Procedure for the Proposed Catalytic Method

A sample of fat, 4 ± 0.1 grams, is accurately weighed in a 100 cc. extraction flask on an analytical balance. Roughly 0.16 grams of stearic acid or 0.20 to 0.60 grams of bentonite are added (0.20 grams for tallow and coconut oil, 0.40 grams for hydrogenated cottonseed oil and 0.60 grams for cottonseed oil). The stearic acid is conveniently added by dropping from a roughly calibrated dropper. The fat containing the stearic acid is heated to 140-150° C. for hydrogenated cottonseed oil and cottonseed oil and to 110-120° C. for tallow and coconut oil by immersing in an oil bath at 160-165° C. for 3 minutes. If bentonite is used, the fats are heated to 100° C. in a water bath or 105° C. oven. The flask is rotated and shaken to distribute the catalyst uniformly in the fat. Then, 4 cc. of 50% aqueous potassium hydroxide is slowly added with shaking and the mixture vigorously agitated with rotary motion for 30 seconds. The flask is loosely stoppered and placed in the 105° C. oven. After 20 minutes it is removed, the soap is dissolved and the solution is cleared, oxidized and the excess oxidant titrated.

SUMMARY

Several methods of saponification of fats for the determination of available glycerol are considered.

1. The Direct Saponification Method.
2. A Method proposed by the A.O.C.S. Committee on Glycerine Determination.
3. The Carius Method.
4. A Method for Rapid Saponification of fats and oils is proposed for laboratory use in determining glycerine yields in which stearic acid or bentonite is added as a catalyst. Upon the addition of potassium hydroxide and vigorous shaking, a fine emulsion is formed provided the proper conditions are regarded. The saponification takes place in a 105° C. oven and is completed in 20 minutes.

The proposed method has the following advantages:

1. The saponification is completed in 20 minutes.
2. No special apparatus is required.
3. Saponification takes place at the comparatively low temperature of 100 to 105° C.
4. The method is simple and involves no unusual technique.
5. The results are in good agreement with both the theoretical and those obtained by other methods.

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CHANGING TRENDS IN DETERGENTS

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Abstract

In the enormously large and varied field of cleaning agents, a review of the changing trends in the field once held chiefly by soaps. and a few chemicals, is of interest. The author has summarized the general theory and ways of preparing many of the new detergents and has indicated the direction of future research to provide many more products which will serve as agents along side of, or as substitutes for many of the old ones.

IN the kaleidoscopic changes of the past few decades we are impressed more and more with the truth of Tennyson's lines:

> "The old order changeth,
> Yielding place to new."

Detergents, like fashions and styles, have also changed and the past few years have witnessed a definite trend into newer fields wherein newer agents have assumed a place alongside of, or as substitutes for the old ones. Many of us still remember the weekly Saturday chore of the small boy, wherein several perfectly good playtime hours had to be sacrificed to the grinding up of several old bricks or some soft rock so that there might be an ample supply of scouring powder for the kitchen knives, pots and pans. Those from New England particularly recall how assiduously every scrap of ham fat and rind was thriftily saved so that in the warm springtime some homemade soap might be made by leaching some of the wood ashes which had accumulated during the winter, by saponifying out in the sunlight in an old earthenware crock. Truly the old order has changed and still continues to change, each month bringing in new agents and newer methods.

We regard a detergent as an agent which functions "to wipe away, wash away, or cleanse." If we accept this definition then we must also believe that there are some detergents which have always been with us. The Biblical story of creation tells us that the good Lord created the heavens, the earth and the waters and all that was contained therein. It would appear then that such detergents as water, sands and clays have been with man from the beginning. Soaps were probably one of man's contributions forced upon the other inhabitants as one of instrumentalities of a higher civilization.

As pointed out by Ittner (Jour. Ind. Eng. Chem. 18, 908 (1926) and *27*, 756 (1935) in his admirable reviews of the history of the soap industry, detergents include quite a large group of agents, viz., soaps and similar bodies, soap builders; dispersion agents for hard waters, enzymes and bleaches; and that large group one may somewhat more generally term the "soap substitutes."

It is quite apparent to most of us that the large developments in the true soaps, i.e., the alkali salts of the higher fatty acids, have concerned themselves largely with improvements in the saponification process, with variations, blending and substitutions of raw materials used, and in glycerine recovery. Large emphasis has been given to physical form. Today we have the various flakes, chips and hollow beads which tend to increase solubility and make for so much convenience in use and of course incidentally, perhaps, for advertising embellishment.

Introduction to the commercial trade of products like cheap trisodium phosphate, sodium hexa metaphosphate and a wide variety of silicates and rosin grades have extended built soap formulas. Activity in this field, especially in the past few years to maintain certain price levels has led to some overdoing of built-soap practice. One must ever keep in mind the real needs of the consumer who is now supplied with a multiplicity of different textiles and other surfaces needing the cleansing action of detergents. The wide use of rayons, the growing practice of daily dab-lot washing of lingerie, stockings, etc., has placed new emphasis on the detergents to be used if consumer satisfaction is to be realized and maintained. We have seen here a wide variety of products offered which have as their basis gentle action both on the materials to be cleaned and on the hands of the user. Newer household interiors with their tiled or lacquered kitchen and bathroom surfaces, porcelain refrigerators, ranges, sinks, lavatories and tubs, chromium plated fixtures, etc., all remind us of the different detergents needed by the housewife today as contrasted with those of her mother's or grandmother's day. All the angles of detergency must be continuously kept in mind—wetting properties, foam building, dispersibility, solubility and effectiveness, if we are to keep abreast of such developments.

Soap, dating back to antiquity, has come down to use as a product ever changing and ever being improved upon from many angles, yet always has there been one shortcoming in the foreground—its tendency to form curds in hard waters. In general we have assumed soaps to be the alkali salts of non-volatile fatty acids or combinations of these fatty acids with certain organic bases. When the alkali soaps come in contact with waters rich in calcium and magnesium salts we find a chemical metathesis ensuing:

$$\left.\begin{matrix}R\,COONa\\R\,COONa\end{matrix}\right> + MgSO_4 \longrightarrow Mg\left<\begin{matrix}R\,COO\\R\,COO\end{matrix}\right. + \left.\begin{matrix}Na\\Na\end{matrix}\right> SO_4$$

Now, inasmuch as the carboxylic acids are weak, such magnesium and calcium compounds hydrolyze further:

$$\left.\begin{matrix}R\,COO\\R\,COO\end{matrix}\right> Mg + \begin{matrix}H\;OH\\H\;OH\end{matrix} \longrightarrow Mg(OH)_2 + 2R\,COOH$$

It is evident then that if some scheme could be devised to produce a method of blocking or eliminating the carboxyl group better detergent results could be obtained. Such blocking, with its consequent overcoming of the curd formation by calcium and magnesium salts, has been shown possible by esterification, amidation or reduction to the alcohol.

In 1931 Adkins and Folkers (Jour. Am. Chem. Soc. *53,* 1095) in a study of hydrogenation of aliphatic acids found that with the proper catalyst, it was possible to obtain the corresponding alcohols having the same number of carbon atoms.

$$\underset{\text{Palmitic Acid}}{CH_3(CH_2)_{14}COOH} \xrightarrow{H} \underset{\text{Cetyl Alcohol}}{CH_3(CH_2)_{14}CH_2OH}$$

This also formed the basis of the early work of H. Berth of the H. T. Böhm firm of the Aktien Gesellschaft in Germany.

Esterification of these alcohols by means of sulfuric acid easily produces the corresponding sulfate, e.g.:

$$CH_3(CH_2)_{14}CH_2OH \xrightarrow{H_2SO_4} \underset{\text{Sulfuric Ester of Cetyl Alcohol}}{CH_3(CH_2)_{14}CH_2OSO_2OH}$$

Upon neutralization of such an ester with NaOH or Na_2CO_3 we obtain the sodium salt:

$$CH_3(CH_2)_{14}CH_2OSO_2OH \xrightarrow{NaOH} \underset{\text{Cetyl Sodium Sulfate}}{CH_3(CH_2)_{14}CH_2OSO_2ONa}$$

In this fashion we obtain derivatives of many of the fatty chain alcohols. Where commercial grades of materials are used, of course, the reactions may leave small amounts of unchanged alcohols, varying amounts of sodium sulfate and some mixtures of end products. Using Lauryl Alcohol we obtain, $CH_3(CH_2)_{10}CH_2OSO_3Na$, which is familiar to us as one of the chief ingredients of the "Gardinols" and "Avirols," etc. Similar products are:

$CH_3(CH_2)_{16}CH_2SO_3Na$
Sodium Octadecyl Sulfate
$CH_3(CH_2)_7CH = CH(CH_2)_7CH_2SO_3Na$
Sodium Oleyl Sulfate

The work of Schrauth and his associates (Ber. *64;* 1314 (1931) indicated the activity of the Deutsche Hydrierwerke in this field. Patents which issued from the work of the Böhm and Hydrierswerke have been licensed in the United States and are being used for the production of these newer detergents.

In Germany the I. G. Farbenindustrie Akt. Ges. has brought out the interesting Igepon products. The Igepon A series are said to be sodium salts of the compounds obtained on the interaction of isthionic acid with oleic acid or its derivatives:

$$CH_3(CH_2)_7CH = CH(CH_2)_7COOCH_2CH_2SO_3Na$$

Igepon A

Isthionic acid is described by Whitmore (Organic Chemistry, 1937 Edition, p. 34; 112; 151 and 169), as beta-hydroxyethane sulfonic acid: $HO\text{-}CH_2\text{-}CH_2SO_3H$. The more stable tauric acid derivative is known as Igepon T, whose formula appears to be:

$$CH_3(CH_2)_7CH = CH(CH_2)_7CON(CH_3)CH_2CH_2SO_3Na$$

It has found some market in this country under special trade names. Sweet (Soap 10, 55 (1934) has given interesting details of these products while Lederer (Angew. Chem. *47,* 119 (1934) reported many tests and measurements made on them. More recently we have seen the introduction of the "Igepals"—Igepal "C," "W," "L" and "F." These are all based upon ethylene chloride combinations and as yet we have seen little detail about them.

Carbide and Carbon Chemicals Corporation has been active in combining various alcohols with halides to produce ethers which upon sulfonation yield good detergents.

Thus:

$$\left.\begin{matrix}\text{Cetyl}\\\text{Dodecyl}\\\text{Oleyl}\end{matrix}\right\}\text{Alcohol} + \begin{matrix}\text{Aliphatic}\\\text{or}\\\text{Aralkyl}\end{matrix}\ \text{Halide} \xrightarrow[\text{+ MgO or Chalk}]{\text{Al powder}} \begin{matrix}\longrightarrow \text{Ethers}\longrightarrow\\\text{Chlorsulfonic Acid}\rightarrow\\\text{Sulfonated Ethers}\end{matrix}$$

Baldwin & Davidson—U. S. Pat. 1,999,315 (4-30-35).

In a French Patent No. 782,835 (1935) this same company has produced a special detergent by combining Methyl Isobutyl Ketone with Ethylhexaldehyde to produce:

$$(CH_3)_2\,CH\,CH_2\,CO\,CH_2\,CHOH\,CH\,(C_2H_5)\,C_4\,H_9$$

Wickert, working for the same company, on undecyl ketol and its derivatives, has shown in U. S. Pat. No. 2,088,015 that if alpha ethyl hexaldehyde is condensed with acetone in the presence of NaOH as a catalyst, it is easy to produce a ketol which is easily converted to an unsaturated ketone by heating to remove water. Hydrogenation of the ketone yields the corresponding alcohol which can be sulfated.

In U. S. Patent 2,088,016 Wickert synthesizes nondecyl ketol, hydrogenates it and then sulfates the resulting secondary nondecyl alcohol. The resulting acid sulfated product is converted to neutral sulfate ester by NAOH, NH_3 or triethanolamine. The sodium salt is said to make a good detergent.

Calcott and Clarkson in U. S. Patent No. 2, 016, 956 (1935) have shown the way of producing new detergents by combining certain aliphatic halides with certain types of amines. By their procedure glucose amine and lauryl alcohol can be made to yield: $C_{12}\,H_{25}NH\,CH_2\,(CHOH)_4\,CH_2\,OH$.

Sulfonated amides of the type of: $R\,CONH\,CH_2\,CH_2\,SO_3\,NA$ have found some favor. Usually these are the sodium salts of the taurine derivatives of oleic acid.

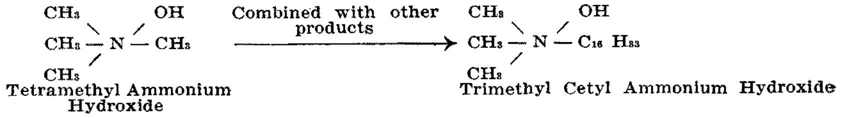
Sulfonated naphthalene compounds have found their way into the field of detergents under a host of trade names. These are either free acid or sodium salt derivatives of sulfonated naphthalenes. We find on the market "Nekal," "Nekal BX," "Alkanol" and Neomerpin X" as examples of such products.

For a number of years the Dow Chemical Company has been interested in making a number of phenol derivatives such as phenyl phenol. When phenyl phenol is produced as sulfate it finds its way onto the market under trade names like "Aresket," "Aresklene" and "Areskap."

In an attempt to use the fatty acids present in the tall oil fraction of pine wood we find a number of detergent preparations in this field.

As wetting agents, derivatives of terpined sulfate have found some use. It is understood that the American Cyanamide Corporation manufacture some products of this type.

Compston (Soap *13*, *17-*), has detailed the possibilities as detergents of the quaternary compounds of Nitrogen containing a long-chain fatty constituent. Thus:



Combination with sulfur-containing compounds has yielded products having both cleansing power and antiseptic power.

In Russia and Japan we find wide usage of detergents which are naphthenic compounds. These are derived from the napthenes which are components of petroleums.

Petroleums → Napthenes → Napthenic Compounds
($C_6\,H_{11}\,COOH$ = Simple Napthenic Acid)

It has been pointed out by Bacharach (Soap *10, 21*) that potash soaps have been made from the naphthenic acids of California crude oil. Such soaps have a high disinfectant value and may some time compete with the more familiar cresylic acid soaps.

The Oranienburger Chemische Fabrik, A. G. in French Patent No. 806,905, have claimed improved wetting agents to be obtained by mixing chlorinated neutral fats, fatty acids, resinic acids or naphthenic acids with ethers of polyhydric phenols which contain at least one free OH group. The products are sulfonated and neutralized.

Aromatic hydrocarbons have been mixed with the esters of higher aliphatic acids containing at least one OH group in the alcoholic residue and such mixtures then condensed and sulfonated. Thus naphthalene and glycerol monostearate may be treated with fuming $H_2\,SO_4$ at 80° C. according to the I. G. Farbenind. A. G. German Patent No. 644,131.

Hilditch (Chem. Age *35*, 558) (1936) has pointed out that Leper Brothers, Ltd., Liverpool, have patented a new synthetic detergent, stable to hard water and stable in an acid medium. It is unique in that it contains no salt forming group. It consists of mono fatty acid esters of one or more polyglycerols. It is said that solubility in water results from the accumulation of aliphatic OH groups in the condensed glycerol molecules. The long chain acyl ester confers desired lathering power and other physical properties.

Enzyme detergents of both the amylolytic and proteolytic types have appeared. In most cases, however, the enzyme reaction may be produced by chemical reagents to advantage. Thus we find the I. G. Farbenindustrie A. G. in British Patent No. 450,467 hydrolyzing protein to the aminocarboxylic acids and then acting on these derivatives with derivatives of a carboxylic acid, an organic sulfonic acid, a carbonic acid ester or a substituted carbonic acid.

Another interesting series of detergents are those described by Hausman in Soap *13*, 24 (1937). Cholesterol may be esterfied with boric acid and mixed with the orthoboric ester of oleic alcohol at 60° C. and then sulfonated. Such detergents are said to be particularly valuable for leather and textiles.

The true organic soaps have been developed by many interesting combinations. Only a few years ago most soap chemists looked upon the triethanolamine soaps as an expensive way of making ammonia soaps. Today they stand on their own feet as valuable adjuncts for dry cleaning and for certain of the "soapless" shampoos. Mixed with naphthenic acid derivatives they have found good service in improving the ordinary liquid soaps by clarifying and lowering the temperature at which the latter congeal or develop turbidity.

We see from all these innovations a definite trend in the detergent field. Never again will we be satisfied with soaps alone. Change, constant change, has been the ever present characteristic of this large field. Just as the pendulum of organic chemistry has swung from its major emphasis on the aliphatic side over predominately to the field of aromatic chemistry, and then back again to the aliphatic field, so, too, can we expect a shift back to a more complete and more intensive study of the detergent products to be derived from the saturated and unsaturated constituents of our natural gases and oils. Such starting materials as ethylene, propylene, butylene, ethane, propane, butane, etc., offer us a great world of possibilities. The newer methods of hydrogenation, condensation, sulfonations and a host of other chemical procedures, coupled with increasingly better tools and control instruments, definitely point to one thing in this large field and that is—continued, definite progress.

Truly—

"The old order changeth,
Yielding place to new."

REPORT OF THE SOAP ANALYSIS COMMITTEE 1937

A MEETING of the Committee was held October 13, 1937, at which the results of the current year's work were reviewed. This report covers the details of these studies including the recommendations and conclusions of the Committee.

During the year the Committee has been engaged in a further study of screen analysis and methods for the determination of combined potassium and sodium oxides in soap.

SCREEN DETERMINATIONS

Two tentative screen test methods have already been adopted by the Society, namely, the hand shake test and Ro-Tap method. Inasmuch as our previous collaborative studies on these methods only included ground soaps, it was decided to make further studies of the two methods as applied to blown or spray-dried soaps. The cooperative sample was a spray-dried soap powder which was tested by the two methods, namely, the tentative hand screening and Ro-Tap methods, the latter revised so that a 100 g. sample was used in the test instead of an 8 oz. sample as prescribed in the method. The A.O.C.S. tentative methods for Screen Determinations appear in the January 1936 issue of OIL AND SOAP. These modified to conform to the committee's present recommendations are given herewith:

HAND SCREENING METHOD

Screens Used:

U. S. Standard, as given in Federal Specifications RR-S-366, "Sieves, Standard, Testing"—8 in. screens being employed.

Procedure:

Nest the No. 12, No. 40 and No. 100 sieves (U. S. Standard or corresponding Tyler sieves) making sure that they are clean and dry and transfer 100 g. (± 0.1 g.) of the well-mixed sample, without previous drying, to the top sieve (No. 12). Shake the sieves simultaneously, occasionally tapping the edge of the bottom sieve on a large rubber stopper or a flat, thick piece of rubber. When the portion of soap passing through the bottom sieve is less than 0.1 g. per minute of shaking (this can be well judged by sifting into a large, dark colored pan), remove the top sieve separately over a clean, dark pan, to be certain that no more of the residue will pass through. Place any material passing through the No. 12 sieve, on the No. 40 sieve, using a small camel's hair brush to remove the material from the catch-pan. Follow the same procedure of sifting for the No. 40 and No. 100 sieves as used for the No. 12 sieves.

NOTE: At least duplicate determinations should be made and averages taken.

Calculations:

1—Calculate the weight of the residue on the No. 12 sieve to percentage retained.

2—Add the weight of the residue retained on the No. 12 sieve to the weight of the residue retained on the No. 40 sieve and calculate the sum to percentage retained on the No. 40 sieve.

3—Add the weight of the residues retained on the No. 12 and No. 40 sieves to the weight retained on the No. 100 sieve and calculate the sum to percentage retained on the No. 100 sieve.

RO-TAP METHOD

Screens Used:

U. S. Standard, as given in Federal Specifications RR-S-366—"Sieves, Standard, Testing"—8 in. screens being employed.

Procedure:

Nest the No. 12, No. 40 and No. 100 sieves, (U. S. Standard or corresponding Tyler Sieves) making sure that they are clean and dry, and transfer 100 g. (± 0.1 g.) of the well-mixed sample without previous drying, to the top sieve, No. 12. Place the nest of sieves in the Ro-Tap machine and run for ten minutes. Carefully weigh the portion held on the No. 12, No. 40 and No. 100 sieves; also, the portion passing through the No. 100 sieves.

NOTE: At least duplicate determinations should be made and averages taken.

TABULATION OF RESULTS

Hand Screening Method

(100 g. sample)

	On No. 12 Mesh	On No. 40 Mesh	On No. 100 Mesh
L. B. Hitchcock	0.0%	57.6%	90.3%
E. R. Luckow[1]	0.0	54.2	89.5
M. L. Sheely[1]	0.0	64.7	90.4
R. C. Newton	0.0 0.0	63.4* 62.8**	90.8 90.1
H. E. Cutts***	...	69.3	94.4
J. E. Doherty	0.0	56.0	90.4
B. S. Van Zile	0.0	68.6	96.3
C. P. Long	0.0	69.1	90.3
Low	0.0%	54.2%	89.5%
High	0.0	69.3	96.3
Average	0.0	62.9	91.4

*Shaking until the amount passing through sieve is less than 0.1 g. per minute.

**Shaking until no perceptible powder passes through sieve.

***Used a 14 mesh screen instead of a No. 12, so no value used under No. 12 mesh column.

[1] These members used in addition to above named sieves, No. 20, No. 60 and No. 80 sieves.

Ro-Tap Method

(100 g. sample)

	On No. 12 Mesh	On No. 40 Mesh	On No. 100 Mesh
E. R. Luckow[1]	0.0%	63.7%	89.2%
M. L. Sheely[1]	0.0	58.9	90.5
R. C. Newton	0.0	67.6	91.4
J. E. Doherty	0.0	59.6	92.8
B. S. Van Zile	0.0	68.6	96.3
C. P. Long	0.0	60.4	87.1
Low	0.0%	58.9%	89.2%
High	0.0	68.6	96.3
Average	0.0	63.1	91.2

[1] These members used in addition to above named sieves, No. 20, No. 60 and No. 80 sieves.