds and scum (2).

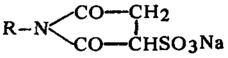
CHEMISTRY OF THE LSDA

In general, bulk can be introduced into the LSDA surfactant molecule in the form of one or more ester or amido groups, ether linkages, or by inclusion of both an anionic and cationic group. Introduction of a second anionic group such as $-COO^-$ or $-SO_3^-$ into an anionic LSDA molecule does not enhance lime soap dispersing properties. The lime soap dispersing ability of a given compound is conveniently measured by a test developed by Borghetty and Bergman (3) that measures the minimum lime soap dispersant requirement (LSDR) in grams to keep 100 g of sodium oleate from precipitating in hard water (333 ppm as $CaCO_3$).

Table I shows a summary of all major classes of LSDA investigated in this laboratory together with the appropriate literature references. The key surface-active properties of

TABLE I

Lime Soap Dispersing Properties and Detergency of Various Lime Soap Dispersants

Compound no.	Structure	Reference no.	LSDR	Formulation detergency[a] (percent of control)[b] EMPA[c]	TF[d]
1	$RCH(SO_3Na)CO_2CH_3$[e]	8, 9	9	95	70
2	$RCH(SO_3Na)CON(CH_2CH_2OH)_2$	24	8	97	79
3	$RCO_2(CH_2)_3SO_3Na$	25	7	87	78
4	$RCON(CH_3)(CH_2)_2SO_3Na$	18	5	95	65
5	$RCON[CH_2CO_2(CH_2)_3SO_3Na]_2$	26	5	85	48
6	$RCONHCH_2CH(OSO_3Na)CH_3$	6	5	97	64
7	$RCONHCH_2CH_2OCH_2CH_2OSO_3Na$	6	4	97	66
8	$RO(CH_2CH_2O)_3OSO_3Na$	17, 27	4	—	—
9	$ArSO_2NHCH_2CH_2OSO_3Na$[f]	7	7	94	90
10	$RCONH(CH_2CH_2O)_{11}H$	28	3	53	69
11	$RCON(CH_2CH_2O)_7H_2$	28	2	50	95
12	$RO(CH_2)_3SO_3Na$	25	9	75	73
13	$RNHCOCH_2CH(SO_3Na)CO_2CH_3$	29	7	90	86
14		30	9	100	68
15	$ArCOCH_2CH(SO_3Na)CO_2CH_3$	31, 32	8	87	100
16	$R\overset{+}{N}(CH_3)_2CH_2CO_2^-$	10	12	65	46
17	$R\overset{+}{N}(CH_3)_2(CH_2)_3SO_3^-$	11	3	92	108
18	$RCONH(CH_2)_3\overset{+}{N}(CH_3)_2(CH_2)_3SO_3^-$	11, 13	2	89	91
19	$R\overset{+}{N}(CH_3)_2(CH_2)_3OSO_3^-$	13	4	102	92
20	$RCONH(CH_2)_3\overset{+}{N}(CH_3)_2(CH_2)_3OSO_3^-$	13	3	91	96

[a] Detergency of 0.2% of solution of formulation containing 64% tallow soap, 19% LSDA, 14% glossy silicate, 1% GMC, and 2% impurities in 300 ppm hard water.

[b] 50% Tripolyphosphate built commercial control detergent.

[c] EMPA 101 presoiled cotton cloth.

[d] Testfabrics presoiled 65% polyester - 35% cotton blend.

[e] R refers to a tallow derived alkyl group.

[f] Ar refers to a dodecylphenyl group derived from a commercial detergent alkylate.

LSDR and detergency are given for the *tallow* derivative of each class, except compounds no. 9 and no. 13, which are derived from a commercial detergent alkylate.

Among the anionic LSDA types the best known one is probably the fatty acid amide of N-methyltaurine or Igepon T type (no. 4 in Table I). While it is a very good detergent by itself and an excellent lime soap dispersant with an LSDR of 5, the commercial product has the disadvantage of high cost and a high sodium chloride content. Some sulfated alkanolamides such as no. 6 and no.7 (Table I) provide a less expensive alternative and provide the same good surface-active properties. Such materials are synthesized by amidation of tallow fatty acid followed by sulfation and neutralization. Although sulfated fatty acid alkanolamides were first synthesized in 1933 (4), the development of a practical sulfation method is quite recent. Neat sulfation of fatty alkanolamides in high yields is nearly impossible because of the high viscosity of the reaction mixture which makes efficient agitation, and hence good contact between sulfating agent and amide, very difficult. In the past, chlorinated solvents were usually added to alleviate this problem. However, current environmental considerations make this approach unattractive. It was now found that cosulfation of a mixture of the monoisopropanolamide (no. 6) and diglycolamide (no. 7) of tallow fatty acid with n-butanol eliminated the viscosity problem (5). The resulting mixture of sulfates, subsequently referred to as TAM, was obtained in a high yield and possessed excellent surface-active properties. These products have somewhat limited hydrolytic stability (6); however, in the presence of soap the sulfated amides are quite stable because of the higher pH.

The analogous alkylarylsulfonamides (no. 9, Table I) possess similar surface-active properties but are somewhat less stable to alkaline hydrolysis than the sulfated fatty alkanolamides (7). These sulfonamide derivatives are of interest, since they are prepared from commercial detergent alkylate or from alkylbenzene sulfonic acids (LAS acid).

Another type of LSDA which was thoroughly investigated was that of the α-sulfo fatty esters (no. 1, Table I). From a raw materials point of view, the methyl ester of α-sulfotallow fatty acid is probably the least expensive anionic LSDA of all the compounds studied. It is prepared from hydrogenated tallow by transesterification and subsequent sulfonation with SO_3, followed by neutralization (8,9). This type of product is produced most advantageously by continuous SO_3 sulfonation. The α-sulfonated methyl esters are less stable to hydrolysis than the sulfated fatty acid alkanolamides no. 6 and no. 7. Furthermore, as Table I shows, they are poorer detergents and lime soap dispersants (LSDR = 9) than the sulfated alkanolamides.

Amphoteric surfactants are the most efficient LSDA studied, and they offer better detergency than the anionics. However, they are inherently more expensive because of costlier starting materials, and some of the reaction steps by which they are made have not been fully investigated.

The simplest members of this group are the betaines obtained via the reaction of an alkyldimethylamine with sodium chloroacetate to give compound no. 16 (Table I).

The analogous amidoamino amphoteric is prepared in two steps starting with amidation of a fatty acid and subsequent reaction with sodium chloroacetate to give a betaine of the structure:

$$RCONHCH_2CH_2CH_2\overset{+}{N}(CH_3)_2CH_2COO^-$$

Both betaines are produced commercially in the U.S. and abroad. The lime soap dispersing (LSDR = 12) and detergency properties of compound no. 16 (10) are slightly inferior to those of anionic LSDA such as sodium methyl α-sulfotallowate as is shown in Table I.

TABLE II

Detergency of Built Soap-LSDA Formulations

Composition of formulation							Detergency as % of control detergent		
% Tallow soap	LSDA type	% LSDA	Builder type	% Builder	% Na_2SiO_3	% Na_2SO_4	TF[a]	EMPA 101[b]	EMPA 104[c]
64.0	TAM[d]	19.0	—	—	14	—	104	97	97
37.5	↓	12.5	STPP[e]	40	10	—	70	82	75
22.5	↓	7.5	↓	60	10	—	98	97	90
15.0	↓	5.0	↓	65	15	—	74	90	87
37.5	↓	12.5	↓	25	10	15	39	66	37
22.5	↓	7.5	↓	40	10	20	43	71	47
15.0	↓	5.0	↓	45	10	25	32	71	50
64.0	TSB[f]	19.0	—	—	14	—	104	97	100
37.5	↓	12.5	STPP	40	10	—	96	98	89
22.5	↓	7.5	↓	60	10	—	94	94	91
15.0	↓	5.0	↓	65	15	—	92	97	90
37.3	↓	12.3	↓	25	10	15	93	100	100
22.5	↓	7.5	↓	40	10	20	97	100	103
15.0	↓	5.0		43	10	25	90	89	84
37.5	↓	12.5	NAT[g]	40	10	—	117	106	105
15.0	↓	5.0	↓	65	15	—	107	103	100
37.5	↓	12.5	↓	25	10	15	90	106	100
22.5	↓	7.5	↓	40	10	20	93	103	106
15.0		5.0		45	10	25	97	103	97

[a] TF Testfabrics, Inc., presoiled polyester-cotton fabric.
[b] EMPA 101, presoiled cotton fabric.
[c] EMPA 104, presoiled polyester-cotton fabric.
[d] TAM=sulfated tallow fatty acid alkanolamide (mixture of compounds no. 6, no. 7, Table I).
[e] STPP=sodium tripolyphosphate.
[f] TSB=tallow derived sulfobetaine (compound no. 17, Table I).
[g] NTA=trisodium nitrilotriacetate.

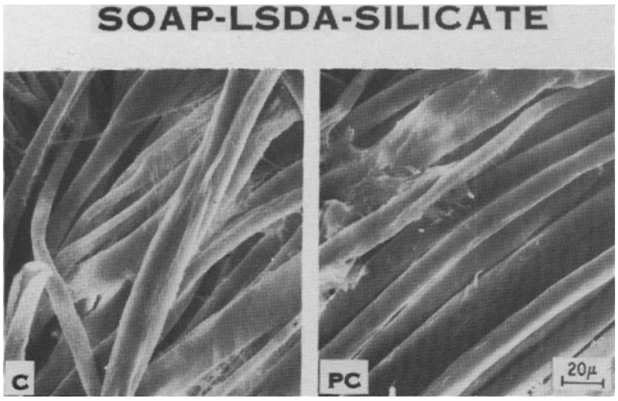


FIG. 1. Photomicrographs of cotton (C) and polyester-cotton blend (PC) fabrics washed 25 times in hard water containing 0.2% of soap-LSDA type detergent.

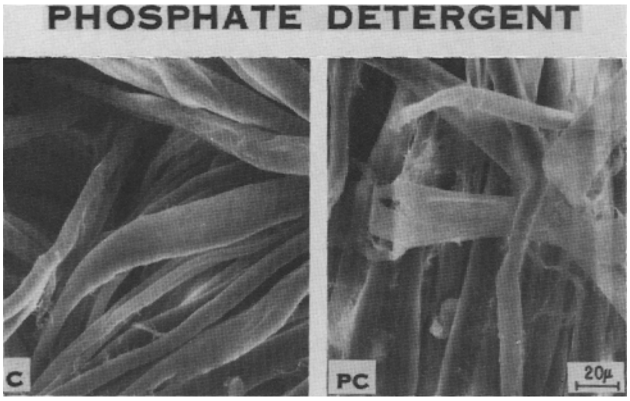
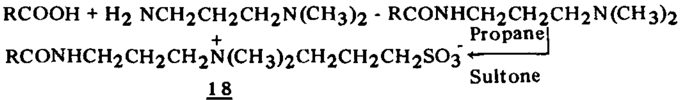


FIG. 2. Photomicrographs of fabrics washed in 0.2% of a high phosphate built control detergent.

Superior LSDA are produced when the anionic group in the molecule is a sulfo $-SO_3^-$ or sulfato $-OSO_3^-$ group. The sulfo compounds are readily prepared by the reaction of a tertiary amine with propane sultone to give compound no. 17. These sulfobetaines have an LSDR of 4-5, depending on the alkyl chain length, and exhibit good detergency (11). When an amido group is introduced into the molecule to form compounds of the structure no. 18 (Table I), the lime soap dispersing power is usually greatly enhanced, and the LSDR drops to 2. These types of compounds are the most potent lime soap dispersants we have encountered so far. The synthetic scheme is as follows:



$$RCOOH + H_2\,NCH_2CH_2CH_2N(CH_3)_2 - RCONHCH_2CH_2CH_2N(CH_3)_2$$
$$RCONHCH_2CH_2CH_2\overset{+}{N}(CH_3)_2CH_2CH_2CH_2SO_3^- \xleftarrow[\text{Sultone}]{\text{Propane}}$$

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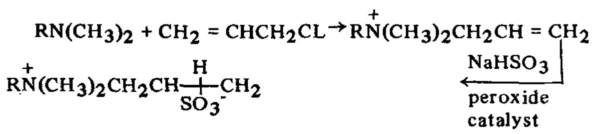
Because of the carcinogenic nature and high cost of propane sultone, its use for commercial syntheses is no longer feasible, and consequently two alternative synthetic routes were developed which lead to closely related compounds. Both involve a two-step reaction scheme (12). In the first synthesis the tertiary amine is first quaternized with allyl chloride, and the resulting quaternary ammonium salt is then treated with sodium bisulfite in the presence of a free radical initiator such as t-butyl perbenzoate to give the sulfobetaine. The overall scheme is as follows.



$$RN(CH_3)_2 + CH_2 = CHCH_2CL \rightarrow R\overset{+}{N}(CH_3)_2CH_2CH = CH_2 \cdot Cl^-$$
$$R\overset{+}{N}(CH_3)_2CH_2CH-\underset{SO_3^-}{\overset{H}{|}}-CH_2 \xleftarrow[\text{peroxide catalyst}]{NaHSO_3}$$

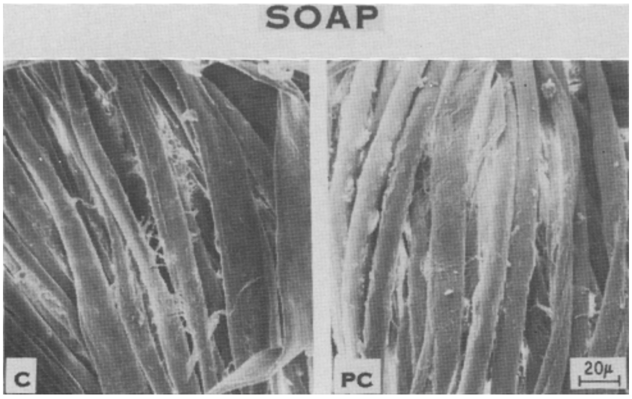


FIG. 3. Photomicrographs of fabrics washed in 0.2% of tallow soap.

The exact position of the sulfo group is not known.

The other synthetic route involves reaction between epichlorohydrin and sodium bisulfite to give the sodium salt of 1-chloro-2-hydroxy-3-propanesulfonic acid, and subsequent reaction with a tertiary amine yields a sulfobetaine according to the following scheme:

$$RN(CH_3)_2 + ClCH_2CHOHCH_2SO_3Na \rightarrow$$
$$R\overset{+}{N}(CH_3)_2CH_2CHOHCH_2SO_3^- + NaCl$$

This type of product is commercially available in the U.S. The surface-active properties of the sulfobetaines obtained via these two alternative routes are the same as that of the sulfobetaine prepared from propane sultone.

The spacing between the anionic and cationic sites of the sulfobetaine molecule effects water solubility and surface activity. The Krafft point is lowered by 50 C or more, and detergency is slightly improved as the bridge between the two sites is increased from C_2 to C_3. Replacement of the sulfo group by sulfate tends to decrease solubility but does not change surface activity (13).

Introduction of an amido group into the sulfobetaine molecule usually improves the LSDR, as stated above, and water solubility is also improved. Introduction of a second amido group does not cause further improvement in the LSDR but increases solubility in water, i.e., lowers the Krafft point (14,15).

The relative positions of the anionic and cationic sites in the molecule are very important. When the quaternary ammonium group is placed at the terminal position of the molecule and the sulfo group is placed away from the end position, the surface-active properties show remarkable decline (16).

FORMULATIONS WITH SOAP-LSDA BLENDS

The detergency of soap is potentiated by addition of an LSDA, and vice versa. Maximum detergency is usually attained when the ratio of soap to LSDA is 80:20, and such a blend washes better than either compound by itself. Further enhancement of detergency is achieved by the addition of builders such as glassy silicates, sodium tripolyphosphate, or sequestering agents like trisodium nitrilotriacetate (NTA) and other organic chelating agents (17). A relatively simple formulation, used in evaluation tests of all LSDA's, consists of the following (18):

64% tallow soap
19% LSDA
14% silicate builder
1% sodium carboxymethylcellulose (CMC)
2% impurities and minor additives

Formulations of this type, in which the LSDA was sodium methyl α-tallowate (no. 1), Igepon T (no. 4), a mixture of the two sulfated alkanolamides no. 6 and no. 7 called TAM, or a tallow derived sulfobetaine no. 17 called TSB, were spray dried successfully on a pilot plant scale. In addition, formulations containing no. 1 or TAM were also dried in a conventional hot air dryer to form flakes. These formulations were evaluated in a Tergometer (18) and the formulation containing no. 1 was also evaluated in several bundle tests. The results indicated that such formulations perform as well in hard (300 ppm) or soft (50 ppm) water as does a high quality commercial detergent built with 50% sodium tripolyphosphate (STPP). The choice of silicate builder is not too critical, and sodium metasilicate performs about as well as a glossy silicate ($SiO_2:Na_2O = 1.6:1$).

Table II shows detergency data for detergents containing the soap-LSDA blend as a major ingredient according to the above formulations as well as for highly built formulations. If desired (and legally permissible), the soap-LSDA blend may be formulated with tripolyphosphate or organic builders in a manner analogous to formulations with linear alkylbenzene sulfonates (LAS). Table II shows the composition of the formulations and their detergency as a percentage of the performance of a commercial detergent containing 50% STPP. The anionic sulfated mixed tallow fatty acid alkanolamide (TAM), and the amphoteric tallow derived sulfobetaine (no. 17, TSB) were used as LSDA, and the builders were STPP and NTA. The table clearly shows the superiority of the high soap-TAM blend formulation over the highly built soap-TAM detergents. While the TAM-containing formulations are adversely affected by the addition of sodium sulfate, the sulfate-free formulations give acceptable detergency although poorer than that of either the control or the high soap-LSDA formulation. On the other hand, formulations containing the amphoteric TSB as the LSDA are essentially unaffected by the addition of sodium sulfate, and differences between the high soap-TSB and the highly built soap-TSB formulations are small. NTA appears to be a better builder than STPP for the soap-LSDA formulations shown in Table II.

MODE OF ACTION OF SOAP-LSDA MIXTURES

It has been frequently assumed that the soap component in soap-LSDA blend acts as a scavenger for hard water ions, whereas the LSDA is solely responsible for detergency. This view does not agree with the experimental findings. All evidence obtained indicates that soap, LSDA, and calcium and magnesium ions are tightly bound together in a suspended particle. Thus fabric washed 25 consecutive times with soap-LSDA formulation in 300 ppm hard water shows no buildup whatsoever of foreign matter when viewed under a scanning electron microscope (Fig. 1); neither does a high phosphate built commercial detergent (Fig. 2), whereas a heavy buildup of soap scum occurs with soap alone (Fig. 3) (19). Analysis of the same fabrics shows very low Ca^{++} and Mg^{++} for the high phosphate built detergent and for the soap-LSDA detergent but a high Ca^{++} and Mg^{++} content for the soap alone. Even more convincing evidence was obtained when a soap-LSDA dispersion in hard water was filtered on a small porosity polymer membrane and analyzed. The filter residue contained all of the soap, all of the LSDA, all of the Ca^{++}, most of the Mg^{++}, but no Na^+. The filtered material could be redispersed in water, and the resulting dispersion exhibited high surface activity including detergency, whereas the filtrate was essentially devoid of surface activity (20). The surface tension behavior of soap-LSDA mixtures likewise indicated a mixed micelle, and the mixture gave surface tension vs. log concentration curves which are typical of single surfactants rather than of mixtures (21).

An interesting phenomenon observed with soap-LSDA blends is that soap and LSDA solubilize each other. For example, a blend of an insoluble LSDA and sodium palmitate, a high Krafft point soap, is more water soluble than either component (22). Since poor solubility of soap, and hence poor detergency in cold water, has been a serious drawback to the use of soap as a detergent, this difficulty can now be overcome by the addition of an LSDA to the soap.

BIOLOGICAL BEHAVIOR

The acute oral toxicity, skin and eye irritation, sensitization and toxicity to fish were determined for three high soap content detergent formulations containing compounds 1, 4, and 6 as the LSDA. It was found that the soap-based detergents are as safe as a high phosphate commercial control detergent (23). With regards to ease and completeness of biodegradation, it was determined that these three soap-LSDA formulations degrade more rapidly and completely than the control. Since these detergents are phosphate-free, it is obvious that they are less objectionable from an environmental point of view than present day commercial detergents.

This new concept of a laundry detergent offers a simple solution to the quest for phosphate-free detergents. It is as safe and effective as a high phosphate built detergent but without the environmentally objectionable features of the latter. Since the present worldwide price trends for petroleum and petrochemicals are expected to continue as crude petroleum becomes scarcer, the use of tallow, a replenishable agricultural by-product, should become very attractive as a raw material for use in built and unbuilt detergents. It is significant that several Japanese firms already are manufacturing and successfully marketing such products. The only imminent problem encountered in the U.S. and several European countries is that there is a shortage of soapmaking facilities. However, just as the detergent industry a generation ago decided to scrap their obsolete soap plants in favor of facilities to produce the so-called "synthetic detergents," there is no reason why present worn out detergent-making facilities cannot be replaced gradually by modern efficient soapmaking facilities.

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