Polymerisation of Tung Oil. VIII. Effects of Various Bitumens and Resins upon the Gelation of Tung Oil.

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The insulating varnishes are made by cooking the mixture of drying oils, bitumens and resins, and their properties are affected eminently by the cooking process. As drying oils, tung oil is one of the most preferable. This paper deals with the results of the effects of various bitumens and resins upon the gelation of tung oil.

(I) Effects of Bitumens. The samples used have the following constants (Tables 1, 2).

Table 1.

Constants of petroleum asphalts.

Kind of Asphalts	Penetration degree (25°C., 100g., 5 sec.)	Softening point (°C.) (Ball & ring method)
S-1	6.0	72.5
S-2	40.7	52.0
S-3	70.0	51.0
B-1	7.0	126.5
B-2	29.0	69.0
B-3	33.5	66.0

S: Straight asphalt
B: Blown asphalt

Table 2.

Softening point of bitumens.

Names of bitumens	Softening point (°C.)
Gilsonite	150.5
Petroleum pitch	108.5
Stearin pitch	82.5
Mineral rubber	137.0
Coal tar pitch	121.0

The measuring methods were the same as those described in the previous reports, the determinations being carried out at 270°C. The relation between gelation time and percentage of petroleum asphalt added to tung oil is shown in Table 3.

Fig. 1 and Fig. 2 show the relation between reciprocals of gelation times ($1/t$) and percentages (x) of straight and blown asphalts added to tung oil.

As shown in these figures, the gelation of tung oil is promoted, when petroleum asphalt is added in an amount less than 10 percent.; but an addition of a larger amount of asphalt tends to prevent the gelation. This sort of inversion is a newly recognized fact. It seems that petroleum asphalt which has a lower softening point has somewhat greater retarding effect on the gelation.

Results with various bitumens are shown in the following.

The inversion was observed at 10% with samples containing gilsonite, mineral rubber, tar pitch, petroleum pitch, and at 25% with those containing stearin pitch.

Table 3. Gelation time of tung oil containing petroleum asphalts.

Kind of asphalts	Percent. of asphalt added (x)	Gelation time (sec.) (t)	$\frac{1}{t}\times 10^4$
S-1	0	938	10.66
	4.96	875	11.43
	9.96	866	11.55
	20.00	944	10.59
	29.82	1101	9.08
	39.90	1585	6.31
S-2	0	939	10.65
	5.00	881	11.35
	9.94	871	11.42
	19.96	973	10.28
	29.50	1228	8.14
	40.00	2398	4.17
S-3	0	937	10.67
	5.00	891	11.22
	9.82	907	11.03
	20.00	1014	9.86
	30.00	1208	8.28
	39.95	1766	5.66
	50.00	>3499	2.86>
B-1	0	938	10.66
	10	754	13.26
	20	799	12.52
	30	992	10.08
B-2	0	933	10.72
	10	798	12.53
	20	861	11.61
	30	1037	9.64
B-3	0	938	10.66
	10	861	11.62
	20	922	10.85
	30	1238	8.08

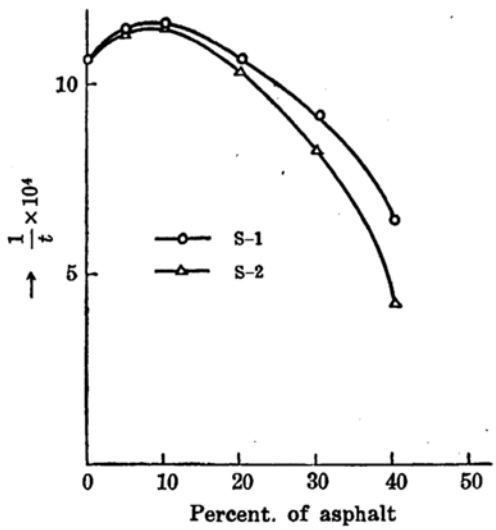

Fig. 1.

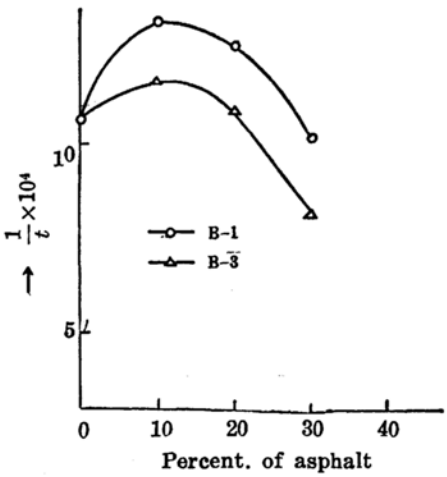

Fig. 2.

Table 4. Gelation time of tung oil containing bitumens.

Kind of bitumens	x (%)	t (sec.)	Kind of bituments	x (%)	t (sec.)
Gilsonite	0	782	Coal tar pitch	0	904
	4.96	752		5.0	870
	10.80	771		10.0	810
	15.31	781		14.9	836
	25.00	792		25.1	969
	35.30	849		35.1	1148
	45.10	953	Stearin pitch	0	776
	54.80	1108		4.96	618
Mineral rubber	0	785		9.95	551
	5.16	723		14.97	546
	9.94	734		24.85	543
	15.56	773		35.0	566
	24.00	814		44.9	649
	35.18	940		54.5	771
	45.00	1056	Petroleum pitch	0	920
	55.00	1447		5.0	764
				10.0	736
				15.0	755
				25.0	761
				35.0	947

The relation between components of asphalt and the inversion. As shown above, every bitumen added in small amount to tung oil promotes the gelation, where when the added amount increases the effect is reversed, and it retards the gelation. This is a phenomenon which is not found in cases of fatty oils, fatty acids, hydrocarbons, etc.

In order to study the relation between components of asphalt and the inversion, following two experiments were undertaken.

(1) The measurements were made with 15°– blown asphalt, which was separated into two parts, soluble and insoluble in hot alcohol. For the purpose of separation, asphalt was heated with 94% alcohol for 5 hours at 120–130° under 7 atmospheric pressure, followed with renewal of alcohol, and heated again under the same conditions. By repeating this treatment four times, the asphalt was separated into soluble and insoluble parts.

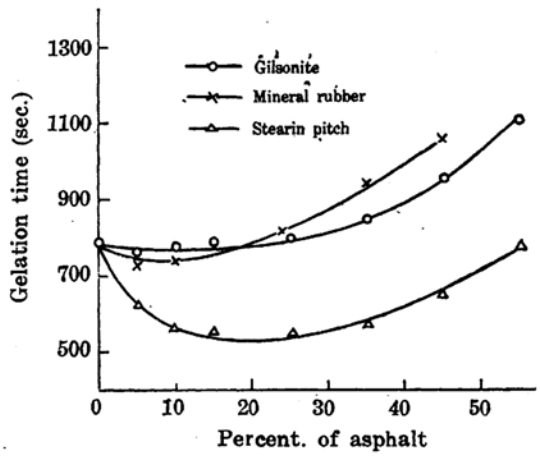

Fig. 3.

Results obtained with soluble and insoluble parts are shown in Table 5.

Table 5. Gelation time of tung oil containing 15°-blown asphalt.

15°-Blown asphalt	x (%)	t (sec.)	15°-Blown asphalt	x (%)	t (sec.)
Alcohol-insoluble part	0	871	Alcohol-soluble part	0	897
	5.0	843		5.0	810
	9.97	809		10.0	800
	14.97	870		14.75	799
	20.0	919		23.60	833
	25.0	998		26.10	894
	30.0	1117		30.00	997

The inversion occurs at 10% with tung oil containing alcohol-insoluble part of blown asphalt and at 15% with that containing alcohol-soluble part.

(2) The components of asphalt are not well known at present, but it is generally accepted that asphalt is composed of petrolen and asphalten. A solution of 5 g. of 5°-blown asphalt in 25 c.c. benzene was poured into 200 c.c. benzine. The precipitate thus obtained was collected and dried to give asphalten, and the filtrate was evaporated to an oily substance, petrolen.

Effects of the petrolen and asphalten upon gelation of tung oil were studied. Results with petrolen are given in Table 6.

Table 6. Gelation time of petrolen of 5°-blown asphalt.

x (%)	t (sec.)	$\frac{1}{t}\times 10^4$
0	917	10.91
5.0	1004	9.96
10.13	1181	8.47
15.0	1392	7.18
20.0	1826	5.48
24.93	2538	3.94
29.94	3671	2.72

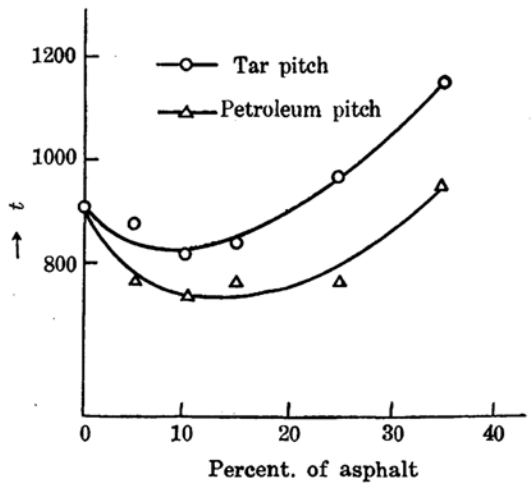

Fig. 4.

The inversion was not found in the experiments with petrolen. As in the case of fatty oils, $1/t$ and x were in a linear relation, and x_∞ was 38.0%.

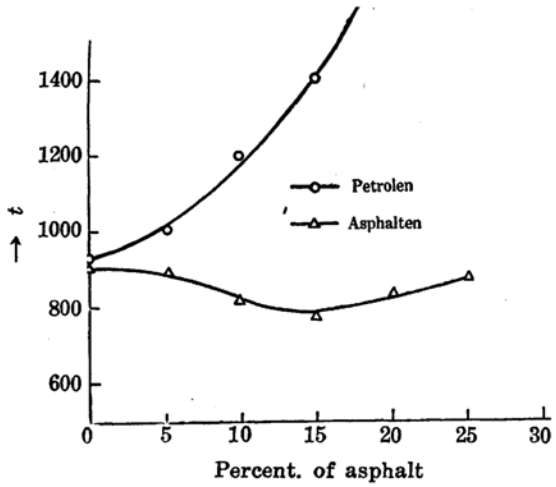

Fig. 5.

Table 7. Gelation time of tung oil containing asphalten of 5°-blown asphalt.

x (%)	t (sec.)
0	899
4.99	886
9.98	801
15.0	768
20.0	827
24.95	861

Results with asphalten are shown in Table 7. In this case the inversion occurred at 15%.

Of the substances reported only α-naphthol indicated the inversion. It can be anticipated that asphalten contains some substances giving a peculiar effect on tung oil.

(II) Effects of Various Resins. Next the effect of various natural and synthetic resins on gelation time of tung oil were examined. Acid values and iodine values of these resins are shown in Table 8.

Table 8.

Resin	Acid value	Iodine value
Copal	134	120.7
Dammar	31.2	83.5
Amber	20.5	61.4
Mastic gum	56.7	124.0
Sandarac gum	134	101.9
Rosin	132.4	130.9
Ester rosin	35.0	115.8
Tamanol No. 125 L	17.8	80.1
Super becacite	28.1	52.7
Bakelite resin No. 254	47.5	66.3
Leuchtol	4.7	55.1
Phthalate resin	7.6	80.4
Coumarone resin	0.5	31.8
Hitachi oil soluble resin	21.4	79.8

Each of these resins was pulverized, weighed, and put into test tubes and suitable quantities of tung oil were added; measurement was carried out at 270°C. in every case.

The gelation times in second were shown in Table 9.

Table 9.

Kind of Resins and Remarks	Addition x (%)	t (sec.)	$\frac{1}{t}\times 10^4$
(1) Copal: An approximately linear relation is found between $1/t$ and x and the value of x_∞ is 91.5%.	0	803	12.45
	4.98	891	11.22
	10 0	936	10.68
	15.1	999	10.00
	20.1	1073	9.32
	25.1	1142	8.75
	30.0	1254	7.97
(2) Dammar: The result is similar to that of copal and the value of x_∞ is 67%.	0	791	12.64
	4.99	857	11.67
	9.95	928	10.77
	14.9	1019	9.81
	19.9	1120	8.98
	24.95	1265	7.91
	30.0	1445	6.92
(3) Amber: The general tendency is the same as the above two resins and x_∞ is 62.5%.	0	882	11.34
	4.97	935	10.70
	10.0	1029	9.27
	15.0	1141	8.76
	19.9	1313	7.62
	24.9	1503	6.65
	29.9	1658	6.03
(4) Mastic gum: A slightly curved line is obtained, x_∞ being 62.5%.	0	879	11.38
	5.36	954	10.48
	10.3	1016	9.84
	14.9	1111	9.00
	19.9	1259	7.94
	24.9	1430	6.99
	30.0	1693	5.91
(5) Sandarac gum: The value of x_∞ is approximately estimated to 87%.	0	892	11.21
	5.0	952	10.51
	10.0	988	10.12
	15.0	1084	9.22
	20.0	1118	8.95
	25.0	1228	8.14
	30.0	1394	7.17
(6) Coumarone resin: A straight line is obtained, x_∞ being 64.5%.	0	843	11.86
	4.99	924	10.82
	10.53	1004	9 96
	14.94	1088	9.19
	19.89	1173	8.52
	25.15	1382	7.23
	31.2	1661	6.02
(7) Ester rosin: A curved line is obtained and x_∞ is 42%.	0	889	11.25
	4.98	947	10.56
	9.96	1002	9.98
	15.0	1114	8.98
	20.0	1358	7.36
	25.0	1661	6.02
	30.0	2742	3.65

Table 9.—(*Concluded*)

Kind of Resins and Remarks	Addition x (%)	t (sec.)	$\frac{1}{t}\times10^4$
(8) Tamanol 125 L: $1/t$ and x bear an irregular relation, this may be probably due to the less soluble nature of the resin in tung oil and the value of x_∞ estimated is 120%.	0	917	10.91
	5.11	927	10.79
	10.0	956	10.46
	13.88	972	10.29
	20.0	1060	9.43
	25.0	1120	8.93
	30.0	1265	8.58
(9) Super beckacite: A slightly gelation-accelerating action is observed.	4.98	909	10.98
	9.90	953	10.49
	14.94	932	10.74
	19.84	904	11.06
	23.97	866	11.55
	29.46	798	12.53
(10) Phthalate resin: A curved line is obtained and the value of x_∞ is less than 60%.	4.90	923	10.83
	10.0	948	10.55
	14.59	978	10.22
	19.92	1034	9.67
	25.00	1055	9.48
	29.64	1128	8.87
(11) Leuchtol: The gelation-preventing action is very strong and the value of x_∞ is approximately 22%.	5.0	928	10.78
	9.83	1062	9.42
	14.74	1554	6.43
	20.0	3642	2.74
(12) Bakelite resin No. 254: An irregular relation, probably due to its less soluble nature in tung oil, is obtained.	0	848	
	5.0	809	
	9.84	751	
	14.76	742	
	19.92	728	
	24.5	761	
	30.0	848	
(13) Oil soluble phenol-formaldehyde resin made by Hitachi Works: The result is the same as above.	0	882	
	4.6	866	
	9.8	889	
	14.9	938	
	19.7	922	
	24.0	942	
	29.7	988	

(14) Rosin:

In order to find the gelation-retarding effect of rosin the following experiments were carried out.

Table 10. Gelation time at 250°C.

x (%)	t (sec.)	$\frac{1}{t}\times10^4$	$\frac{1}{x}\left(\frac{1}{t_0}-\frac{1}{t}\right)\times10^4$
0	1910 (t_0)	5.236	—
5	1954	5.118	0.0256
10	2095	4.773	0.0463
15	2301	4.346	0.0593
20	2582	3.873	0.0682
25	3120	3.205	0.0812

Table 11. Gelation time at 260°C.

x (%)	t (sec.)	$\frac{1}{t}\times10^4$	$\frac{1}{x}\left(\frac{1}{t_0}-\frac{1}{t}\right)\times10^4$
0	1324	7.553	—
5	1366	7.321	0.0044
10	1460	6.849	0.0704
15	1563	6.277	0.0857
20	2039	4.904	0.1325
25	3030	3.300	0.1701

Table 12. Gelation time at 270°C.

x (%)	t (sec.)	$\frac{1}{t}\times10^4$	$\frac{1}{x}\left(\frac{1}{t_0}-\frac{1}{t}\right)\times10^4$
0	955	10.47	—
5	985	10.17	0.060
10	1066	9.38	0.109
15	1250	8.00	0.164
20	1598	6.26	0.210
25	3025<	—	—

Table 13. Gelation time at 290°C.

x (%)	t (sec.)	$\frac{1}{t}\times10^4$	$\frac{1}{x}\left(\frac{1}{t_0}-\frac{1}{t}\right)\times10^4$
0	441	22.68	—
5	491	20.37	0.462
10	574	17.42	0.526
15	753	13.28	0.621
20	1371	7.29	0.769
25	3720<	2.69>	0.800<

Table 14. Gelation time at 300°C.

x (%)	t (sec.)	$\frac{1}{t}\times10^4$	$\frac{1}{x}\left(\frac{1}{t_0}-\frac{1}{t}\right)\times10^4$
0	365	27.4	—
5	397	25.2	0.442
10	510	19.6	0.779
15	703	14.2	0.878
20	2203	4.54	1.143
25	4800<	2.08	—

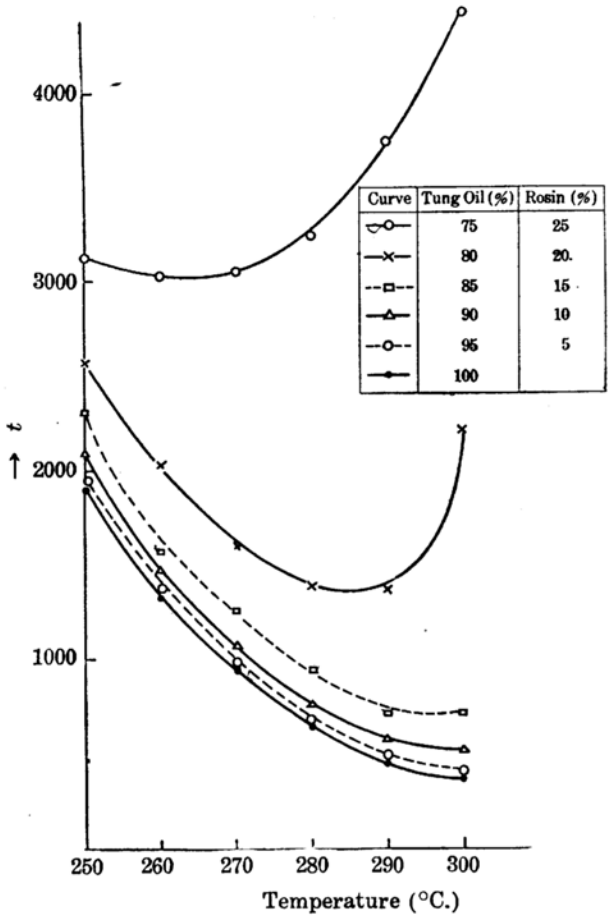

Fig. 6. Relation between Gelation-time and Temperature

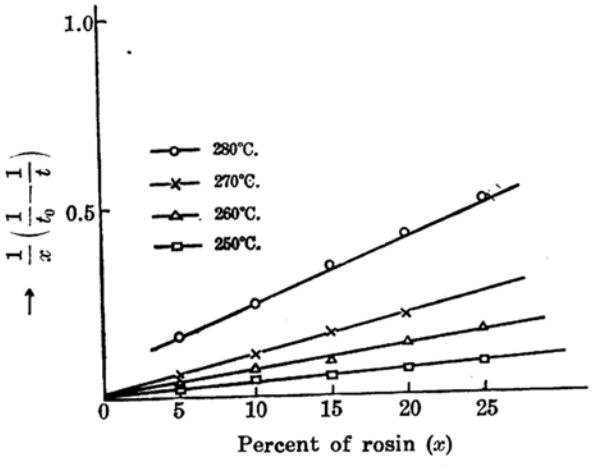

Fig. 7.

The relations between gelation time and temperature are shown in Fig. 6.

The general tendency is the same as that of fatty acid.

The relations between $\frac{1}{x}\left(\frac{1}{t_0}-\frac{1}{t}\right)$ and x are shown in Fig. 7.

From Fig. 7 it is noticed that the reciprocals of gelation time $(1/t)$ may be expressed by the quadratic equation of x.

Summary.

(1) Studies on the effects of straight asphalts, blown asphalts, gilsonite, petroleum pitch, stearin pitch, mineral rubber, coaltar pitch, etc. on the gelation time of tung oil lead to the conclusions that the gelation is promoted with bitumen added in an amount less than 10–15 percent., but is prevented with an addition of larger amount of bitumen. The inversion was noticed as the amount of substances added increase.

(2) Petroleum asphalt with a lower softening point has a somewhat greater gelation preventing effect.

(3) 15° blown asphalt was separated into alcohol soluble and insoluble parts. As in the case of the original asphalt, the inversion was found in the experiments with the soluble and insoluble parts.

(4) 5° blown asphalt was separated into asphalten and petrolen, and effects on gelation were studied. As in the case of ordinary neutral substances, the linear relation of $1/t$ and x was observed in the experiments with petrolen, but as in the case with original asphalt, the inversion was noticed when asphalten was used.

(5) The gelation-retarding effects of various natural and synthetic resins were observed. Among them copal, dammar, amber, coumarone resin have retarding effects, and $1/t$ and x bear a linear relation.

The relation $1/t$ and x for mastic, leuchtol, phthalate resin, ester rosin, sandarac, tamanol are not linear.

Generally speaking, the relations of $1/t$ and x for neutral and soluble resins are linear, but those of the less soluble resins are not linear.

About the effect of rosin upon gelation of tung oil, many measurements were carried out and the relation of $1/t$ and x are shown to be expressed by a quadratic equation. The influence of temperature on the gelation times of tung oil mixed with rosin is similar to that of fatty acid.

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