The Iodine Number of Tall Oil

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Reported Iodine Numbers of Tall Oil

Tall oil, the natural mixture of fatty and rosin acids recovered from pine wood in the alkaline paper pulp process, finds increasing use in many fields, as an abundant literature attests (24).

With its growing importance in the drying oil field much interest has been shown in its iodine number. The iodine numbers of tall oil reported in the literature are tabulated in Table 1. This data shows a variation of from 100 to 210.

TABLE 1

Iodine Numbers of Tall Oil Reported in the Literature

No.	Material	Iodine Numbers		Reference	
		Value	Method	Author	No.
1	Crude tall oil	110-128	.....	Patch	20
2	Crude tall oil	115	.....	Dittler	7
3	Crude tall oil	160	.....	Botto-Micca	5
4	Crude tall oil	118	.....	Lorentz	18
5	Crude tall oil	140-150	Wijs	West Virginia Pulp & Paper Co.	25
6	Crude tall oil settled for 2-10 days	200-210	Hanus	Hasselstrom	12
7	Refined tall oil	100-160	Hanus	Frankel & Pollak	9
8	Refined tall oil	188.2	Wijs	Niesen	19
9	Refined tall oil	106	.....	Heubschner	13
10	Refined tall oil	117	.....	Wallach	23
11	Refined tall oil	117.6	.....	Keghel	16
12	Refined tall oil	147.5	.....	Fricke	10
13	Tall oil refined by settling at —10 to 25°C.	165-175	Hanus	Hasselstrom	12
14	Tall oil fatty acids	100	.....	Duesberg	8
15	Tall oil fatty acids	176	.....	Botto-Micca	5
16	Tall oil fatty acids	125-135	.....	Christmann	6
17	Tall oil rosin acids	160.3	Hübl	Niesen	19
18	Tall oil abietic acid	155-165	Hanus	Christmann	6
19	Tall oil glycerol esters				
	—12% rosin	139	.....	Tobias	22
20	—20% rosin	129	.....	Tobias	22
21	—33% rosin	122	.....	Tobias	22
22	Tall oil glycol esters	123	.....	Tobias	22

Variables Influencing Iodine Numbers

The Wijs method as adopted by the American Oil Chemists' Society (2), the Association of Official Agricultural Chemists (4), and the American Society for Testing Materials (3) calls for 30 minutes reaction time for all oils and fats except tung, linseed, and perilla oils. For these oils the Wijs method as adopted by the American Oil Chemists' Society specifies that one hour be used. This procedure also stipulates that the temperatures used with tung, linseed, and perilla oils be 20-25°C. while the A.S.T.M. procedure calls for a temperature of 25 ± 2°C. for all oils and fats. The Wijs method as adopted by all three of the above organizations requires that the excess iodine be from 100 to 150% based on the iodine absorbed.

Although the literature affords very little information on suitable conditions for determining the iodine numbers of tall oil, there is much information on the iodine numbers of the two main groups of constituents of tall oil. The Hanus, Hübl-Walker, and Wijs iodine numbers of linseed and tung oils were reported by van Reibritz (21) to vary with the temperature and time of absorption. He recommended the Wijs method for speed, reliability, and reproducibility. Hyde (14) stated that the absorption period for non-drying oils using a Wijs solution was about 15 minutes while a shorter period was required for drying oils. He reported the Hanus solution was less rapid than the Wijs solution and that an operation time of 24 hours was used with the Hübl method. According to Lewkowitch (17), Vol. 1, page 407, 30 minutes was sufficient for the completion of the reaction in the case of oils and fats having iodine numbers less than 100, while semi-drying oils required about an hour and drying oils required from 2 to 6 hours depending on the degree of unsaturation.

The iodine numbers of rosin acids have been shown to vary widely with the conditions used. Lewkowitsch (17), Vol. 1, page 408, found that the Wijs solution gave very much higher and more capricious results than did the Hübl method. Grun and Jonko (11) reported that the iodine number of rosin determined by the Wijs method differed from the value found by the Hübl method and that both varied widely with the time of absorption and the amount of excess iodine used. Lewkowitsch (17), Vol. 1, page 620, gave data showing that the Hübl iodine number of rosin continued to increase after 18 hours absorption since iodine numbers of 160.3 and 172.6 were obtained for 18 and 52 hours reaction time respectively. As reported by Smetham and Dodd (17), Vol. 1, page 619, grade N rosin gave Wijs iodine numbers of 171.2 and 270.5 for 10 minutes and 4 hours absorption respectively. The iodine number of rosin was shown by McIlhiney (17), Vol. 1, page 619, to vary with the time of absorption and the excess iodine used to a much greater extent than was the case with oils and fats. He concluded that the iodine number did not furnish useful results in the case of rosin.

Materials

Samples of crude and distilled tall oil and tall oil abietic acid were tested. The crude tall oil used, LIQRO, was the material obtained by acidifying crude tall oil soap produced at the Charleston, South Carolina plant of the West Virginia Pulp and Paper Company. This tall oil had the following composition:

Fatty acids	46%
Rosin acids	47%
Sterols and other unsaponifiables	7%

The distilled tall oil used, INDUSOIL, was obtained from the Covington, Virginia plant of the West Virginia Pulp and Paper Company. In this plant crude tall oil is vacuum distilled, abietic acid crystallized out, and the resulting oil redistilled. The abietic acid used, as obtained from the above refining process, was a pale amber crystalline solid.

Since the two main constituents of tall oil are unsaturated fatty acids and rosin acids, it was of interest to correlate the iodine values of technical oleic acid, raw linseed oil, and grade N wood rosin.

Experimental

Tests were made to determine the effect of the amount of excess iodine and the time and temperature of absorption on the iodine number.

The Wijs method of analysis was used except that no blank determinations were made. From 5 to 12 samples were analyzed at a time, so instead of running two blanks with each sample the solutions were standardized before and after each series of analysis. Lewkowitsch (17) Vol. 1, page 407, found that "Wijs solutions kept for 5 or 6 months did not appreciably change their 'strength'. Hence in ordinary work a blank test is not required in each case."

To confirm this blanks were run at the two extremes of the conditions used in these experiments, 21°C. for 30 minutes and 32°C. for 2 hours. No Wijs solution was consumed.

In determining the effect of excess iodine the weight of sample used was varied so that the volume of Wijs and sodium thiosulfate solutions required would not exceed one 50 ml. burette. In determining the effect of the temperature of the absorption the sample was weighed into a glass stoppered, 250-ml. Erlenmeyer flask. The chloroform was added and the flask placed in a bath at the desired temperature for about one hour. The flask was then taken from the bath, the desired quantity of Wijs solution added and then returned to the bath for the reaction period. For each temperature used, samples with various excesses of iodine were tested.

A similar procedure was used in determining the effect of the time of absorption except that the samples were allowed to remain in the bath from 0.5 to 2 hours at 26.7°C.

The following equation describes the relation of the volume of Wijs solution, the excess iodine and the sample weight:

$$W \times N \times 1269 = A \times (E + 100) \times S$$

where W = Wijs solution, ml.
N = Wijs solution normality
A = Iodine number
E = Excess iodine, %
S = Sample, grams

In our procedure S was first calculated for W = 25.0 by guessing the probable value of A. Samples were then weighed out of approximately the weight S. The actual weights were then used and W calculated for the desired value of E. The iodine number was then computed by

$$12.69 \times \frac{(W \times N) - (T \times M)}{S}$$

where T = $Na_2S_2O_3$ solution, ml.
M = $Na_2S_2O_3$ solution, normality

The % excess iodine was

$$100 \times \frac{(T \times M)}{(W \times N) - (T \times M)}$$

The Effect of Excess Iodine

The data given in figure 1 shows that the iodine numbers of tall oil abietic acid and crude and distilled tall oil increase with an increase in the per cent excess iodine. The tall oil abietic acid shows the greatest rate of change with excess iodine while the distilled tall oil, which contains the least rosin acids, shows the least variation in iodine number. This would indicate that the rosin acids in tall oil are the principal cause of variations in iodine numbers with excess iodine.

The Effect of the Temperature of Absorption

The data plotted in figures 2, 3, and 4 show that the iodine numbers also vary with the temperature

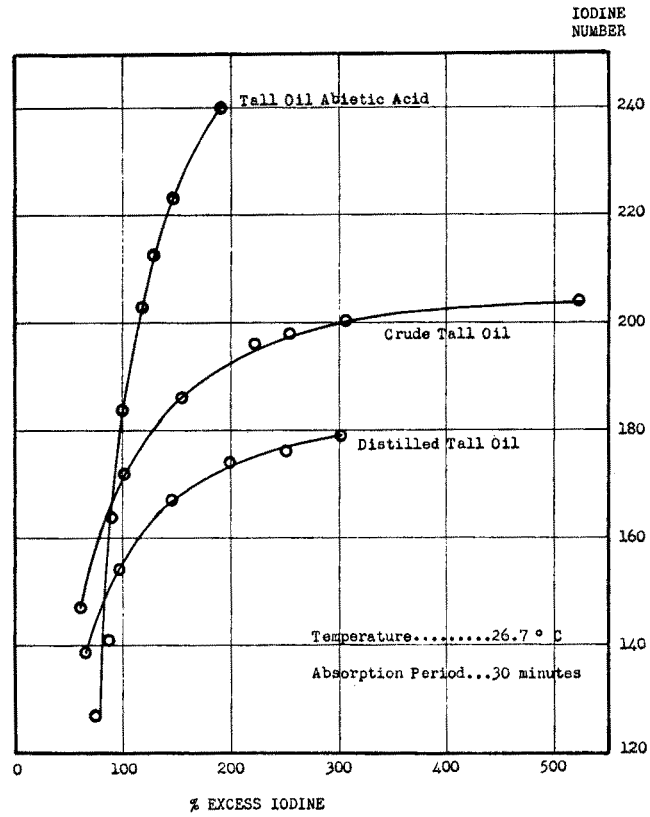

FIG. 1. The effect of excess iodine on the iodine number of tall oil abietic acid, crude tall oil, and distilled tall oil.

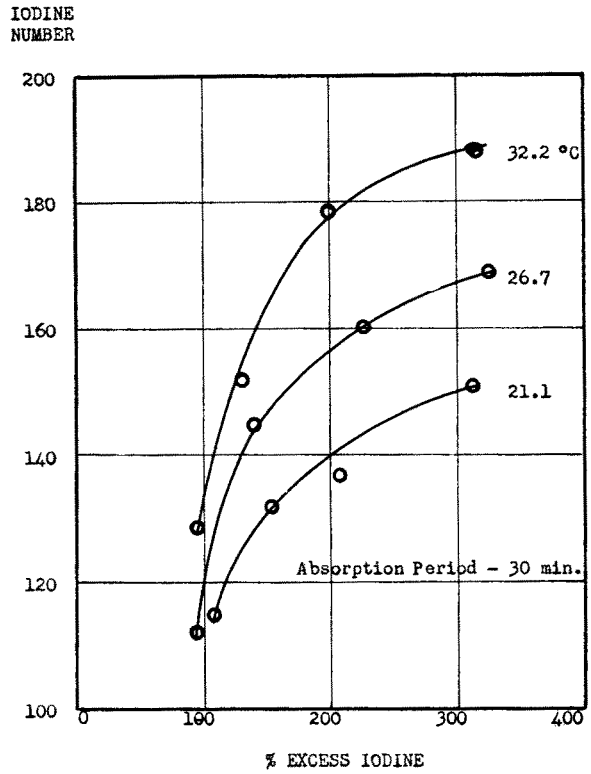

FIG. 2. The effect of the temperature on the iodine number of tall oil abietic acid.

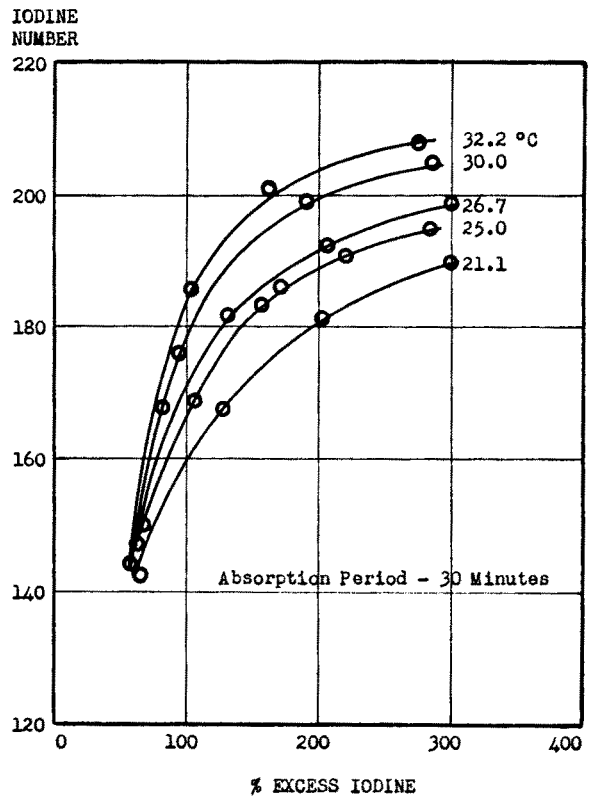

FIG. 3. The effect of the temperature on the iodine number of crude tall oil.

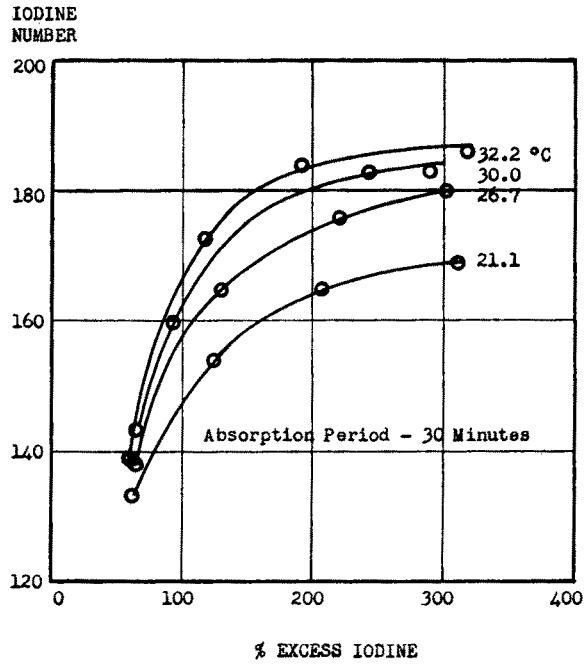

FIG. 4. The effect of the temperature on the iodine number of distilled tall oil.

of absorption. Data taken from these curves for 250% excess iodine show that a change in the absorption temperature from 21.1 to 32.2°C. will change the iodine numbers 38, 22, and 18 points, respectively, for the abietic acid and crude and refined tall oil. Again it is the abietic acid which is affected most while the distilled tall oil shows the least effect, indicating that the rosin acids cause most of the variation.

The Effect of the Time of Absorption

The data plotted in figures 5, 6, and 7 show how the iodine numbers vary with the time of absorption. Increasing the time of reaction from ½ to 2 hours with 300% excess iodine resulted in an increase in

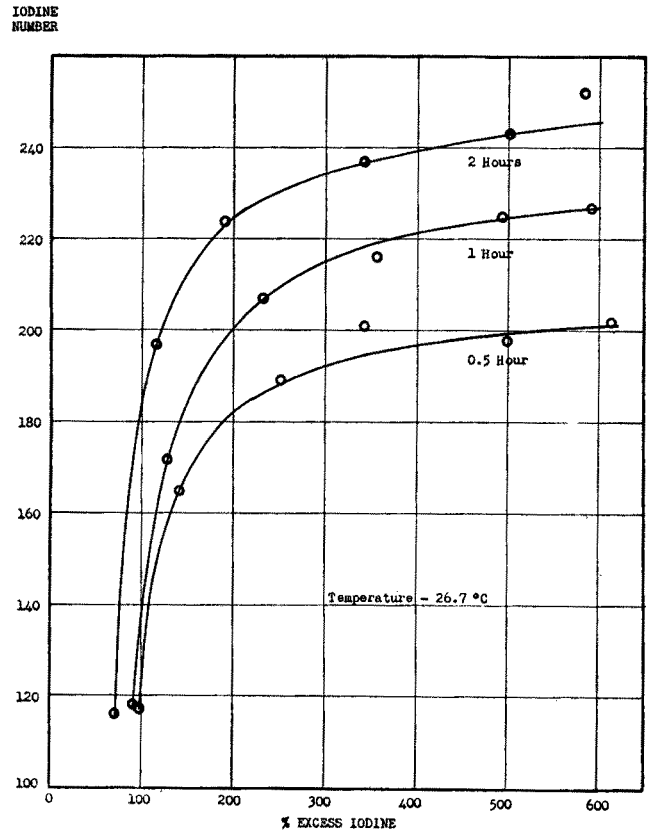

FIG. 5. The effect of the time of absorption on the iodine number of tall oil abietic acid.

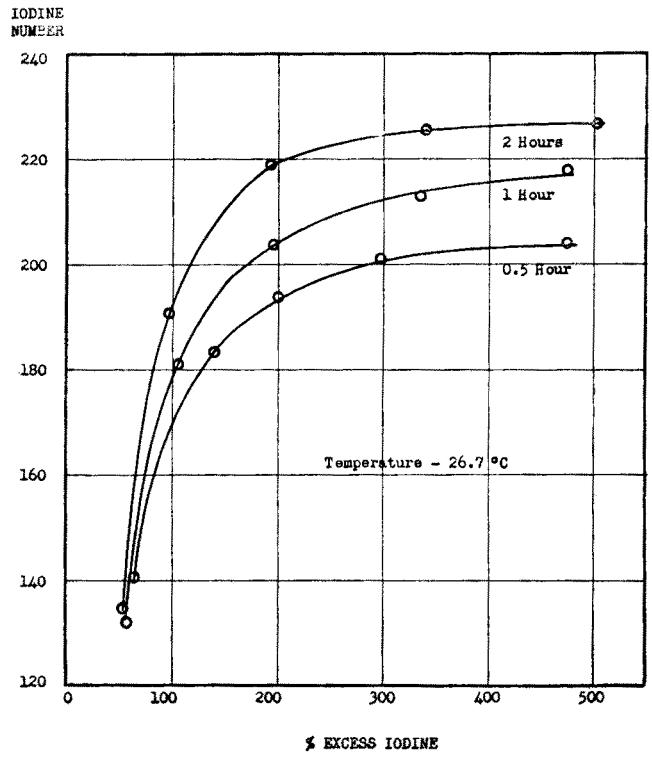

FIG. 6. The effect of the time of absorption on the iodine number of crude tall oil.

the iodine numbers of 44, 24, and 20 points, respectively, for the abietic acid and crude and refined tall oils. The data again shows that the greatest variations were obtained with the samples containing the most rosin acids.

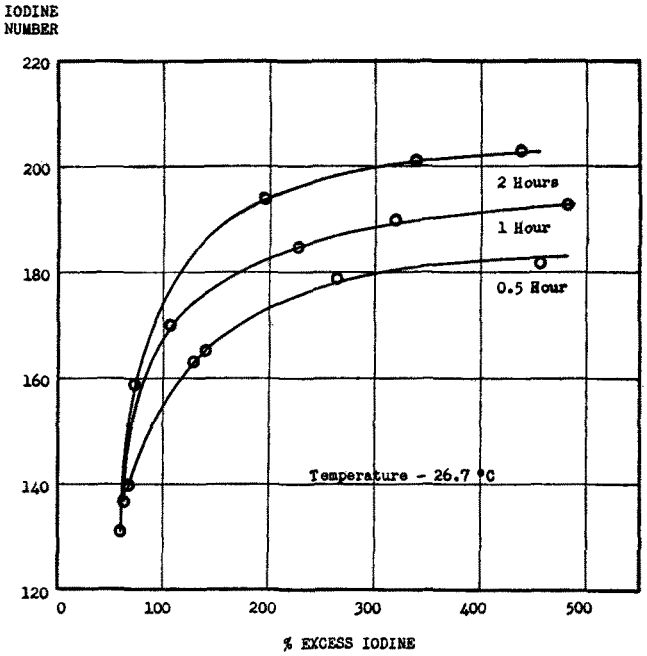

FIG. 7. The effect of the time of absorption on the iodine number of distilled tall oil.

The Iodine Numbers of Related Materials

Since the two main constituents of tall oil are unsaturated fatty acids and rosin acids, a few tests were made using wood rosin, raw linseed oil, and oleic acid. The data obtained, table 2, shows very little variation in the iodine numbers of the linseed oil and oleic acid with changes in the time of absorption and excess iodine used. On the other hand, wood rosin, figure 8, gave much the same variations in iodine numbers as were obtained with tall oil and tall oil abietic acid.

TABLE 2

The Effect of Excess Iodine and Time of Absorption on the Iodine Number of Rosin, Linseed Oil, and Oleic Acid

Time of Reaction Hours	Grade N Wood Rosin		Linseed Oil		Oleic Acid	
	Iodine No.	% Excess Iodine	Iodine No.	% Excess Iodine	Iodine No.	% Excess Iodine
0.5	121	89	180	63	90.5	69
	192	225	179	201	90.3	96
	203	378	177	387	90.8	123
	211	475	.....	.....	92.1	144
	212	586	.....	.....	92.0	169
1.0	.....	.....	.....	.....	87.5	64
	.....	.....	.....	.....	87.9	205
	.....	.....	.....	.....	88.7	378
	.....	.....	.....	.....	89.3	598
2.0	120	81	181	63	.....	.....
	173	99	181	171	.....	.....
	215	157	182	315	.....	.....
	229	233	181	555	.....	.....
	238	388	.....	.....	.....	.....

Discussion

The results obtained agree with the data reported in the literature in that the iodine numbers of rosin acids, unlike fatty acids, vary widely with the amount of excess iodine used, the time of absorption, and the temperature during the reaction period. Tall oil exhibits similar but somewhat smaller variations in Wijs iodine values.

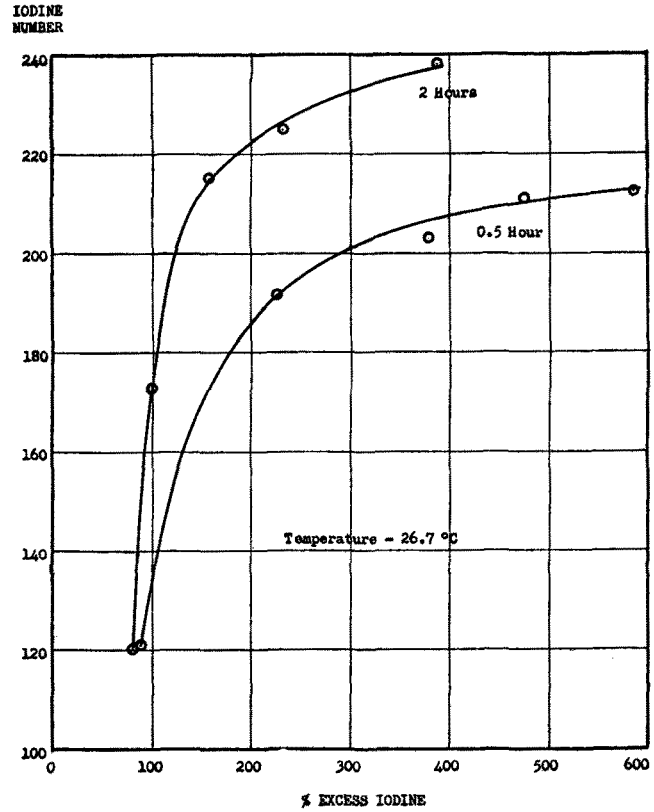

FIG. 8. The effect of excess iodine and time of absorption on the iodine number of wood rosin.

The tall oil abietic acid used in these experiments, a crystalline power, oxidizes readily. It will be seen that the iodine numbers of abietic acid in figures 1, 2, and 5 do not agree for the same reaction time and temperature. The differences are believed to be due to the oxidation of the sample.

Additional restrictions and some modification in the standard conditions of the Wijs method permits reproducible results, using tall oil. The degree of restriction depends upon the reproducibility required. The data presented above were used for selecting the conditions necessary for a reproducibility of 1% in the iodine number.

The Wijs method calls for an excess of from 100 to 150% iodine. For tall oil a high rate of change in the iodine numbers with excess iodine occurs within this range. The data given in table 3, taken from figure 6 at 30-minute reaction time, shows that in order to reduce the variation in iodine number of crude tall oil to $\pm$ 0.25%, the variation in excess iodine would have to be reduced to $\pm$ 10% at an excess of 300%. With more than 300% excess iodine, if not more than one 50 ml.-burette of Wijs or sodium thiosulfate solutions is to be used, the sample weight becomes so small as to affect the precision with the ordinary balance.

Without knowing the iodine number beforehand it is impossible to add the amount of Wijs solution necessary to give the excess iodine desired to a precision of 10%. Therefore, it is necessary that determinations be made on about 4 samples in which the excess iodine is varied. The results obtained are then plotted and the iodine number at the desired excess iodine read from the curve.

TABLE 3

Per Cent Variation in the Iodine Number of Crude Tall Oil With Excess Iodine

Excess Iodine Range	Iodine No.	Per Cent Variation ±
125±25	170-186	4.5
175±25	186-194	2.1
225±25	194-198	1.0
275±25	198-201	0.75
325±25	201-203	0.5
125±10	176-182	1.0
175±10	189-192	0.75
225±10	195-197	0.5
275±10	199-200.5	0.4
300±10	200.5-201.5	0.25
325±10	201.5-202.5	0.25

The Wijs method as adopted by the American Oil Chemists' Society calls for a 30-minute reaction time for most oils and fats, and for one hour with linseed, tung, and perilla oils. Data taken from figure 6 for crude tall oil with 300% excess iodine shows a variation in the iodine number of 11 points for a 30-minute change in the reaction time. For a variation of ± 0.25% or ± 0.5 points this corresponds to a reaction time varying by ± 1.5 minutes.

The Wijs method as adopted by the American Oil Chemists' Society and the Association of Official Agricultural Chemists does not mention a temperature of absorption for most oils, but a temperature of 20-25°C. is given for tung, linseed, and perilla oils. The American Society for Testing Materials procedure specifies that 25 ± 2°C. be used. For crude tall oil and 250% excess iodine, figure 3, the iodine number increased from 186 to 208 at 21.1 and 32.2°C., respectively. This corresponds to a change of ± 2% for 25 ± 2°C. A variation in the temperature of ± 0.5°C. would cause ± 0.5% change in the iodine number.

The maximum variation then totals 1% as shown below:

Condition	Iodine No. % Variation
30 ± 1 minute time	± 0.25
25 ± 0.5°C. temperature	± 0.50
300 ± 10% excess iodine	± 0.25
Total	±1.0

Where less precision is permissible, some control may be reduced but in no case could the present broad standard conditions be applied to tall oil or rosin for useful results.

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Abstracts

Oils and Fats

Edited by
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PHOTOMETRIC DETERMINATION OF ACETONE-INSOLUBLE MATERIAL IN SOYBEAN OIL. C. A. Murray and E. B. Oberg. *Ind. & Eng. Chem., Anal. Ed. 14*, 785-7 (1942). A photometric procedure has been described for the detn. of acetone-insol. material and break in solvent-extd. soybean oil. The photometric method is rapid, possesses an av. precision of approx. 0.005 break % and is relatively free of errors introduced by differences in technique. A direct empirical relation has been found between acetone-insol. material and break in solvent-extd. soybean oils.

THE VITAMIN D CONTENT OF ENGLISH BUTTER FAT THROUGHOUT THE YEAR. K. M. Henry and S. K. Kon. *Biochem. J. 36*, 456-9 (1942). The vitamin D potencies of the fat of butters churned at approx. monthly intervals from the milk of the Shinfield herd have been measured between March 1940 and March 1941. The assay was done by the prophylactic bone ash method against the international standard on groups of 11 or 12 rats, all comparisons being between littermates. The values of the non-saponifiable residue varied from less than 0.1 i.u./g. fat in the months of Nov.-March to 0.55 i.u./g. in July and 0.97 i.u./g. in August. The latter figure may be too high. The values for untreated fat were invariably higher than those measured after sapon., the difference being much more marked in winter than in summer.

THE APPLICATION OF LABELING AGENTS TO THE STUDY OF PHOSPHOLIPID METABOLISM. I. L. Chaikoff. *Physiol. Revs. 22*, 291-317 (1942).