THE DETERMINATION OF ROSIN ACIDS IN FATTY ACIDS BY THE REFRACTOMETER

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ROSIN possesses a refractive index which is much higher than that of any other stock regularly used for soap making. For this reason the presence of small amounts of rosin can be readily detected in mixtures of rosin and fatty acids by the refractometer.

This paper is primarily confined to the analysis of mixtures of rosin and fatty acids of known refractive indices. In these cases, applicable chiefly to the manufacturing control of soaps containing rosin, very accurate results can be obtained. The error which seems to be inherent in the Wolff method can be avoided.

Experimental

Several series of mixtures of known proportions of tallow and rosin were prepared. The tallow used in these experiments contained about .1 per cent free fatty acids. The rosin was of the W. G. grade. The refractive indices of the tallow and the mixtures were obtained, after which they were saponified, acidified, and a reading of the mixed acids taken. These mixtures were prepared in the following manner: A master solution of rosin in tallow was first prepared containing the percentages of rosin required by the highest one of the series desired. This in no case was above 40 per cent of rosin. To a weighed amount of this rosin solution the necessary amount of tallow to obtain the desired concentration was added.

TABLE I

Per Cent Rosin Added	Refractive Index at 48° C. Before Saponification	Refractive Index at 48° C. After Saponification	% Rosin Acids Present After Saponification* (Calculated)
1	2	3	4
10.0	1.4621	1.4532	10.2
12.5	1.4640	1.4553	12.8
16.7	1.4670	1.4590	17.0
20.0	1.4689	1.4614	20.3
25.0	1.4731	1.4660	25.4
33.3	1.4800	1.4732	33.8
40.	1.4847	1.4789	40.5

*The percentage yield of rosin acids from rosin was taken to be 97, that of tallow acids 95.
One per cent of rosin elevates the refractive index of a rosin-tallow mixture to the extent of about .0008.

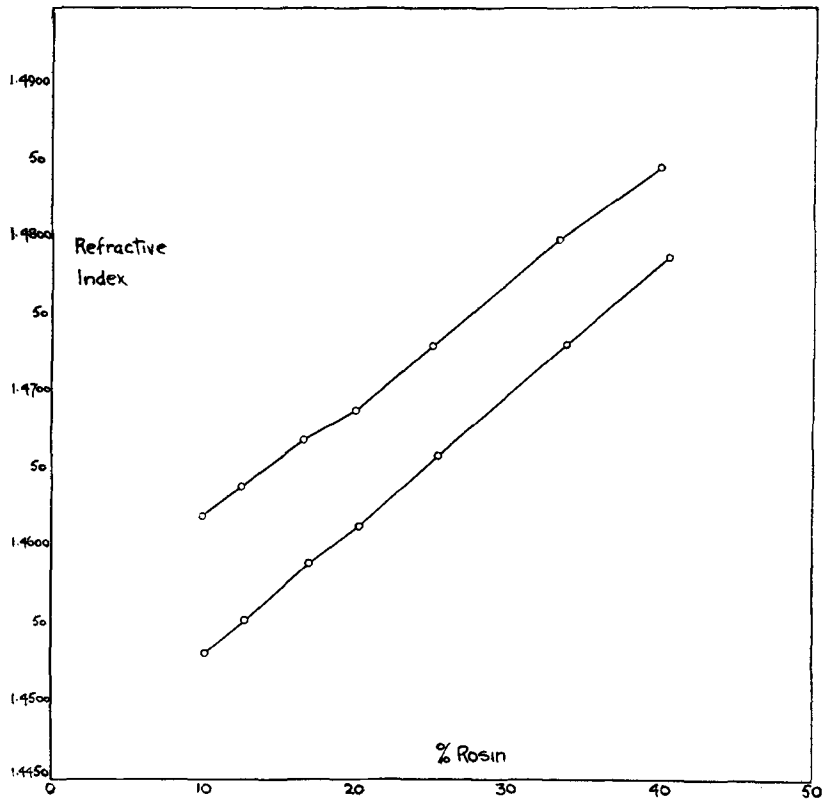

Figure 1—Chart showing refractive indices of tallow-rosin mixtures before and after saponification

First Series

The first series of mixtures contained from 10 to 40 per cent rosin. The readings obtained in this first series of experiments are shown in Table 1 above and also on the chart (Fig. 1). These figures when plotted show the relationship to be almost linear. The upper curve shows the figures obtained before saponification and the lower one those after saponification.

Second and Third Series

Two other series of experiments were carried out. In the first one mixtures were prepared containing .5 per cent of rosin up to and including 10 per cent and a further experiment with mixtures containing from 10 to 40 per cent of rosin inclusive. The figures obtained are shown in table 2 and graphically on the chart (Fig. 2).

It will be noticed that these mixtures were tested for rosin content by the Wolff method. The figures shown in the last column were obtained after the deduction of a blank of 1 cc. from all titrations.

TABLE II

Per Cent Rosin Added	Refractive Index at 48° C. Before Sap.	After Sap.	Per Cent Rosin Acids Calculated on 97-95 Basis	Wolff Method Using 3 Gms.	Modified
1	2	3	4	5	6
0	1.4551	1.4454	0	2.94	0.06
0.50	1.4555	1.4458	0.51	3.34	).46
1.02	1.4559	1.4463	1.04	4.18	.30
2.00	1.4565	1.4471	2.05	4.99	2.11
3.00	1.4572	1.4480	3.07	5.97	3.09
5.00	1.4588	1.4497	5.10	8.13	5.25
7.50	1.4603	1.4516	7.67	10.76	7.88
10.00	1.4621	1.4534	10.20	13.08	10.20
10.00	1.4620	1.4534	10.20	13.03	10.15
15.00	1.4656	1.4573	15.25	18.44	15.56
20.00	1.4692	1.4614	20.30	23.21	20.33
25.00	1.4729	1.4657	25.35	28.58	25.70
30.00	1.4766	1.4702	30.40	33.22	30.34
35.00	1.4803	1.4743	35.45	38.12	35.24
40.00	1.4841	1.4787	40.50	43.13	40.25

By this modification close checks to the amounts actually added can be obtained. Column 5 shows the figures which would be obtained without deduction of this blank. These figures are all about 2.88 per cent too high.

The upper line of the chart shows the figures obtained before saponification and the lower one those obtained after saponification. These curves are not quite linear and deviations from the straight line relationship are probably accounted for by the varying densities of the different rosin-tallow mixtures which produce the same effect on the refractive index as variations in temperature. These figures confirm the findings of the first series of experiments.

As in the previous chart the lower curve approaches the higher one. This is due to the loss of glycerol in decreasing proportion with increase of rosin. The dotted lines on the chart show that they would meet somewhere in the neighborhood of the point which corresponds to 100 per cent rosin indicating a refractive index for rosin of approximately 1.528.

The Method

The method for the determination of rosin acids in mixtures of rosin and fatty acids is based upon the results shown in these two tables. As previously mentioned this method is applicable primarily to the manufacturing control of soaps containing rosin. In actual practice two samples are first obtained. One of these is a sample of the stock before the addition of rosin. This may be either in the form of soap or fat. The other sample is of the rosin which is to be added to the soap. A portion of mixed fatty acids is obtained from the first sample, by acidification in the case of the soap. Fat must, of course, be first saponified and then acidified. A refractometer reading is taken of the mixed fatty acids. A mixture is then prepared (using the mixed fatty acids and the rosin) containing rosin in the actual percentage which is desired in the finished soap. It may be necessary to saponify the mixture after the addition of rosin if in the actual manufacturing process the soap is grained out after the rosin change and if very accurate results are desired, but this would not be necessary for a manufacturing control. A slight correction could be used, however, if considered necessary. The degree of error introduced by not saponifying the mixture will not be more than 3 per cent on the percentage of rosin present.

The mixture is saponified as follows: 30 grams of the mixture is added to 60 grams of a solution of Potassium Hydroxide and glycerin contained in a 300 cc. beaker at 100° C. (250 grams of KOH to 1 liter of glycerin). The whole is heated until complete saponification has taken place, the temperature being kept below 150° C. The soap solution is then diluted to 150 cc. with cold water, 3 drops of Methyl Red introduced and dilute HCl poured in while stirring until the color of the lower layer remains red. The temperature is then allowed to cool to between 30° C. and 35° C., and the whole washed with about 150 cc. of ether in a separatory funnel. The ether layer is then run into a 250 cc. extraction flask and the ether completely evaporated. One to two grams of anhydrous sodium sulphate is then sprinkled into the warm acids to remove water, the whole thoroughly mixed and allowed to stand until clear. The supernatant acids are then poured off through a filter paper into a 50 cc. beaker and heated to about 80° C. for two minutes. The refractive index of this mixture is then determined.

Since it has been established that the percentage of rosin in mixtures of fatty acids and their refractive indices have almost a straight line relationship, from the two figures obtained, a curve is constructed which shows the per-

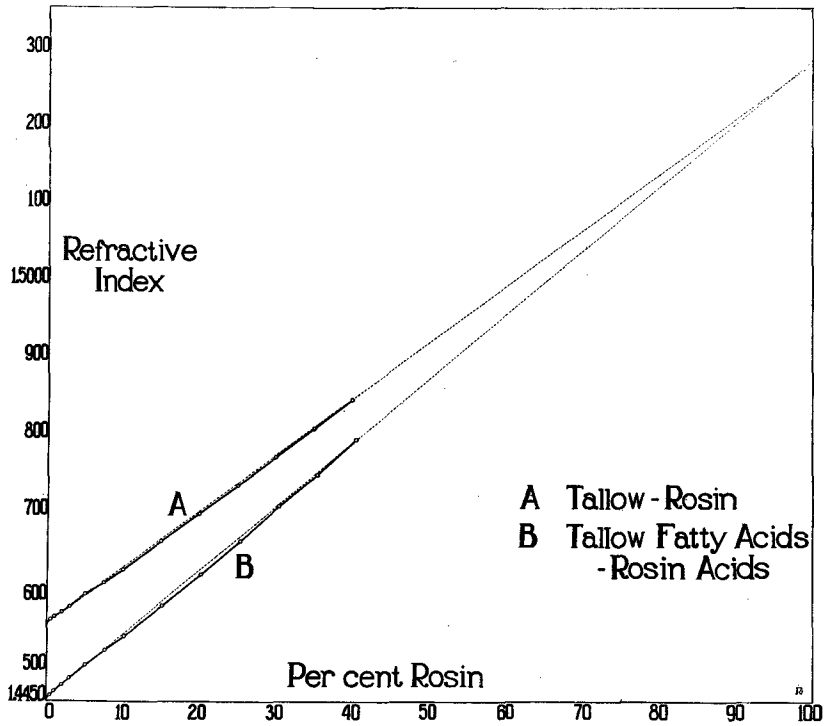

Figure 2—Chart showing refractive indices and precentages of tallow-rosin mixtures before and after saponification revealing almost linear relationship

centage of rosin acids corresponding to the refractive index of the mixture. The index of the fatty acids occupies the zero mark and that of the mixture coinciding with the actual rosin content.

These points are connected by a straight line.

Samples of the product in process after the addition of rosin are acidified (after saponification if necessary), the fatty acids obtained and the refractive index read. The rosin content can then be obtained from the chart. An Abbe refractometer is used to make these tests at a temperature of 48° C.

Test Experiment

Using 2 samples, 1 neutral tallow and the other 25-75 rosin tallow mixture, 7 samples containing various percentages of rosin in tallow were prepared. These samples were tested for rosin content by the refractometer. They were also tested by the modified Wolff method.

TABLE III

	Per Cent Rosin Added	Per Cent by Refractometer	Per Cent by Wolff Method (Modified)
	1	2	3
1.	24.50	24.50	24.21
2.	19.30	19.00	19.06
3.	14.25	14.20	13.91
4.	11.25	11.20	11.04
5.	10.10	9.80	9.98
6.	8.90	8.20	8.65
7.	3.50	3.40	2.74

The percentages actually added are shown in column 1. The results reported after testing by the refractometer are shown in column 2 and the results reported by the Wolff method in column 3.

The curve used in this experiment was constructed on the basis

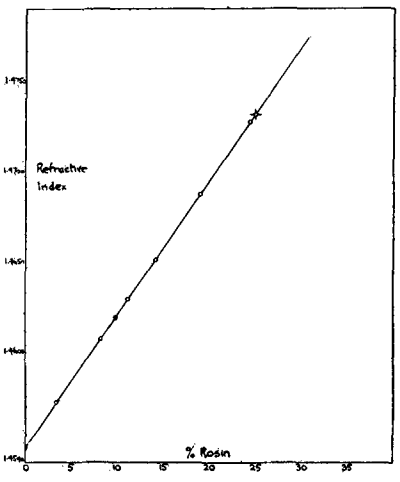

Figure 3—Chart used in test experiment. The straight line is based upon the refractive indices of the neutral tallow (1.4451) *and the 25 per cent rosin-tallow mixture* (1.4732)

of the readings obtained from the two component mixtures—that is, tallow and 25-75 rosin-tallow mixture. Most of the figures are therefore slightly below the theoretical. This, no doubt, is due to the varying density of the solutions. A correction could be applied in cases such as this, but in actual practice—that is, where the method is used as a manufacturing control, the curve would be based upon the fats without rosin and the actually desired percentage of rosin in the final product, therefore, as the samples tested in the course of control would be close to this figure, the error would be reduced to a minimum.

Lewkowitsch mentions[1] that "the presence of free fatty acids in oils and fats appears to affect the refractive index to a marked degree," but the refractive index of either the fatty acids or the neutral fat of a given material is a constant, the refractive index decreasing with increase of free fatty acids. For the purpose of the test experiment neutral tallow was used instead of fatty acids as a matter of convenience. As a matter of interest, however, in these experiments, the indices of the neutral tallow-rosin mixtures were taken and have been shown.

It frequently happens that a boil is made on the nigre of a previous boil which contained rosin. In this case it will be necessary to ascertain the rosin content of the nigre by taking a reading of the separated acids and using the chart which was made for the particular boil to which it belongs. By comparing the rosin content of the nigre with the figure obtained for the new boil previous to the addition of fresh rosin and knowing the weights of both new stock and nigre, a figure can be obtained which will represent fatty stock alone.

Applicability of This Method to Mixtures of Unknown Tallows and Rosin

Although no claims are made as to the reliability of this method other than for the purpose stated above—that is, as a manufacturing control and where actual samples of the components of the mixture can be obtained and refractive indices determined separately, it is possible to obtain approximate figures on samples of soap, the component stocks of which are unknown. In this case it is necessary to determine the possible variation between the different grades of the possible stocks used in the mixture. A number of tests were carried out to determine the variation which might be expected between rosins of different grades and also the variation in the refractive indices of tallows.

Variation in Tallows

The refractive index of the fatty acids of 139 samples of beef tallows of various grades were tested giving an average figure of 1.4463, the highest being 1.4476 and the lowest 1.4451.

It was noticed that the higher grade tallows tend to be lower in refractive index and the lower grade samples higher (this also seems to apply to the various grades of rosin, the lighter grades having a lower refractive index).

Variation of the Refractive Index of Rosin of Different Grades

In order to obtain an idea of what variation might be expected in rosin of different grades, a number of samples were obtained and readings taken. These readings could not conveniently be read directly by the Abbe refractometer at 48° C., but a series of figures were obtained by preparing from these samples 25 per cent rosin-tallow mixtures. The detailed figures appear in the following table.

TABLE IV

Rrefractive Indices of 25% Rosin in Beef Tallow Using Various Grades of Rosin

		——Refractive Index at 48° C.——		
	Grade	25% Rosin Tallow Mixture	Tallow	Rosin (By Extrapolation)
Gum Rosin	B	1.4730	1.4543	1.5291
	D	1.4723	1.4543	1.5263
	E	1.4726	1.4543	1.5275
	F	1.4727	1.4543	1.5279
	G	1.4729	1.4543	1.5287
	I	1.4727	1.4543	1.5279
	K	1.4724	1.4543	1.5267
	M	1.4725	1.4543	1.5271
	N	1.4723	1.4543	1.5263
	WG	1.4724	1.4543	1.5267
	WW	1.4721	1.4543	1.5255
Wood Rosin	M	1.4721	1.4543	1.5255
	N	1.4723	1.4543	1.5263
	I	1.4724	1.4543	1.5267
Average		1.4725	1.4543	1.5270
Highest	1.5291			
Lowest	1.5255			
Spread	.0036			

No study has been made of the relationship between these figures and the characteristics of the various grades of rosin tested. It might be of interest as a subject for future work to determine whether or not the saponification values, unsaponifiable matter content or physical characteristics such as color or melting point of a rosin

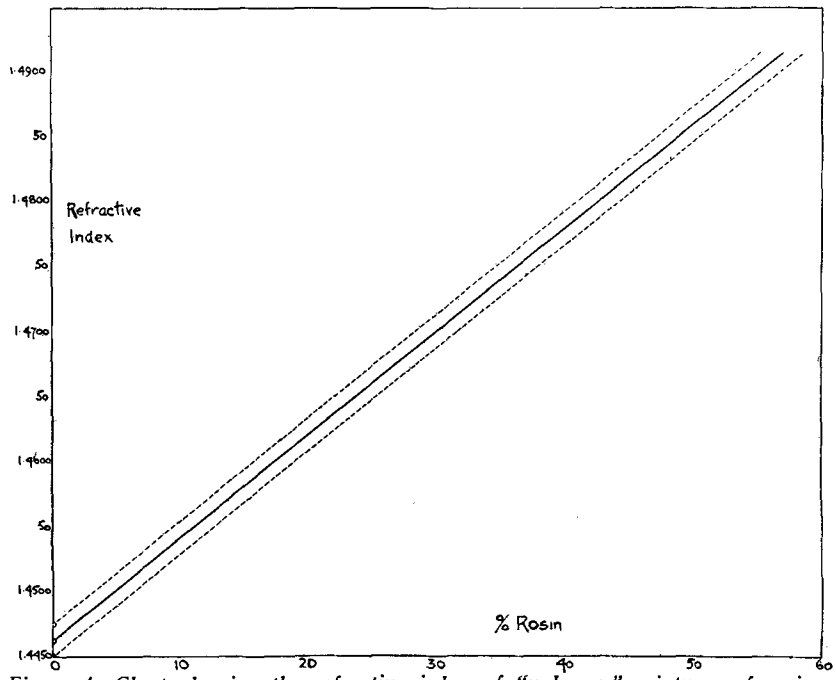

Figure 4—Chart showing the refractive index of "unknown" mixtures of rosin-acid and tallow fatty acids. This chart is based upon the figures obtained from 139 samples of tallow, and 14 samples of various grades of rosin. The upper and lower limits are shown by the dotted lines

bears any definite relationship to its refractive index.

TABLE V

Rrefractive Indices of 25% Rosin in Beef Tallow Using Various Grades of Rosin After Saponification

		——Refractive Index at 48° C.——		
	Grade	25% Rosin Tallow Mixture	Tallow Fatty Acids	Rosin Acids* (By Extrapolation)
Gum Rosin	B	1.4656	1.4448	1.5270
	D	1.4651	1.4448	1.5250
	E	1.4653	1.4448	1.5258
	F	1.4653	1.4448	1.5258
	G	1.4655	1.4448	1.5266
	I	1.4653	1.4448	1.5258
	K	1.4652	1.4448	1.5254
	M	1.4653	1.4448	1.5258
	N	1.4652	1.4448	1.5254
	WG	1.4653	1.4448	1.5258
	WW	1.4649	1.4448	1.5242
Wood Rosin	M	1.4648	1.4448	1.5238
	N	1.4649	1.4448	1.5242
	I	1.4651	1.4448	1.5258
Average		1.4652	1.4448	1.5254

*Computations based upon the assumption that the acids after saponification are present in the proportions of 25.35 per cent rosin to 74.65 per cent tallow.

Highest — 1.5270
Lowest — 1.5232
Spread — .0028

By testing the refractive index of a mixture containing unknown amounts of rosin in tallow and referring to this chart, the percentage of rosin can be obtained. The possible error when using the average figure shown by the center line and testing a mixture containing approximately 25 per cent of rosin is not more than 1.7 per cent of rosin. The spread at this point is — 1.7 to + 1.6. The average figure in this chart is probably on the low side, as, for the regular run of rosin soaps low grade tallows are used and this figure includes a substantial percentage of high grade tallow which would not regularly be used in rosin soap. This does not take into account the possibility of such unknown soap containing coconut oil. The presence of oils of low refractive index such as coconut* would increase the possible error. This method can be adapted for the determination of the percentage of coconut oil in mixtures of coconut oil and tallow.

The Abbe refractometer was used for this work and is recommended for this method. The Butyro refractometer is unsuitable for two reasons, first, the range of the Butyro scale is from 1.4220 to 1.4895, and therefore a mixture containing over 50 per cent rosin and giving a reading higher than 1.4895 cannot be read. The other reason is that owing to the prisms of the Butyro refractometer being adjusted, as they are, for butter fat or similarly colored substances, mixtures containing rosin show a colored fringe at the critical line, making it almost impossible to obtain an accurate reading.*

Katrakis and Megaloikonomou[2] published a method in 1929 for the determination of rosin in Rosin-Japanese-wax mixtures by the refractometer.

A direct refractometric method for the determination of oil in paraffin wax was published by Diggs and Buchler[3] in Industrial and Engineering Chemistry, 1927. Although this paper deals with mineral oils, the principle of their method is much the same as that set forth in the present paper. Apart from these references a search of the literature reveals the fact that very little directly pertinent to this subject has been published. This is the more surprising in view of the increasing recognition of the value of the refractometer in testing fats and oils. It must be obvious to all that physical and physico-chemical methods are taking a more and more prominent place in our laboratories and there is no doubt that in this direction we must look for progress in analytical technique.

*The refractive index of 64 samples of CNO Fatty Acids gave the following figures: Lowest 1.4329 (Butyro 13.7°); Average 1.4331 (Butyro 14.0°); Highest 1.4333 (Butyro 14.3°).

*It has been pointed out that it may be possible to overcome both these difficulties by working at a higher temperature and using a suitable filter between the source of light and prisms.

[1]Lewkowitsch, 1921, Volume 1, page 345.

[2]Katrakis, C. G., and Megaloikonomou. Pratika de l'Academie d'Athens 3:564. (Abstracted in Chemisches Zentralblatt 1929, I:2843 and Chemical Abstracts 24: 3660.)

[3]Diggs, S. H., and Buchler, C. C. Industrial and Engineering Chemistry 19: 125. (1927.)

NOTICE

The Journal Committee is desirous of obtaining some missing numbers of our former publication OIL & FAT INDUSTRIES in order to complete the files. We have been unable to complete our work on the 10-year index because of the lack of the following numbers:

Oil & Fat Industries, No. 2—1925.

Oil & Fat Industries, No. 4—1926.

Oil & Fat Industries, Nos. 3 and 7—1927

Doubtless some of our older members have these journals tucked away somewhere in their files.

The Journal Committee will much appreciate it if you will make a search and either give or loan us the missing numbers.

W. H. IRWIN, Chairman, Journal Committee.