Notes On The McNicoll Method For Determination Of Rosin In Soap

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THE two methods most commonly employed in the determination of rosin in soap are the Wolff[1] and Twitchell Methods[2]. The Wolff Method has been adopted as the official A. O. C. S. procedure after a cooperative study by the Soap Analysis Committee. It has been generally recognized that both of these methods are rather cumbersome and time consuming. Moreover, neither method gives results which are strictly correct for all percentages covered over a wide range. Although the McNicoll[3] Method was recommended some seventeen years ago, it appears that very little attention has been given to it in this country.

The McNicoll Method is based on the fact that aliphatic acids are converted into methyl esters by naphthalene-β-sulphonic acid in anhydrous methyl alcohol solution, whereas rosin remains unchanged. The equation for the reaction may be written as follows:

$$RCOOH + CH_3OH \rightleftharpoons RCOOCH_3 + H_2O$$

As is evident, this is a reversible reaction. Hence, a dehydrating agent must be present in the system to throw the reaction to the right. The main difference between the McNicoll Method and the Twitchell and Wolff Methods is that in the McNicoll Method, naphthalene-β-sulphonic acid is used as the dehydrating agent whereas in the Twitchell Method hydrochloric acid is used, and in the Wolff Method concentrated sulfuric acid is used.

The detailed description of the method as we employed it in our work is as follows:-

Reagents — (1) a solution of naphthalene-β-sulphonic acid (40 g.) in pure dry methyl alcohol (1 litre); (2) N/5 alcoholic potassium hydroxide solution.

Method — Approximately 30 gms. of the soap to be tested are dissolved in hot water, acidified with dilute (1:4) sulfuric acid and boiled gently to split the soap. The complete sample is then transferred to a separatory funnel and the fatty acids are washed free of mineral acids with hot water. The washed fatty acids are then filtered and dried. About 2 gms. of the fatty acids thus prepared are weighed into a 300 ml. Erlenmeyer flask, dissolved in 20 ml. of the naphthalene-β-sulphonic acid reagent and boiled gently under a reflux condenser for 30 minutes. A few small glass beads are added to insure regular ebullition. A blank test should be carried out at the same time with 20 ml. of the reagent alone. The contents of both flasks are then cooled and titrated immediately with N/5 alcoholic potassium hydroxide using 0.5 ml. of 0.5 per cent alcoholic solution of phenolphthalein as the indicator. In calculating per cent rosin in the fatty acids, 346 is used as the mean molecular weight.

Calculations:

$$\frac{(\text{Titra. of Sample} - \text{Titra of Blank}) \times \text{Normality} \times 0.346 \times 100}{\text{Weight of Sample}} = \% \text{ Rosin}$$

The McNicoll Method as published by the British Subcommittee in their report No. 5[5] specifies that the calculations be based on a molecular weight of 326 for the rosin acids. They calculate the rosin acids as percentage of the total fatty matter and subtract 1 per cent from the percentage so obtained. The calculations of all our work were based on a molecular weight of rosin of 346 and no deductions were made from our actual results.

Based on our experience, the McNicoll Method has a distinct advantage over the Twitchell and Wolff Methods in that it is more accurate and much quicker and easier to run. In fact, the McNicoll procedure parallels very closely a saponification determination both in manipulation and in time consumed. It requires about 45 minutes to an hour to make a test. The Wolff and Twitchell Methods are considerably more involved, requiring more manipulation and handling of solutions and necessitate between 3½ and 4 hours to obtain results.

The Wolff Method (one and two esterification) and the McNicoll Method were employed in testing seven samples of prepared tallow fatty acids containing known amounts of rosin. As a matter of expediency and to minimize the number of manipulations, the samples were prepared by adding accurately weighed amounts of rosin to tallow fatty acids instead of preparing soaps containing these various percentages of rosin. The data obtained are shown below in TABLE I. All results in this paper are calculated on a mean molecular weight of 346 which is considered to be a good average of the common rosins on the market[4].

In addition to the set of results shown in TABLE NO. I, we have tried out the McNicoll Method on four other groups of fatty acid-rosin combinations. . Each set of tests was performed by a different

TABLE NO. I

Actual Per Cent Rosin Present		Wolf Method 1 esterification	Wolf Method 2 esterifications	McNicoll Method
1%		4.97%	3.87%	1.67%
		5.01	4.04	1.32
	Average	4.99%	3.96%	1.49%
2		5.93%	4.95%	2.43%
		5.92	4.83	2.38
	Average	5.93%	4.89%	2.41%
5		8.45%	7.71%	5.20%
		8.52	7.76	5.11
	Average	8.49%	7.74%	5.16%
10		13.26%	11.81%	10.10%
		13.27	11.67	10.11
	Average	13.27%	11.74%	10.11%
20		22.78%	21.40%	20.58%
		22.77	21.17	20.24
	Average	22.78%	21.29%	20.41%
30		32.52%	30.86%	30.68%
		32.54	30.88	30.00
	Average	32.53%	30.87%	30.34%
40		42.09%	40.49%	41.34%
		41.74	40.43	40.44
	Average	41.92%	40.46%	40.44%

It will be noted that except for the lower rosin concentration (1.5%) there is very little variation between the McNicoll figures and the known rosin contents.

operator and in every instance the results obtained emphasized the accuracy and the merits of the McNicoll Method.

The above data as well as previous work indicates that the accuracy of the Wolff Method increases as the percentage of rosin is increased. The deviations from the actual rosin contents obtained by the three methods are recorded in TABLE II.

*The deviations obtained on the Twitchell Method as shown in TABLE No. II were obtained on a separate series of rosin-tallow mixtures and indicate that the accuracy of the Twitchell Method decreases with the increase in percentage of rosin.

The McNicoll Method as described by the British subcommittee in their report Report No. 5, calls for the use of 20 ml. of a solution of naphthalene-β-sulphonic acid made up 40 grams in 1 liter of absolute methyl alcohol. Tests were also conducted to determine the effect of a more concentrated solution of naphthalene-β-sulphonic acid than called for in the method. It was thought that possibly a higher concentration solution of the reagent might act more efficiciently at the lower rosin percentages. The higher concentration was made up by dissolving 40 grams of the reagent in 800 ml. of methyl alcohol and using 25 ml. instead of 20 ml. as called for in the method. This modification gave results shown in TABLE NO. III.

Figures in TABLE NO. III indicate that it is not necessary to use a higher concentration of reagent than called for in the method since results are in close agreement using either concentration of reagent.

Tests were conducted to determine whether the grade of rosin used in the soap had any effect on the McNicoll determination. Accordingly, a pale grade of gum rosin (WW) and a dark grade of rosin (H) were incorporated in amounts of 20% and 35% in tallow fatty acids. McNicoll determinations are indicated in TABLE NO. IV.

From the results obtained in TABLE IV it appears that the grade of rosin does not influence the accuracy of this method.

All of the work thus far has been conducted on samples containing gum rosin. Due to the fact that wood rosins are sometimes used in place of gum rosin in the manufacture of soap, we have

TABLE NO. II

Actual Per Cent Rosin Present	McNicoll Method Deviation from Actual	Wolff Method Deviation from Actual	Twitchell Method* Devia. from Actual
1%	0.49% High	2.96% High	0.11% High
2	0.41 "	2.89 "	0.18 "
3	—	—	0.08 Low
5	0.16 "	2.74 "	0.82 "
10	0.11 "	1.74 "	1.28 "
15	—	—	2.10 "
20	0.41 "	1.29 "	—
25	—	—	4.08 "
30	0.34 "	0.87 "	—
40	0.89 "	0.46 "	—

TABLE NO. III

Actual Per Cent Rosin Present		Regular Concentration of Reagent	Increased Concentration of Reagent
0		2.05%	1.60%
		1.68	1.22
	Average	1.86%	1.41%
5		6.60%	6.55%
		6.68	6.31
	Average	6.64%	6.43%
20		21.98%	21.22%
		21.04	21.35
	Average	21.51%	21.28%
35		36.39%	36.05%
		36.37	36.33
	Average	36.39%	36.19%

TABLE NO. IV

Actual Per Cent Rosin Present	WW Rosin % Rosin Found	H Rosin % Rosin Found
20%	20.75%	20.19%
	20.65	20.00
	20.70%	20.10%
35	35.88%	35.55%
	35.65	35.21
	35.77%	35.38%

TABLE NO. V

Actual Per Cent K Wood Rosin	% Rosin Found
20%	20.76%
	21.02
	20.89%
35	36.25%
	36.36
	36.31%

TABLE NO. VI

Per Cent Rosin Actual	% Rosin Found (Before Saponification)	% Rosin Found (After Saponification)
20%	21.98%	20.40%
	21.04	20.02
	21.51%	20.21%
35	36.39%	35.05%
	36.37	35.50
	36.38%	35.28%

TABLE NO. VII

	% Rosin McNicoll Method	% Rosin Wolff Method
Soap No. 1	24.54%	25.32%
Soap No. 2	41.42	41.80
Soap No. 3	35.90	35.00
Soap No. 4	29.15	30.70
Soap No. 5	28.15	28.15

made up samples combining wood rosin with tallow fatty acids and tested them with results as shown in TABLE V.

The indications are that *after* saponification, the results obtained are about a percent lower than *before* saponification.

Five Brands of yellow laundry soaps purchased on the market were tested by the Wolff and McNicoll Methods. Data are indicated in TABLE VII. The results by the McNicoll Method are in line with those obtained by the Wolff Method.

The figures as shown in TABLE V indicate that the McNicoll Method is equally as accurate for wood as for gum type rosin.

In making all of the foregoing tests, the various samples were prepared by adding the desired quantity of rosin to pure tallow fatty acids. Inasmuch as the rosin undergoes no saponification in this manner, it was thought advisable to determine the effect of saponification of the rosin-tallow mixtures on the McNicoll determination. Hence, two samples containing definite amounts of rosin-tallow fatty acids were completely saponified, then split with the mineral acid and the mixed fatty acids separated by washing, filtering and drying. The results of the McNicoll rosin determination before and after saponification are indicated in TABLE NO. VI.

On the basis of the data obtained, the following facts have been established with regard to the McNicoll Method.

1. It is rapid and easy to run; a decided advantage in this respect over both the Wolff and Twitchell Methods.
2. It produces reliable and consistent results.
3. It is not appreciably influenced by the grade or type of rosin contained in the soap.
4. It yields satisfactory results when applied to laundry soaps containing rosin.

References:
1. Chem. Ztg., 38, 369-70, 382-3, 430 (1914); C. A., 8 (1914) 2495
2. J. Soc. Chem. Ind., 804 (1891)
3. J. Soc. Chem. Ind., 124T (1921)
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5. Analyst, V.62, (1937)

THE IODINE VALUE OF TUNG OIL

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THE fact that the apparent iodine value of Tung oil varies with the conditions under which it is determined was apparently first noted in 1909 by Boughton[1] who mentions temperature, time of reaction, concentration of reagent and weight of oil as controlling factors. Notable attempts at standardising the test include that of A. C. Chapman[2], who proposed the use of 0.1 gram of oil dissolved in 20 ml. of purified carbon tetrachloride with 30 ml. of 0.2—N Wijs solution and allowed the reaction to proceed for three hours in the dark.

Thus it will be seen that the difficulties of the problem have been recognised for about 30 years and standardisation of the test in one form or another has been practised for nearly as long.

Evidence in our possession in 1930, but not mentioned in our paper, indicated clearly that the "instantaneous" figure obtained from the 30 minute and 3 hour figures is independent of the excess of reagent and of the temperature of reaction within the limits of ordinary laboratory temperatures.

Reference to our paper will show that there is additional proof that the "instantaneous" figure corresponds to the two double bond absorption, since otherwise percentages of elaeostearic acid calculated from it and the Tom's bromine value[5] would not correspond with those obtained by our polymerisation method.

We therefore feel that the following method, which has stood the test of eight years' application, is preferable to that put forward by von Mikusch:

It has however been realized only in comparatively recent years — as J. D. von Mikusch points out in this journal[3] — that such standardisations gave empirical figures which did not correspond to any definite degree of halogenation.

We ourselves were concerned some eight years ago with the problem discussed by von Mikusch at a time when we were searching for methods of determining elaeostearic acid in the oil. It is interesting to note that we approached the problem on similar lines and, although we did not discuss the effect of temperature, we dealt with the effect of varying the times of contact of oil and different halogenating reagents in a paper read before the Society of Public Analysts in 1930.[4]

The conclusions we then came to are now confirmed bv von Mikusch[3] who agrees that the iodine value corresponding to absorption by exactly two of the three double bonds of elaeostearic acid may theoretically be obtained by absorption for zero time.

In our experiments we found that certain irregularities developed when the time of reaction was limited to less than 5 minutes. On this account we preferred to make two determinations — one of 30 minutes duration, and the other of 3 hours — and to extrapolate from these to the figure for zero time. Alternatively we found that a single figure obtained with the quantities of reagents described by Chapman[2] and only 20 minutes time of reaction is sufficiently close to the "instantaneous" figure for practical purposes.

METHOD

Weigh out 0.08 to 0.10 gram of filtered tung oil into a 300 ml. flask. Add 20 ml. of cp. chloroform or carbon tetrachloride and 30 ml. of 0.2-N Wijs solution.