Polymerisation of Tung Oil. IX. Comparison of Gelation Phenomena of Tung Oil and Oiticica Oil.

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The main constituent of tung oil which is one of the most rapidly drying fatty oils, is the glyceride of α-eleostearic acid, and has three double bonds in conjugated form. Recently oiticica oil produced in South America has been found to have powerful drying nature as comparable to that of tung oil. The main constituent of oiticica oil is licanic acid and its constitution is believed to be $CH_3(CH_2)_3$ CH=CH CH=CH CH=CH $(CH_2)_4$ CO $(CH_2)_2$ COOH, and its unsaturated nature is considered similar to α-eleostearic acid, therefore the gelation tendency of oiticica oil also is supposed to be similar to tung oil. The author reported formerly about the results of gelation of tung oil and it is interesting to ascertain that the conclusion obtained from the study of tung oil concerning gelation may be applied to oiticica oil which has the similar constitution as tung oil.

Table 1. Constants of oiticica oil.

Density (15/15)	0.9771
Iodine value	148.9
Refractive index (20°C.)	1.5130
Acid value	4.93
Saponification value	183.7

Experimentals. In this experiment the following oiticica oil was used.

The characteristic constants of the fatty oils used are shown in Table 2.

Table 2.

Kind of oil	Density (15°C.)	Refractive index (20°C.)	Iodine value	Saponification value	Acid value
Japanese wood oil	0.9347	1.5037	155.4	196.0	3.2
Tung oil	0.9422	1.5185	168.5	180.0	6.9
Linseed oil	0.9329	1.4818	182.2	190.6	11.1
Soya bean oil	0.9247	1.4750	134.8	195.7	1.4
Camellia oil	—	1.4694	79.8	191.9	5.0

The method of determining the gelation times is the same as in the previous reports and the experiment was carried out at 270°C.

Table 3.

Added Substances (%)	Gelation time (t) (sec.)	$\frac{1}{t}\times 10^4$
(1) Tung oil*		
0	1291	7.75
20	1218	8.21
40	1138	8.79
60	1082	9.24
80	1030	9.71
100	970	10.31
(2) Linseed oil		
0	1290	7.75
5	1442	6.94
10	1639	6.10
15	1921	5.21
20	2260	4.43
(3) Soya bean oil		
0	1415	7.07
5	1630	6.13
10	1890	5.29
15	2258	4.43
20	2849	3.51
25	3960	2.53
(4) Camellia oil		
0	1199	8.34
5	1368	7.31
10	1620	6.17
15	1982	5.05
20	2497	4.01
(5) Stearic acid		
0	1209	8.27
2.5	1459	6.85
5.0	1877	5.33
7.5	2690	3.72
10.0	3889	2.52
(6) Cetyl alcohol		
0	1200	8.33
2.5	1470	6.80
5.0	1996	5.02
7.5	3295	3.05
10.0	4700	2.13
(7) Rosin		
0	1209	8.27
2.5	1250	8.00
5.0	1285	7.78
7.5	1344	7.44
10.0	1403	7.13

* The relations between gelation times and percent. of tung oil are shown in Fig. 1.

Table 3.—(*Concluded*)

Added Substances (%)	Gelation time (t) (sec.)	$\frac{1}{t}\times 10^4$
(8) 5° blown asphalt**		
0	1200	8.33
5	1132	8.83
10	1260	7.94
15	1609	6.21
(9) Japanese wood oil		
0	1120	8.93
20	1221	8.15
40	1350	7.41
60	1500	6.67
80	1697	5.89
100	1928	5.18

** The results are shown in Fig. 2.

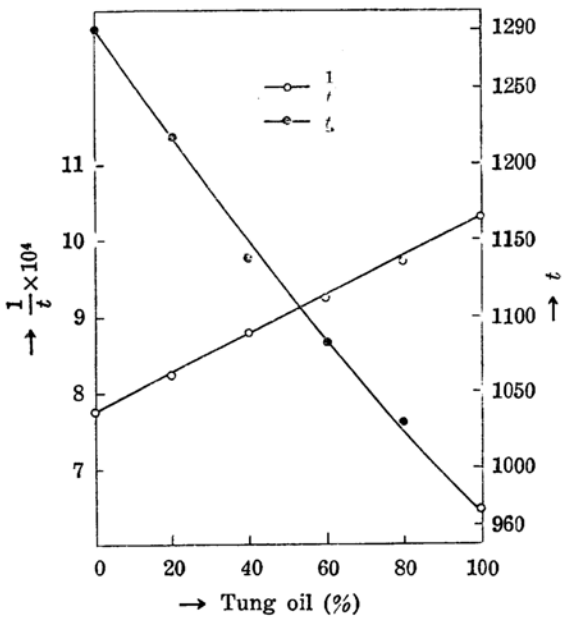

Fig. 1. The relation between gelation time and percentage of tung oil added.

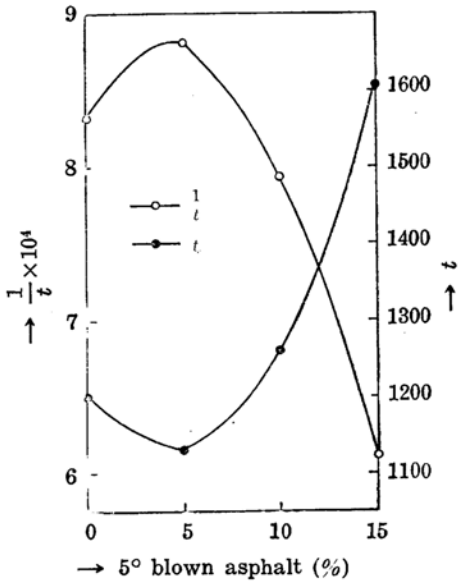

Fig. 2. The relation between gelation time and percentage of 5° blown asphalt added.

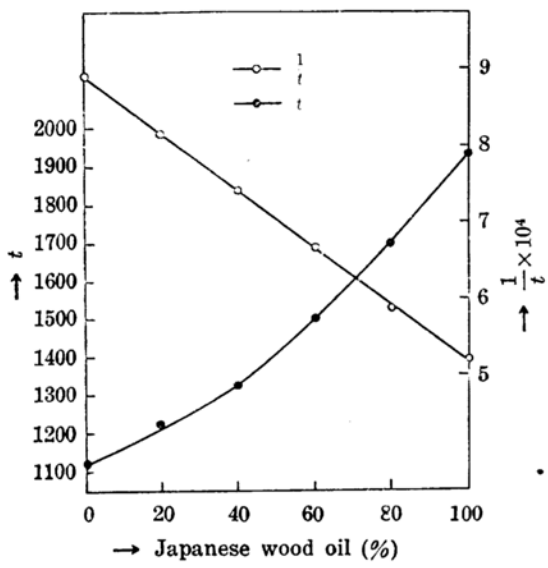

Fig. 3.

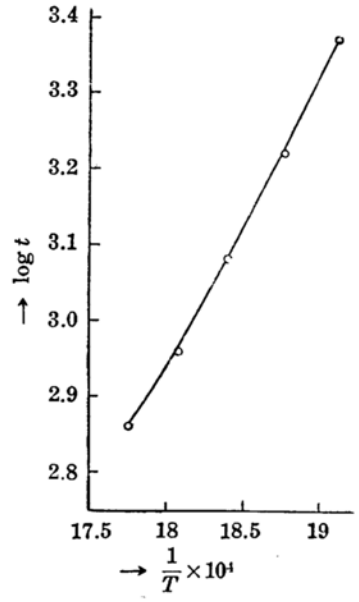

Fig. 4.

Relation between gelation times and temperatures. The gelation times of oiticica oil are shown in Table 4.

Table 4. Gelation time of oiticica oil.

Temp. (°C.)	Gelation time	$\frac{1}{t}\times10^4$	log t
250	2358	4.24	3.373
260	1660	6.02	3.220
270	1207	8.28	3.082
280	914	10.94	2.961
290	730	13.70	2.863

The relation between log t and $1/T$ is shown in Fig. 4.

The gelation times of the mixture of 50% of oiticica oil and 50% of tung oil are shown in Table 5.

Table 5.

Temp. (°C.)	Gelation time
250	2105
260	1383
270	989
280	745
290	595

The relations between gelation times and temperatures are shown in Fig. 5.

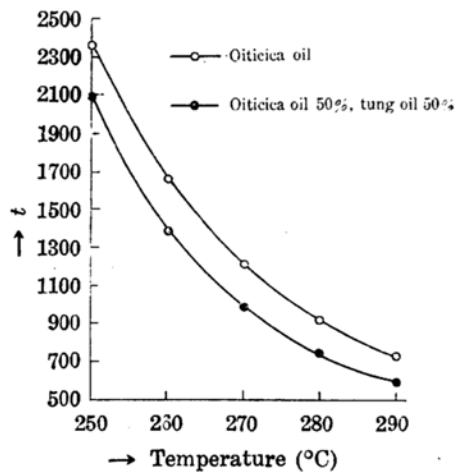

Fig. 5.

Discussion of Results. The general tendency of the gelation phenomena of oiticica oil is similar to that of tung oil.

Table 6.

Substances	x_∞ at 270°C. (%)
Japanese wood oil	236
Linseed oil	46
Soya bean oil	39
Camellia oil	37.5
Stearic acid	14.5
Cetyl alcohol	12.7

The gelation time is prolonged by the addition of fatty oils and the relations between the reciprocals of gelation times and the percentage of added fatty oils are linear, and the values of x_∞ were obtained by extrapolation.

The value of x_∞ increases according to the increasing degree of the unsaturation of fatty oil.

The gelation preventing action of stearic acid and cetyl alcohol are very strong as compared to fatty oils.

The temperature dependence of the gelation time of oiticica oil is similar to that of tung oil.

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

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