

distillation. The rosin acids crystallized from tall oil contained the highest percentage of abietic acid, but the sum of abietic and neoabietic acids was only slightly higher.

The rosin acids from acid refined tall oil contained appreciably less abietic and neoabietic acid than the others.

Before spectrophotometric analysis the rosin acids were isolated from the tall oils in about 95% yield by cyclohexylamine precipitation.

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Acetone Numbers of Thermally Polymerized Drying Oils¹

OLIVER GRUMMITT, ALBERT ARTERS, and JAMES STEARNS,
Sherwin-Williams Company, Cleveland, Ohio²

THIS investigation of acetone numbers of bodied drying oils is part of a program to develop tests and analytical methods in order to correlate the properties of these oils with their performance as coating vehicles. Specifications on a bodied oil frequently give only the kind of oil, viscosity, acid number, and color, but it is well known that oils having essentially the same specifications may produce paints and varnishes of widely different properties. This variation may be due to unknown differences in composition. Bodied oils consist of varying proportions of monomeric glycerides, polymeric glycerides, and decomposition products, both acidic and neutral. Tests and analytical methods which measure or reflect these components should be useful in predicting the vehicle properties of the oil.

The acetone number is defined as the quantity of acetone, expressed in grams per 100 g. of oil, which is required to produce a permanent cloudiness in the oil at 25°C. (2, 4, 6). It is a quantitative measure of the well-known property of bodied oils of becoming less soluble with increasing viscosity. Related to this determination is the acetone extract (5, 7), the acetone point (8), and the Behr process of extracting the unpolymerized portion of bodied oils with acetone (3).

One would expect the acetone number to be a function of the relative amounts of monomeric and polymeric glycerides and of the nature of the polymer, particularly its molecular weight distribution and degree of cross linking. Such information should aid in understanding the behavior of bodied oils as vehicles.

Experimental

The procedure given here is based on the published methods (2, 4, 6). In several respects it is believed to be an improved method.

Anhydrous acetone is made by allowing 1.5 l. of reagent grade acetone and 200 g. of anhydrous calcium sulfate (Drierite) to stand in a 2-l. r.b. flask with standard taper joint, protected with a drying tube, for three days with occasional shaking. About 70% of the acetone is distilled directly from this flask and the drying agent in a dry all-glass apparatus into the dry bottle of an automatic burette apparatus.³ The bottle is protected with a drying tube to prevent moisture from entering during distillation. The clean, dry burette with its drying tubes is fitted to the bottle.

To check the water content of the acetone its specific gravity at 25°C./25°C. is determined with a calibrated g.s. 50-ml. volumetric flask. Values in the range of 0.7864-0.7872, which indicate a water content of 0.00-0.24%, show that the acetone is satisfactory. A standardization procedure for checking the acetone is described below.

Duplicate 30-g. samples of oil, weighed to the nearest 0.01 g., are weighed into clean, dry 250-ml. Erlenmeyer flasks. A rubber nipple is slipped over the mouth of the flask and the flask is immersed in a constant temperature water bath so that the water level is about 1 in. above the oil sample. The bath is held at 25 ± 0.1°. After allowing at least 15 minutes for the sample to reach 25°, the tip of the burette containing acetone is inserted through the nipple.

The flask is swirled gently while acetone is added

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² Address: Sherwin-Williams Laboratory, Western Reserve University, Cleveland 6, O.

³ The water jacket for the burette as described in the A.S.T.M. method (2) is not considered to be necessary if the titration is done as specified here. The excellent reproducibility is evidence for this statement (v. i.).

slowly from the burette so that the temperature of the mixture remains at 25°. Each addition of acetone produces a dense cloudiness which disappears as the mixture is agitated. As the end point is approached, the cloudiness persists for longer periods of time, and the acetone is added dropwise until the addition of one to two drops produces a permanent dense cloudiness. The flask is wiped dry, weighed to the nearest 0.01 g., and the weight of acetone found by difference with the sample weight. The number is calculated from the following equation:

$$\text{Acetone No.} = \frac{\text{Wt. of acetone used} \times 100}{\text{Wt. of oil sample}}$$

Characteristics of the Determination

Reproducibility. The determination of the acetone number is satisfactorily reproducible if the variables discussed below are controlled. For example, a bodied alkali refined linseed oil whose acetone number was about 94 was run five times. The maximum deviation from the average value was ± 0.16 .

Effect of Temperature. Since increasing temperature increases the mutual solubility of a bodied oil and acetone, the acetone number becomes greater. Figure 1 shows data for a bodied linseed oil of acetone number 92 over the temperature range of 19.5 to 26.5°. It will be noted that the relationship is almost linear and that the increase per degree is about 2.5. Therefore satisfactory reproducibility requires that the temperature be held at $25 \pm 0.1^\circ$ during the titration.

Effect of Water. Acetone dried as described above contains 0.12-0.15% of water. Increasing the concentration of water in the acetone decreases its solvency rapidly and the acetone number becomes smaller. Ta-

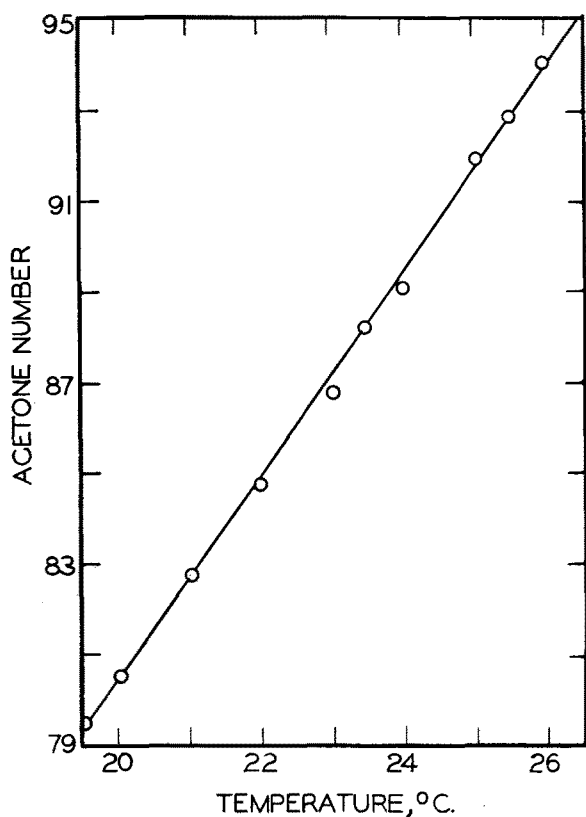


FIG. 1. Effect of temperature on acetone number of a bodied linseed oil. (Viscosity: 60.6 Gardner-Holdt seconds.)

ble I shows data for a bodied linseed oil of acetone number 92 obtained by varying the water content from 0.15 to 1.10%.

TABLE I
Effect of Water on the Acetone Number of a Bodied Linseed Oil
(Visc.: 60.6 G-H seconds)

% Water in Acetone	Acet. No.	% Decrease
0.15	91.6
0.35	85.9	6.3
0.71	74.6	18.6
1.10	65.9	28.0

It will be noted that at 1% water the acetone number has dropped about 25%. The effect of water was studied with bodied oils of various viscosities and acetone numbers, and it was found that the higher the number the greater the effect of water on it. The possibility of using the more readily available 99% acetone, instead of a specially dried grade, was investigated. This has the disadvantage that the range of acetone numbers as a function of viscosity becomes narrower. Therefore properly dried acetone should be used.

Water in the oil sample is much less important than water in the acetone. Bodied oil samples are usually dry unless there has been an accidental contact with water. Several samples used in this work were dried by bubbling in dry nitrogen at 100°. The effect on the acetone number was negligible. Saturating with water the bodied linseed oil used in the experiments of Table I decreased the acetone number about 1%. Therefore drying the oil sample is ordinarily unnecessary.

Color of the Oil. To determine if the visibility of the end point was affected by the color of the oil a bodied linseed sample of color 7 (Gardner-Holdt), viscosity 60 G-H seconds,⁴ acetone number 92, was darkened to a color of 15 by heating a sample with 1% of p-toluenesulfonic acid monohydrate at 90-100° for one hour, stirring occasionally, and filtering. The acid number and viscosity were not changed. The acetone number of this oil was determined several times. The values ranged within 1-2% of the original value, indicating that the usual reproducibility probably cannot be achieved with very dark samples.

Determination of End Point. A Coleman nephelometer was tried in order to detect the end point more precisely. While this is much more sensitive than the eye, it is not possible to hold the sample sufficiently close to 25° in the conventional instrument, and the error introduced by temperature change more than offsets the accuracy of determining the end point.

Standardization. For any analytical or test procedure it is important that a standard be available. Since a uniform bodied oil would not be readily accessible to everyone, other standards were sought. The ideal standard would be a pure, easily obtained substance whose behavior on titration with acetone closely paralleled that of a bodied oil. After trying a number of organic liquids and aqueous solutions of salts such as potassium acid phthalate, it was concluded that a 33.3% aqueous solution of sugar met the requirements. On titration with acetone, according to the regular procedure, the solution first be-

⁴ Viscosities in G-H (Gardner-Holdt) seconds are found by measuring the rate of rise of an air bubble in a standard tube; see ref. (6), p. 299. For conversion to other viscosity units see J. Am. Oil Chem. Soc., 36, 347 (1949).

TABLE II
Acetone Numbers of Linseed Oil Bodied at $300 \pm 3^\circ\text{C}.$ ^a

Time	Visc.	Acet. No.	Acid No. ^b	Color ^c
<i>min.</i>	<i>sec.</i>			
255	10.8	268.1	6.4	8
305	17.8	183.3	7.6	9
350	26.0	155.3	8.2	9
390	35.2	137.7	9.1	10
430	48.7	120.4	9.7	10
445	56.0	115.5	9.8	10
460	63.5	111.1	9.9	10
475	72.0	107.8	10.2	10
490	81.4	104.1	10.5	10
505	92.1	101.1	10.8	11
520	108.8	98.9	11.0	11
535	133	95.4	11.2	11
565	176	91.6	11.4	12
580+	237	89.2	11.6	12

^a 2,500 g. of alkali-refined linseed oil in a 5-l, three-necked r.b. flask heated by a Glas Col mantle and stirred by a glass stirrer. Samples of 30-35 g. were withdrawn with a pipette.

^b A.O.C.S. Tentative Method Ka 2-47.

^c Gardner-Holdt.

comes cloudy, due to precipitation of the sugar, at an acetone number of 124. This value can be reproduced within $\pm 0.16\%$. Water in the acetone in excess of 0.12-0.15% decreases the number considerably, although to a smaller degree than for the bodied linseed oil (Table I). Therefore it is recommended that this solution, which is easily made from cane sugar and distilled water, be used as a standard.

Acetone Numbers of Various Oils

Bodied Linseed Oil. To determine the change in acetone number with viscosity, alkali refined linseed oil was bodied in glass at $300 \pm 3^\circ\text{C}.$ to a viscosity of 237 G-H seconds. Samples were withdrawn at various time intervals for measurement of viscosity, acetone number, acid number, and color (Table II, Figures 2 and 3).

The increase in viscosity is accompanied by a decrease in acetone number, and the greatest decrease, about 170 units, is in the lower viscosity range of 10-100 seconds. At high viscosities, 100-240 seconds, the

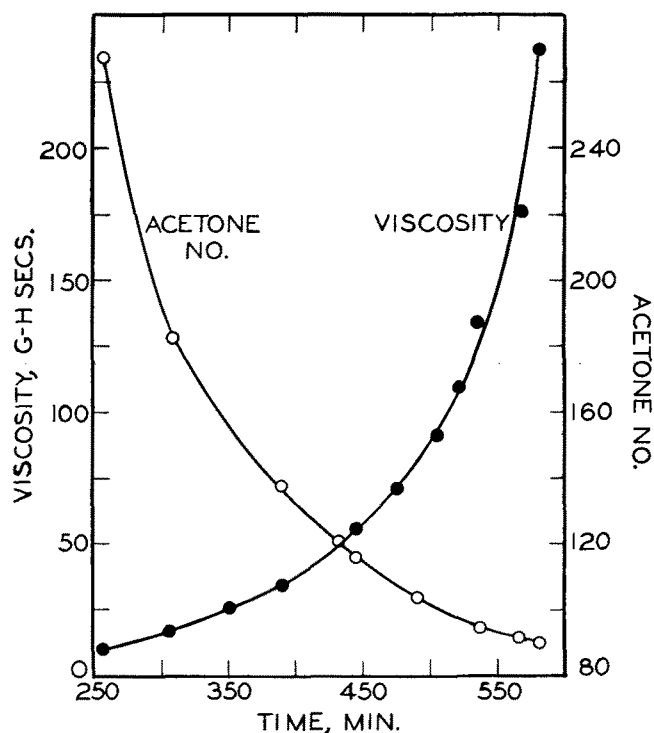


FIG. 2. Viscosity and acetone number vs. heating time for A. R. linseed oil bodied at $300 \pm 3^\circ\text{C}.$

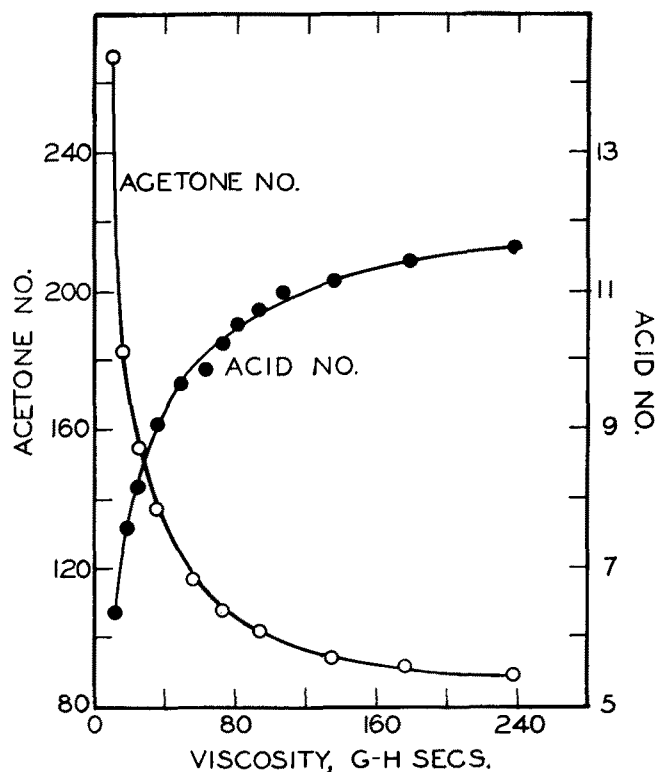


FIG. 3. Acetone number and acid number vs. viscosity for A. R. linseed oil bodied at $300 \pm 3^\circ\text{C}.$

change in acetone number is relatively small, only about 10 units. Linseed oils of even higher viscosities (Table IV) approach a limiting value of about 80.

Attempts to obtain a straight line relationship of acetone number to viscosity by plotting log quantities and/or reciprocal quantities were only partly successful. In the viscosity range of 14-60 seconds the acetone number plotted against the reciprocal of the viscosity is a straight line. Above and below this range the line curves.

Effect of Acids. Since fatty acids are generally soluble in acetone, their presence as decomposition products in a bodied oil should increase the acetone number. To estimate the magnitude of the effect acetone numbers were determined on mixtures of a vacuum-bodied, low acid number linseed oil and linseed acids. The data of Table III show that the acetone number increases rapidly and the viscosity decreases rapidly with increasing concentration of acids in the oil.

In the concentration range studied the change in acetone number is a linear function and the viscosity change is almost linear. The rate of viscosity change

TABLE III
Acetone Numbers and Viscosities of Vacuum Bodied Linseed-Linseed Acids Mixtures^a

% Linseed Acids	Acid No.	Visc.	Acet. No.	% Change	
				Visc.	Acet. No.
.....	2.8	63	78.8
1.25	5.0	57	84.3	-9.5	+7.0
3.8	9.6	48	90.3	-23.8	+14.7
6.3	14.9	42	98.2	-33.4	+24.6
8.8	20.0	35	105.2	-44.5	+33.2
11.5	25.6	30	114.0	-52.5	+44.7

^a These mixtures were made from Archer-Daniels-Midland's OKO S-70 vacuum bodied linseed oil and distilled linseed acids.

with acid concentration is somewhat greater than the rate of acetone number change (Table III).

To make the acetone number entirely dependent on the monomer and polymer components of the oil, the acids should be completely removed and the number and viscosity of the residual oil measured. Work now in progress on the removal of acids shows that this is not readily accomplished. It must be remembered that a comparison of the acetone numbers of bodied oils of the same viscosity must include consideration of the acid content. The oils with higher acid numbers would show higher viscosities and lower acetone numbers if the acid content were reduced to that of the other oils. Since the composition of the acids in bodied oils is not known, and since it is probably not constant in various oils, there does not appear to be any quantitative method of calculating the acetone number and viscosity of an acid-free bodied oil.

The use of linseed acids in these mixtures does not, of course, simulate the higher and lower molecular weight acids actually present in bodied linseed oil, but this seemed to be the best way of carrying out these determinations.

Effect of Type of Oil. Acetone numbers of various bodied oils were measured to learn the effect of the kind of oil (Table IV).

TABLE IV
Acetone Numbers of Various Bodied Drying Oils

Oil	Acet. No.	Visc.	Acid No.
Linseed, raw ^a	(145)	<i>sec.</i>	2.5
Linseed, A. R. ^a	∞	<1	0.3
Linseed, A. R., bodied ^a	94	61	10
Linseed, A. R., bodied ^a	80	261	17
Linseed, A. R., bodied ^a	84	930	27
Soya, A. R., bodied ^b	118	59	24
Safflower, A. R. ^b	120	57	12
Dehydrated castor ^a	133	61	4
Tung, bodied ^b	285	55	5
80% Soya - 20% Tung ^a	86	62	11
Linseed - 5% maleic ^b	>350	61	26
Linseed, OKO S-70 ^c	79	58	3
Linseed, A. R., blown ^a	>350	100	3

^a Commercial oils obtained from the Sherwin-Williams Company, Cleveland, O.

^b Prepared in glass in the laboratory. Soya and safflower were bodied at $300 \pm 3^\circ$, tung at 200° , and the linseed - 5% maleic at 275° .

^c Archer-Daniels-Midland.

The value of 145 for raw linseed oil is not a true acetone number because acetone precipitates solid matter. The alkali refined unbodied oil is completely miscible with acetone and therefore has an infinitely high acetone number. The next three oils are commercial bodied linseed oils of viscosities 61, 261, and 930 seconds. It will be noted that the acetone numbers vary only from 94 to 80 since these viscosities fall in the higher viscosity range where the acetone number is comparatively constant. The second and third oils show reversed numbers with respect to viscosity, probably because of the high acid content of the latter.

The next group of six oils were all about 60 seconds in viscosity. Compared to the 61-second linseed oil, soya has a higher number, but its acid number is also considerably higher (*v.i.*). Safflower is close to soya, but its acid number is lower. Both dehydrated castor and tung have high acetone numbers despite their low acid values. The copolymer soya-tung oil

is very close to linseed. The 5% maleic-treated linseed has an acetone number in excess of 350.

The last two oils are special linseed oils. The vacuum bodied OKO S-70 has a lower acetone and acid number than linseed. The blown linseed resembles the maleinized oil in having a number above 350.

A further comparison of linseed and soya was made by bodying each oil in the laboratory at $300 \pm 3^\circ$ under exactly the same conditions. The data of Table V show that the acetone numbers of these oils at the same viscosities are very close despite the acid number difference. It is plain that the acetone number could not be used to differentiate these two oils. Safflower likewise shows no significant difference. However the comparatively high values for dehydrated castor, tung, maleic-linseed, and the blown linseed are significant.

TABLE V
A Comparison of Bodied A. R. Linseed and A. R. Soya
($300 \pm 3^\circ\text{C}$., 2,500 g. oil in glass,
agitated, open to air)

Linseed			Soya		
Visc.	Acet. No.	Acid No.	Visc.	Acet. No.	Acid No.
24.0	158	8.1	24.2	159	19.3
56.0	115	9.8	55.0	120	21.9
92.0	101	10.8	92.0	112	23.6

Effect of Temperature of Bodying. Alkali-refined linseed oil was bodied at $275 \pm 2^\circ$, $300 \pm 3^\circ$, and $315 \pm 2^\circ\text{C}$., samples were withdrawn at various time intervals, and acetone numbers were found. The results are shown graphically in Figure 4.

At equal viscosities in the range of 10-240 seconds the oil bodied at the lower temperature had higher acetone numbers. This was true despite the higher

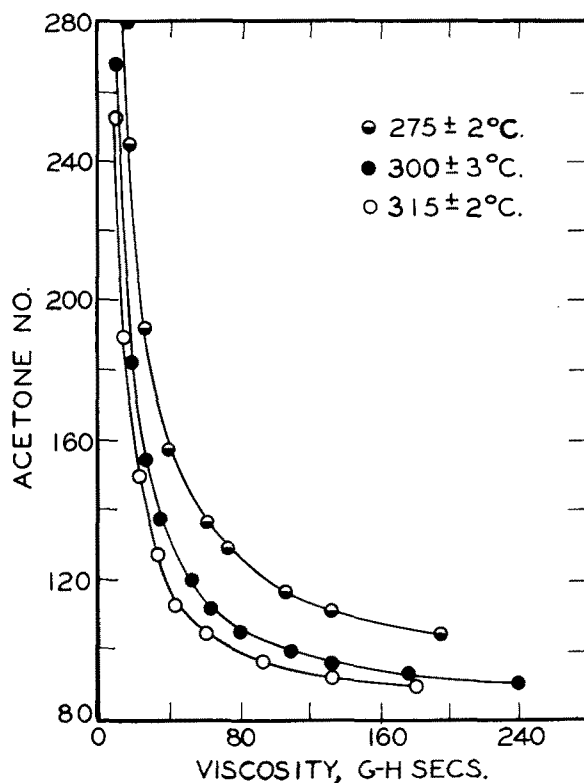


FIG. 4. Effect of bodying temperature on acetone numbers of A. R. linseed oil.

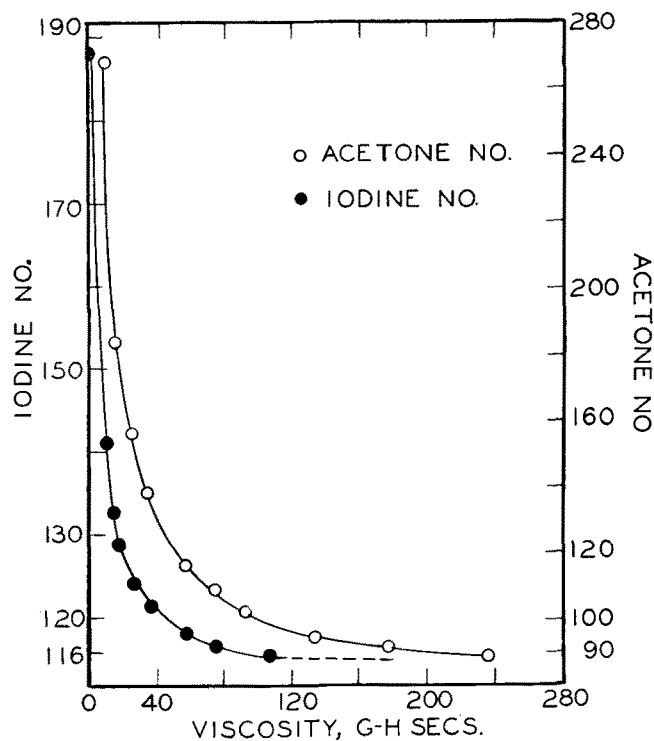


FIG. 5. Acetone numbers and iodine numbers vs. viscosity for A. R. linseed oil bodied at $300 \pm 3^\circ\text{C}$.

acid numbers produced at higher temperatures. The difference in acetone numbers is greater in comparing the 275 and 300° oils than for the 300 and 315° oils.

It is expected that the effect of other bodying conditions can be studied later. Of particular interest would be the acetone numbers of catalytically bodied oils.

Discussion

This work shows that the acetone number may be a function of several properties of bodied oils. These include a) the kind of oil, b) its viscosity, c) the amount of acids, d) processing conditions such as temperature and air-blowing, and e) the presence of modifying agents such as maleic anhydride.

As far as the acetone number is concerned, oils appear to be of two types: the non-conjugated ones, including linseed, soya, and safflower, which show lower numbers at equal viscosities than the conjugated oils, dehydrated castor and tung. The high value of tung compared to dehydrated castor suggests that the acetone number will be higher when the degree of unsaturation and conjugation is higher.

In the case of linseed, a non-conjugated oil, the acetone number varies inversely with viscosity up to a viscosity of about 200 seconds. The spread in acetone number within that viscosity range is from an infinitely high value to about 90. The rate of change of number with viscosity is conspicuous in that the greatest decrease in number is during the initial period of bodying where the rate of viscosity

increase is low (cf. Figures 2 and 3). This is reminiscent of the change in iodine number, and the plot of acetone number and iodine number against viscosity for the linseed oil bodied at $300 \pm 3^\circ$ shows a remarkable similarity in rate of change of the numbers (Fig. 5).

Thus the acetone number of a given oil depends on the degree of unsaturation rather than its average molecular weight if we accept the view that *intra* dimerization precedes inter polymerization (1).

The effect of the acids formed by decomposition during bodying is two-fold: the viscosity of the oil is probably lowered by the acids⁵ and the acetone number is increased. These effects must be kept in mind when comparing acetone numbers of various oils.

In general, the effects of acids, air-blowing during bodying, and treatment with maleic anhydride, all of which lead to high acetone numbers, are related in that oxygen-containing compounds are produced in the oil, and this added polarity increases the tolerance for acetone.

The explanation of the effect of bodying temperature is probably that higher temperatures lead to higher molecular weight, less soluble polymers with the result that the acetone number is lower.

Summary

The effect on the determination of the acetone numbers of thermally polymerized drying oils of temperature, water, color, and method of determining the end point has been reported. A simple standardization has been developed. With proper precautions a reproducibility of ± 0.16 at an acetone number of 94 can be obtained.

From a study of various bodied oils it is concluded that the acetone number is a function of the kind of oil, its viscosity, amount of acids present, processing conditions such as temperature and oxidation by air, and the addition of polar modifying agents such as maleic anhydride.

The acetone number promises to be a useful constant of bodied oils.

⁵ Work in progress on the isolation of acids from bodied oils shows that in the case of a 60-second linseed oil about 75% of the acids, as calculated by the acid number, are distillable at high vacuum and have an approximate molecular weight of 18 carbon atom acids. These acids lower viscosity. The effect of the remaining 25% is not known.

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