• *Technical*

Status of Synthetic Detergent Bars[1]

JOHN W. McCUTCHEON, Consulting Chemist, New York, New York

ATTEMPTS to make synthetic bars are not new and can be dated back almost 25 years. It was not until World War II that the so-called salt water soaps were formulated and used on a commercial basis. Attempts to make a synthetic type of bar soap in a milled form were somewhat later and followed the war. One of the first products of this nature was trade-named Vel.

Since we are confining our attention to milled bars, we may say that the beginning of this phase of development was about 12 years ago. About five or six years later a second product, trade-named Zest, began to be test-marketed. However only within the last two years or less may it be said that synthetic bars have become established on a national basis and have made an impression on the 250,000-ton-market for toilet soaps.

The difficulty in formulating such products is evident from the lack of competition in this field. Many patents have been issued, many suggestions made, but few practical formulae have been produced. One of the earliest difficulties was the fact that overenthusiasm in the use of detergents tended to prevent the bar from being free-rinsing. This was a greater drawback than had been anticipated. It has since been solved.

Now what incentives exist for the manufacture of a synthetic bar? Such advantages are four-fold: a) a synthetic bar is usable equally well in hard and soft water; b) it does not form a sticky curd in hard water to produce the so-called bathtub ring; c) it washes from the skin more freely than a soap; and d) the pH may be brought closer to that of a normal skin.

Detergent bars may be considered as consisting of a detergent, a binder, and such auxiliary products as color, perfume, whitener, and stabilizer. It is highly desirable for the product to be milled and plodded on equipment similar to that used for a standard toilet soap bar. Its specific gravity may be close to that of soap and its plodding temperatures may be in excess of soap but should not exceed about 130° to 140°F. because of deleterious effects on color, perfume, stability, etc. Moisture control is generally very narrow for most formulations, and in some cases a plus or minus one-half per cent may make the difference between a hard rubbery mass and a soft putty, both equally difficult to mill.

There are exceptions to such manufacturing conditions, but when such conditions are altered greatly, the product generally falls into another class not under consideration here (4).

There are three approaches to formulation of such products: a) where soap is the base and a detergent is added; b) where a detergent is the base and a soap is added as the binder; and c) where the bar contains no orthodox soap and the binder is a supplementary type of material such as a polygylcol ethylene ether, etc. (1).

In cases a) and b) the soap need not necessarily be the orthodox soap used in toilet bars but may be derived from soap of hydrogenated tallow, from salts of hydroxystearic acid as previously discussed.

The detergents used may be of two classes, a normal detergent and an abnormal detergent. The normal detergent is one which is not precipitated in hard water and includes such classes of materials as the alkyl aryl sulfonates, alkyl sulphates, fatty taurates, etc. They may consist also of mixed products of this class and may include nonionic foam boosters.

The abnormal detergents may be classed as such products as do precipitate in hard water but do so in such a way that they produce a fine nonsticky curd. Materials such as these are the substituted fatty acids, such as salts of *alpha* sulfonated stearic acid (5, 6), *alpha* hydroxystearic and the lactone condensation products of primary fatty amines (2).

The binders in addition to soap are very numerous, as shown by a study of the patent literature, but generally speaking a binder should be sought which most closely resembles soap in its physical characteristics such as its water solubility, plasticity, and compatibility with the other ingredients of the mixture. Under this definition salts of *alpha* sulfonated stearic acid may be considered either as a binder or a detergent base, depending on its function in the formula.

All raw materials used must be stable, colorless, odorless, commercially available from at least two suppliers, and should be priced within a range to permit competitive pricing of the product. At the present time synthetic toilet bars range in retail price from about 50% to 200% above their soap counterparts. It is unfortunate in the author's opinion that such products have been classified as "cosmetics." Their relationship to toilet soap is exactly the same that detergent powders bear to soap powders.

The supplementary materials in the formula such as color, whitener, perfume, etc., do not differ substantially from those presently employed in soaps. Of course, each type of formulation will require its own individual treatment. Acceptable formulae may differ considerably from one another and from soap, as is illustrated in Table I.

The primary requirements of a successful detergent bar is that it must have all the physical and chemical

TABLE I

	Typical toilet soap	Detergent bar No. 1	Detergent bar No. 2
	%	%	%
Moisture	12	6	10
Mineral matter	0.5	2	8
Soap	85.5	30	20
Detergent	....	30	50
Auxiliaries such as plasticizers, binders, cold cream, etc	....	30	10
Perfume, whiteners, stabilizers, etc	2	2	2

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TABLE II

	Soap	A	B	C	D	E
pH of 1% solution	8.7	8.0	8.0	7.5	8.2	7.8
Foam power in moderate hard water, rated 0–10	10	4	3	7	9	8
Foam power in water of 600 p.p.m. as $CaCO_3$	....	4	3	5	7	5
Texture under use test	Good	Poor	Bad	Good	Good	Fair
Feel of bar after soaking and air drying	Slimy	Slimy	Firm	Firm	Slimy	Slightly slimy
Sloughing effect under conditions yielding a 10% loss to soap	10%	35%	5%	4%	11%	14%

characteristics of soap, that is, it must not slough away when left wet, must have a smooth texture, must not crack, must foam well, and have good detergency without skin defatting (3). In addition, the synthetic bar must not leave a bathtub ring, must foam and have good detergency in the hardest water, and should take advantage of a low pH value. How well these ideals have been approached may be noted from the following tabulation, Table II, based on a few typical examples of commercial and experimental formulations. Soap is used as a basis for comparison.

An examination of the above table indicates that D most closely resembles soap, with E a close second. Both represent satisfactory synthetic bar formulations when consideration is given to their superior foam power in hard water and to their low pH values as compared to soap. Example C however, except for slightly inferior foam power, greatly excels soap in its resistance to wasting away, its feel under semi-dry conditions, and its low pH value which approaches that of a normal skin. This type of formulation would be very satisfactory. Formulations A and B would be unsatisfactory on foam value, and A in particular on its tendency to slough away.

It thus appears that synthetic bars of excellent quality can be made from presently available raw materials that are superior to soap except in perhaps a few minor details and that their impact on the 250,000-ton-a-year market is at present being felt in the trade. It is the author's opinion that the future will see a great shift in this market from soaps to detergents although the effect of this change will not be as devastating on the tallow market as that produced by detergent powders. This view is based on the part soap and tallow derivatives may play in the future formulation of such products.

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N-Bromosuccinimide in the Conjugation of Fatty Acids and Oils

D. D. NANAVATI, BHOLA NATH, and J. S. AGGARWAL,[1]
National Chemical Laboratory, Poona, India

CREATION of new conjugated double bonds for improving the drying properties of fatty oils or acids of low unsaturation has been frequently reported. This may be brought about through chlorination, followed by dehydrochlorination (1), dehydration of hydroxylated fatty oils (2, 3), or introduction of hydroxyl groups by oxidation accompanied by dehydration (4).

Methods for effecting conjugation by the isomerism of polyunsaturated fatty acids are well known (5, 6). Brode *et al.* (7) have shown that debromination of tetrabromo derivative of 9:12-linoleic acid produces to some extent conjugated unsaturated acids. Recently Teeter *et al.* (8) reacted *tert*-butyl hypochlorite with methyl oleate, methyl linoleate, and some vegetable oils under various conditions and then by thermal dehydrochlorination introduced conjugation, principally of diene and triene type. In the case of methyl oleate they found that the products consisted mostly of a mixture of allylic and nonallylic monochloro derivatives and a saturated dichloro derivative, possibly methyl 9,10-dichlorostearate. Methyl linoleate was converted by *tert*-butyl hypochlorite and methanol to methyl dimethoxy dichlorostearate; its thermal decomposition resulted in the formation of a 21.7% methyl diketostearate. Teeter *et al.* explained these reactions by a free-radical chain process. More recently Arnold (9) has obtained a patent on the use of alkali metal hypochlorite for the same purpose.

Ziegler *et al.* (10) have shown that a hydrogen atom on a methylene group adjacent to an ethylenic double bond may easily be replaced with bromine by means of N-bromosuccinimide. By this reaction Teeter (8) introduced bromine in the allylic position in methyl esters of soybean fatty acids and methyl linoleate. Schmid and Lehmann (12) brominated methyl elaidate and methyl brassidate with N-bromosuccinimide and, after dehydrobromination, isolated 9:11-octadecadienoic and 13:15-docosadienoic acids. Gunstone (13) has however pointed out that the properties of the

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[1] Present address: Regional Research Laboratory, Hyderabad, Deccan, India.