Polymerisation of Tung Oil. VI. Effects of Fatty Acids, Fatty Alcohols and Several Organic Substances upon the Gelation of Tung Oil.

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I. Fatty Acids. It is a well known fact that the addition of any acidic substance retards the gelation of tung oil when cooked[(1)], and the gelation time of tung oil increases in proportion to the increasing degree of acidity of the oil[(2)]. The interpretation of the mechanism for this retarding action has been attempted by some investigators[(3)], but it is likely that there is not yet a definite theory hereabout.

The measuring methods of the gelation time etc. were the same as those described in the previous report.

(1) *Simple fatty acids.* The Merck's pure stearic, oleic and linolic acids were used. The gelation times measured in second are shown in Table 1 and 2.

Table 1.

	Temp. (°C.)	0%	5%	7.5%	10.0%	12.5%	15.0%
Stearic acid	260	1386	1626	—	1957	—	—
	270	940	1115	1250	1397	1501	1768
	280	682	819	928	1053	1199	1482
Linolic acid	260	1340	1526	—	1769	1959	2226
	270	937	1068	1160	1262	1380	1592
	280	682	782	869	956	1050	1334

Table 2. Oleic acid.

Temp. (°C.)	0%	5%	7.5%	10.0%	12.5%	15.0%	20.0%
320	282	378	—	1560	—	—	—
310	349	475	—	781	—	4980	—
300	405	520	580	722	1130	2988	—
290	532	643	—	830	—	1482	—
280	702	834	908	1036	1192	1476	9720
270	961	1132	1207	1327	1765	1892	2820
260	1320	1575	1727	1911	2132	2369	3588
250	1995	2253	—	2699	—	3420	—

(1) R. Bürstinbinder, *Farben Ztg.*, **23** (1917), 243; H. Rhodes, J. Potts, *Chem. Metall. Eng.*, **29** (1923), 533.
(2) H. A. Gardner, *Chem. Absts.*, **15** (1921), 1081.
(3) Krumbhaar, *ibid.*, **9** (1915), 2155; L. A. Jordan, *J. Chem. Ind.*, **53** (1934), 1.

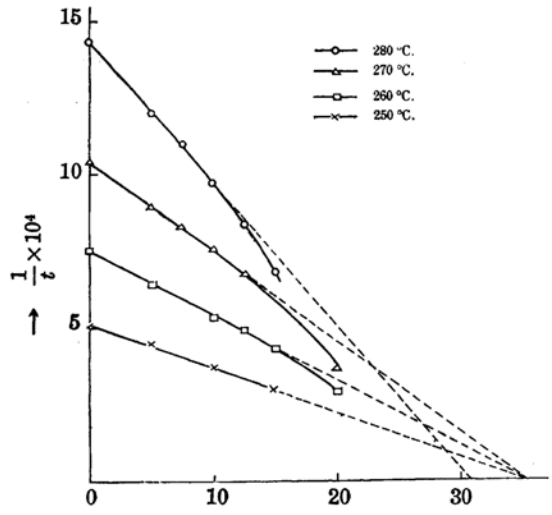

Fig. 1.

The relations between the reciprocals of gelation time ($1/t$) and the percentage of oleic acid (x) present are shown in Fig. 1.

(2) *Mixed fatty acids.* The fatty acids of tung, linseed, soyabean and sesame oils were prepared by the saponification of the respective oils by the usual methods. The gelation times are shown in the following tables.

Table 3. Tung oil acids.

Temp. (°C.)	6.9%	9.8%	14.4%	19.8%
270	1046	1150	1318	1570
280	730	808	945	1151

Table 4. Linseed oil acids.

Temp. (°C.)	5.07%	10.2%	15.0%	20.2%
270	1016	1196	1466	1948
280	726	884	1121	1677

Table 5. Soya bean oil acids.

Temp. (°C.)	5.09%	10.1%	14.7%	19.6%
270	1062	1278	1578	1771
280	775	938	1236	2269

Table 6. Sesame oil acids.

Temp. (°C.)	5.0%	10.9%	15.0%	20.3%
270	1152	1482	1764	2601
280	801	1063	1427	2361

The linear relations exist between $1/t$ and x, when x is less than 15%, beyond which curved lines are obtained. The values of x_∞ can be

Table 7. x_∞ (at 270°C.)

Stearic acid	32.0%
Oleic acid	33.5
Linolic acid	38.0
Fatty acids of sesame oil	33.3
Fatty acids of soya bean oil	34.0
Fatty acids of linseed oil	35.0
Fatty acids of tung oil	42.0

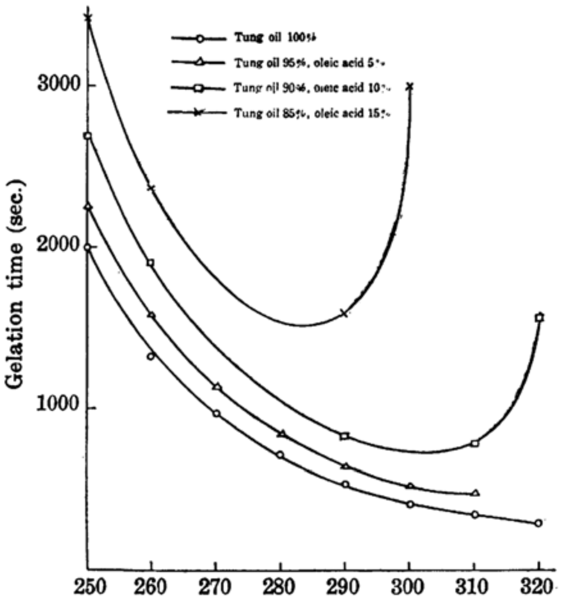

Fig. 2.

calculated from the initial inclination of the lines. The results thus obtained are summarized in the following table.

From the above results it is concluded that the value of x_∞ becomes greater as the degree of unsaturation of fatty acid increases.

The temperature effect of the gelation time of the system added with oleic acid is shown in Figs. 2 and 3.

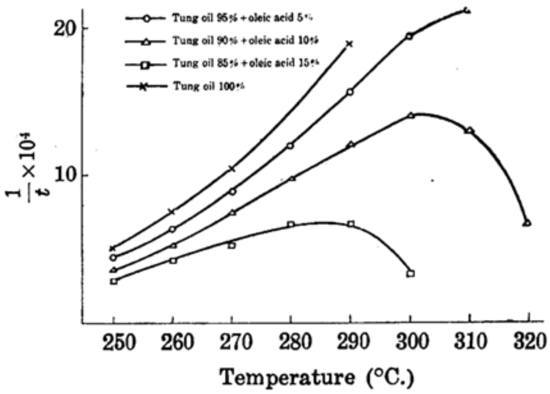

Fig. 3.

In general, oleic acid behaves like linseed oil.

II. Fatty Alcohols. Next, the effects of fatty alcohols which from the standpoint of esterification have the natures opposite to those of fatty acids, were measured. Numerical data are shown below.

(1) *Glycerine* (30° Be′).

Table 8.

Temperature	Glycerine added x (%)	Gelation time t (sec.)	$\frac{1}{t} \times 10^4$
280°C.	0	674	14.84
	5.25	1589	6.29
	7.76	2731	3.66
	19.20	3650<	2.74>
290°C.	0	436	22.94
	5.11	620	16.13
	9.09	2794	3.58
	11.92	3484<	2.87>

As glycerine does not mix with tung oil, the measurement was carried out by weighing both materials into the test tubes, and the mixture was stirred with a glass rod during the first two minutes while the determination was carried on.

From the $1/t-x$ curve it is seen that the gelation-retarding action of glycerine becomes more intense as the amount of glycerine increases, than it could be expected from the linear relation of initial part. The results obtained without stirring the mixture are shown in Table 9.

Table 9.

Temperature	x (%)	t (sec.)	$\frac{1}{t}\times 10^4$
270°C.	0	885	11.30
	5.26	958	10.44
	10.08	1045	9.57
	13.50	1085	9.22
	20.60	1257	7.96

The gelation time is greatly affected by the mechanical stirring; and the value of x_∞ may be considered to be less than 10%, when the system of tung oil and glycerine is violently stirred.

(2) *Cetyl alcohol* $C_{16}H_{34}O$.

Table 10.

x (%)	t (280°C.)	t (270°C.)	t (260°C.)
0	671	919	1344
5	740	1054	1474
10	897	1309	1965
15	1159	1705	2486

The relation of $1/t$ to x is given by a curved line V, the value of x_∞ becoming 31% when estimated from the data with samples containing 10 to 15% of cetyl alcohol.

(3) *Oleyl alcohol* $C_{18}H_{36}O$.

Table 11.

x (%)	t (280°C.)	t (270°C.)	t (260°C.)
0	665	906	1346
5	763	1097	1542
10	902	1295	1844
15	1210	1619	2256

The general tendency is the same as that of cetyl alcohol and x_∞ becomes 32.5%.

(4) *Mono-glyceride of oleic acid.*

Table 12.

x (%)	t (280°C.)	t (270°C.)	t (260°C.)
0	660	902	1306
5	766	1035	1489
10	998	1388	1887
15	1731	2227	2879
20	3439	4182	4860

Mono-glyceride of oleic acid is prepared as usual by heating glycerine and an equivalent amount of oleic acid with 1% of sulphuric acid.

The relation of $1/t$ and x is nearly linear and the value of x_∞ is 24.5% at 270°C. The gelation-preventing power is very intense.

(5) *Mono-glycol ester of oleic acid.*

Table 13.

x (%)	t (280°C.)	t (270°C.)	t (260°C.)
0	635	902	1300
5.43	724	1030	1512
10.00	863	1231	1728
15.73	1162	1502	2090
20.40	1684	2121	2712

The mono-glycol ester of oleic acid is synthetized in the same way as the case with mono-glyceride. The general tendency is the same as in mono-glyceride, the value of x_∞ amounting to 35%.

Fig. 4 shows the results obtained for four systems of tung oils added respectively with 10, 20% of oleyl alcohol, and 9.7, 13.5% of mono-glyceride.

At elevated temperatures near 300°C. the gelation time reaches a minimum value and again it increases

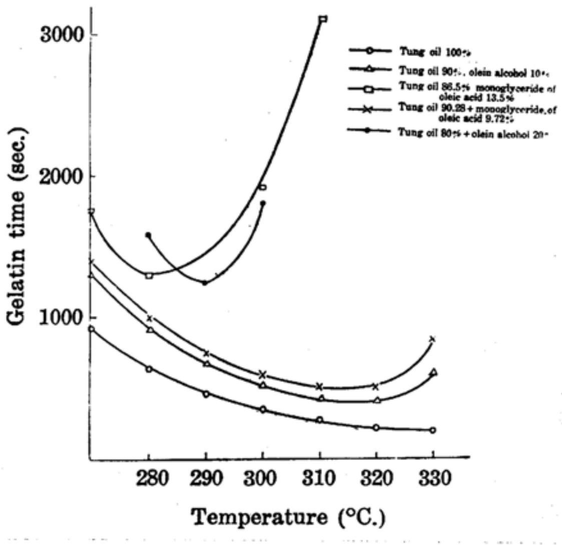

Fig. 4.

as the temperature increases. This tendency is the same as in fatty acids.

The fact that glycerine has a remarkable gelation-retarding action has been reported by Rhodes and Potts, but on the effect of mono-glyceride and fatty alcohols no report has been published.

In the cases of monovalent alcohol such as oleic, cetyl and mono-glycol ester, the values of x_∞ become 33, 31 and 35% respectively. On the other hand in the polyvalent alcohols such as glycerine, glycerine mono-ester, x_∞ amount to 10 and 14%. The peculiar behavior of glycerine is thus anticipated.

It is known that the exchange of glycerine radical occurs when fatty oil is heated with alcohols(4). Therefore the exchange of alcohol radical plays a part in the gelation-retarding effect of glycerine.

From the results of author's experiments monovalent alcohols have the retarding effect comparable to that of fatty acids. It follows therefore that another consideration should be given for this case.

III. Several Organic Substances. (1) *Hydrocarbons.* (a) Solid paraffin (Solidifying point 53°C.).

Table 14.

Solid paraffin (%)	Gelation time (sec.)
0	1247
15	1719
20	1952

The percentage of solid paraffin added (x) behaves linearly to the reciprocals of the gelation time ($1/t$) and the value of x_∞ is 56%.

(b) Mobile oil A (Boiling range 195~230°C. at 1 mmHg.).

Table 15.

x (%)	t (sec.)
10	1102
15	1226
20	1428

The linear relation also exists in this case between $1/t$ and x, the value of x_∞ being 53%.

(2) *Organic acids.* (a) Aromatic acids. The gelation-retarding effects of benzoic acid, cinnamic acid and phthalic acid anhydride were tested and their results are shown in Fig. 5.

The gelation-retarding effects of benzoic acid and cinnamic acid are very remarkable and the value of x_∞ become 18 and 25%, respectively. Phthalic acid anhydride has also retarding effect, but not so remarkable as the former two acids, probably on account of its less soluble nature in tung oil.

(b) Aliphatic polybasic acids. Succinic, malic, citric and tartaric acids were tested and their results are shown in Fig. 6.

Malic acid has a strong effect and the value of x_∞ is 19% at 270°C. Succinic acid has a poor gelation retarding action and citric acid shows practically no effect. Tartaric acid has, on the other hand, an accelerating action.

(c) Miscellaneous acids. Tannic and gallic acids, and pyrogallol were tested and their results are shown in Fig. 7.

(4) H. H. Young, H. C. Black, *J. Am. Chem. Soc.*, **60** (1938), 2603.

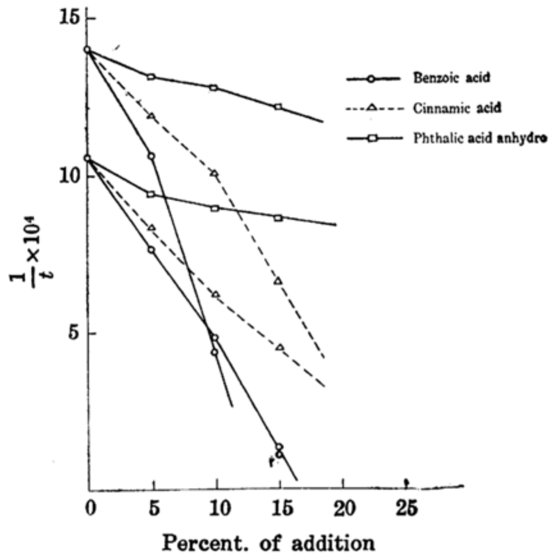

Fig. 5.

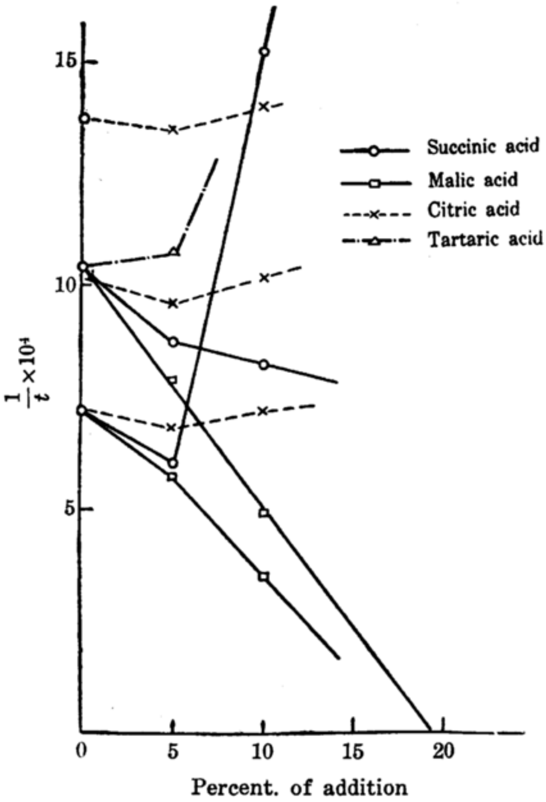

Fig. 6.

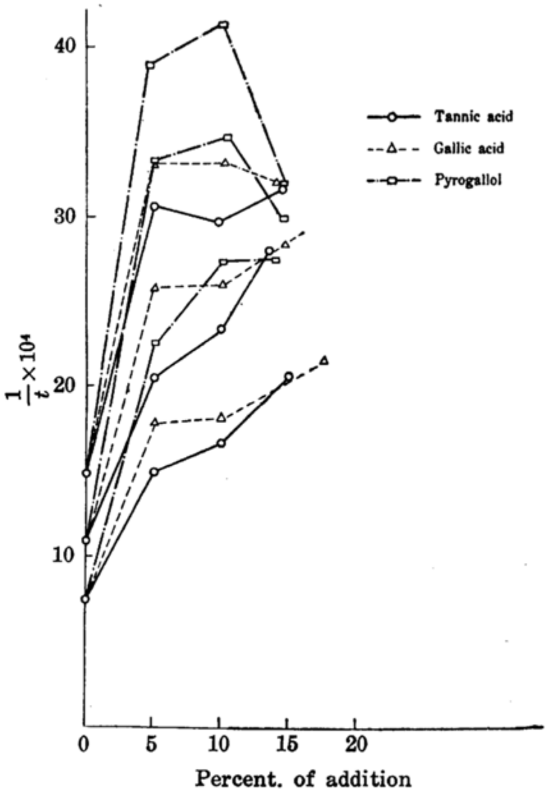

Fig. 7.

These acids have poor solubility in tung oil, but all of them have weak accelerating effects.

(3) *Aromatic substances.* (a) α-Naphthylamine.

Table 16.

x (%)	t (sec.)
0	898
4.90	1015
9.98	1170
15.0	1381

The linear relation exists between $1/t$ and x and the value of x_∞ becomes 42.3%.

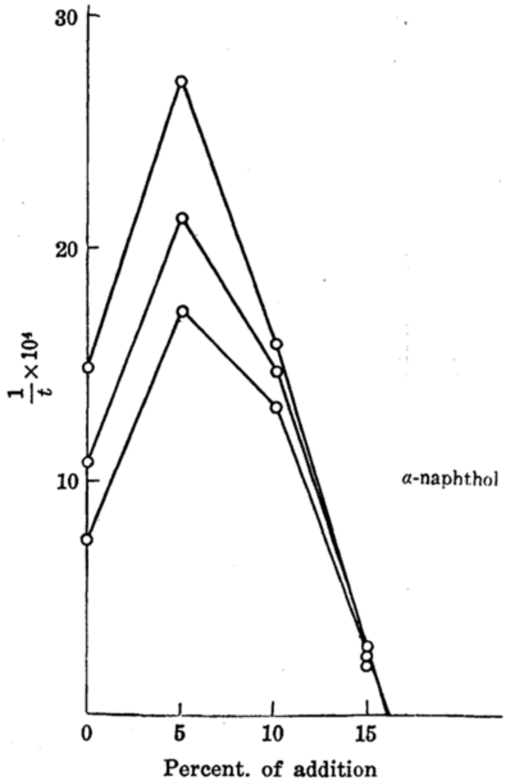

Fig. 8.

(b) Hydroquinone.

Table 17.

x (%)	t (sec.)
0	888
5	908
10	926
15	947

The linear relation exists between $1/t$ and x and the value of x_∞ amounts to 236%.

(c) α-Naphthol. The results are shown in Fig. 8. Up to 10% addition it has an accelerating effect, but beyond this limit it acts inversely and prevents the gelation.

(d) β-Naphthol. The relation between $1/t$ and x appears to form a curved smooth line and in this case no inversion is observed.

(4) *Esters.* Of the plasticizers for cellulose ester lacquers, butyl stearate, tricresyl phosphate, triacetin and Sipalin AOM (methylcyclohexanol ester of adipic acid) were tested. They have also the gelation retarding effects and the linear relations are held between $1/t$ and x in each case. The value of x_∞ at 270°C. are summarized in the following table.

Table 18.

Substances	x_∞ (%)
Butyl stearate	44.8
Tricresyl phosphate	62.5
Triacetin	54.0
Sipalin AOM	57.0

Summary.

(1) The effects of fatty acids, fatty alcohols, and other several organic substances upon the gelation of tung oil were studied.

(2) As simple fatty acids, stearic, oleic and linolic acid, as mixed fatty acids, tung oil, linseed oil, soya bean oil and sesame oil acids were used. The gelation-preventing actions of these acids are stronger than that of fatty oils and the relation of $1/t-x$ are linear, when x is less than 15%, beyond which curved lines are obtained. The value of x_∞ becomes greater as the degree of unsaturation of fatty acids increases.

(3) As fatty alcohols, glycerine, cetyl alcohol, oleyl alcohol, monoglyceride of oleyl acid, monoglycol ester of oleic acid were used. The

gelation-preventing actions of these monovalent alcohols are strong and their order are similar to that of fatty acids.

Glycerine and monoglyceride of oleic acid have very strong gelation-preventing actions and their retarding nature is probably due to special chemical reaction such as exchange of glycerine radicals.

(4) Among the several organic substances tested by the author, neutral substances such as solid paraffin, mobile oil, butyl stearate, triacetin, tricresyl phosphate, Sipalin AOM, α-naphthylamine, hydroquinone, β-naphthol have the retarding effects and the linear relations exist between $1/t$ and x. Benzoic acid, phthalic acid anhydride and malic acid have remarkable retarding effects, but their relations between $1/t$ and x are irregular.

Tartaric, tannic and gallic acids and pyrogallol have accelerating actions. The behavior of α-naphthol is very noteworthy; that is, it accelerates the gelation of tung oil when the amount of addition is less than 10%, but beyond this limit it retards the gelation of tung oil.

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