Polymerisation of Tung Oil, IV. Effects of Various Natural Fatty Oils upon the Gelation of Tung Oil.

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It is well known that the gelation of tung oil on heating may be delayed or prevented by the addition of certain substances. Considerable amount of works have been done along this line,[1] but as to the quantitative relation between gelation time and the amount of substances added to tung oil, only a few informations have been published.

There are known various types for curves of the gelation time and the amount of added substances, but as for the nature of the curve nothing is said. The work described in this article was undertaken for the purpose of determining the comparative effects of various fatty oils in preventing the gelation of tung oil on heating, with a hope to throw light on the explanation of gelation phenomenon of tung oil.

Experimentals. The apparatus consists of an oil bath (the diameter being 20 cm., height 17 cm.) which was maintained at a required constant temperature. The cover of the bath is provided with four openings through which the ordinary test tube, whose size was predetermined by measuring the height of 5 c.c. of alcohol taken in it (expressed in cm. unit), was dipped in bath so that the lower 9 cm. of the test tube was immersed in the oil. Five c.c. of a mixture, containing known proportion of tung oil and added substances, was put in a test tube, a glass rod (its diameter being 3 mm., length 16 cm.) was inserted in, and the test tube was put into the oil bath. The time required for the oil to gelatinize was then measured and noted. The determination was repeated for the same mixture a few times and the mean value was calculated.

The samples used have the following constants (Table 1).

Table 1.

Kind of oils	d_{15}^{15}	n_D^{20}	Iodine value	Acid value
Tung oil (A)	0.942	1.518	164.5	3.17
Tung oil (C)	0.941	1.517	166.8	4.64
Japanese wood oil	0.935	1.501	168.2	1.44
Perilla oil	0.935	1.483	199.3	5.71

(1) R. Birstinbinder, *Farben Ztg.*, **23** (1917), 243; *Chem. Umschau Fette, Oele Wachse*, **36** (1929), 36; Krumbhaar, *Chem. Abstrs.*, **9** (1915), 2155; J. Marcusson, *Zt. deut. Oele Fette Ind.*, **43** (1923), 162; H. Hardert, *Farbe und Lack*, 1928, 558; H. Brendel, *ibid.*, 1932, 145; L. A. Jordan, *J. Oil Colour Chem. Assoc.*, **17** (1934), 47.

Table 1.—(*Concluded*)

Kind of oils	d_{15}^{15}	n_D^{20}	Iodine value	Acid value
Linseed oil	0.934	1.480	171.1	4.31
Hemp seed oil	0.927	1.479	162.7	2.08
Soya bean oil	0.922	1.475	131.4	1.12
Maize oil	0.923	1 475	122 1	0 94
Sesame oil	0.923	1.474	115.2	1.19
Rape oil	0.917	1 473	99.4	1.90
Olive o l	0.918	1.470	83.0	4 37
Camellia oil	0.917	1.469	80 9	8.43
Castor oil	0.975	1.479	84.8	1.79
Sardine oil	0.934	1.483	194.4	4 66
Hardened fish oil	—	—	17.1	2.24
Liquid paraffin	0.882	1.479	—	—

From the preliminary experiments it was found that the gelation time is affected by the heating temperature, by the size of the test tube as well as by the kind of tung oils.

One of the examples is shown in Table 2, in which the gelation time of tung oil (A) were measured at 290°C. in three kinds of test tubes, widely different in size.

Table 2.

% of linseed oil added to tung oil	Gelation time in sec. Size of test tube (he ght of 5 c.c. in cm.)		
	3.1 cm.	3.5 cm.	4.5 cm.
0	485	478	465
10.00	565	559	549
15.01	633	623	620
20.04	701	699	685

The absolute value of the gelation time is affected remarkably by the size of test tube. The relation between the reciprocals of the gelation time (t) and percentage of linseed oil (x) are shown in Fig. 1.

It is a very important new fact that in all cases $1/t$ and x are in linear relations and the limiting value of x at $t=\infty$ (hereafter denoted as x_∞) converge on one point, in spite of wide differences in dimension of test tubes.

(1) *Gelation time for the system of Japanese wood oil and tung oil (A).*

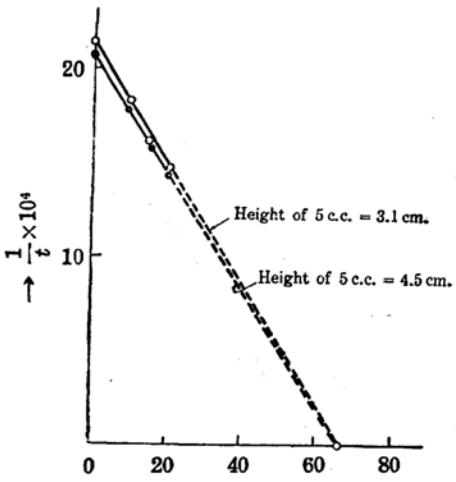

Fig. 1.

Results at 290°C. in test tubes of 3.7 cm. are given in Table 3.

Table 3.

Percent. of Japanese wood oil added to tung oil.	Gelation time (sec.)
0	467
10	513
20	555
30	640
40	730
50	862
60	1033
70	1237
100	3848

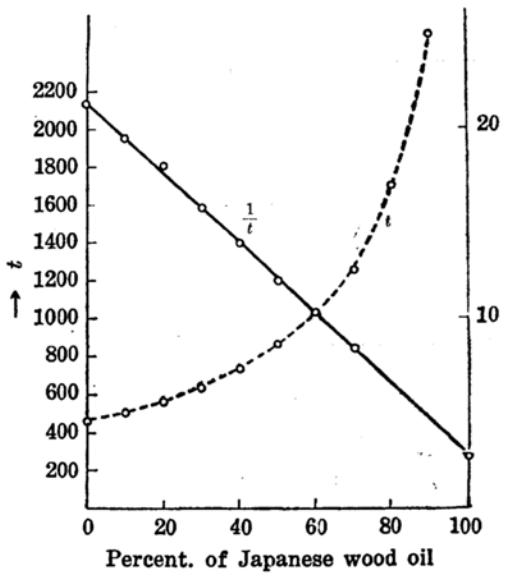

Fig. 2.

The relations of $t-x$ and $1/t-x$ are shown in Fig. 2. x and $1/t$ form a straight line in the whole range of Japanese wood oil.

(2) *The gelation time of the system of tung oil and linseed oil.* From the preliminary experiments it was noticed that the amount of added substance necessary to make the gelation time of tung oil be infinitely long, increases a little, when the heating temperature falls from 290 to 280°C., so the gelation time of the system of tung oil and linseed oil was measured in wide temperature range. It was found that the temperature of 270°C. is most suitable to determine the relation between $1/t$ and x.

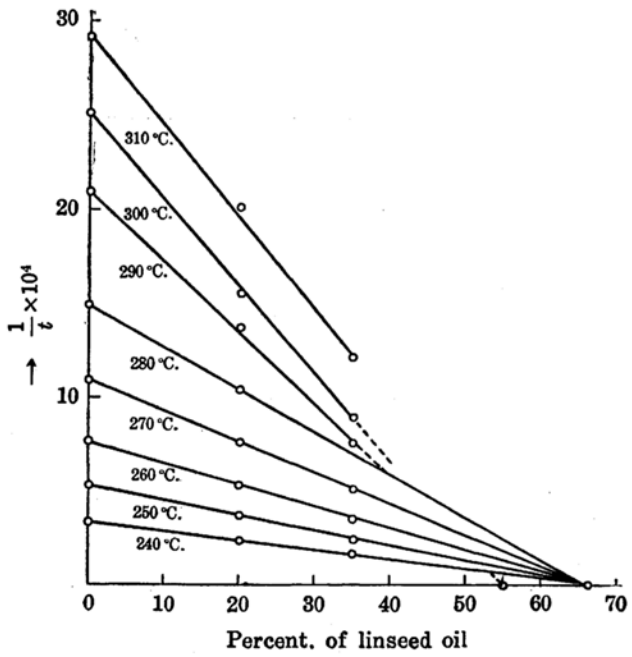

Fig. 3.

The results are shown graphically in Fig. 3.

From Fig. 3 it was found that below 280°C. lines of $1/t$- x converge

on one point of 67% and above 290°C. they shift gradually to the origin according as temperature increases: above 310°C. the rectilinear relationship is no more formed. The temperature of 270°C. is the most suitable for measuring the time of gelation by reason that above this temperature relation of $1/t-x$ is unstable and below this temperature the gelation time becomes too great.

The values of x at $\frac{1}{t}=0$ (x_∞) obtained from graphs are shown in Table 4.

Table 4.

Temperature (°C.)	x_∞ (%.)
305	52.0
300	54.0
295	56.5
290	61.5
280	67.0
270	67.0
260	67.0
250	66.5
240	67.5

(3) *Effects of temperature upon the gelation time.* The gelation time of tung oil is prolonged by lowering the heating temperature. L. A. Jordan and W. E. Wornum[2] measured the gelation time of many kinds of tung oils. F. T. Walker[3] treated their results and stated that the relation of the gelation time and temperature can be expressed by a hyperbola, whose equation is $(T\text{-}m)\times t=k$, where m and k denote constants, T the temperature, t the gelation time.

If the above be true, $1/t$ and T should be in linear relation. From Fig. 4. neither from the case of tung oil only, nor from that added by 20% linseed oil straight lines can be obtained.

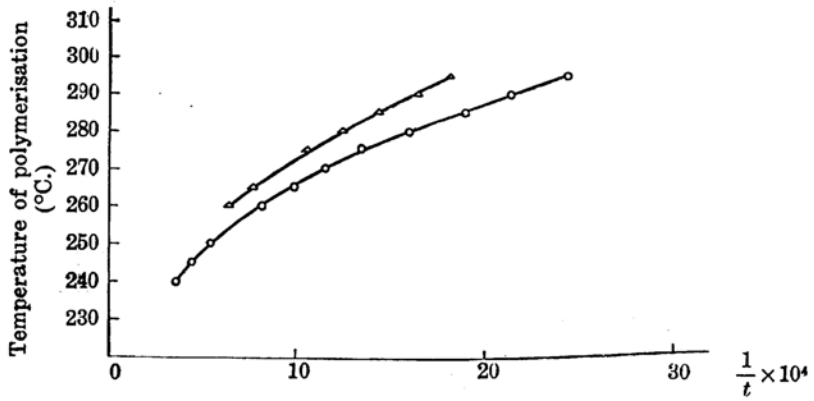

Fig. 4. Upper curve: 80% Tung oil+20% linseed oil.
Lower curve: Tung oil.

The relation between gelation time and temperature is shown in Fig. 5. It is seen that the gelation time of tung oil decreases according

(2) *J. Soc. Chem. Ind.*, **53** (1934), 1.
(3) *Ibid.*, **53** (1934), 104.

to increasing degree of temperature, but at temperature higher than 300°C. the decreasing amounts become less and less, and at last the gelation time of the system containing 20% linseed oil reaches a minimum value at 330°C., then again it increases.

It is known that the acidic substance prevents the gelation and also that when the fatty oil is heated at high temperature the cracking of glycerine radical occurs,[4] so it is reasonable that at high temperature the gelation of tung oil is prolonged.

(4) *Effects of various fatty oils.* The gelation time of various fatty oils mixed in tung oil (C) was measured at 270 and 280°C. and the results are shown in Table 5.

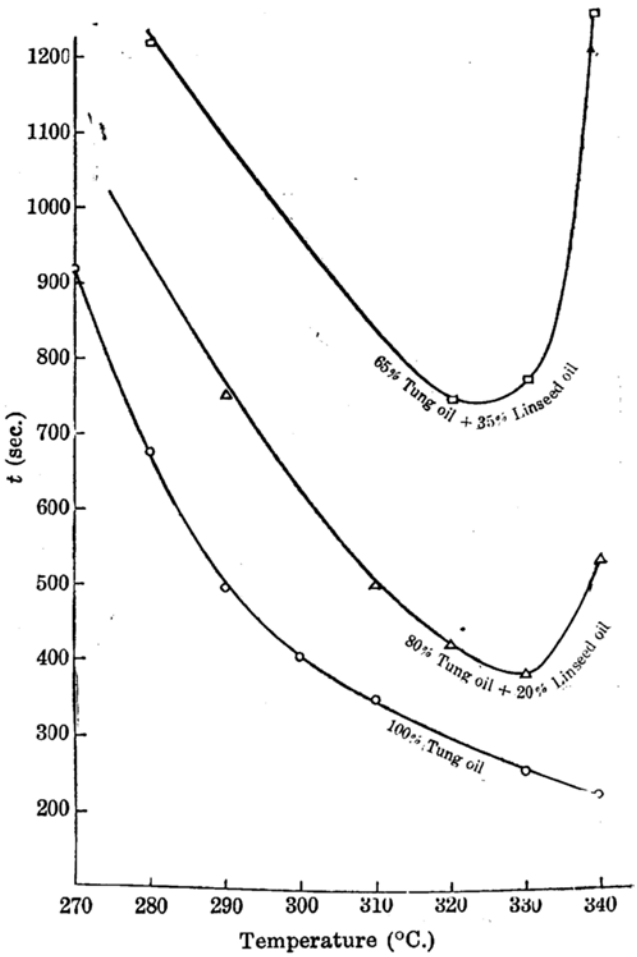

Fig. 5.

Table 5.

Kind of oils	Temperature (°C.)	Gelation time	
		% added to tung oil	
		20%	30%
Perilla oil	270	1298	1534
Hemp seed oil	270	1324	1710
	280	952	1216
Soya bean oil	270	1325	1727
	280	1023	1309
Maize oil	270	1353	1742
	280	1001	1293

(4) R. Sändig, Dissertation, Leipzig (1934), 26; Kürz, *Zt. angew. Chem.*, **49** (1936), 235.

Table 5.—(*Concluded*)

Kind of oils	Temperature (°C.)	Gelation time	
		% added to tung oil	
		20%	30%
Rape oil	270	1396	1823
	280	989	1364
Camellia oil	270	1434	1879
	280	1044	1408
Sesame oil	270	1485	2079
	280	1120	1638
Castor oil	270	1393	1815
Sardine oil	270	1483	1983
	280	1075	1440
Hardened fish oil	270	1351	1745
	280	957	1213
Liquid paraffin	270	1397	1873
	280	982	1355

For any oil $1/t$ and x are in linear relation and the lines of 270 and 280°C. converge on one point.

Discussion of Results. The gelation time of tung oil within the limit of experiments is prolonged by the addition of other fatty oil without exception. The retarding nature of any fatty oils are similar to that of Japanese wood oil (Fig. 2). For any kind of added oils $1/t$ and x show linear relation when measured in test tubes of the same dimension. This relation is expressed by

$$\frac{1}{t} = \frac{1}{t_0} - ax = b - ax \,, \qquad (1)$$

where a denotes a constant, t_0 the gelation time of tung oil. a and b vary widely according to experimental conditions, but the value of x when $t = \infty$, i.e. the amount of added substance necessary to make the gelation time of the mixture to be infinitely great, is fixed, not affected by the dimension of test tubes. It is therefore considered that x_∞ is a specific property of the substance in gelation phenomenon of tung oil.

x_∞ of various oils at 270 and 280°C. are shown in Table 6.

From the above table it is concluded that drying oils such as perilla, linseed, hempseed are less effective and for the perfect prevention of gelation the amount of more than 67% of them should be added, while semi- and non-drying oils are more effective. This is expected from the fact that at high temperature the drying oils have themselves the tendency of polymerisation and gel-formation.

Table 6—x_∞ (%).

Kind of oils	270°C.	280°C.
Perilla oil	75.5	—
Linseed oil	67.0	67.0
Hemp seed oil	67.0	69.0
Maize oil	64.5	64.5
Soya bean oil	63.0	63.5
Rape oil	63.0	63.5
Camellia oil	59.0	59.0
Sesame oil	53.0	54.5
Sardine oil	58.0	59.0
Hardened fish oil	65.0	66.5
Castor oil	62.0	—
Liquid paraffin	60.4	60.7

As a general idea x_∞ of common fatty oils increases according to increase of iodine values. The effects of castor oil, hardened fish oil and liquid paraffin were measured for the purpose of comparison, they have specific effects respectively.

Summary.

(1) The gelation time of the system of tung oil and linseed oil was measured at 240–310°C. In the range of 240–280°C. the lines of $1/t$–x converge on one point.

(2) The relation between gelation time and the amount of addition of any fatty oil is expressed by $1/t=1/t_0-ax$, and the value of x at $t=\infty$ is considered as a characteristic constant of added fatty oil.

(3) Gelation preventing effects of various natural fatty oils were measured at 270 and 280°C. Drying oils are less effective than non-drying oils due to their tendency of polymerisation.

(4) The temperature dependance of gelation time was discussed.

In conclusion, the author wishes to express his sincere thanks to Dr. K. Baba, Dr. T. Yosioka, and Mr. K. Yokota for their kind guidance.

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