Polymerisation of Tung Oil. V. Effects of Treated Fatty Oils upon the Gelation of Tung Oil.

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As the nature of fatty oil is markedly affected by various treatments, the effect of several kinds of fatty oil treated by different ways upon the gelation time of tung oil is dealt in the present paper.

Cooked drying oils. Drying oils such as linseed or perilla oils are usually cooked and at the end of cooking they turn by oxidation or polymerisation into a gelatinous state, therefore the gelation preventing action of these oils upon tung oil should be affected by their cooking degree. To obtain the relation between x_∞ and the cooking degree, the following experiments were done. The measurements of gelation times carried out at 270°C. were the same as in the previous report.

I. Oxidised and polymerised linseed oils. The cooked oils were obtained by oxidising linseed oil at 100°C. with oxygen, and by polymerising it at 287°C. in carbon dioxide atmosphere.

Table 1. Raw linseed oil.

(iodine value 172.4).

x (%)	t (270°C.)	t (280°C.)
10.40	1040	730
20.00	1228	841
30.15	1576	1075
x_∞	67%	66%

Table 2. Oxidised linseed oil No. 1.

(iodine value 140.8).

x (%)	t (270°C.)	t (280°C.)
10.22	989	691
20.21	1167	828
30.86	1367	950
x_∞	85%	86%

Table 3. Oxidised linseed oil No. 2.

(iodine value 124.1).

x (%)	t (270°C.)	t (280°C.)
10.40	944	688
20.71	1036	751
30.97	1165	843
x_∞	122%	122%

Table 4. Oxidised linseed oil No. 3.

(iodine value 115.9).

x (%)	t (270°C.)	t (280°C.)
15.0	971	719
30.6	1068	798
x_∞	196%	198%

Table 5. Polymerised linseed oil No. 1.

(iodine value 161.0).

x (%)	t (270°C.)
0	882
5.23	942
15.1	1106
30.9	1595
x_∞	69%

Table 6. Polymerised linseed oil No. 2.

(iodine value 140.3).

x (%)	t (270°C.)
7.73	947
10.00	1010
15.00	1067
30.00	1430
x_∞	73%

Table 7. Polymerised linseed oil No. 3.

(iodine value 124.1),

x (%)	t (270°C.)
10.58	985
20.55	1146
29.28	1230
x_∞	87%

Table 8. Polymerised linseed oil No. 4.

(iodine value 122.2).

x (%)	t (270°C.)
15.04	1085
30.40	1435
x_∞	88%

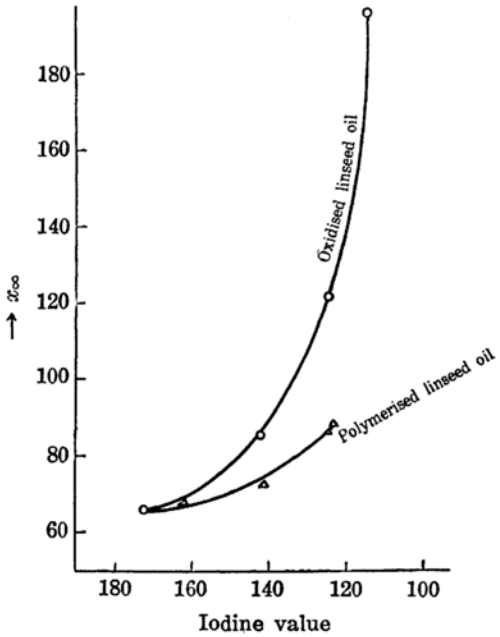

Fig. 1.

The relation of x_∞ to the iodine value of cooked oils is shown in Fig. 1.

From Fig. 1 it is noticed that the value of x_∞ increases with the increase of cooking degree; that is, the gelation-preventing action becomes weaker, as the cooked oil itself has the gelation tendency.

For the same cooking degree, the value of x_∞ for the oxidised linseed oil is greater than that for the polymerised oil. This coincides with the fact that the drying power of oxidised oil is always greater than that of polymerised oil[1].

II. Oxidised perilla oil. The gelation retarding effect of the oxidised perilla oils oxidised at 100°C., 200°C. and 300°C. was measured.

(1) M. Tatimori, *Hitachi Hyoron*, **20** (1937), 43.

Perilla oil taken in 1l. beaker were oxidised, by air-blowing at temperatures of 100°C., 200°C. and 300°C. respectively. The oxidised oils then had the following constants.

Table 9.

Kind of oil		Abbreviation	Iodine value
Raw Perilla oil		200 (0)	210.0
Oxidised at	100°C.	170 (100)	175.5
,,	200°C.	170 (200)	177.6
,,	300°C.	170 (300)	177.5
,,	100°C.	150 (100)	160.4
,,	200°C.	150 (200)	156.5
,,	300°C.	150 (300)	149.9
,,	100 C.	140 (100)	140.7
,,	200°C.	140 (200)	140.9
,,	300°C.	140 (300)	137.5

Table 10.

Kind of oil and Remarks	Amount of addition (x %)	Gelation time (t, sec.)	Kind of oil and Remarks	Amount of addition (x %)	Gelation time (t, sec.)
200 (0): The relation between $1/t$ and x is linear and the value of x_∞ becomes 59.5%.	0 10 20 30 40 50	881 1040 1254 1622 2338 3899	150 (200): A curved line is obtained, the estimated value of x_∞ is 84%.	0 10 20 30 40 50	885 950 1050 1184 1375 1590
170 (100): The relation of $1/t$ and x forms a convex curve, the estimated value of x_∞ is 62%.	0 10 20 30 40 50	888 1017 1140 1409 1794 2695	150 (300): A straight line is obtained, x_∞ is 89%.	0 10 20 30 40 50	870 980 1120 1269 1498 1777
170 (200): The relation of $1/t$ and x forms nearly a straight line and x_∞ is 66%.	0 10 20 30 40 50	884 1057 1170 1524 1935 2842	140 (100): A curved line is obtained.	0 10 20 30 40 50	886 899 940 982 1018 1086
170 (300): The relation between $1/t$ and x is linear and x_∞ is 66%.	0 10 20 30 40 50	885 1144 1348 1660 2197 3130	140 (200):	0 10 20 30 40 50	884 910 983 1074 1177 1298
150 (100): A curved line is obtained, the estimated value of x_∞ is 67%.	0 10 20 30 40 50	886 942 1032 1200 1464 2040	140 (300): The relation between $1/t$ and x is linear and x_∞ is 110%.	0 10 20 30 40 50 100	884 930 1018 1101 1255 1422 5012

The relations between the reciprocals of gelation times and the amount of addition of oils are shown in Fig. 2.

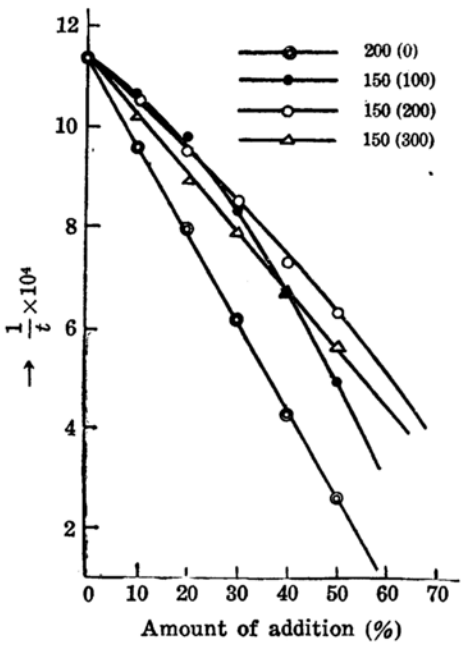

Fig. 2.

From the above rsults it is concluded that with the addition of oxidised oils at 300°C. the relation of $1/t$ and x are linear, on the contrary in the cases of oxidised oils at 100°C. curved lines are obtained and in the cases of oxidised oils at 200°C., those of the beginning of cooking, a straight line, but those of the increased degree of cooking curved lines are obtained.

It is supposed that oxidised fatty oil prepared at low temperature contains a substance which has special action upon the gelation of tung oil. M. Nakamura[2] reported that oxidised fatty oil prepared at temperatures lower than 160°C. contains a peroxide, while high temperature oxidation oil does not contain it. The author conformed from a qualitative experiment that the oil oxidised at 100°C. contains peroxide, while that oil oxidised at 300°C. does not contain it.

Therefore the curved nature of the relation between $1/t$ and x is supposed to be due to the peroxide contained in the oil.

III. Effect of benzoyl peroxide. To verify the above presumption the effect of benzoyl peroxide were studied.

Table 11. Effect of perilla oil added with 5% of benzoyl peroxide.

x (%)	t (sec.)
0	885
10	1032
20	1168
30	1512
40	2111
50	3762

Table 12. Effect of perilla oil added with 10% of benzoyl peroxide.

x (%)	t (sec.)
0	878
10	981
20	1125
30	1353
40	1775
50	2911

(2) *J. Chem. Ind. Japan*, **40** (1937), 448.

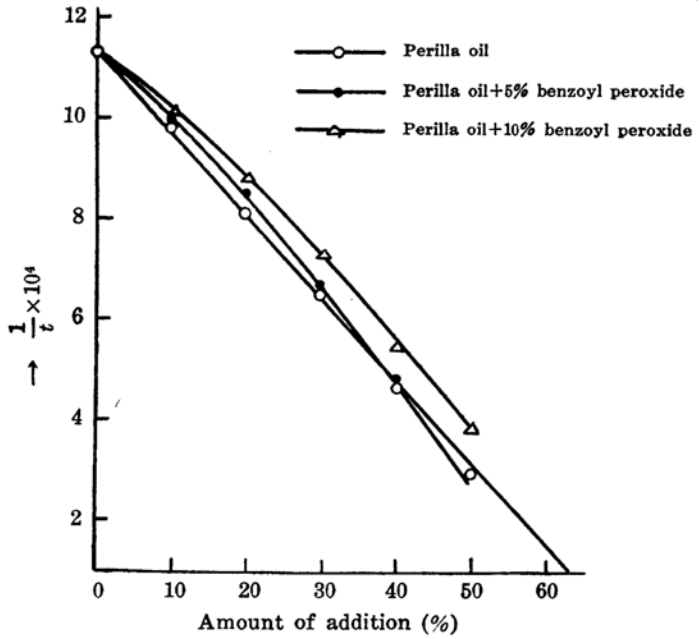

Fig. 3.

The nature of the curve is similar to that of oxidised perilla oil prepared at 100°C.

From the above results benzoyl peroxide has a great accelerating action upon the gelation of tung oil. It is a well known fact that peroxides have accelerating actions upon the polymerisation of butadiene and styrol. It is concluded that the curved nature of $1/t$–x relation of oxidised perilla oil is due to the superposed effects of retarding action of oxidised perilla oil and of accelerating action of peroxide contained in it. The relation of x_∞ to the degree of cooking of oxidised oil prepared at 300°C. is shown in Table 14.

Table 13.

Effect of benzoyl peroxide.

x (%)	t (sec.)
0	883
0.1	860
0.3	837
0.5	810
0.8	760
1.0	730
10.0	349
20.0	148
30.0	23

Table 14.

Kind of oil	x_∞ (%)	Iodine value
200 (0)	59.5	210.0
170 (300)	66.0	177.5
150 (300)	89.0	149.9
140 (300)	110.0	137.5

The value of x_∞ increases according to the increase of cooking degree. This tendency is similar to that of the cooked linseed oil.

Table 15. Brominated soya bean oil (Br content 31.3%).

x (%)	t (270°C.)
0	904
1.09	885
2.07	958
3.00	1410

The gelation preventing action is very strong and the value of x_∞ is less than 6%.

Table 16. Brominated soya bean oil (Br content 16.4%)

x (%)	t (270°C.)
0	903
1.19	791
2.27	1088
3.00	3818

The value of x_∞ is 3.5%.

Table 17. Brominated oleic acid (Br content 17.7%).

x (%)	t (270°C.)
0	1086
1.43	1291
2.00	1994

The value of x_∞ is less than 3.0%.

IV. Brominated fatty oils.

Brominated fatty oils and fatty acids have a strong gelation—retarding action. On heating the brominated fatty oil the hydrogen bromide is evolved. It is supposed therefore that the gelation—preventing action of brominated oils is due to the isomerizing action of hydrogen bromide exerting on the conjugated double bond of the tung oil molecule.

Summary.

1. The gelation—preventing actions of oxidised and polymerised linseed oil were measured. The value of x_∞ increases with the increasing degree of cooking and the value for oxidised oils is always greater than that for polymerised oils of the same cooking degree.

2. Perilla oil was oxidised at 100°C., 200°C. and 300°C. to the degrees of iodine values 170, 150, 140 and the effects upon the gelation were measured. In the cases of oxidised oil prepared at 300°C. the relation of $1/t \sim x$ was linear and the value of x_∞ increase according to the increase of cooking degree. In the cases of oxidised at 100°C. and 200°C. curved lines were obtained. This tendency is supposed to be due to the peroxide contained in it.

3. The effect of benzoyl peroxide also was examined. Benzoyl peroxide has a strong gelation accelerating action. The effect of perilla oil added with benzoyl peroxide is similar to that of perilla oil oxidised at low temperature.

4. The gelation—preventing action of brominated oils is very strong and the value of x_∞ is less than 4%. Therefore, these substances can be used as a strong gelation—preventing agent.

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