cellent wetting, detergent and softening properties."

Conclusion

From the foregoing, it is right easily seen that the sulphonated compounds have a close relation to the textile industry, especially that section which deals with scouring, dyeing, mercerizing, printing and finishing of yarns and fabrics.

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REPORT OF THE SOAP ANALYSIS COMMITTEE

By M. L. SHEELY, CHAIRMAN

SOAP SECTION

A Report Read Before the 8th Fall Meeting, A.O.C.S.

Publication of Complete Set of Methods of Analysis

At the meeting of the Soap Analysis Committee a year ago it was decided to adopt as the official methods of analysis of the society the Standard Methods of the American Chemical Society with certain exceptions. These exceptions included:

1. Alternative method for moisture in highly filled soaps.
2. Revised method for unsaponified and unsaponifiable.
3. Revised method for rosin.
4. Minor changes in some methods and correction of all reference notes.

It was further decided to republish the complete methods with the above noted changes and this was accordingly done in the May, 1934, issue of OIL AND SOAP.

Rosin Determination

During the course of the past year the committee has been engaged in a further study of the revised method for the determination of rosin in soap. The method is known as the Wolff Method, Modified (OIL AND SOAP, 11, 90, 1934), and consists in a double esterification of the fatty acids from the soap, the remaining detail being practically the same as the original Wolff method. The final result is obtained by a titration of the unesterified rosin and calculated to rosin by a factor corresponding to a molecular weight of 346.

Four samples, containing 0, 5%, 20% and 35% rosin in fatty acids were distributed among all members of the committee. The complete tabulated results are shown in Table I.

For the purpose of showing the effect of the second esterification, both first and second esterification results are shown. It is obvious from the table that the method still cannot be considered anything but approximate, although in general the results indicate fairly close agreement among the ten laboratories collaborating. The average of all results on the sample containing no rosin is 2.39%, the low and high figures being 1.40 and 3.32% respectively. From a comparison of these figures with results obtained by the committee last year using the same method but a different sample of fatty acid, it is apparent that the magnitude of the blank determinations may depend to some extent on the type of fatty acids involved. The committee is of the opinion that, as a result of this positive blank, a note to the effect that in all cases where less than 5% rosin is found the actual presence or absence of rosin should be checked by means of a qualitative test.

From a study of the results on the samples containing definite amounts of added rosin, varying from 5% to 35%, it is noteworthy that the method gives somewhat high results on samples containing up to and including 20% rosin, whereas at 35% rosin content slightly low results are the rule. The average of the 10 laboratories' results on the sample containing 5% rosin is 6.89%; on the sample containing 20% rosin, 20.51%; on the sample containing 35% rosin, 34.01%. At first thought, it would appear that a practical solution of the problem would be the application of a decreasing factor as the percentage of rosin increases. When such a sliding correction is applied to the present results, the percentages check fairly close with the actual percents of rosin present. However, when similar corrections are applied to last year's results the agreement would not be considered good. Consequently, the committee does not feel that it has sufficient data available to establish a table of corrections which will universally apply to all fatty acid-rosin mixtures.

In this connection it should be noted that the molecular weight of rosins will vary widely and as a consequence the titration factor used will influence results correspondingly. The rosin used in these samples was H grade having an acid number of 164, corresponding to a molecular weight of 342.1 or a N/2 factor of 0.171. However, the factor 0.173 was used in all the tabulated figures since this factor is considered to be a good average of the common rosins on the market. A meeting of the committee was held October 10, 1934, and data of the A. S. T. M. Committee D-17 on the constants of rosin were presented as follows:

	Gum Rosin		Wood Rosin	
		(Aver.)		(Aver.)
Acid number	158-172	165.0	150-158	154
Molecular weight	355.1-326.2	340.0	374.0-355.1	364.3
N/2 factor	0.1776-0.1631	0.1700	0.1870-0.1776	0.1822

This would indicate that the N/2 factor may vary from 0.163 to 0.187 or approximately a 14% variation. Consequently, it would seem inadvisable to strive for greater accuracy than this in any method involving the molecular weight of rosin.

Results by Mr. Long using methyl alcohol instead of ethyl alcohol were also submitted as follows:

% Rosin	1st Est.	2nd Est.
0	3.11	2.25
5	5.88	4.67
20	19.72	18.51
35	32.70	30.62

These results are not as satisfactory as those reported by the official method, although it should be noted that German practice specifies methyl alcohol as the esterifying medium.

Several members of the committee were of the opinion that the method in its present form is not detailed enough to follow closely and inasmuch as this may account in part for the variations noted, a recommendation to revise the procedure is recorded as a part of this report. The revised detailed method is as follows:

Summarizing, the committee wishes to make the following recommendations:

1. *Rosin Method.* This method is further revised to describe in more complete detail the actual manipulations of the method. No major changes of the procedure have been made since it is felt that the basic method is better than any heretofore published. The revised detailed method is published as a part of this report and is recommended for adoption as a tentative method.

2. *Factor to Be Used in Converting Silica* (SiO_2) *to Sodium Silicate.*

The factor used in the present methods is 1.26 corresponding to a ratio of Na_2O to SiO_2 of approximately 1:3.85. It was the recommendation of the committee that this factor be changed to 1.308 which, incidentally corresponds to the ratio of Na_2O to SiO_2 in N brand sodium silicate, namely 1:3.25. While it is recognized that

TABLE NO. 1—RESULTS OF CO-OPERATIVE WORK ON SAMPLES FOR ROSIN DETERMINATION (1934)
WOLFF METHOD MODIFIED

	Sample No. 1 0.0% Rosin		Sample No. 2 5.0% Rosin		Sample No. 3 20% Rosin		Sample No. 4 35% Rosin	
Laboratory	1st Est.	2nd Est.	1st Est.	2nd Est.	1st Est.	2nd Est.	1st Est.	2nd Est.
1	3.21%	2.26%	7.84%	6.68%	23.00%	21.53%	37.85%	35.40%
2	3.03	2.06	8.17	7.28	22.38	20.52	36.57	34.56
3 (a).......	2.9	1.4	...	5.7	20.9	18.6	34.6	31.7
(b).......	4.2	2.1	7.9	6.7	21.9	19.7	36.2	34.0
4	3.42	2.42	7.86	6.92	21.94	21.11	36.31	34.60
5	4.3	2.6	8.4	7.4	22.6	21.4	37.4	36.1
6 (a).......	3.24	2.99	8.48	8.56	22.75	20.93	36.67	31.66
(b).......	3.80	3.03	8.04	7.52	22.32	20.76	35.81	33.13
7	3.01	2.15	7.77	6.22	21.91	19.75	36.49	32.59
8	5.32	3.32	7.58	6.80	22.88	19.16	36.72	33.93
9	....	1.50	....	5.68	.....	22.16	.....	35.15
10	3.25	2.9	8.4	7.25	22.7	20.5	37.2	35.05
High		3.32		8.56		22.16		36.10
Low		1.40		5.68		18.6		31.66
Average ..		2.39		6.89		20.51		34.01

N/2 Factor used in all tests, 1 cc. = 0.173 rosin.

(a) 1st report.

(b) 2nd report.

October 11, 1934.

other ratio silicates are also in use, it was felt that this ratio is more in line with that of the silicates in common use in the industry.

3. It was further recommended that the committee should undertake as its next major studies the following:

a. Determination of free alkali in soap.

b. Volatile hydrocarbons in soap by the method suggested by Mr. Long.

The active members of this committee are as follows:

C. P. Long, Procter & Gamble Co., Ivorydale, Ohio.

R. C. Newton, Swift & Co., Chicago, Illinois.

L. F. Hoyt, Larkin Co., Inc., Buffalo, N. Y.

R. B. Trusler, Davies-Young Soap Co., Dayton, Ohio.

M. A. Beck, Van Camp Oil Prod. Co., Louisville, Ky.

W. A. Peterson, Colgate-Palmolive-Peet Co., Jersey City, N. J.

H. P. Trevithick, New York Produce Exchange, New York, N. Y.

J. M. Burmaster, The Southern Cotton Oil Co., New Orleans, La.

H. C. Bennett, Los Angeles Soap Co., Los Angeles, Cal.

H. E. Cutts, Stillwell & Gladding, Inc., New York, N. Y.

F. W. Smither, Bureau of Standards, Washington, D. C.

J. E. Doherty, Lever Bros. Co., Cambridge, Mass.

M. L. Sheely, Chairman, Armour Soap Works, Chicago, Ill.

Determination of Rosin in Soap

Revised October 11, 1934

ROSIN — Wolff's Method, Modified. *Preparation of fatty and rosin acids.* Dissolve 5 g. (±0.01 g.) of the sample in 100 to 200 cc. of hot distilled water in a 250 cc. beaker, add a slight excess of dilute sulfuric acid (1:1), heat on the steam bath until the fatty acids collect in a clear layer, cool to room temperature, transfer to a separatory funnel, washing the beaker free from fatty and rosin acids with small portions of ethyl ether, adding the ether washings to the separatory funnel. Add about 50 cc. of ethyl ether to the separatory funnel which is then given a whirling movement to dissolve the fatty and rosin acids. After the solid acids are dissolved in the ether, allow the aqueous solution to stand for at least five minutes. Draw off the aqueous portion into another separatory funnel designated as No. 2, add about 30 cc. of ethyl ether to funnel No. 2, shake vigorously, allow to stand for at least five minutes and then draw off the aqueous portion into another separatory funnel designated as No. 3. Transfer the ether extract to separatory funnel No. 1. Wash the aqueous liquid three more times, using for each washing about 30 cc. of ethyl ether. Then discard the aqueous liquid and add the ether washings to funnel No. 1. Now add about 50 cc. of distilled water to the collective ether extract in funnel designated as No. 1, shake vigorously and allow to stand for five minutes. Draw off the aqueous solution into another separatory funnel. Repeat this operation, combining the water washings until the ether is free from acid, using methyl orange as indicator. Add 50 cc. of ethyl ether to the water washings, shake the separatory funnel vigorously and allow to stand for at least five minutes. Draw off and discard the aqueous solution and wash the ether layer with small portions of distilled water until free from acid, using methyl orange as indicator. Transfer the total ether extract to a 250 cc. Erlenmeyer flask, evaporate off the ether slowly on a steam bath and dry one hour in an oven at 105° C., cool and dissolve in 20 cc. of absolute alcohol.

First Esterification: Add 10 cc. of a solution of one volume of concentrated sulfuric acid (Sp.Gr. 1.84) and four volumes of absolute ethyl alcohol, bring to boil on the steam bath and boil exactly four minutes under a reflux condenser. Remove from the steam bath, add to the liquid about five times its volume of 7 to 10 per cent sodium chloride solution. Transfer to a separatory funnel, washing the Erlenmeyer flask with small portions of ethyl ether, the ether washing being added to the aqueous solution in the separatory funnel. Add about 30 cc. of ethyl ether to the separatory funnel, shake vigorously, and allow to stand for at least five minutes. Draw off the aqueous solution into another separatory funnel designated as No. 2. Add about 30 cc. of ether to funnel No. 2, shake vigorously, allow to stand for at least five minutes and then draw off the aqueous layer into another separatory funnel designated as No. 3. Repeat the extraction of the aqueous solution three more times. Then discard the aqueous liquid and add the combined ether solutions to separatory funnel No. 1. Add 50 cc. of sodium chloride solution (7-10%) to the ether extract in funnel No. 1, shake vigorously and allow to stand for at least five minutes. Draw off the aqueous solution into another separatory funnel. Repeat this operation until the washings are neutral to methyl orange, all salt water washings being combined. Add 50 cc. of ether to the washings in the separatory funnel. Shake the funnel vigorously, allow to stand for at least five minutes and then draw off and discard the aqueous salt solution. Add 50 cc. of sodium chloride solution and wash the ether layer until the aqueous salt solution is neutral to methyl orange. Dry the ether extract by the addition of about 3 g. of anhydrous sodium sulphate to the separatory funnel, filter into a 250 cc. Erlenmeyer flask and evaporate off the ether slowly on the steam bath to dryness.

Second Esterification: Cool and dissolve the residue in 20 cc. of absolute ethyl alcohol and then proceed as above under "First Esterification." Titrate rosin or rosin soap as desired. (1 cc. N/2 alkali = 0.173 g. rosin or 0.188 g. rosin soda soap.) If the true fatty acid soap is desired, subtract the rosin soap from the total anhydrous soap obtained under C-III.

The above method gives somewhat high results on all low percentages of rosin. On the higher percentages, it is approximately correct. The committee recommends in all cases where the rosin content is found to be less than 5%, the actual presence or absence of rosin should be checked qualitatively by the Liebermann-Storch test, which is as follows:

1 to 2 cc. of the sample of fatty acids are shaken in a test tube with 5 to 10 cc. C.P. acetic anhydride with gentle warming on a steam bath. After cooling, pour 1 to 2 cc. in a white porcelain dish and allow a drop or two of sulfuric acid (Sp.Gr. 1.53) to run down the side of the vessel. If rosin is present, a fugitive violet coloration changing to a brownish tinge is immediately produced at the margin of contact of the reagents. The test should be checked with a sample of fatty acids to which a small amount of rosin has been added.

(Sulfuric acid of 1.53 Sp.Gr. is prepared by diluting 34.7 cc. of concentrated C.P. sulfuric acid (Sp.Gr. 1.84) with 35.7 cc. of distilled water.)