Polymerisation of Tung Oil. VII. Effects of Various Inorganic Substances upon the Gelation of Tung Oil.

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(Received November 28, 1940.)

The effects of various inorganic substances upon the gelation of tung oil at elevated temperatures being little known, the author carried out this experiments to obtain the effects of inorganic substances upon the gelation time of tung oil.

Each of the reagents was added to tung oil with 10% by weight and the measurements were done at 273°C, and the results were compared with the blanc tests.

The reagents were pulverized as fine as possible and the sifted parts were used. The substances which affect the metallic net of the standard sieve, or which could not be pulverized were directly weighed into the test tube.

Experimentals. The results were shown in Tables 1 (substances having no or little effects), 2 (accelerating effects), 3 (retarding effects). The number in the Tables are the values calculated from $(t-t_0)/t_0$, where t and t_0 are the gelation times of tung oil added with reagents and that of the blanc test. Therefore the plus sign means the gelation retarding action and the minus sign, the gelation accelerating one.

Table 1.

$(t-t_0)/t_0$ (%)	Substances
0	Hg, Bi, $(NH_4)_2Cr_2O_7$.
0～+1.0	$Ba(NO_3)_2$, $Co(NO_3)_2$, K_2CrO_4, $Na_2C_2O_4$, KBr.
+1.0～2.0	KNO_3, $NaHPO_3 \cdot 3H_2O$ $Na_2HPO_4 \cdot 12H_2O$, $Na_2SO_3 \cdot 7H_2O$, NaBr, C_2O_4Ce.
+2.0～3.0	$AlK(SO_4)_2 \cdot 12H_2O$, NH_4Cl.
+3.0～4.0	Sb_2O_3, $PbCl_2$, KNO_2, Cr_2O_3, $Al_2(SO_4)_3 \cdot 18H_2O$.
+4.0～5.0	K_2SO_4, $CH_3COONa \cdot 3H_2O$, $BaSO_4$.
0～−1.0	Na_2SO_4, KI, $NaNO_3$, SnO_2, Al_2O_3, Sb.
−1.0～2.0	$CaCl_2 \cdot xH_2O$, $BaCl_2$, Hg_2Cl_2, $FeSO_4 \cdot 7H_2O$.
−2.0～3.0	$MnCl_2 \cdot 4H_2O$, $KHSO_4$, $Fe_2(SO)_3$, $MnSO_4 \cdot 4H_2O$, C_2O_4Pb, Lead Arsenate.
−3.0～4.0	Ni (plate), $CaSO_4$, ZnS, $(NH_4)ClO_4$.
−4.0～5.0	$Sr(NO_3)_2$, Cd, NaCl, $Cr(NO_3)_3$.

Table 2.

$(t-t_0)/t_0$ (%)	Substances
− 5∼ 10	$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, $CdSO_4 \cdot 8H_2O$, $(NH_4)_2SO_4$, $K_2Cr_2O_7$, $CuCl_2$, Cu_2Cl_2, $CrCl_3 \cdot xH_2O$.
−10∼ 20	$Fe(NH_4)_2(SO_4)_2 \cdot 12H_2O$, Zn, $HgSO_4$, $MgSO_4$, $CuSO_4 \cdot 5H_2O$, $(Hg)_2CrO_4$.
−20∼ 30	NH_4NO_3, $KClO_3$, $(CH_3COO)_2Cu \cdot H_2O$.
−30∼ 40	CuO, Cu_2O, $Ni(NO_3)_2$, $Hg(NO_3)_2$, CH_3COOHg.
−40∼ 50	$Th(NO_3)_4 \cdot 4H_2O$, HgO, $UO_2(NO_3)_2$, $CoCl_2 \cdot 6H_2O$.
−50∼ 60	$Bi(NO_3)_2$.
−70∼ 80	Na.
−80∼ 90	$HgCl_2$.
−90∼100	$ZnCl_2$, ICl_3, $FeCl_3 \cdot 6H_2O$, $AlCl_3$, I_2, $SnCl_4$ $POCl_3$.

Generally halides have very strong gelation accelerating actions.

Table 3.

$(t-t_0)/t_0$ (%)	Substances
+ 5∼ 10	$(NH_4)_2S_2O_8$, $CuCO_3 \cdot Cu(OH)_2$, $NaHPO_4$, Uranium acetate, KCNS, Fe, Cu, $AgNO_3$, Sn.
+10∼ 20	LiCl, CoO, NaOCl, $Mn(OH)_2$, Mn-Borate.
+20∼ 30	ZnO, Al.
+40∼ 50	$(HCOO)_2Pb$, Mg, KCN, Na-Oleate, Al-Stearate.
+50∼ 60	$Ca(NO_3)_2$, $NaHCO_3$, $KMnO_4$.
+90∼100	$SbCl_3$.
+100∼200	$Mg(NO_3) \cdot xH_2O$, $Pb(NO_3)_2$, $H_3AsO_4 1/2H_2O$, Animal Charcoal.
+100	No gelation MgO, PbO, PbO_2, Pb_3O_4, P (red), $(CH_3COO)_2Mn$, $(CH_3COO)_2Pb$, Se, NaOH, KOH.
+300	No gelation MnO, Na_2O_2, Na_2HAsO_3, $NaHSO_3$, $NaNO_2$, As_2O_3, S_2Cl_4, Na_2S, $Na_2S_2O_3 \cdot 5H_2O$, $MgCl_2 \cdot 6H_2O$.

Generally basic substances have strong gelation retarding actions.

Next, about the effects of sulphur and selenium, experiments were carried out in more detail. It is known that sulphur and selenium have special chemical action (a kind of isomerisation) upon the drying oil[1], but no report has been published about the effects upon the gelation of tung oil.

I. Effect of Sulphur. As it was difficult to mix sulphur in tung oil uniformly, the carbon disulphide solution of sulphur was added and after

(1) T. P. Hilditch and H. Jasperson, *J. Soc. Chem. Ind.* London, **58** (1939), 233; H. I. Waterman, C. Van Vlodrop, F. Althiusius, *ibid.*, **57** (1938), 87; J. Rinse, *Rec. trav. Chim.*, **51** (1932), 529.

Table 4.

Time lapsed from addition of sulphur (min.)	Gelation time (sec.)
30	1337
60	1366
90	1411
150	1426
210	1454
270	1478

evaporating the solvent the measurements were carried out at 270°C. by usual method.

In Table 4 the results of gelation times of tung oil added with 0.013% of sulphur were given. The gelation time increases with the lapse of time from addition of sulphur.

In the following experiments the measurements were done at 30 min. after addition of sulphur.

Table 5. (Tung oil 100%).

Amount of S (%)	Gelation time (t)	$\frac{1}{t}\times10^4$	log t
0	830	12.05	2.919
0.005	1032	9.69	3.014
0.010	1212	8.25	3.084
0.015	1404	7.12	3.147
0.020	1586	6.32	3.200
0.025	1793	5.58	3.254
0.030	2018	4.97	3.305

Table 6. (Tung oil 95%, Soya bean oil 5%).

S (%)	t	$\frac{1}{t}\times10^4$	log t
0	855	11.69	2.932
0.005	1139	8.77	3.057
0.010	1379	7.24	3.139
0.015	1680	5.95	3.225
0.020	1896	5.29	3.278
0.025	2311	4.32	3.364
0.030	2567	3.90	3.409

Table 7. (Tung oil 90%, Soya bean oil 10%).

S (%)	t	$\frac{1}{t}\times10^4$	log t
0	1125	8.89	3.051
0.005	1307	7.62	3.116
0.010	1671	5.95	3.223
0.015	1970	5.06	3.295
0.020	2446	4.00	3.388
0.025	2838	3.52	3.453
0.030	3436	2.90	3.536

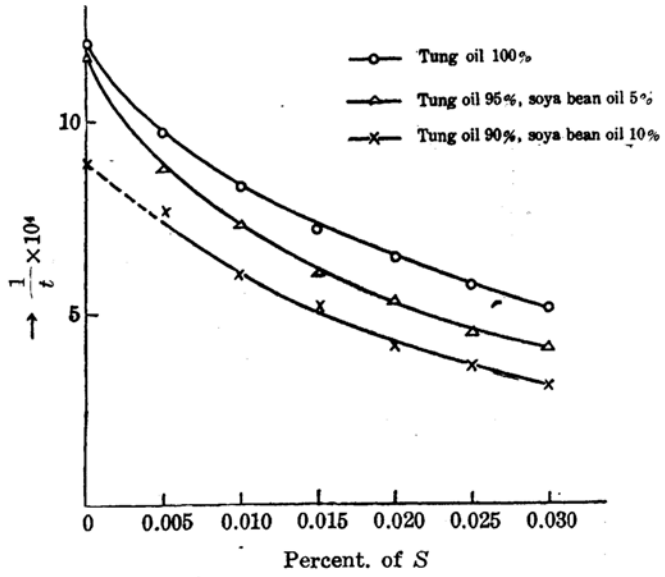


Fig. 1.

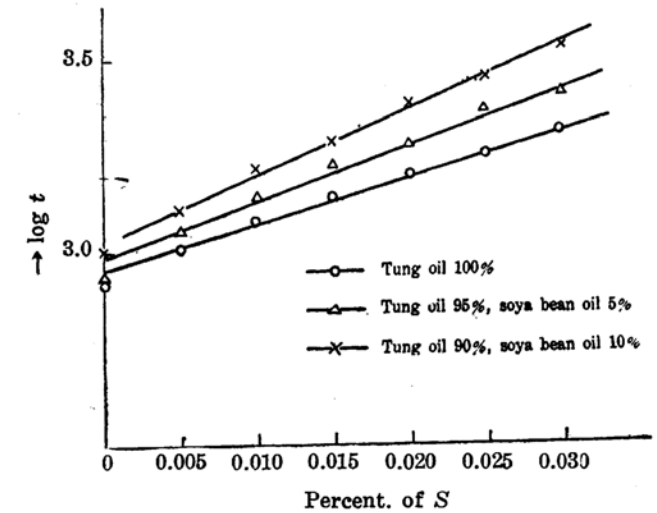


Fig. 2.

As shown in Fig. 1, from the relations between $1/t$ and x curved lines were obtained. In Fig. 2 relations of log t–x were shown. Except the initial points linear relations were obtained.

II. Effect of Selenium. The experiments were conducted as same as that of sulphur. In this case the solvent was not evaporated off, but the blanc test was done (Table 8).

Table 8. Effect of carbon disulphide.

Amount of carbon disulphide (g./5 g. tung oil)	%	t
0	0	1024
0.1	2	1090
0.2	4	1155
0.3	6	1200
0.4	8	1220
0.5	10	1245
0.6	12	1280
0.7	14	1310
0.8	16	1335
0.9	18	1352

The solvent has a little gelation retarding action.

Table 9. (Tung oil 100%).

Amount of solution added (g.)	Se (%)	t	$\frac{1}{t}\times 10^4$	$\log t$
0	0	1018	9.82	3.008
0.5	0.0139	1646	6.08	3.216
0.6	0.0167	1860	5.38	3.270
0.7	0.0195	1980	5.05	3.297
0.8	0.0222	2165	4.62	3.336
0.9	0.0250	2397	4.17	3.380
1.0	0.0278	2640	3.99	3.422
2.0	0.0556	5400<	1.85>	3.73<

Table 10. (Tung oil 95%, Soya bean oil 5%).

Amount of solution added (g.)	Se (%)	t	$\frac{1}{t}\times 10^4$	$\log t$
0	0	1130	8.85	3.053
0.1	0.0027	1355	7.38	3.131
0.3	0.0082	1718	5.82	3.235
0.4	0.0110	2052	4.87	3.312
0.5	0.0137	2240	4.46	3.351
0.7	0.0192	3090	3.24	3.481
0.9	0.0247	4170	2.40	3.620

Table 11. (Tung oil 90%, Soya bean oil 10%).

Amount of solution added (g.)	Se (%)	t	$\frac{1}{t}\times 10^4$	$\log t$
0	0	1300	7.69	3.114
0.1	0.0028	1695	5.89	3.229
0.2	0.0056	2122	4.71	3.328
0.3	0.0083	2430	4.12	3.386
0.5	0.0140	3275	3.05	3.515
0.6	0.0168	3780	2.65	3.578
0.7	0.0196	4565	2.19	3.659

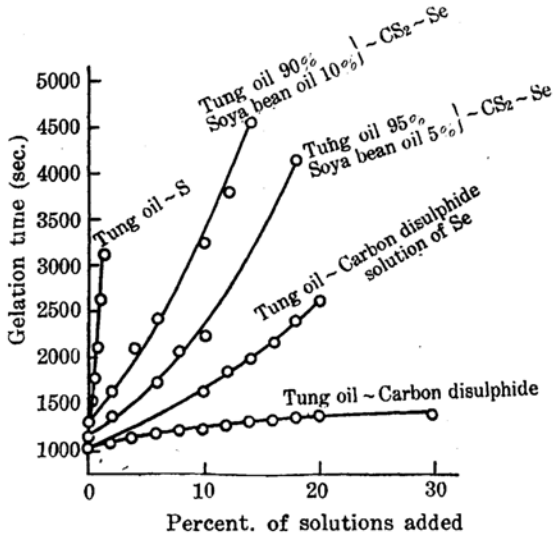


Fig. 3.

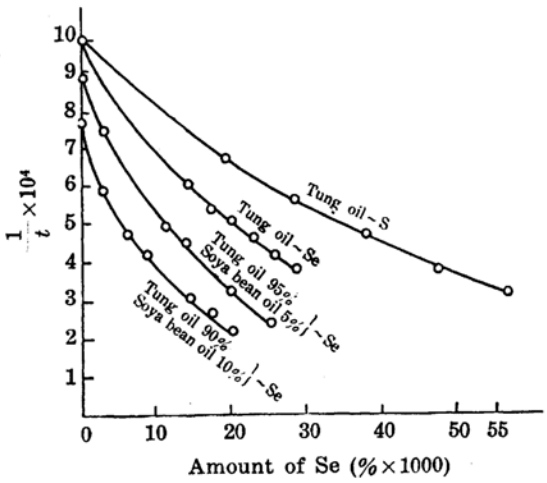


Fig. 4.

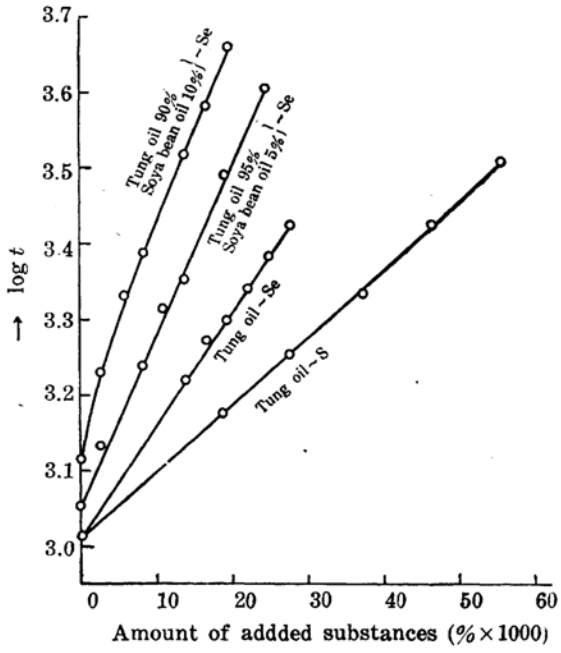


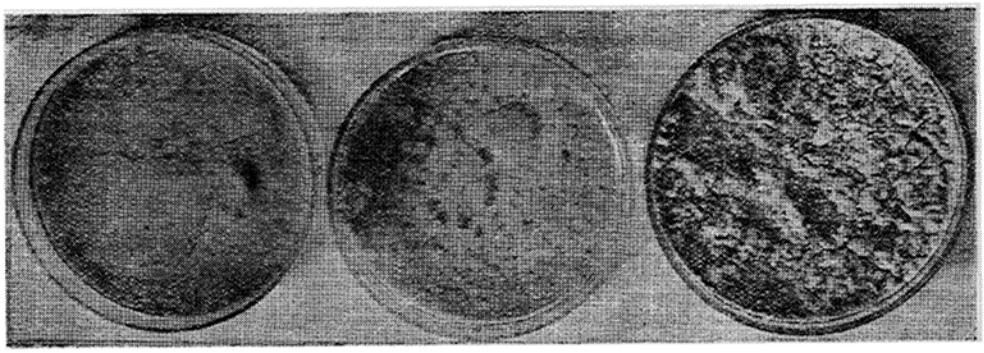
Fig. 5.

The comparison of the effects of sulphur and selenium with the same conditions was shown in Fig. 4. Selenium has stronger gelation retarding action than sulphur.

III. Isomerisation. Isomerisation of tung oil by S, Se and I_2 were examined. 10 g. of tung oil was taken in a glass dish (80, 15h) and irradiated by a ultraviolet lamp (100–110 V. 4 A.), distance of lamp and sample being 35 cm.

The photographs of tung oil added with 0.05% of reagents, after irradiation of 10 hours, were shown in Fig. 6.

Iodine has the strongest isomerisation power and the next is selenium.



Selenium Sulphur Iodine

Fig. 6.

Summary.

(1) As inorganic reagent besides sulphur and selenium, 16 kinds of elements, 28 of halides, 18 of nitrates, 23 of sulphates, 17 of oxides and 29 of other miscellaneous substances were used. Many of the halides have strong gelation accelerating actions and magnesium compounds have strong gelation retarding actions.

Metallic sodium acts gelation accelerating and manganese, compounds which are used as oxidation catalysers in paint industry, act as gelation retarding catalysers. Generally speaking acidic substances have gelation accelerating and basic substances have gelation retarding action.

(2) Gelation retarding power of S and Se are very strong and the gelation time of tung oil becomes infinitely long when added with 0.05% of regents. At the same concentration the gelation retarding action of Se is stronger than that of S.

(3) The relation between the logarithm of gelation time and the amount of S added is linear. These results can be applied also to the systems of mixture of tung oil and soya bean oil.

(4) S, Se and I_2 have isomerisation action upon tung oil at room temperature when irradiated by ultraviolet light.

(5) The gelation time of tung oil increases with the lapse of time from addition of S, so there is an intimate connection between the isomerisation and the gelation retarding action.

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

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