that the above method is found to be simpler and more rapid than the gravimetric train method, without sacrifice of accuracy. Experiments in our laboratory in applying the new method to materials other than soap products indicate that the procedure has general utility. On materials such as 50 per cent liquid caustic soda, where the carbonate content of the product as shipped is normally only 0.1-0.3% calculated as sodium carbonate, no difficulty is experienced in obtaining reproducible and accurate results. This aspect of the method has been verified by adding very small known amounts of sodium carbonate and finding the increment.

Examples of results in using the method in the examination of a variety of soap products are presented in Table II. Convenient quantities of sample are indicated in each case. The degree of agreement which may be anticipated in routine use of the method is illustrated in these results, which represent duplicate determinations in each case.

Notes on the Method

Suggestion has been made that funnel "D" might be dispensed with and absorbent solution measured directly into flask "B," thus simplifying the apparatus and making it unnecessary to rinse funnel "D." Evacuation by the aspirator pump might then be made thru funnel "C." We are unable to say at this time whether the method will give the same results with this modification, but the suggestion appears to be well worth trying.

Another suggestion has been made to the effect that the spent absorbent solution be titrated directly with standard HCl instead of sodium bicarbonate solution. We have tried this variation, but in our experience the end point is not as satisfactory.

TABLE II
CARBON DIOXIDE DETERMINATIONS ON TYPICAL PRODUCTS

Product	Sample First Taken Grams	Grams CO_2	% CO_2	Calculated as Equivalent Na_2CO_3 %
C. P. Na_2CO_3	0.5206	0.2148	41.25	99.41
C. P. Na_2CO_3	0.4989	0.2074	41.57	100.18
A textile soap	25	0.0898	0.36	0.87
A textile soap	25	0.0848	0.34	0.82
A nationally advertised washing powder	3	0.1498	4.99	12.02
A nationally advertised washing powder	3	0.1500	5.00	12.06
Another nationally advertised soap powder	3	0.0623	2.08	5.02
Another nationally advertised soap powder	3	0.0616	2.06	4.97
A well known rosin soap	10	0.1273	1.27	2.96
A well known rosin soap	10	0.1274	1.27	2.96
A prominent cleanser	6	0.2162	3.60	8.67
A prominent cleanser	6	0.2168	3.61	8.70
A nationally advertised white floating soap	50	0.0474	0.095	0.23
A nationally advertised white floating soap	50	0.0460	0.092	0.22
A well known chip soap	15	0.2357	1.57	3.78
A well known chip soap	15	0.2329	1.55	3.74

SOME NOTES ON THE DETERMINATION OF GLYCEROL IN FATS

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THE accurate and rapid determination of glycerol that can be produced by saponifying fats is of great importance to the soap and allied industries. That it is still a great vital problem is indicated by the recent articles regarding rapid saponification[1,2] and rapid determination of glycerol[3], and the activity of the Committee on Glycerol Determination.

The usual method of analysis of fats for available glycerol divides itself into three operations: saponification, oxidation, and titration or determination of excess oxidant. Each of these operations may be performed in a number of different ways, and considering the many slight variations in the various procedures an almost innumerable number of ways of performing the entire analysis are available. It is the purpose of this paper to consider briefly, first, a few of the methods:

I. The direct saponification method.

II. The method proposed by the A. O. C. S. Committee on Glycerol Determination.

III. The method involving the use of a Carius tube; also to propose and discuss a new method.

IV. The catalytic method, using stearic acid or bentonite as catalysts, and, finally, to compare the results of the analyses and the time involved.

I. The Direct Saponification Method

This method, used for fats relatively high in free fatty acids, calls for a 4-gram sample of fat to which is added 50% aqueous potassium hydroxide and distilled water, and the mixture refluxed for 1¼ hours. After addition of hot water, it is placed on the steam bath overnight. In the morning, the solution is transferred quantitatively to a 300 cc. beaker and acidified, and the fatty acids removed. The solution is cleared with aluminum sulphate and sodium hydroxide, and the glycerol determined by the iodiometric method. To an aliquot portion are added standard potassium dichromate solution and concentrated sulphuric acid. This solution is then boiled for 15 minutes and cooled. Potassium iodide solution is added and the liberated iodine is titrated with standard sodium thiosulphate solution, using starch as the indicator. This method, although it works satisfactorily for fats relatively high in free fatty acids, is entirely unsatisfactory for fats low in free fatty acids, in that the saponification is incomplete.

II. The Method Proposed by the A. O. C. S. Committee

The Glycerine Analysis Committee of the A. O. C. S. recently proposed for cooperative work a method of saponification in which 5 grams of the melted fat are mixed with 5 cc. of 50% aqueous potassium hydroxide and heated to 105° C. for four 15-minute periods. At the end of each period, thorough mixing of the fat and the potassium hydroxide is essential. Potassium dichromate is used as the oxidizing agent, the excess titrated with ferrous ammonium sulphate solution, using potassium ferricyanide as an outside indicator.

A. O. C. S. samples of refined coconut oil, cottonseed oil, hydrogenated cottonseed oil, and tallow, all high-grade, were saponified by this method and the oxidation and titration operations were done by two methods, (1) the iodiometric method for glycerol in soap and (2) that described by the committee. The results are given in Table I.

TABLE I
PERCENTAGE GLYCEROL

	A. O. C. S. Coconut Oil		A. O. C. S. Cottonseed Oil		A. O. C. S. Hydrogenated Cottonseed Oil		A. O. C. S. Tallow	
Theo.	13.95		10.68		10.65		10.84	
	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
Expt. No. 1	13.92	13.95	10.40	10.65	(*10.11)	(*10.34)	.....	.....
Expt. No. 2	14.03	13.98	(*7.52)	(*7.35)	10.52	10.63	10.84	10.94
Expt. No. 3	14.38	14.06	10.69	10.66	10.54	10.58	11.27	11.04
Expt. No. 4	14.29	14.10	10.65	10.64	10.49	10.41	10.92	10.84
Avg.	14.16	14.02	10.58	10.65	10.51	10.54	11.01	10.95
Dev.	+.21	+.07	—.10	—.03	—.14	—.11	+.17	+.11
Largest Dev.	.43	.11	.28	.04	.06	.24	.43	.20
Expt. No. 5	14.12	13.82	*8.65	*8.66	*9.44	*9.50	11.10	10.83
Expt. No. 6	14.09	13.00	*9.85	*9.83	*9.99	*9.92	10.92	10.82

*Saponification incomplete.

TABLE III
PERCENTAGE GLYCEROL BY THE CARIUS METHOD

	Coconut Oil	Cottonseed Oil	Hydrogenated Cottonseed Oil	Tallow
Theoretical	13.95	10.68	10.65	10.84
Test No. 1	*13.54	10.53	10.94	11.07
Test No. 2	14.02	11.45	11.15	10.60
Test No. 3	*13.72	(*10.10)	10.89	10.94
Test No. 4	*12.41	10.84	10.86	11.20
Test No. 5	*	10.87	10.99	11.12
Test No. 6	*	.....	10.69	11.16
Avg.	.....	10.92	10.92	11.01
Dev. of Avg.	.....	+.24	+.27	+.17
Largest Dev.	.....	+.79	+.50	+.36

*Saponification incomplete.

It will be noted that in all cases of the first four experiments, except in one case for cottonseed oil and one for hydrogenated cottonseed oil, in which saponification is obviously incomplete, the results are in fairly good agreement with the theoretical values, calculated from the saponification and acid values. The deviation of the average of the results from these is positive for coconut and tallow and negative for cottonseed oil and hydrogenated cottonseed oil. Except for hydrogenated cottonseed oil, the deviations are greater when the glycerol is determined by method (1) than by method (2).

While this method is very satisfactory for coconut oil and for tallow, it is not entirely reliable for cottonseed oil and hydrogenated cottonseed oil, as in one case of the first four for each of these oils given in Table I saponification was incomplete. In Experiments No. 5 and No. 6, performed by an analyst unfamiliar with the method, both results for these two oils were low. This is in agreement with the fact[4] that while coconut oil, palm kernel oil, and castor oil will saponify quite easily, tallow and hydrogenated oils, etc., saponify much more slowly; and that the ease of saponification is inversely proportional to the fraction of unsaturated glycerides present. That the method is an improvement is shown by the fact that tallow is here included in the group that is quite easily saponified while cottonseed oil and hydrogenated cottonseed oil remain in the group that is difficult to saponify. We believe the reason for its improved success is the intimate mixing caused by the mechanical stirring which liberates the oil particles occluded by the soap formed in the initial reaction. The emulsion is very stable in the 105° C. oven in which the saponification takes place.

Again the excess potassium hydroxide is small. With greater excess there is a tendency for the soap when formed to salt out, thereby causing the emulsion of the oil and aqueous caustic solution to break down.

III. The Method Involving the Use of a Carius Tube

The idea was suggested in our laboratory that the saponification operation be made in a Carius tube. In this method, 5 grams of fat or oil is placed in a Carius tube, 50% potassium hydroxide solution added (3 cc. for tallows and palm oils and 4 cc. for coconut oils), and the Carius tube heated in a steam bath to melt any oil which may have spattered on the wall of the tube when it was introduced. Twenty-five cc. of distilled water are added, washing down the walls of the tube, which is then sealed and annealed, thoroughly shaken and heated overnight in the Carius oven at 130-135° C. The oxidation is done by means of potassium dichromate, the excess of which is titrated with sodium thiosulphate solution using starch as the indicator.

Results by this method compared with those of Method I as well as those determined from the ester values are given in Table II.

TABLE II
PERCENTAGE GLYCEROL

Stock	From Ester Value	By Method I	By Carius Method
Acidulated coconut oil	5.08	6.45	6.38
Unrefined tallow	9.25	9.99	9.79
Acidulated Palm oil	5.54	6.67	6.66
Unrefined Palm oil	9.56	9.77	9.79
Refined tallow	10.80	....	10.73
Refined tallow	10.73	....	10.74

It will be seen that in the first four cases the results of Method I and the Carius Method agree very well, but both vary from the percentage glycerol determined from the ester value. The variation is greater for the acidulated oils than for the unrefined oils, a fact which is in agreement with laboratory experience. Method I is not applicable to such oils as refined tallow, but it will be noted in these cases that the results of the Carius Method agree very well with those calculated from the ester values.

This work was extended to the refined and pure oils, the results of which are given in Table III.

After this set of experiments was completed it was found that coconut oil requires a lower temperature than the other oils, and probably if the effect of temperature were studied, a condition for complete saponification could be ascertained.

The averages of several determinations for cottonseed oil, hydrogenated cottonseed oil, and tallow vary +0.24, +0.27, and +0.17 per cent, respectively, from the calculated values obtained from the saponification and acid numbers, while the greatest deviation of a single determination differed from the theoretical value by +0.79, +0.50, and +0.36 per cent, respectively. These deviations are greater than is desirable. It may be that by improved methods of oxidation and titration greater accuracy may be obtained.

The potassium hydroxide attacks the glass of the Carius tube during the prolonged heating and when the sulphuric acid is added in excess to convert the soap to fatty acids, silicic acid is precipitated. When the excess sulphuric acid is neutralized with sodium hydroxide the silica causes a fugitive end point and may possibly be responsible for the high results noted. The etchings on the inside of the Carius tube are of such appearance as to raise considerable doubt as to just when all the soap jell and glycerol has been washed out. More work should be done on this method as it seems to offer possibilities.

IV. The Catalytic Method

The use of α-naphthol, β-naphthol, and thymol[4] as catalysts in saponification has been described and increased efficiency demonstrated. It has been stated that bentonite[5] is probably the most active and generally useful catalyst for this purpose. The use of a catalyst, which in this case is actually an emulsifying agent was thus suggested for laboratory saponification.

A. Stearic Acid

On the basis of easy saponification of oils containing free fatty acids, small quantities of stearic acid were added to refined and purified fats when these were to be saponified and the percentage of glycerol determined, and it was found that oils which could not be saponified by the direct method were then readily saponified. Conditions and amounts of stearic acid and 50% potassium hydroxide were varied to determine those most satisfactory for complete saponification of an oil of the hardened cottonseed type, which we shall designate as Oil A.

The quantity of potassium hydroxide was first varied from 4 to 8 cc. to determine which gave the best emulsion. The data are given in Table IV.

On the basis of this and similar experiments, 4 cc. of 50% aqueous potassium hydroxide was chosen as standard.

From experience it was known that for this particular Oil A, the best emulsion resulted when the potassium hydroxide was added to the oil which was heated to a temperature of 140-150° C. However, to ascertain the exact influence of temperature, a series of experiments in which the temperature was increased by 10° C. for each member of the series over the previous member, with the first one at 100° C., was performed. The observations made are recorded in Table V.

TABLE V
INFLUENCE OF TEMPERATURE ON STATE OF EMULSION
4 Grams of Oil A
4 cc. of 50% KOH
4% Stearic Acid

Temp. ° C.	State of Emulsion
100 110 120 130	Incomplete, mixture partially solidified before complete emulsion was effected.
140	Very fine and uniform.
150	Very fine and uniform.
160	Slightly grainy.
170	Grainy.
180	Very grainy.
200	Complete separation into two phases.

The earlier experience was definitely substantiated and 140-150° C. was selected as the standard temperature of the oil when the potassium hydroxide was added. A single saponification was made, with the initial temperature of the oil at 160-170° C., and the percentage of glycerol determined and found to be 10.26% as compared with 10.68%, calculated from the saponification and acid values. In other words, a grainy emulsion will not lead to complete saponification.

The next factor to be studied was that of quantity of stearic acid most efficient in producing a good emulsion. The amount was varied from 0 to 6.4% of the weight of the Oil A in increments of 0.8%. The appearance of the resulting emulsions is listed in Table VI.

TABLE VI
INFLUENCE OF PER CENT STEARIC ACID ON APPEARANCE OF EMULSIONS
4 Grams Oil A
4 cc. 50% KOH
Temp. 140-150° C.

% Stearic Acid	Appearance of Emulsion
0	Coarse, separating on standing
0.8	Coarse, separating on standing
1.6	Finer, slight separation
2.4	Fair, very slight separation
3.2	Good
4.0	Fine, self-supporting
4.8	Fine, self-supporting
5.6	Fine, self-supporting
6.4	Fine, self-supporting

Four per cent of stearic acid was found to produce as fine an emulsion as larger amounts, and that quantity was then standardized as the most efficient.

After these conditions were established, the time factor was studied. A series of determinations was made, in which each one was started five minutes after the previous one, the first one being kept in the 105° C. oven for 25 minutes. Table VII gives the results of this series as well as those of a second series in which 20 minutes was the time limit.

TABLE IV
APPEARANCE OF EMULSION WITH VARYING AMOUNTS OF KOH
4 Grams of Oil A
4% Stearic Acid
Temp. 140-150° C.

Vol. 50% KOH	Appearance of Emulsion
4 cc.	Very good—no separation on steam bath.
5 cc.	Fair—some separation on steam bath.
6 cc.	Poor—distinct separation on steam bath.
7 cc.	Poor—separation on steam bath.
8 cc.	Poor.

TABLE VII
PROGRESS OF SAPONIFICATION WITH TIME IN 105° C. OVEN
Theoretical Percentage of Glycerol in Oil A = 10.68.

SERIES 1

Time in Oven (Min.)	% Glycerol	Percentage Saponification
0	2.26	21
5	9.13	86
15	9.71	91
20	10.72	100
25	10.55	99

SERIES 2

Time in Oven (Min.)	% Glycerol	Percentage Saponification
0	3.25	30
5	9.20	86
10	10.31	97
15	10.49	98
20	10.58	99
20	10.60	99

From these data it was concluded that 20 minutes was sufficient time for complete saponification.

Originally this heating was attempted on a hot plate in conformity with the direct saponification method, but it was observed that the high temperature destroyed the emulsion and in spite of continued heating and shaking for two hours the saponification was observed to be far from complete.

Having now determined the best conditions for saponification using stearic acid as the catalyst, we turned our attention to α-naphthol suggested by Silman[4] and bentonite suggested by Smith[5].

B. α—Naphthol

Although α-naphthol may be an excellent catalyst for rapid saponification, it was found to be unsuitable for use in analysis involving the determination of glycerol, as it is apparently oxidized by the potassium dichromate solution since the apparent percentage of glycerol is considerably higher than that calculated from the ester value. When a blank was run, without the fat, and the correction applied to the apparent percentage, the result was lower. This coincides with the fact that the α-naphthol is readily soluble in the fatty acids and only slightly soluble in water. Even if this were not the case, the use of α-naphthol as a catalyst would be more cumbersome than stearic acid since it involves a blank determination.

C. Bentonite

Bentonite, on the other hand, was found to be very satisfactory. Instead of adding it to the caustic solution as suggested by Smith[5], it was added to the melted fat prior to the addition of the caustic. It forms a good emulsion and the results are comparable with those of the determination in which stearic acid was used.

It is, possibly, not so neat a catalyst as stearic acid in that the suspended bentonite causes the resulting soap solution to be cloudy and it is impossible by visual inspection to determine whether or not the saponification or subsequent solution of soap is complete.

Approximately 5% of the weight of the fat was chosen as the quantity of bentonite to be used. The length of time of saponification in the 105° C. oven was ascertained by two series of determinations of percentage glycerol available from Oil A, similar to those made for stearic acid. The results are found in Table VIII.

TABLE VIII

PROGRESS OF SAPONIFICATION WITH TIME IN 105° C. OVEN

Catalyst - Bentonite

Time (Min.)	% Glycerol	Percentage Saponification
SERIES 1		
0	2.76	26
5	3.73	35
10	8.88	83
15	10.56	99
20	10.55	99
SERIES 2		
Time (Min.)	% Glycerol	Percentage Saponification
15	10.66	100
20	10.62	100
25	10.61	99

Again 20 minutes was selected as a reasonable length of time for complete saponification.

The catalysts, stearic acid and bentonite, were then applied to the saponification of the highly purified oils; Coconut Oil, Tallow, Hydrogenated Cottonseed Oil, and Cottonseed Oil. It was found that a temperature of 140-150° C. for the initial temperature of the oils when the caustic is added was too high for Coconut Oil and Tallow and that good emulsions are not formed. A temperature of 110-120° C. is far superior. Also larger quantities of bentonite are required for Hydrogenated Cottonseed Oil and Cottonseed Oil than for Tallow and Coconut Oil. Data for stearic acid and bentonite as catalysts are given in Table IX.

TABLE IX

PERCENTAGE GLYCEROL, USING ACID AND BENTONITE AS CATALYSTS IN SAPONIFICATION

Oil	Temp.	Percentage Glycerol (Stearic Acid)	Percentage Glycerol (Bentonite)	Percentage Glycerol Calculated from Sap. & Acid Values
Coconut	110-120° C.	14.07 14.05	14.10 14.15	13.95
Tallow	110-120	10.88	10.77	10.85
Hydrogenated cottonseed	140-150	10.64	10.64	10.65
Cottonseed	140-150	10.80	10.60	10.68

There is excellent agreement between the values obtained with the two catalysts and these in turn agree very well with those calculated from the saponification and acid values.

Considerable care must be exercised in the clarification of the aqueous solution containing the glycerol for Coconut Oil, as it apparently contains an appreciable quantity of non-glycerol oxidizable matter, which if not removed gives increased reduction of the potassium dichromate and, therefore, high results for percentage glycerol.

Conclusion

A recapitulation of the results obtained by the various methods is given in Table X.

TABLE X

PERCENTAGE GLYCEROL BY VARIOUS METHODS

Oil	Theoretical	Comm. Thio	Comm.	Carius	Catalysts Stearic Acid	Catalysts Bentonite
Coconut	13.95	14.16	14.02	.....	14.06	14.12
Cottonseed	10.68	10.58	10.65	10.92	10.80	10.60
Hydrogenated cottonseed	10.65	10.51	10.54	10.92	10.64	10.64
Tallow	10.84	11.01	10.95	11.01	10.88	10.77

The results given under "Committee Thiosulphate" are those obtained by saponification according to the method proposed by the Committee and the glycerol determined by the thiosulphate method while those under Committee are determined by the entire method as proposed by the Committee. The results of the latter are in better agreement with the theoretical than the former.

A survey of the results reveals that no one of these methods is greatly superior to the others with respect to accuracy, it being possible in most cases to ascribe the variation to the limits of error for the method. The results obtained by the Carius Method are slightly higher than those of the other methods, which may or may not be significant.

The method involving the use of catalysts, either stearic acid or bentonite, is simple, rapid and apparently as reliable as the other methods discussed. Stearic acid gives a clear solution when the oils are saponified which is not true for bentonite. Bentonite has the advantage that the initial temperature of the oil need be no higher than 100° C., so that instead of heating the flask containing the oil in an oil bath at 160° C., it may be heated in the same 105° C. oven where the saponification is completed. If a 105° C. oven is not available, the heating preliminary to and during saponification may be done by partially immersing the flask containing the fat in boiling water.

The advantage of the catalytic method of saponification is the fact that the time is greatly reduced. The time required for this method is only 20 minutes as compared with at least an hour and a half for the committee method and overnight for the Carius method.

Judging from the results given in Table X, the percentages of glycerol obtainable from fats may be determined to a fair degree of accuracy in the shortest time by the catalytic method of saponification and the potassium dichromate and sodium thiosulphate method of oxidation and titration. However, a higher degree of precision may possibly be attained with somewhat increased time by saponifying by the catalytic method, oxidizing with potassium dichromate and titrating with ferrous ammonium sulphate.

Further work is being undertaken to apply the use of diphenylamine[3] as an indicator in the titration of the excess potassium dichromate with ferrous ammonium sulphate and to determine the applicability of electrometric titrations to this analysis. Both of these methods hold promise of success and may add to the accuracy of the method as well as a reduction of time for the analysis.

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