Polymerisation of Tung Oil. II. Gelation of Tung Oil by Catalytic Action of Iodine.

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The author hitherto studied about the polymerisation and gelation of tung oil at high temperature such as 260–280°C. and obtained several interesting results.(1) When neutral substances were added to tung oil, the reciprocals of gelation times of the mixture had a linear relation to the amount of addition and from which the values of ∞, the amount of addition necessary to make the gelation time of tung oil infinitely long, were obtained. This value is considered to be proportional to the gelation accelerating action of the added reagent.(2) It has been proved also that these conclusions could be applied to the other drying oils which have similar constitution to that of tung oil.(3) But in the presence of the catalytically acting substances such as S, Se, the gelation was strongly retarded and the relation between the gelation time and the amount of addition was different from that of neutral substances and the logarithm of gelation time was proportional to the amount of addition(4).

It is known that several acidic substances such as I_2, HNO_2, HCl, FeCl, S_2Cl_2, $AlCl_3$, $ZnCl_2$, $SbCl_3$, have gelation accelerating action upon tung oil at room temperature(5). These facts were used usually as the identification and estimation of tung oil, but reports were not published in details.

Experimentals. Iodine as catalyser and chloroform as solvent were used at first and the measurements were carried out at 25°C. Tung oil (density at 25°C. 0.9356) was weighed in a 200 c.c. three necked bottle into which chloroform solution of iodine was poured under stirring and the gelation time was measured. When the polymerisation of tung oil proceeded considerably, a small gelatinous mass floated on the surface of the sample and after a while the whole mass sticked to the stirring rod, this instant was noted as the gelation time. Between the times of gelation beginning and gelation finishing the difference of 3–10% was observed. As the gelation of tung oil at low temperature is a kind of catalytic reaction, the degree of mixing of tung oil and iodine has a considerable effect on the absolute value of gelation time. The dimension of the apparatus used in this experiment is shown in Fig. 1.

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(1) M. Tatimori, this Bull., **13** (1938), 142; *J. Soc. Chem. Ind. Japan*, Supptl. Bd., **41** (1938), 39, 100; **42** (1939), 162; **43** (1940), 102, 136.

(2) The summarizing report of the gelation of tung oil will be published later.

(3), (4) Not yet published.

(5) J. Marcusson, *Angew. Chem.*, **33** (1920), 235; Mclhiny, *Ind. Eng. Chem.*, **4** (1912), 96; Nagel and Grüss, *Wissenschaft. Veröff. Siemens Konzern*, **4** (1925), 284; M. Th. Fransçois, *Bull. Sci. Pharmacol.*, **41** (1934), 269.

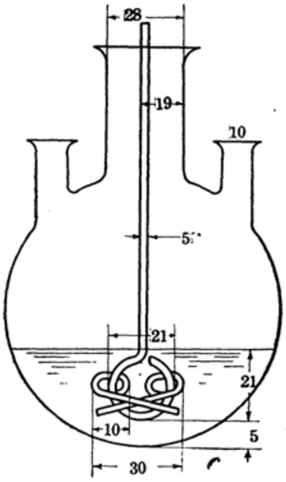

Fig. 1.

The gelation time is affected by the velocity of stirring and decreases according to the increase of the velocity of revolution. In the following experiments the revolution of 360 per minute was used.

From the results of the several experiments, the next relation has been found,

$$\log t = ax + b/zx \qquad (1).$$

Where t is the gelation time in second, x the volume of tung oil, (30-x) the volume of solvent, z the weight of iodine in gram, a and b the constants.

It is known that $\log t$ has a minimum value at $x=b/za$, by differentiating the equation (1) and when x is kept constant the relation between $\log t$ and $1/z$ is linear. These are proved experimentally.

Experiments were conducted with the systems of tung oil—chloroform—iodine, tung oil—glacial acetic acid—iodine, and tung oil—soya bean oil—chloroform—iodine.

The above formula could be applied to all these systems. One of the examples were shown in Table 1.

Table 1.

Volume of oil (Tung oil 95% Soya bean oil 5%) x c.c.	Volume of Solvent. (30−x) c.c.	Amount of Iodine zg.	Gelation time t (sec.)	$\log t$	$\frac{1}{x}$	$\frac{1}{z}$
10	20	0.1775	838	2.923	0.1000	5.634
12	18	,,	521	2.717	0.0833	,,
15	15	,,	442	2.645	0.0677	,,
20	10	,,	650	2.813	0 0500	,,
23	7	,,	932	2.969	0.0435	,,
10	20	0.3550	46	1.663	0.1000	2.817
10	20	0.3195	70	1.845	,,	3.130
10	20	0.2840	108	2.033	,,	3.521
10	20	0.2485	172	2 236	,,	4.024
10	20	0.2130	308	2.489	,,	4.693

Next the effects of solvent were examined. The gelation times of the systems of 10 c.c. of tung oil and 20 c.c. of solvents were measured at 25°C. The results were shown in Table 2.

From Table 2 it was noticed that iodine in the solvents containing halogens has great accelerating action upon the gelation of tung oil and in the solvents containing oxygen has no or very weak gelation accelerating action. It is a very remarkable fact that the colour of iodine solution

Table 2.

Solvent	Amount of iodine	Gelation time (sec.)
Pentane	Saturated solution	11450
Hexane	,,	3340
Cyclohexane	0.355 g. (a)	2745
Tetraline	a	7890
Benzene	,,	286
Toluene	,,	680
Xylenes	Saturated sol.	>18000
Petroleum ether	,,	>16800
Benzin	,,	1340
Mineral spirit	,,	430
Kerosine	,,	5030
Solvent naphtha	,,	965
Chloroform	a	61
Carbon tetrachloride	,,	125
Bromoform	,,	1595
Ethylene dichloride	,,	11.5
Trichloroethylene	,,	50
Ethylene dibromide	,,	92
Chlorobenzene	,,	15
Para-aldehyde	,,	4150
Glycerine dichlorohydrine	,,	22
Glacial acetic acid	,,	15.2
Acetic acid anhydride	,,	10.2
Lactic acid	Saturated sol.	1545
Triacetin	a	135
Ethyl acetate	,,	6560
Nitrobenzene	,,	2.5
Carbon disulphide	,,	280
Ether	,,	> 9600
Acetone	,,	> 7800
Methyl ethyl ketone	,,	>15000
Butyl alcohols	,,	> 6600
Benzyl alcohol	,,	> 7000
Butyl acetates	,,	> 9600
m-cresol	,,	>30000
Aniline	,,	>19800
o-toluidine	,,	>18000

in the oxygen containing solvent is yellowish brown, on the other hand the colour of the iodine solutions which have strong gelation accelerating action are of violet tint. But the solvents from glycerine dichlorohydrine to nitrobenzene in Table 2 are exceptions and in spite of yellowish brown tint, have a strong gelation accelerating action.

In Table 3 the colour of iodine solutions were shown.

The solvents not shown in the Table have the violet tint as that of chloroform. The colour of the solution was determined by the Rovibond's Tintometer using 1/16 inch cell.

Table 3.

Solvent	Amount of iodine	Yellow	Red	Blue
Chloroform	0.355 g. (a)	—	54.0	0.8
Xylenes	Saturated sol.	20.0	28.0	—
Ethyl acetate	a	10.0	45.0	—
Butyl acetates	,,	20.0	23.0	—
Benzyl alcohol	,,	22.0	32.0	—
Acetone	,,	30.0	8.5	—
Methyl ethyl ketone	,,	30.0	4.4	—
Butyl alcohol	,,	7.0	33.0	—
m-cresol	,,	4.6	52.6	—
Aniline	,,	0.5	0.1	—
Glycerine dichlorohydrine	,,	20.0	33.0	—
Lactic acid	Saturated sol.	30.0	9.0	—
Acetic acid anhydride	a	14.0	30.0	—
Glacial acetic acid	,,	40.0	25.0	—
Triacetin	,,	35.0	21.0	—
Para-aldehyde	,,	12.0	35.0	—
Nitrobenzene	,,	5.2	40.0	—

It is a new fact that the violet solutions of iodine have strong gelation accelerating action. The gelation times of the mixture of two solvents were shown in Tables 4 and 5.

Table 4.

Solvent	Gelation time (sec.)	Dielectric constant at 25°C	Abbreviation (see Fig. 3)
(1) Benzene-nitrobenzene (% of nitrobenzene)			
0	286	2.28	—
5	105	3.10	105
10	47.5	4.25	110
15	22.5	5.45	115
25	10.5	8.08	125
50	7.5	14.9	150
75	6.0	24.0	175
100	2.5	35.0	—
(2) Benzene-chloroform (% of chloroform)			
25	158	2.74	225
50	115	3.25	250
75	87.5	3.91	275
(3) Benzene-chlorobenzene (% of chlorobenzene)			
25	128	3.18	325
50	65.5	3.96	350
75	30.5	4.79	375

Table 5.

Solvent	Gelation time (sec.)	Colour		
		Yellow	Red	Blue
Chloroform-acetone (% of acetone)				
5	128	—	66.0	—
10	268	5.0	66.0	—
15	623	7.0	55.0	—
25	2700	25.0	34.0	—
50	No gelation	40.0	13.0	—
75	,,	51.0	9.5	—
Chloroform-ether (% of ether)				
5	78	—	62.0	0.5
15	228	—	57.0	0.5
25	1028	—	56.0	0.5
50	3170	10.0	38.0	—
75	>9600	15.0	30.0	—
Chloroform-butyl acetates (% of butyl acetates)				
5	178	1.0	87.5	—
10	433	3.0	87.0	—
15	1093	5.0	66.0	—
25	3280	5.0	73.0	—
50	>9000	12.0	51.0	—
75	No gelation	20.0	40.0	—
Chloroform-benzyl alcohol (% of benzyl alcohol)				
5	713	—	66.0	0.4
10	2218	—	63.0	0.3
15	5550	3.0	56.0	—
25	22200	—	54.0	0.4
50	No gelation	2.0	46.0	—
75	,,	12.0	40.0	—
Chloroform-*m*-cresol (% of *m*-cresol)				
25	113	—	63.0	—
50	6780	5.0	56.0	—
75	No gelation	7.0	54.0	—
Chloroform-aniline (% of aniline)				
25	No gelation	2.0	2.0	—
50	,,	3.0	0.5	—
75	,,	2.5	0.4	—
100	,,	2.0	0.3	—

According to the increase of the amount of solvent containing oxygen both the yellowish tint and gelation time of tung oil increase. And the gelation time increases according to the increase of yellowish tint of iodine solution.

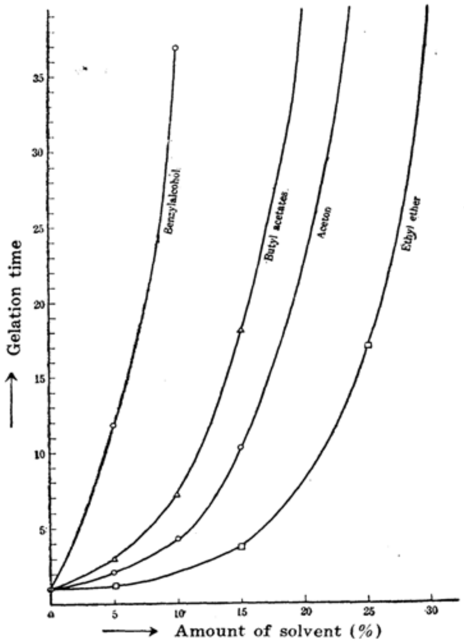

Fig. 2.

The gelation times of the mixture of two solvents were shown in Fig. 2.

Several papers were published[(6)] about the relation between the solutional state of iodine and its colour. At present it is believed that iodine in the violet solution dissolves in molecular state like its vapour state and in the yellowish brown solution dissolves in solvated form.

As to the chemical activities of iodine solutions having violet and yellowish brown tints few reports were known[(7)].

It is a very interesting fact that great difference in the catalytic actions of iodine solutions upon the polymerisation of tung oil was observed. The catalytic action of iodine solutions is considered to be due to the iodine in molecular state, and not to the solvated iodine. Inversely its dissolved state can be proved by the catalytic action of iodine solutions upon the gelation of tung oil.

Generally speaking the gelation accelerating action of iodine is strong in solvents having high dielectric constant.

The relations between dielectric constants and gelation times were shown in Fig. 3, both in logarithmic scale.

Greater part of solvents situate on a smooth curve.

Summary.

(1) The gelation times of tung oil catalysed by iodine in various organic solvents were measured.

(2) The relation between gelation time t, concentration of tung oil x and amount of iodine z is expressed by the formula

$$\log t = ax + b/zx \ .$$

(6) Lachmann, *J. Am. Chem. Soc.*, **25** (1903), 50; Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry", vol. II, p. 110.

(7) H. Gautier and G. Charpy, *Compt. rend.*, **111** (1890), 645.
L. Carcano, *Bull. Chim. Farm.*, **47** (1908), 5.

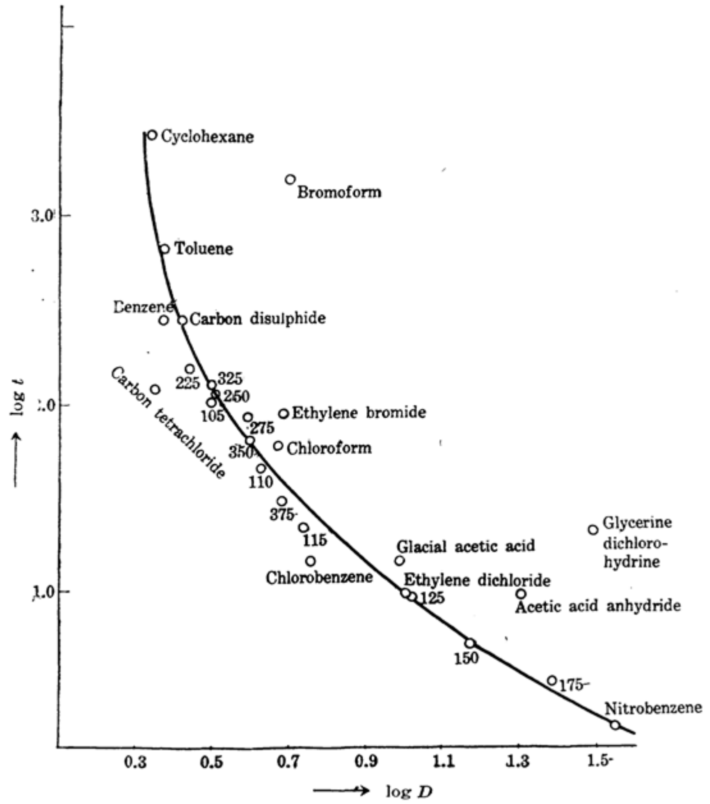

Fig. 3.

(3) In the solution having violet tint, iodine has a strong gelation accelerating action, but in the yellowish brown solution the accelerating action of iodine is very weak.

(4) Organic acids and nitrobenzene are exceptions of the above fact (3) and in spite of yellowish brown tint, have strong gelation accelerating action.

(5) In the iodine solutions of mixed solvents the gelation time increases with the increase of yellowish tint.

(6) Difference in catalytic action of iodine solutions is considered to be due to the difference of molecular state of iodine in the solution. Generally solvated solution of iodine has poor catalytic action.

(7) Generally iodine in the solvent having high dielectric constant shows strong gelation accelerating action.

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