2. The SO_3 type of sulfonation requires no aging or digestion period and no drowning steps to remove spent acid. This simplification results in a significant reduction in the time required to complete the operation. Depending upon the particular process and equipment used, this reduction can be as great as 60%.
3. The increased activity and lower salt content resulting from straight SO_3 sulfonation offer an obvious advantage to the manufacturer or potential manufacturer of liquid formulations. It has also been reported by some observers that the sulfonate odors are improved as a result of SO_3 sulfonation. Color of sulfonate is equal to that from oleum sulfonation.
4. Smaller volume equipment is required for a given quantity of alkylate.
5. The use of a higher sulfonation temperature than with oleum facilitates heat removal.

Disadvantages

1. The equipment required for the vaporization and handling of SO_3 is more extensive than that for handling oleum. This may be at least partially offset by reduction in equipment required for spent acid removal.
2. The high sulfonic acid viscosity necessitates more efficient heat transfer equipment.
3. The pH drift of the neutralized product from sulfonation without an acid heel might result in the requirement of a reneutralization step.

Acknowledgment

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The Determination of Small Amounts of Trimethylene Glycol in High Gravity and Chemically Pure Glycerine

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IN 1919 Rojahn (1, 2) prepared tables for determining trimethylene glycol in high gravity and C. P. glycerines based upon the specific gravity and the water content. These tables are useful although it has long been recognized that they are slightly in error (3) due to the lack of sufficiently pure material and the shortcomings of the available methods. For this reason and because more exact data were available on the specific gravity of glycerol (4) and the more accurate Fischer volumetric method for water (5), it seemed appropriate to bring this phase of glycerine analysis up to date.

Analyses of sweet water concentrates have shown the presence of from 5 to 10% propylene glycol and 50 to 60% trimethylene glycol (6). These two compounds have very similar boiling points so that some propylene glycol will no doubt be present in high gravity and C. P. glycerine whenever trimethylene glycol is present. Refined glycerine usually does not contain a determinable amount of trimethylene glycol. Chemical methods like those of Pohle and Mehlenbacher (6) are satisfactory and generally applicable to samples containing more than 3% propylene and trimethylene glycols but cannot be considered suitable for smaller amounts. In the lower range the specific gravity and water methods must be employed.

The glycerol content of C. P. and high gravity glycerines can be determined most accurately by the specific gravity method (2) and somewhat less accurately from the water content determined by the Fischer volumetric method (5). When the sample contains only water and glycerol, 100 — % water equals the glycerol, and these results agree with the glycerol found by the specific gravity method. When the sample also contains trimethylene glycol, the percentage of glycerol found by the two methods does not agree, and the exact glycerol content is uncertain. Lawrie (3) gives a table for determining trimethylene glycol in high gravity glycerine from the specific gravity and water content of the sample. However it covers only the range of 0 to 3.0% trimethylene glycol when the water content varies between 0 and 2.5% so that the limited range for moisture will not include C. P. glycerines which contain approximately 5% water. Therefore a procedure was sought which would not require a table and could be applied to most of the conditions that are encountered in C. P. and high gravity glycerines.

The procedure which was investigated involved measuring the specific gravity at 25°/25°C. (8) and the water content by the Fischer volumetric method (5). Trimethylene glycol, including similar constituents, is calculated from these measurements and the change in specific gravity (0.0023) caused by a change of 1% in trimethylene glycol content. The factor (0.0023) was calculated from data in Lawrie's book (7) and was checked experimentally. The trimethylene glycol is calculated as follows:

A = % water by A.O.C.S. Fischer volumetric method (5)
B = specific gravity at 25°/25°C. by A.O.C.S. Method (8)
C = % glycerol from water content = 100-A
D = specific gravity at 25°/25°C. of a glycerol-water solution with a glycerol content of C.

$$\text{Trimethylene glycol, }\% = (D-B)/0.0023 = E$$

$$\text{Glycerol, }\% = 100-(A+E)$$

TABLE I

Properties and Composition of Compounds Used in Preparing Known Mixtures

Compound	Sp. gr. 25°/25° C.	Water, %	Trimethylene glycol, %	Propylene glycol, %	Glycerol, %
C. P. glycerin[a]	1.2492	4.9	0.0	0.0	95.0
High gravity glycerine (containing trimethylene glycol)[b]	1.2583	0.5	1.1	....	98.4
Trimethylene glycol (6)	1.0533	0.0	100.0	0.3	0.0
Propylene glycol (6)	1.0377	0.0	0.0	100.2	0.0

[a] Glycerol from specific gravity measurements.
[b] Trimethylene glycol and glycerol from method described above.

TABLE II

Analyses of Known Mixtures Prepared from Compounds Listed in Table I

Sample	Trimethylene Glycol and Propylene Glycol, %[a] Present							
	Water, %		Trimethylene glycol	Propylene glycol	Total	Found	Glycerol, %	
	Present	Found					Present	Found
C. P. glycerine								
1	5.0	4.9	0.6	....	0.6	0.6	94.4	94.5
2	4.9	4.8	1.1	....	1.1	1.1	94.0	94.1
3	4.9	4.8	2.8	....	2.8	2.8	92.3	92.4
4	4.9	4.8	....	0.9	0.9	1.1	94.2	94.1
5	4.9	4.8	0.9	0.9	1.8	2.0	93.3	93.2
6	4.9	4.7	....	2.5	2.5	2.8	92.6	92.5
7	4.8	4.8	2.6	2.5	5.1	5.3	90.1	89.9
8	4.8	4.8	4.9	....	4.9	4.7	90.3	90.5
High gravity glycerine (containing trimethylene glycol)								
9	0.5	0.5	1.5	0.3	1.8	1.9	97.7	97.6
10	0.5	0.5	2.0	....	2.0	2.0	97.5	97.5
11	0.5	0.5	3.6	....	3.6	3.7	95.9	95.8
12	0.5	0.5	1.1	0.9	2.0	2.1	97.5	97.4
13	0.5	0.5	2.0	0.9	2.9	2.9	96.6	96.6
14	0.5	0.5	1.1	2.5	3.6	3.7	95.9	95.8

[a] The amount of trimethylene glycol present is normally several times the amount of propylene glycol.

Analyses of sweet water concentrates (6) have shown that propylene glycol is present along with trimethylene glycol, and it is difficult to prepare trimethylene glycol free from propylene glycol by distillation from sweet water concentrates. Thus whenever trimethylene glycol is present in C. P. or high gravity glycerines, some propylene glycol may also be present. In the above formula the two glycols are calculated as trimethylene glycol since it is generally present in quantities several times larger than the propylene glycol.

The accuracy of the proposed method was investigated by analyzing known mixtures of glycerol, trimethylene glycol, propylene glycol, and water. The properties and compositions of the compounds used in preparing the known mixtures are given in Table I.

The results of the tests on the known mixtures are given in Table II.

Trimethylene glycol and similar constituents calculated as trimethylene glycol were determined within 0.2% of the amount present. This is greater precision than can be expected from tests between different laboratories. The between laboratories variation expressed as the standard deviation is ± 0.13 for the specific gravity method and ± 0.20 for the Fischer volumetric method (9). Under these conditions single tests can be relied upon with 95% confidence only when the value for trimethylene glycol is more than 0.5%. The certainty of smaller amounts might be established by using the average of 2, 3, 4, or more analyses.

Summary

A method has been developed for the determination of small amounts of trimethylene glycol together with similar constituents in C. P. and high gravity glycerines. The various constituents in known mixtures were determined within 0.2% of the amount present. The method is simple and accurate and utilizes proven A.O.C.S. Methods.

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The Function of Fatty Acids in Metallic Soaps[1]

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METALLIC soaps are compounds of metals and fatty acids, which are characterized by water repellency, solubility in some organic liquids, extremely small particle size, and purity of the metal content.

Although the cation or metal part of these compounds plays an important role in such uses as driers, ceramic glazes, and mildewproofing, the fatty acid fraction has a more important function because it governs the physical properties, such as melting point, particle size, fluffiness, unctuousness, and solubility.

In view of the fact that most of the industrial uses of metallic soaps depend on their physical characteristics, it is apparent that the choice of the fatty acid is an important one. The method of manufacture and the application of metallic soaps to the production of waterproofing compounds, lubricants, paints, varnishes, lacquers, inks, rubber, plastics, and waxes to a large extent depends on the fatty acid employed.

As a rule low titer, liquid fatty acids produce metallic soaps which have low melting points and good solubility while the higher titer fatty acids produce soaps which have rather high melting points, poorer solubility, and greater water repellency.

The methods of manufacture of metallic soaps are definitely related to the melting point of the fatty acid and the metallic soap resulting from it. With liquid fatty acids it is easier to react them with oxides, carbonates, or acetates. The metallic soaps from these fatty acids also have relatively low melting points which allow them to be melted and dried

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