in the production of greases such as those described by the patents quoted.

### Summary

1. Pure calcium, barium, and magnesium stearates have been prepared.

2. X-ray diffraction powder diagrams of these metallic soaps have been obtained as standard references for analysis.

3. The probability of the non-existence of basic alkaline earth and mixed acid soaps were shown.

4. The probable course of reactions taking place during the production of greases at high temperatures involving the presence of excess base is outlined.

REFERENCES

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# Report of Soap Analysis Committee*

# AOCS—ASTM Committee D-12, 1945

DURING the last few years the soap companies were called upon to furnish the armed services with special types of soaps for use in soft, hard, and sea water. The composition of these products differed from normal soaps in that they contained in addition to soda soap, synthetic detergents and inorganic salts, the latter consisting essentially of sodium sulfate and sodium chloride, which are normal constituents of the synthetic detergents. Because of the presence of the synthetic detergents and inorganic salts the official analytical methods commonly used for normal soaps were found, for the most part, to be inapplicable to these products. Accordingly, a set of special analytical methods had been developed by the Soap Analysis Committee in cooperation with the laboratories of the Army and Navy departments. During 1944 the committee made a comprehensive study(1) on three cooperative samples of soap containing synthetic detergents using these methods, and at its annual meeting in 1944 the committee voted the tentative adoption of these methods. Some slight revisions had been made in these methods, and it was the consensus to analyze additional samples of soap in 1945, following strictly the revised procedures as tentatively adopted.

Since the work in 1944 did not include a study of the starch determination in these types of soaps, it was agreed to analyze a sample of soap of the synthetic detergent type containing this ingredient. Therefore two samples of these special soaps representing commercial production were used in these studies by 13 collaborating laboratories. The compilation of results submitted by the various laboratories is shown in Tables I and II.

Sample No. 45-1 represented a bar containing moisture, anhydrous soap, active synthetic detergent, and neutral inorganic salts. Sample No. 45-2 was a similar type except that it contained approximately 20% starch. Some of the members of the committee questioned the factor of 0.9 which is used in the official soap methods in converting the dextrose by the Munson-Walker method to starch. To check on this point a sample of starch representing the same material used in the manufacture of Sample No. 45-2 was submitted to the members of the committee with a request that they determine the actual factor thereon. In Table II under column "Starch" Result A represents figures obtained using the official factor 0.9 whereas Result B represents figures obtained using the actual factor determined on the sample of starch used in the preparation of Sample No. 45-2. The actual starch factor obtained by the individual laboratories is shown in the last column of this table. A detailed method for determining starch in the sample of soap was submitted to the participants in this work and is included as a part of this report.

In examining the results shown in Tables I and II, it will be noted that the figures for the most part can be considered in fairly close agreement. Although there appears to be some divergence in results in some of the determinations, it was the consensus that the methods are quite satisfactory for these types of soaps and that with more experience with these procedures operators should be able to obtain more accurate and uniform results.

### Recommendations

I. SOAPS CONTAINING SYNTHETIC DETERGENTS

The committee voted the official adoption of the methods for analyzing soaps containing synthetic detergents with the stipulation that the following revisions be made thereto:

a. *Anhydrous Soap.* Instead of weighing the fatty acids in the anhydrous soap determination the fatty acids are to be titrated with alkali in the presence of alcohol, evaporated to dryness, and weighed as anhydrous soap. Because of the hygroscopic nature of this soap a caution is to be included in the method to cool in a desiccator before weighing.

b. *Fatty Matter.* The present tentative method calls for evaporating the petroleum ether on the steam bath and dry the residue (fatty matter) in an oven at 100 to 105° C. to constant weight. This will be changed to read as follows: "Evaporate on a steam bath until the odor of petroleum ether is no longer perceptible and then dry for one-half hour in an oven at 105° ± 2° C."

c. *Starch Factor.* The committee voted to change the present factor of 0.9, which is used in converting dextrose to starch, to 0.93.

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* Presented at fall meeting of the American Oil Chemists' Society, Nov. 7-9, 1945, Chicago.

## TABLE I.

1945 AOCS-ASTM Cooperative Studies—Soap Containing Synthetic Detergents Sample No. 45-1 (Synthetic Detergent = 55% Nacconol HG and 45% Ultrawet 40B) (Basis Active Synthetic). (Moisture—Figures represent actual determinations reported. All other constituents are calculated to 25% $H_2O$ basis.)

| | Moisture-Matter Volatile at 105°C. | Free Alkali as NaOH | Free Acid as Oleic | Anhydrous Salt-Free Soda Soap | Alcohol Soluble Matter | Matter Insoluble in Water | Total Alk. of Mat. Ins. in Alcohol (Calc. as $Na_2CO_3$) | Sodium Silicate (1 $Na_2O$: 3.25 $SiO_2$) | Fatty Matter | Chloride in Alcohol Sol. Matter (as NaCl) | Rosin | Syn. Det. (By Diff.) | Cal. of Neutral Inorganic Salts |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *Pct.* | *Pct.* | *Pct.* | *Pct.* | *Pct.* | *Pct.* | *Pct.* | *Pct.* | *Pct.* | *Pct.* | *Pct.* | *Pct.* | *Pct.* |
| Lab. No. 1 | 22.4 | 0.02 | ...... | 41.3 | 65.7 | 0.05 | 0.2 | 0 | 2.4 | 2.1 | 0 | 19.9 | 11.15 |
| Lab. No. 2 | 22.3 | 0 | 0 | 39.2 | 67.9 | 0 | 0 | 0.1 | 1.3 | 1.9 | 0 | 25.8* | 8.9 |
| Lab. No. 3 | 19.38 | 0.01 | ...... | 42.32 | 66.41 | 0 | 0.36 | 0.03 | 1.84 | 0.28* | 0 | 22.00 | 8.51 |
| Lab. No. 4 | | | | | | | | | | | | | |
| Analyst A | 21.00 | 0.04 | ...... | 43.03 | 66.16 | 0 | 0.12 | 0 | 1.67 | 2.35 | 0 | 19.11 | 11.07 |
| Analyst B | 19.68 | ...... | 0.13 | 41.81 | 65.31 | 0.16 | 0.24 | 0 | 2.44 | 1.88 | 0 | 19.18 | 11.17 |
| Lab. No. 5 | 20.9 | 0.03 | ...... | 37.6* | 66.4 | 0.08 | 0.11 | 0.05 | 2.8 | 1.96 | 0 | 24.1 | 10.3 |
| Lab. No. 6 | | | | | | | | | | | | | |
| Analyst A | 21.67 | 0.02 | ...... | 40.71 | 66.45 | 0 | 0.15 | 0.10 | 1.29 | 1.91 | .... | 22.54 | 10.30 |
| Analyst B | 21.88 | 0.03 | ...... | 42.46 | 66.56 | 0.03 | 0.20 | 0.10 | 1.36 | 1.77 | 0 | 20.97 | 9.98 |
| Lab. No. 7 | 19.4 | 0.01 | ...... | 38.9 | 65.8 | 0 | 0.05 | ...... | 1.5 | 1.5 | .... | 23.2 | 10.6 |
| Lab. No. 8 | 20.52 | 0.01 | ...... | 39.78 | 66.20 | 0.04 | 0.10 | 0.02 | 1.65 | 2.65 | 0 | 22.11 | 11.31 |
| Lab. No. 9 | 21.56 | 0.01 | ...... | 43.51 | 68.10 | 0.07 | 0.37 | 0.08 | 1.00 | 1.71 | 0 | 21.94 | 8.08 |
| Lab. No. 10 | 21.49 | 0.02 | ...... | 41.50 | 66.26 | 0 | 0.16 | 0.11 | 1.39 | 2.11 | 0 | 21.26 | 10.69 |
| Lab. No. 11 | 21.49 | ...... | 0.13 | 41.33 | 67.01 | 0.62* | 0.51 | 0.06 | 1.46 | 2.12 | 0 | 21.62 | 9.48 |
| Lab. No. 12 | 19.37 | 0.01 | ...... | 40.95 | 66.28 | 0.05 | 0.22 | 0.04 | 2.93 | 2.32 | 0 | 20.08 | 10.76 |
| Lab. No. 13 | 20.5 | 0.02 | ...... | 40.3 | 63.6* | 0.02 | 0.6 | 0.03 | 0.8 | 1.6 | 0 | 20.8 | ...... |
| Average | | 0.02 | ...... | 41.22 | 66.41 | 0.04 | 0.22 | 0.05 | 1.79 | 2.00 | 0 | 21.29 | 10.16 |
| High | | 0.04 | ...... | 43.51 | 68.10 | 0.16 | 0.6 | 0.11 | 2.93 | 2.65 | .... | 24.1 | 11.31 |
| Low | | 0.00 | ...... | 38.9 | 65.31 | 0.00 | 0.00 | 0.00 | 1.0 | 1.50 | .... | 19.11 | 8.08 |
| % Deviation from the mean** | | 0.01 | ...... | 1.07 | 0.51 | 0.03 | 0.14 | 0.04 | 0.44 | 0.24 | .... | 1.02 | 0.83 |

* Not included in average.

** Deviation from the mean represents the sum of the variance of individual values from the arithmetical average, divided by the number of values included in the average.

## TABLE II.

1945 AOCS-ASTM Cooperative Studies—Soap Containing Synthetic Detergents—Sample No. 45-2 (Synthetic Detergent = 100% Nacconol). (Moisture—Figures represent actual determinations reported. All other constituents are calculated to 15% $H_2O$ basis.)

| | Moisture-Matter Volatile at 105°C. | Free Alkali as NaOH | Free Acid as Oleic | Anhydrous Salt-Free Soda Soap | Alcohol Soluble Matter | Matter Insoluble in Water | Total Alk. of Mat. Ins. in Alcohol (Calc. as $Na_2CO_3$) | Sodium Silicate (1 $Na_2O$: 3.25 $SiO_2$) | Fatty Matter | Chloride in Alcohol Sol. Matter (as NaCl) | Rosin | Syn. Det. (By Diff.) | Cal. of Neutral Inorganic Salts | Starch | | Starch Factor |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | | | | Result A | Result B | |
| | *Pct.* | *Pct.* | *Pct.* | *Pct.* | *Pct.* | *Pct.* | *Pct.* | *Pct.* | *Pct.* | *Pct.* | *Pct.* | *Pct.* | *Pct.* | *Pct.* | *Pct.* | |
| Lab. No. 1 | 12.3 | ...... | 0.71 | 40.6 | 55.2 | 20.0 | 0.4 | 0.48 | 2.0 | 0.3 | 0 | 12.3 | 9.7 | 20.8 | 22.4 | 0.967 |
| Lab. No. 2 | 14.7 | ...... | 0.8 | 39.7 | 53.8 | 21.0 | 1.1 | 0.4 | 0.8 | 0.4 | 0 | 12.3 | 9.7 | 19.5 | 20.6 | 0.955 |
| Lab. No. 3 | 13.38 | 0.09 | ...... | 40.61 | 53.60 | 20.70 | 1.07 | 0.23 | 1.33 | 0.02 | 0 | 11.64 | 9.69 | 19.47 | | |
| Lab. No. 4 | | | | | | | | | | | | | | | | |
| Analyst A | 13.25 | 0.06 | ........ | 34.83* | 52.73 | 20.87 | 1.52 | 0.33 | 1.32 | 1.18* | 0 | 15.41* | 11.06 | 19.78 | 21.29 | 0.97 |
| Analyst B | 13.89 | 0.02 | 0.14 | 40.94 | 54.93 | 20.95 | 1.23 | 0.69 | 1.76 | 0.36 | 0 | 11.87 | 8.25 | 20.05 | ...... | ...... |
| Lab. No. 5 | 14.0 | 0.03 | ...... | 39.0 | 54.0 | 21.0 | 0.92 | 0.26 | 2.2 | 0.37 | .... | 12.43 | 9.5 | 19.8 | 21.4 | 0.978 |
| Lab. No. 6 | 13.95 | ...... | ...... | 40.06 | 52.93 | 20.99 | 0.97 | 0.19 | 0.73 | 0.03 | 0 | 12.11 | 10.14 | 19.49 | 20.40 | 0.942 |
| Lab. No. 7 | 12.3 | ...... | 1.1 | 37.3* | 54.1 | 21.0 | 1.0 | ...... | 1.2 | 0.3 | .... | 15.3 | 9.3 | 19.5 | 20.6 | 0.95 |
| Lab. No. 8 | 13.62 | 0.01 | 0.60 | 38.52 | 54.17 | 20.70 | 0.85 | 0.22 | 1.45 | 0.51 | 0 | 13.69 | 9.79 | 19.53 | 20.56 | 0.947 |
| Lab. No. 9 | 13.89 | 0.23* | ...... | 40.43 | 54.68 | 20.58 | 1.44 | 0.67 | 0.59 | 0.48 | 0 | 13.17 | 8.77 | 20.34 | 21.03 | 0.93 |
| Lab. No. 10 | 14.94 | 0.06 | ...... | 39.79 | 54.77 | 20.41 | 0.75 | 0.33 | 0.94 | 0 | 0 | 14.04 | 9.07 | 19.62 | ...... | ...... |
| Lab. No. 11 | 11.58 | ...... | 1.28 | 41.14 | 54.65 | 18.86* | 0.51 | 0.66 | 0.89 | 0.36 | 0 | 12.26 | 11.30 | 18.86 | 20.22 | 0.965 |
| Lab. No. 12 | 10.82 | ...... | 1.14 | 50.33* | 54.00 | 20.78 | 0.36 | 0.61 | 1.93 | 0.78 | 0 | 0.95* | 10.66 | 19.24 | 20.23 | 0.946 |
| Lab. No. 13 | 13.9 | 0.24 | ...... | 40.8 | 54.4 | ...... | ...... | 0.24 | 0.6 | 0.3 | .... | 12.7 | ...... | 20.5 | 21.0 | 0.92 |
| Average | | | | 40.14 | 54.14 | 20.75 | 0.93 | 0.41 | 1.27 | 0.35 | 0 | 12.59 | 9.76 | 19.75 | 20.88 | 0.952 |
| High | | | | 41.14 | 55.2 | 21.00 | 1.52 | 0.69 | 2.2 | 0.78 | .... | 14.04 | 11.30 | 20.8 | 22.4 | 0.978 |
| Low | | | | 38.52 | 52.73 | 20.00 | 0.36 | 0.19 | 0.59 | 0.00 | .... | 11.64 | 8.25 | 18.86 | 20.22 | 0.930 |
| % Deviation from the mean** | | | | 0.60 | 0.55 | 0.23 | 0.28 | 0.16 | 0.45 | 0.13 | .... | 0.59 | 0.63 | 0.40 | 0.49 | 0.017 |

* Not included in average.

** Deviation from the mean represents the sum of the variance of individual values from the arithmetical average, divided by the number of values included in the average.

## II. Potash Paste Soaps

The committee voted to move from tentative to official the Methods for the Determination of Free Alkali and Potassium Carbonate in Potash Paste Soaps (1).

## III. Rewriting of Soap Methods

The American Oil Chemists' Society has undertaken the job of rewriting and standardizing according to a definite pattern all its analytical procedures including the soap methods. Accordingly, a subcommittee was appointed during this year with the approval of the main committee for the purpose of reviewing the rewriting of the soap methods. The main committee voted to grant the subcommittee authority to make editorial revisions and minor changes in technique which they believe are necessary and which will not affect the general principle of any method. After all the revisions are made, the methods will then be referred to the Uniform Methods Committee for approval.

## IV. Methods of Sampling Soaps and Preparation of Samples for Analyses

The chairman was authorized to appoint a subcommittee to study and develop suitable methods for sampling soaps and the preparation of samples for analysis.

The personnel of the Soap Analysis Committee is as follows:

H. C. Bennett
R. Bernstein
E. W. Blank
J. N. Borglin
L. F. Hoyt
C. P. Long
L. B. Parsons
B. N. Rockwood
J. E. Simpson
F. W. Smither
Foster D. Snell
B. S. Van Zile
M. L. Sheely, chairman
E. Randa, vice chairman

### REFERENCE

1. Report of Soap Analysis Committee, AOCS; ASTM Committee D-12, 1944, Oil & Soap, *22*, 62-68, March (1945).

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## Method for Determination of Starch in Soap

### Reagents:

Copper sulfate—Solution A—Weigh 34.639 grams of C. P. $CuSO_4 \cdot 5H_2O$, dissolve in 150 ml. of distilled water, filter through asbestos, and make up to 500 ml. in a volumetric flask.

Alkaline tartrate—Solution B—Weigh 173 grams of Rochelle salts (sodium potassium tartrate $KNa\ C_4H_4O_6 \cdot 4H_2O$), dissolve in 150 ml. distilled water, and add 50 grams of NaOH. Stir the mixture frequently until dissolved. Dilute to 500 ml., allow to stand 2 days and filter through prepared asbestos.

Hydrochloric acid—Dilute, HCl conc. C. P. in dist. water, 1:1.

Hydrochloric acid—Dilute, HCl conc. C. P. in dist. water, 1:3.

Sulfuric acid—Dilute, $H_2SO_4$ C. P. conc. in distilled water, 1:4.

Nitric acid—Dilute, $HNO_3$ C. P. conc. in distilled water, 1:3.

NaOH—Approximately 10% (15° Bé).

Alcohol—Freshly boiled ethyl alcohol, 95% and neutral to phenolphthalein; either Formula No. 3A or No. 30 of the U. S. Internal Revenue Bureau.

Ether—Ethyl ether.

Phenolphthalein indicator—1% solution in neutral, redistilled alcohol.

Asbestos—Long fibre Amphibole variety, see preparation.

### Preparation of Asbestos for Use

Digest the asbestos for 2 to 3 days in 1:3 HCl. Wash free from acid with distilled water. Digest 2 to 3 days in 10% NaOH. Drain off bulk of NaOH and add sufficient hot alkaline tartrate solution (B) of the same strength used for the sugar solution to cover the asbestos well. Place on the steam bath, stirring occasionally for 2 to 3 hours. Wash the asbestos free from alkali. Pour off the solution. Rinse with water and then digest the asbestos several hours with 1:3 $HNO_3$. Wash free from acid. Add distilled water and shake into a fine pulp. Store in a flask or wide mouthed bottle in water suspension.

### Apparatus

Beakers—400 ml. and 250 ml.

Volumetric flasks—250 ml., 500 ml. accurately standardized.

Pipettes—An accurately standardized 50-ml. pipette is used in sampling from the volumetric flask. Two 25-ml. pipettes are used to pipette Fehling's solution.

Timer—Any suitable timer.

Flasks—500-ml. Erlenmeyer flasks provided with reflux condensers.

Gooch crucible—A 30-mm. Gooch crucible, prepared and weighed.

### Preparation of Gooch Crucible

The crucible should be used with an asbestos mat prepared as follows and not a paper filter mat. With the crucible in position over the suction flask and with gentle suction, make an asbestos film ¼" thick and wash thoroughly with distilled water to remove fine particles of asbestos. Wash the crucible with 10 ml. of alcohol, then 10 ml. of ether, dry for 30 minutes at 105° C., cool in a desiccator and weigh.

### Procedure for Analysis

Cut the soap into thin flakes to aid in rapid solution. Weigh at once a sample weight that will not give over 1 gram of starch into a 400-ml. beaker. Add 200 ml. hot, neutral alcohol. Cover the beaker and heat on the steam bath, swirling occasionally until the soap is in solution. Filter through a filter paper or a Gooch crucible with suction. (A paper filter pad may be used for this filtration). Wash the residue on the Gooch or filter paper with hot alcohol until free from soap. Wash, neutral to phenolphthalein the alcohol insoluble on the filter with distilled water at not over 60° C. without drying. The amount of starch should not be over 1 gram. If so, a smaller sample should be used.

Transfer the insoluble material to a 500-ml. Erlenmeyer flask provided with a reflux condenser, washing the last traces from the paper with a spray of warm water (not over 60° C.). Add water up to 200 ml. and 20 ml. 1:1 HCl. Boil for 2½ hours. Cool and nearly neutralize with sodium hydroxide. Transfer to a 250-ml. volumetric flask, cool to room temperature (25° to 30° C.), and make to volume. Filter enough through a clean dry paper to give a 50-ml. aliquot.

Transfer 25 ml. each of the copper sulfate solution (A) and alkaline tartrate solution (B) into a 400-ml. beaker. Add a 50-ml. aliquot to the 400-ml. beaker. Distilled water should be added to give 50 ml. if a smaller sized aliquot is used. The aliquot used must not be so large that no excess of Fehling's Solution remains after the boiling. Heat so that boiling begins in 4 minutes and continue the boiling for exactly 2 minutes. Keep the beaker covered with a watch glass during the heating. (It is important that boiling begins in 4 minutes and it is continued for exactly 2 minutes. To regulate the burner it is advisable to make a preliminary test using 50 ml. of the reagent and 50 ml. of water before proceeding with the actual determination. A timer should be used.)

Without diluting, filter the cuprous oxide at once on a weighed prepared Gooch crucible using gentle suction. Wash the cuprous oxide thoroughly with distilled water at about 60° C., then with 10 ml. cold 95% alcohol and finally with 10 ml. of ether making certain that the filter is below the boiling point of alcohol or ether when used. Dry for 30 minutes in an oven at 105° C., cool in a desiccator and weigh as cuprous oxide.

### Calculations

Refer to the amount of dextrose equivalent to the weight of cuprous oxide in Munson and Walker's Tables.* Usually the dextrose is given in milligrams. The weight dextrose should be placed on a gram basis by shifting the decimal point 3 places to the left.

*Result A:* 1. $\text{Weight of Starch} = \text{Weight of Dextrose} \times 0.90$

2. $$\%\ \text{Starch} = \frac{\text{Weight of starch Eq. 1} \times 500}{\text{Weight of original sample}}$$

*Result B:* 3. $\text{Weight of Starch} = \text{Weight of Dextrose} \times ??^{**}$

4. $$\%\ \text{Starch} = \frac{\text{Weight of starch Eq. 3} \times 500}{\text{Weight of original sample}}$$

** Actual factor determined on sample of starch (dry basis).

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* Methods of Analysis, A.O.A.C., 5th Edition 1940, pages 671 to 676; Handbook of Chemistry and Physics, 24th Edition, pages [illegible] to 1407; J. Am. Chem. Soc. *28*, 663, 1906.