and sometimes mysterious art to an increasingly exact science capable of precise physical and chemical control from raw materials to finished lubricants.

Grease lubricants are primarily used in those applications where oils are unsatisfactory because of seepage and leakage. Because greases possess the characteristics of better adherence and resistance to seepage or leakage, they are also becoming increasingly preferred to oils in many applications wherein frequent replenishing is necessary when oil is used, but where such relubrication is inefficient or impractical. Greases are accordingly finding increased applications where performance for long periods without attention for shut-downs and relubrication is desired.

The future trends in grease lubricants may accordingly be summarized as:

1. Increasing importance in the over-all field of lubrication.
2. Development of improved greases having combined properties of high melting points, good water resistance, and exceptional stability for long service under severe conditions of load, temperature, and environment.
3. Improved methods of production including continuous rather than batch manufacture, mechanical homogenization and dispersion, etc.
4. Emphasis on the purity, composition, and stability of the fats and fatty acids utilized in making the metal soap bases.

With further respect to the fatty materials used in lubricating greases, it is well known that trace impurities of iron, copper, nickel, and lead in fats or fatty acids will act as active oxidation catalysts in greases exposed to elevated temperatures. Since oxidation stability of grease lubricants is receiving much attention, increased interest in fats containing minimums of catalytic impurities is indicated.

Because of the emphasis on temperature stable and oxidation resistant greases, much attention is also being given to oxidation inhibitors and similar additives. Study of the natural inhibitors present in many natural fats and the development of improved or stabilized fats is accordingly of much interest to grease manufacturers.

Lastly, grease chemists are paying considerable attention to metallic soaps prepared from substantially single component fats or fat acids instead of the heterogeneous mixtures existing in natural fats. There thus seems to be a fertile field for cultivation in fats and acids of more uniform and definite composition than the natural fats and roughly fractionated constituents therefrom.

The grease industry will certainly be interested in developments and improvements in fat technology along the lines mentioned and will welcome the cooperation of fat processors in the constant effort to produce better lubricants.

Acknowledgment

REFERENCES

1. "Grease Production and Fat-Fatty Acid Consumption by the Lubricating Grease Industry," by Sydney Bevin and C. W. Georgi, The Institute Spokesman, 7, No. 12, March, 1944.
2. "Structure of Lubricating Greases," by B. B. Farrington and W. N. Davis, Industrial & Engineering Chemistry, 28, No. 4, 414-416 (April, 1936).
3. "Metallic Soaps," Mallinckrodt Chemical Works, St. Louis, Mo. (1946).
4. U. S. Patent Reissue 22,299, April 13, 1943. C. E. Earle.
5. "The Effect of Fatty Acid Molecular Weight on Lithium Greases," The Institute Spokesman 10, No. 4, July, 1946.
6. U. S. Patents 2,033,148 (March 10, 1936) and 2,154,383 (April 11, 1939). T. F. Ott and P. S. Clarke.

Report of the Glycerine Analysis Committee
October, 1946

THE Glycerine Analysis Committee has conducted collaborative analyses by three methods on three samples of glycerine and two types of organic impurities most frequently found in commercial glycerine products. The analytical methods investigated were:

1. Apparent Specific Gravity—Pycnometer Method 25°/25°C.
2. Moisture by Karl Fischer Method.
3. Determination of Glycerol by Oxidation with Periodic Acid.

As a result of these studies your committee recommends adoption of the procedures listed above, and herein described in detail, as tentative methods of the Society. The specific gravity method includes the table prepared by Bosart and Snoddy for conversion of apparent specific gravity into percent glycerol.

Preparation of Samples

Sample 1-A was a commercial C. P. glycerine distilled from selected salt crude and believed to be of high purity. Samples 1-B and 1-C were prepared from 1-A by dilution with about 5 and 12% distilled water.

Sample 2-A was a commercial trimethylene glycol. Such a product may be expected to contain normally about 1% glycerol. Sample 2-B was a crude polyglycerol, chiefly the dimer. From the mode of preparation, and data collected during the process, it was believed to contain about 20% glycerol. Samples 2-C and 2-D were prepared by addition of 80% 1-A to 20% 2-A, and 80% 1-A to 20% 2-B, respectively.

Periodic Acid Method

A summary of the analyses reported by eight members of the committee is shown in Tables I and II. No difficulty was reported in the analysis of samples 1-A, 1-B, and 1-C. Samples 2-A and 2-B gave some trouble, chiefly in selection of proper size of sample. Polyglycerols apparently are oxidized to some extent by periodic acid, but without production of formic acid which results from the oxidation of glycerol. Trimethylene glycol reduces periodic acid, but to a somewhat smaller extent. In the presence of considerable oxidizable impurities insufficient periodic acid may be left to accomplish the desired oxidation of glycerol itself unless the sample size is held to a smaller weight than is indicated by note 6 of the method. This trou-

TABLE I

Commercial C. P. Glycerines of Varying Water Content

Sample No.	1-A			1-B			1-C		
% Apparent Glycerol from	Sp. Gr.	Moisture	Periodic Acid	Sp. Gr.	Moisture	Periodic Acid	Sp. Gr.	Moisture	Periodic Acid
Pohle	95.8	95.8	96.3	91.17	91.1	91.55	84.35	84.4	84.6
Parsons	95.9	95.75	95.95	91.2	91.15	91.0	84.4	84.45	84.5
Luckow	....	....	96.00	....	....	90.63	....	....	83.73
Bennett	95.82	95.63	96.12	91.11	91.18	91.42	84.26	84.24	84.42
Whyte	95.45	95.36	95.47	91.12	91.00	91.00	84.41	84.13	84.19
Van Zile	95.6	95.2	95.45	90.85	90.65	90.45	84.1	83.75	84.0
Andrews	95.76	95.83	96.43	91.00	91.14	91.64	84.19	84.47	85.10
Colt	95.70	95.65	95.9	91.13	91.05	91.25	84.32	84.25	84.6
Average	95.72	95.60	95.95	91.08	91.04	91.12	84.29	84.24	84.40

ble is not encountered in the analysis of reasonably pure samples. Two methods for controlling size of sample have been suggested by members, and they will doubtless be the subjects of further investigation by the committee.

TABLE II

% Apparent Glycerol by Periodic Acid Method In Presence of Common Impurities

	Commercial Trimethylene Glycol	Crude Diglycerol (About 20% Glycerol)	80% 1-A 20% 2-A	80% 1-A 20% 2-B
Sample No.	2-A	2-B	2-C	2-D
Pohle	1.05	20.2	77.6	81.3
Parsons	0.86	19.6	76.5	80.4
Luckow	0.97	19.15	76.11	80.27
Bennett	1.17	22.46	77.27	80.31
Whyte	1.06	19.65	76.64	79.93
Van Zile	1.15	19.2	75.85	79.7
Andrews	0.99	20.01	76.68	80.77
Colt	......	......	76.85	80.7
Average	1.04	20.04	76.69	80.42
Calculated from 80% 1-A + 20% 2-A			76.97	......
Calculated from 80% 1-A + 20% 2-B			......	80.77

The committee checked selection of 5.4 and 6.2 pH as endpoints in titration of blanks and oxidized samples respectively. One member prefers a pH for both about 0.4 lower than these prescribed values but his experience is believed to be abnormal. The periodic acid method is regarded as a useful addition to our analytical repertoire. In the words of the Swift and Company chemists, who worked out its details,— "This method has served and is serving the excellent purpose of making possible the accurate determination of glycerol in the presence of impurities which interfere with other procedures. The authors do not propose to submit it as a substitute for either the dichromate or acetin methods but rather as an added tool to fill a previous gap."

Moisture by Fischer Method

Details of the method were furnished by Swift and Company Research Laboratories. Several members employed a closed system with mechanical stirring and a potentiometric titration apparatus. While it is not our intention to preclude the use of such excellent equipment, the method, as written with visual endpoint, is regarded as satisfactory except for samples dark in color.

Specific Gravity Method

The method is essentially that of Procter and Gamble Company. Conversion of specific gravity to glycerol by use of the table is obviously applicable to samples in which water is the only impurity.

H. C. BENNETT   W. D. POHLE
E. W. COLT   B. S. VAN ZILE
R. N. DUPUIS   L. K. WHYTE
E. R. LUCKOW   J. T. R. ANDREWS,
L. B. PARSONS   *chairman*

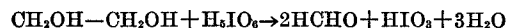# Determination of Glycerol by Oxidation With Periodic Acid

Scope

Applicable to any glycerine solution. Especially useful in the analysis of samples containing oxidizable organic impurities and certain hydroxylated compounds which interfere with the dichromate and acetin procedures. This method is more specific for glycerol than any other recognized procedure.
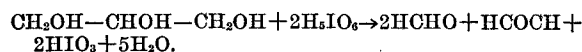
Reference

Bradford, Pohle, Gunther, and Mehlenbacher, Oil & Soap *19*, 189-93 (Nov. 1942).

Principle

Investigators have shown that at room temperatures, periodic acid oxidizes polyalcohols containing two or more adjacent hydroxyl groups, splitting the compound between the carbon atoms attached to these hydroxyl groups. The end hydroxyl groups are oxidized to aldehydes and the inner HCOH groups are oxidized to formic acid. For example, the reaction with ethylene glycol can be represented by the equation—

$$CH_2OH-CH_2OH+H_5IO_6 \rightarrow 2HCHO+HIO_3+3H_2O$$

and the reaction with glycerol is

$$CH_2OH-CHOH-CH_2OH+2H_5IO_6 \rightarrow 2HCHO+HCOOH+2HIO_3+5H_2O.$$

Trimethylene glycol and other polyalcohols in which the hydroxyl groups are not adjacent are not oxidized at normal temperatures. In the reaction with glycerol, the betahydroxyl group is oxidized to formic acid and the adjacent groups are oxidized to formaldehyde. Therefore, the amount of formic acid produced is a measure of the glycerol present.

Reagents and Solutions

Periodic acid solution—Dissolve 20 grams of periodic acid in one liter of water. If the solution is not clear, filter through sintered glass filter. Store the solution in a dark, glass stoppered bottle. The oxidizing power of this solution decreases slowly with time. A blank must be run each day analyses are made.

Sodium hydroxide—0.1250 N. Standardize with potassium acid phthalate, using phenolphthalein indicator.

Methyl red—Dissolve 0.1 gram in 100 ml. 95% alcohol.

Sodium hydroxide—Approximately 0.05 N.

Sulfuric acid—Approximately 0.2 N.

Apparatus

Fifty-ml. burette, accurately calibrated.

Fifty-ml. pipette, accurately calibrated.

Variable speed stirrer.

Glass electrode pH meter.

Procedure

The amount of excess periodic acid in the glycerol-periodic acid reaction is critical. Therefore it is neces-

sary to know the approximate concentration of the sample to be analyzed. Sometimes trial tests must be made to locate the approximate range. Refer to Table I for the size sample to be weighed.

TABLE I

Weight of Sample to be Taken for Analysis Based Upon the Glycerine Content

% Glycerol in product to be analyzed	Size of sample to be selected if entire sample is used for analysis	Size of sample to be selected if same is to be diluted to 2 liters and 50 ml. withdrawn for analysis	Size of sample to be selected if same is to be diluted to 500 ml. and 50 ml. withdrawn for analysis
100	.1200 to .1500	4.8 to 6.0	
90	.1330 to .1670	5.3 to 6.7	
80	.1500 to .1880	6.0 to 7.5	
70	.1720 to .2180	6.9 to 8.6	
60	.2000 to .2500	8.0 to 10.0	
50	.2400 to .3000	9.6 to 12.0	
40	.3000 to .3750	12.0 to 15.0	
30	.4000 to .5000	16.0 to 20.0	
25	.4800 to .6000		4.0 to 5.0
20	.6000 to .7500		4.8 to 6.0
15	.8000 to 1.000		6.0 to 7.5
10	1.200 to 1.5		8.0 to 10.0
8	1.5 to 1.88		12.0 to 15.0
7	1.72 to 2.18		15.0 to 18.8
6	2.0 to 2.5		
5	2.4 to 3.0		
4	3.0 to 3.75		
3	4.0 to 5.0		
2	6.0 to 7.5		
1	12.0 to 15.0		
0.9	13.3 to 16.7		
0.8	15.0 to 18.8		
0.7	17.2 to 21.8		
0.6	20.0 to 25.0		
0.5	24.0 to 30.0		
0.4	30.0 to 37.5		
0.3	40.0 to 50.0		
0.2	60.0 to 75.0		

All weighing must be accurately and rapidly made. Weighings are conveniently made in a small beaker, pouring from this into a flask or beaker.

If the glycerine content is 30-100%, weigh into a 2-liter volumetric flask, make to volume with distilled water, mix well, pipette 50 ml. into a 600-ml. beaker, and cover with a watch glass.

If the glycerine content is 10-30% follow the same procedure, using a 500-ml. volumetric flask instead of a 2-liter.

If the glycerine content is below 10% pour directly from weighing beaker into 600-ml. beaker, add about 50 ml. distilled water, and cover with a watch glass.

Add one drop of the methyl red indicator to the sample in the 600-ml. beaker, acidify with the 0.2 N sulfuric acid. Neutralize with the 0.05 N sodium hydroxide to the yellow color which corresponds with a pH of about 6.2. If the color of this solution interferes with the detection of the color changes of the indicator, use the pH meter and in this case adjust to the pH to which the final titration is to be carried. Add with a pipette 50 ml. periodic acid, shake gently to effect thorough mixing, cover with a watch glass and allow to stand for one hour at room temperature. At the same time prepare a blank containing only 50 ml. water, with no glycerol, and run along with the sample.

After allowing the sample to stand for one hour, dilute to 240-250 ml. and titrate with the 0.125 N sodium hydroxide using a glass electrode pH meter to determine the endpoint. The sample should be agitated with a stirrer during the titration. The blank is titrated to a pH of 5.4 and the sample to a pH of 6.2. If the actual fraction of sample being titrated contains more than 0.1 gram salt, titrate to the corrected endpoint shown in Table II.

TABLE II

The Endpoint for the Alkali Titration of Solutions Containing Sodium Chloride

Grams of Sodium Chloride in the sample titrated	pH to which the titration should be carried *
0.0	6.20
0.1	6.20
0.2	6.19
0.3	6.17
0.4	6.16
0.5	6.15
1.0	6.08
2.0	6.02
4.0	5.96
6.0	5.85
10.0	5.75
15.0	5.63
20.0	5.54
25.0	5.46

When the titration approaches the endpoint add the alkali in increments of 0.1 ml. to and past the equivalence point. Record the volume of sodium hydroxide and the corresponding pH when within 0.1-0.2 ml. of the endpoint and do likewise after passing the endpoint. From these data, calculate the actual alkali required to titrate to the proper endpoint.

Calculation of endpoint

V_1 = Volume of alkali before endpoint—pH_1 corresponding to V_1

V_2 = Volume of alkali after endpoint—pH_2 corresponding to V_2

V_x = Volume of alkali at endpoint—pH_x corresponding to V_x and obtained from Table II

$$V_x = V_1 + (V_2 - V_1)\ \frac{pH_x - pH_1}{pH_2 - pH_1}$$

Calculation of percentage of glycerol

X = Ml. sodium hydroxide to titrate sample

Y = Ml. sodium hydroxide to titrate blank

N = Normality of sodium hydroxide

W = Weight of sample

$$\% \text{ Glycerol} = \frac{(X-Y) \times N \times 0.092094 \times 100}{W}$$

Notes on Method

1. If the sample contains an appreciable amount of buffering material, always adjust the pH with pH meter to the endpoint to which the sample will be titrated. In some instances the buffering action may be sufficiently great to tend to prevent good reproducibility of results.

2. In order to produce accurate results extreme care is necessary in all manipulations. The burette should be read to 0.01 ml., using a magnifier. This analysis must be carried out in an atmosphere free from acid or alkaline vapors. A suitable temperature is from 25 to 31°C.

3. When analyzing samples of salt containing more than 2% glycerol, dissolve in 50 ml. of water. For samples containing less than 2% glycerol, dissolve in 100 ml. of water.

4. Use 25 grams of salt for all samples containing less than 0.5% glycerol.

5. Cork should not be used to stopper any of the flasks used in this determination or in any other way be allowed to come in contact with any of the materials used in or for the analysis.

6. The titration for the formic acid (titration of the sample minus the titration of the blank) must be not less than 30% and not more than 40% of the blank titration. This is to insure the proper ratio of periodic acid to sample, that is, the correct excess of reagent.

7. Very careful manipulation is required throughout the periodic acid method. This is readily appreciated when it is realized that the glycerol in the sample is equivalent to approximately 10 ml. of the standard alkali and that 0.01 ml. of the standard alkali is equivalent to 0.1% of the actual glycerol. The determination must be carried out

in an atmosphere free from acid or alkaline vapors which might be absorbed and influence the titration. In some cases, the buffering action of some samples, especially glycerine foots, has been found to be so great that it was impossible to obtain accurate results.

The determination of glycerol in widely varying samples has been found to agree with 0.4% or less of the actual glycerol present. The glycerol content of crude glycerines as determined by the periodic acid method has, in general, been found to be higher than that as determined by the acetin procedure.

Method for the Determination of Moisture In Glycerine Using the Fischer Reagent

Scope

Applicable to distilled glycerines. May be applied to many organic solvents which show no interfering reactions or colors.

Reagents

A. Fischer Reagent:

1. Preparation:

   502 grams anhydrous pyridine, Barrett's—2A—refined or Eastman Kodak No. 214-H.
   102.5 grams sulfur dioxide, anhydrous.
   202 grams iodine, reagent quality.
   1000 ml. anhydrous methanol, du Pont's or equivalent.

   Discharge the SO_2 from a drum through a tube into and beneath the surface of the pyridine. This mixture is stable and may be prepared and held as a stock solution. When ready to use, add methanol and cool under tap water. Add the iodine slowly with constant shaking and cooling. This reaction will get out of hand if allowed to proceed too rapidly. Allow the reagent to stand for 24 hours before standardizing or using.

   For storage of reagent and methanol solvent a bottle and burette assembly, such as Scientific Glass Apparatus Company, No. J-740, is recommended.

2. Standardization:

   a. Pipette two or three 10-ml. portions of the methanol-water standard into 125-ml. Erlenmeyer. Keep stoppered until ready to titrate.

   b. Fill Fischer reagent burette and discard first 2 to 3 ml. at tip of burette.

   c. Titrate standard with reagent. Rotate flask to keep color dispersed. The endpoint is the change from yellow to red and the red should persist for at least 5 minutes when the flask is immediately stoppered after reaching the endpoint. Add reagent in increments of 0.2 ml. when nearing the endpoint.

   d. Each ml. reagent in grams of $H_2O =$

   $$\frac{M(\text{from C-3-C})}{\text{Ml. reagent required}} = F$$

   Reagent must be restandardized daily because there is usually a slow but gradual decrease in its water equivalence.

B. Methanol-Water Standard:

1. Weigh accurately 10.000 grams of distilled water and pour into a 1-liter volumetric flask. Rinse the beaker thoroughly with anhydrous methanol and pour rinsings into flask.

2. Add sufficient anhydrous methanol to bring the volume to 1 liter. Each ml. of this solution then contains 0.0100 gram of water in addition to the original water content of the methanol. Protect this standard from change in concentration by any positive means.

3. Determine total water content of methanol standard as follows:

   a. Titrate 10-ml. portion of the standard with Fischer Reagent=A.

   b. Titrate 10-ml. portion of the methanol used in preparation of the standard with Fischer Reagent=B.

c. $M = 0.1 + \dfrac{0.1B}{A-B}$ = total grams of water per 10 ml. of standard

Example: A=20
B=1.5
M=0.1081

This factor must be established with each lot of standard immediately after preparation. With this information, it is not essential that the same methanol be used in the standard as is used for solvent.

Caution:

All reagents and solution must be kept well protected by an efficient desiccant to prevent water absorption from the atmosphere.

C. Methanol Solvent

Anhydrous methanol, maintained in a bottle-burette assembly.
Anhydrous methanol absorbs water rapidly so it must always be well protected.

Procedure

1. Titrate 10 ml. of the solvent with the reagent to determine the blank.

2. Weigh into a 125-ml. Erlenmeyer flask, a sample of such size that from 10 to 45 ml. of reagent will be required, but not to exceed 10 grams.

3. Add 10 ml. of solvent and titrate with Fischer Reagent until color changes to red. This color should persist for at least 5 minutes.

4. % water in glycerine equals

   $$\frac{(\text{titration of sample—titration of blank}) \ 100 \ F}{\text{Weight of sample}}$$

Note

1. When sample contains large amounts of water, weigh an appropriate amount into a volumetric flask, make to volume with anhydrous methanol, mix and titrate a convenient aliquot.

2. Glycerine absorbs water very rapidly. Keep the sample protected from the atmosphere at all times.

3. This procedure, employing a visual endpoint, is not intended to preclude the use of any satisfactory apparatus, of which several are available, in which the endpoint is obtained potentiometrically. The use of a closed system, with mechanical stirring, is to be encouraged, though it is not essential to accurate analysis. The method as prescribed will yield satisfactory results on any distilled glycerine not too dark in color to obscure the visual endpoint.

Apparent Specific Gravity at 25°/25°C:

Pycnometer Method

Scope

Applicable to any liquid or solution, but intended primarily for distilled glycerines.

A. *Apparatus*

1. Pycnometer, or specific gravity bottle, of the Leach type of 25, or preferably 50-ml. capacity. The thermometer should be graduated to 0.2°C. and should be calibrated against a Bureau of Standards certified thermometer at 25.0°C. The range of the thermometer is preferably from about 10°C. to 40°C.

2. Bath—A well insulated bath capable of holding from four to eight pycnometers. A convenient size holding four instruments is twelve inches in diameter and seven inches high. It is made of tin or lead clad sheet metal and insulated with one-inch cork. A small motor-driven pump to circulate the water is desirable, though hand or motor stirring will suffice. Automatic thermostatic control is desirable but not essential. The bath is adjusted and maintained at 25°±0.1°C. by manual or automatic thermal regulation. A deeper bath to provide for greater

TABLES FOR SPECIFIC GRAVITY AND PER CENT GLYCEROL

Glycerol Per cent	Apparent Specific Gravity				True Specific Gravity			
	15/15°C.	15.5/15.5°C.	20/20°C.	25/25°C.	15/15°C.	15.5/15.5°C.	20/20°C.	25/25°C.
100	1.26557	1.26532	1.26362	1.26201	1.26526	1.26501	1.26331	1.26170
99	1.26300	1.26275	1.26105	1.25945	1.26270	1.26245	1.26075	1.25910
98	1.26045	1.26020	1.25845	1.25685	1.26010	1.25985	1.25815	1.25655
97	1.25785	1.25760	1.25585	1.25425	1.25755	1.25730	1.25555	1.25395
96	1.25525	1.25500	1.25330	1.25165	1.25495	1.25470	1.25300	1.25140
95	1.25270	1.25245	1.25075	1.24910	1.25240	1.25215	1.25045	1.24880
94	1.25005	1.24980	1.24810	1.24645	1.24975	1.24950	1.24780	1.24615
93	1.24740	1.24715	1.24545	1.24380	1.24710	1.24685	1.24515	1.24350
92	1.24475	1.24450	1.24280	1.24115	1.24445	1.24420	1.24250	1.24085
91	1.24210	1.24185	1.24020	1.23850	1.24185	1.24155	1.23985	1.23825
90	1.23950	1.23920	1.23755	1.23585	1.23920	1.23895	1.23725	1.23560
89	1.23680	1.23655	1.23490	1.23320	1.23655	1.23625	1.23460	1.23295
88	1.23415	1.23390	1.23220	1.23055	1.23390	1.23360	1.23195	1.23025
87	1.23150	1.23120	1.22955	1.22790	1.23125	1.23095	1.22930	1.22760
86	1.22885	1.22855	1.22690	1.22520	1.22860	1.22830	1.22660	1.22495
85	1.22620	1.22590	1.22420	1.22255	1.22595	1.22565	1.22395	1.22230
84	1.22355	1.22325	1.22155	1.21990	1.22330	1.22300	1.22130	1.21965
83	1.22090	1.22055	1.21890	1.21720	1.22060	1.22030	1.21885	1.21695
82	1.21820	1.21790	1.21620	1.21455	1.21795	1.21765	1.21595	1.21430
81	1.21555	1.21525	1.21355	1.21190	1.21530	1.21500	1.21330	1.21165
80	1.21290	1.21260	1.21090	1.20925	1.21265	1.21235	1.21065	1.20900
79	1.21015	1.20985	1.20815	1.20655				
78	1.20740	1.20710	1.20540	1.20380				
77	1.20465	1.20440	1.20270	1.20110				
76	1.20190	1.20165	1.19995	1.19840				
75	1.19915	1.19890	1.19720	1.19565	1.19890	1.19865	1.19700	1.19540
74	1.19640	1.19615	1.19450	1.19295				
73	1.19365	1.19340	1.19175	1.19025				
72	1.19090	1.19070	1.18900	1.18755				
71	1.18815	1.18795	1.18630	1.18480				
70	1.18540	1.18520	1.18355	1.18210	1.18515	1.18495	1.18330	1.18185
69	1.18260	1.18240	1.18080	1.17935				
68	1.17985	1.17965	1.17805	1.17660				
67	1.17705	1.17685	1.17530	1.17385				
66	1.17430	1.17410	1.17255	1.17110				
65	1.17155	1.17130	1.16980	1.16835	1.17135	1.17110	1.16960	1.16815
64	1.16875	1.16855	1.16705	1.16560				
63	1.16600	1.16575	1.16430	1.16285				
62	1.16320	1.16300	1.16155	1.16010				
61	1.16045	1.16020	1.15875	1.15735				
60	1.15770	1.15745	1.15605	1.15460	1.15750	1.15725	1.15585	1.15445
59	1.15490	1.15465	1.15325	1.15185				
58	1.15210	1.15190	1.15050	1.14915				
57	1.14935	1.14910	1.14775	1.14640				
56	1.14655	1.14635	1.14500	1.14365				
55	1.14375	1.14355	1.14220	1.14090	1.14360	1.14340	1.14205	1.14075
54	1.14100	1.14080	1.13945	1.13815				
53	1.13820	1.13800	1.13670	1.13540				
52	1.13540	1.13525	1.13395	1.13265				
51	1.13265	1.13245	1.13120	1.12995				
50	1.12985	1.12970	1.12845	1.12720	1.12970	1.12955	1.12830	1.12705
49	1.12710	1.12695	1.12570	1.12450				
48	1.12440	1.12425	1.12300	1.12185				
47	1.12165	1.12150	1.12030	1.11915				
46	1.11890	1.11880	1.11760	1.11650				
45	1.11620	1.11605	1.11490	1.11380	1.11605	1.11595	1.11475	1.11365
44	1.11345	1.11335	1.11220	1.11115				
43	1.11075	1.11060	1.10950	1.10845				
42	1.10800	1.10790	1.10680	1.10575				
41	1.10525	1.10515	1.10410	1.10310				
40	1.10255	1.10245	1.10135	1.10040	1.10240	1.10235	1.10125	1.10030
39	1.09985	1.09975	1.09870	1.09775				
38	1.09715	1.09705	1.09605	1.09510				
37	1.09445	1.09435	1.09335	1.09245				
36	1.09175	1.09165	1.09070	1.08980				
35	1.08905	1.08895	1.08805	1.08715	1.08895	1.08885	1.08790	1.08705
34	1.08635	1.08625	1.08535	1.08445				
33	1.08365	1.08355	1.08270	1.08190				
32	1.08100	1.08085	1.08005	1.07925				
31	1.07830	1.07815	1.07735	1.07660				
30	1.07560	1.07545	1.07470	1.07395	1.07550	1.07535	1.07460	1.07385
29	1.07295	1.07285	1.07210	1.07135				
28	1.07035	1.07025	1.06950	1.06880				
27	1.06770	1.06760	1.06690	1.06625				
26	1.06510	1.06500	1.06435	1.06370				
25	1.06250	1.06240	1.06175	1.06115	1.06240	1.06230	1.06165	1.06110
24	1.05985	1.05980	1.05915	1.05860				
23	1.05725	1.05715	1.05655	1.05605				
22	1.05460	1.05455	1.05400	1.05350				
21	1.05200	1.05195	1.05140	1.05095				
20	1.04935	1.04935	1.04880	1.04840	1.04930	1.04925	1.04875	1.04830
19	1.04685	1.04680	1.04630	1.04590				
18	1.04435	1.04430	1.04380	1.04345				
17	1.04180	1.04180	1.04135	1.04100				
16	1.03930	1.03925	1.03885	1.03850				
15	1.03675	1.03675	1.03635	1.03605	1.03670	1.03670	1.03630	1.03600
14	1.03425	1.03420	1.03390	1.03360				
13	1.03175	1.03170	1.03140	1.03110				
12	1.02920	1.02920	1.02890	1.02865				
11	1.02670	1.02665	1.02640	1.02620				
10	1.02415	1.02415	1.02395	1.02370	1.02415	1.02410	1.02390	1.02370
9	1.02175	1.02175	1.02155	1.02135				
8	1.01935	1.01930	1.01915	1.01900				
7	1.01690	1.01690	1.01675	1.01660				
6	1.01450	1.01450	1.01435	1.01425				
5	1.01210	1.01205	1.01195	1.01185	1.01205	1.01205	1.01195	1.01185
4	1.00965	1.00965	1.00955	1.00950				
3	1.00725	1.00725	1.00720	1.00710				
2	1.00485	1.00485	1.00480	1.00475				
1	1.00240	1.00240	1.00240	1.00235				

bulk of water, thus holding fluctuations in temperature to a minimum, is desirable, but not essential. If this type of bath is employed, the pycnometers should rest on a false bottom of wire mesh or perforated metal and at a depth such that immersion of the pycnometer will be to the neck of the instrument. Any suitable thermometer, graduated to 0.1° or 0.2°C., and accurately calibrated, may be used to register the temperature of the bath.

3. A sensitive analytical balance and set of weights accurately calibrated. Weighings must be made to nearest milligram.

B. *Procedure*

1. Calibration of Pycnometer—Clean and dry the pycnometer assembly thoroughly and obtain its weight to nearest 0.001 gram. Fill it with freshly boiled distilled water which has been cooled to about 20°C. Insert the thermometer and place in bath with cap of side arm removed. Allow the temperature to rise until the temperature of the pycnometer thermometer and that of the bath are identical, i.e. 25.0°±0.1°C. This may require from 20 to 30 minutes. When this condition has been obtained, remove excess water from the tip of side arm and replace cap. Remove pycnometer from bath and dry thoroughly with a clean towel, avoiding too brisk rubbing which tends to induce a static charge. Weigh pyconometer and contents, dry again with towel and reweigh to nearest milligram.

Weight of pycnometer + water — weight of pycnometer = weight of water in pycnometer at 25.0°C.

2. Determination of Glycerine Specific Gravity—The glycerine sample must be free from air bubbles. If not, they may be removed by warming and allowing them to rise to the surface, or this action may be hastened by centrifuging. During all of these operations precautions must be taken against loss of moisture from the sample by

evaporation or gain in moisture because of its well known hygroscopic nature. Cool the glycerine to about 20°C. and fill the cleaned, dried and tared pycnometer by pouring the sample carefully down the side of the neck until both side arm and neck overflow. Insert the thermometer carefully and examine for air bubbles. If none are visible, place the assembly, with side arm cap removed, in the bath and bring to 25°C. temperature exactly as in B-1. Carefully remove excess glycerine from tip of side arm, replace cap, dry and weigh as described in B-1.

Weight of pycnometer + sample — weight of pycnometer = weight of sample in pycnometer at 25°C.

C. *Calculation*

Apparent specific gravity at 25°/25°C.=

$$\frac{\text{Weight of sample in pycnometer at } 25°C.}{\text{Weight of water in pycnometer at } 25°C.}$$

Notes

1. For a given pycnometer, once the water weight is accurately established, the calibration need not be repeated unless some change in the weight of the pycnometer assembly occurs. It is strongly recommended that the weight of each pycnometer, dry and empty, be taken before each determination. This precaution is an insurance against change in weight by chipping or accidental interchange of caps, etc.

2. For conversion of apparent specific gravity of distilled glycerines from 25°/25°C. to other temperatures and for translation of specific gravity into percent glycerine, the tables prepared by Bosart and Snoddy, Ind. & Eng. Chem., *19*, pp. 506 at seq. (April, 1927) shall be employed. These tables also permit calculation of true specific gravity and density from apparent specific gravity. It is obvious that these tables are applicable only to solutions of glycerol in which water is the only impurity.

The Effect of Some Inorganic Salts in Dilute Solution on the Formation of Calcium and Magnesium Soaps[1]

GILBERT D. MILES and JOHN ROSS
Colgate-Palmolive-Peet Company, Jersey City, N. J.

BUILDERS, in the jargon of the soap technologist, are materials which are considered to aid detergent action and foaming properties of soap solutions. Alkali carbonates, phosphates, and silicates of various complexity are commonly used as builders.

The most direct means of aiding the detergency of soaps in hard water is the prevention of the formation of calcium or magnesium soaps. This paper is concerned with this function of builders. No attempt has been made to measure the influence builders have on detergency except insofar as can be surmised from their effectiveness in preventing direct loss of soluble soaps to form calcium and magnesium soaps.

The reaction mixture from calcium and magnesium salts, builders, and a commercial soap or even a relatively pure soap, is a complex colloidal system. As long as excess soap is present as a surface active agent, complete precipitation from these dilute solutions has not been possible. Consequently, any direct analysis of the reaction products has not been permissible, and indirect evidence must be resorted to.

Using an indirect method based on the foam stability of the total soluble soap present, we have attempted to interpret these reactions on the basis of solubility products.

In a previous paper (1) it was shown that the foam stability of solutions of soaps of pure fatty acids is a function of concentration and pH, and for each concentration of each pure soap there was a pH range within which the foam stability was at a maximum. It was also observed that for the soaps of the straight chain saturated fatty acids studied, the presence of dispersed calcium or magnesium soaps in the solutions did not affect the foam stability of the remaining soap. This was not the case for all the soaps of unsaturated fatty acids. For example, sodium oleate solutions showed reduced foam stability in the presence of the corresponding calcium soap.

These observations have been utilized in the method followed in the present investigation. For each pure soap, we have selected a concentration which is sufficiently critical with respect to foam stability in the pH range for maximum foam so that the pour foam test used (2) permits the measurement of a reduction in soap concentration of about 10 per cent. When