Polymerisation of Tung Oil. I.

By Monzi TATIMORI.

(Received December 4, 1937.)

I. **Introduction.** It is well known that drying oils such as linseed, perilla, and tung oil are used for coating materials after special treatment generally called cooking.

Tung oil⁽¹⁾ is one of the most unsaturated oils and is important in paint and varnish industry. Its iodine value is about 260 as measured by hydrogenation method⁽²⁾ and its polymerisation velocity is far greater than that of linseed oil. Therefore it has the disadvantage of gelation⁽³⁾ and there are several devices and patents⁽⁴⁾ to avoid it.

Most fatty oils are composed of glycerides of fatty acids such as stearic, oleic, linolic, and linolenic acid and obey the rule of proportionality between iodine value and density.⁽⁵⁾ Tung oil, however, is an exception,⁽⁶⁾ and it is supposed that the tung oil acids have distinctly different constitutions from that of linseed oil acids. There are many theories⁽⁷⁾ on the constitutional formula of α-eleostearic acid, the main constituent of the tung oil acids. At present it is generally accepted that its most probable constitutional formula is

$$CH_3\text{-}(CH_2)_3\text{-}CH{=}CH\text{-}CH{=}CH\text{-}CH{=}CH\text{-}(CH_2)_7\text{-}COOH.^{(8)}$$

The cooking of a drying oil at high temperatures in the absence of oxygen is accompanied by an increase in the viscosity, density, and apparent molecular weight of the oil and by a decrease in iodine value

---

(1) This oil is obtained from the seed of *Aleurites Fordii*, and is called Chinese wood oil.

(2) L. A. Jordan, *J. Soc. Chem. Ind.*, **53** (1934), 1.

(3) Gelation is the phenomenon that an oil solidifies suddenly and becomes an insoluble and unfusible mass.

(4) H. Brendel, *Farbe u. Lack*, **1932**, 145; H. Hardert, *ibid.*, **1928**, 558.

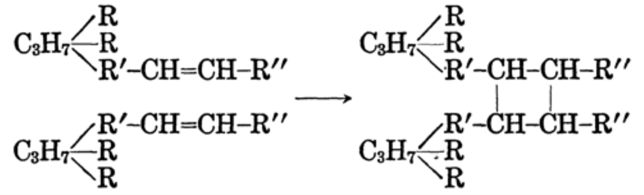
(5) K. Yokota and M. Tatimori, not yet published.

(6) The iodine value of tung oil is ca. 165 by Wijs method and is smaller than that of linseed oil.

(7) M. S. Cloez, *Compt. rend.*, **81** (1875), 469; **82** (1876), 501; **83** (1876), 943; M. L. Maquenne, *ibid.*, **135** (1902), 696; T. Kametaka, *J. Chem. Soc.*, **83** (1903), 1042; Fokin, *J. Russ. Phys.-Chem. Soc.*, **38** (1906), 419; R. Majima, *Ber.*, **42** (1909), 674.

(8) The formula was proposed by Boeseken and Ravensway, *Rec. trav. chim.*, **46** (1927), 619.

and saponification value, unless heat treatment is effected at unusually high temperature. Most authorities agree that these changes are due to the polymerisation of fatty acid radicals, although some investigators propose different hypothesis as to the exact mechanism.(9) According to Rhodes and Welz(10) the polymerisation of tung oil proceeds in the following schema, forming a tetramethylene linkage by the union of a pair of ethenoid groups,



$$\begin{array}{l} C_3H_7\!\left\langle\begin{array}{l}R\\R\\R'\text{-}CH{=}CH\text{-}R''\end{array}\right. \\ \\ C_3H_7\!\left\langle\begin{array}{l}R'\text{-}CH{=}CH\text{-}R''\\R\\R\end{array}\right. \end{array} \longrightarrow \begin{array}{l} C_3H_7\!\left\langle\begin{array}{l}R\\R\\R'\text{-}CH\text{-}CH\text{-}R''\end{array}\right. \\ \qquad\qquad\quad | \quad\;\; | \\ C_3H_7\!\left\langle\begin{array}{l}R'\text{-}CH\text{-}CH\text{-}R''\\R\\R\end{array}\right. \end{array} \qquad (1).$$

While Fonrobert(11) supposed that tung oil polymerises after monomolecular reaction as can be concluded from the fact that the decrease in the evolution of heat is too small for bimolecular reaction, when tung oil is diluted by the addition of linseed oil.

It is desirable to study the polymerisation phenomena from the standpoint of chemical kinetics, as few papers have been published along this line. R. H. Kienle(12) studied the kinetics of the baking of tung oil film and found that it proceeds as a first order reaction. While Fuller(13) pointed out that the reaction constant calculated as the first order reaction is not constant, but has a maximum. J. Rinse(14) studied the polymerisation by measuring the refractive index. To compare polymerisation velocity for different temperatures he drew curves of refractive index and temperature, measuring time from the moment when the temperature reached 220°C. neglecting the polymerisation below 220°C. He did not treat the results kinetically. The present author studied the polymerisation of tung oil quantitatively and found that it is a second order reaction.

II. Experimental Procedure. An oil bath provided with an electric heater, a stirrer, and a mercury temperature regulator, was filled with

---

(9) By polymerisation of oil, we mean the result of changes by heating. There may be chances for reactions such as intramolecular and extramolecular polymerisation of glycerides, isomerisations of fatty acid radicals, and cracking and condensation of glycerine radicals.

(10) Rhodes and Welz, *Ind. Eng. Chem.*, **19** (1927), 68.

(11) Fonrobert, *Farben-Ztg.*, **40** (1935), 477, 505, 533, 560, 586.

(12) R. H. Kienle, *Ind. Eng. Chem.*, **22** (1930), 1370.

(13) Fuller, *ibid.*, **23** (1931), 1458.

(14) J. Rinse, *Rec. trav. chim.*, **51** (1932), 529.

soya bean oil and heated. The temperature was kept constant and a three necked 300 c.c. flask, which contained 250 g. of tung oil, was dipped in it and a gentle stream of carbon dioxide was passed over the surface of the oil. When the required temperature was reached the first 10 c.c. of the oil was taken as a sample in a test tube and chilled quickly by inserting it in cold water. The time was measured from that moment. Samples were withdrawn at suitable intervals and the run was continued until finally the oil gelatinised.

The material used had the following constants: density = 0.9418, refractive index (n_D^{20}) = 1.5191, iodine value (Wijs method) = 166.8, acid value = 1.8.

III. **Experimental Results.** For each sample density, iodine value, relative viscosity, and refractive index were measured.

Increase in density. The density was measured at 15°C. The results are shown in Fig. 1.

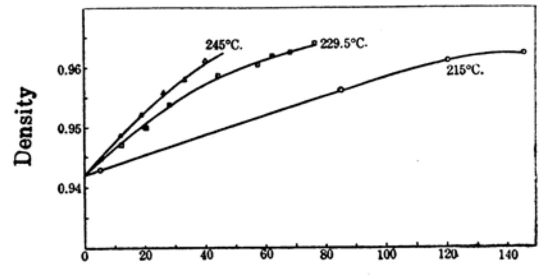


Fig. 1.

Decrease in iodine value. The iodine value is affected by the ratio of halogen solution to oil, by the duration of contact, and by the reaction temperature.

The Wijs reagent used was 0.1 N solution of iodine monochloride, with 2% excess of iodine to chlorine and the temperature was kept exactly at 20°C. during two hours.

If we denote by f the factor of thiosulphate solution for the titration of Wijs solution, by A the number of titration of blank Wijs solution, by B that of actual measurement, and by m the weight of oil, the iodine value is calculated as $(A - B)f/m$ and the ratio Z of halogen solution to oil as Bf/m.

Determinations for each sample were made for two or three values of Z, and the iodine value corrected for $Z = 239.9$ was obtained from the graph of log $[(A - B)f/m]$ versus log Z. The results are shown in Tables 1–3.

Increase in relative viscosity. Samples were dissolved in benzene to 2 and 3% and the viscosity was measured at 30°C. by an Ostwald viscometer described in the previous report.(15) The viscosity constant K_0 was

---

(15) M. Tatimori, *J. Soc. Chem. Ind., Japan*, **39** (1936), Suppl. binding, 473 B.

Table 1. (206°C.)

Time of heating (min.)	Iodine value
0	—
30	163.7
60	158.1
90	154.3
120	150.4
150	147.9
180	144.9
210	141.1

Table 2. (230°C.)

Time of heating (min.)	Iodine value
0	160.6
8	157.8
16	154.4
24	151.7
32	148.7
40	146.8
48	144.6
56	142.3
64	140.1
72	139.2

Table 3. (245°C.)

Time of heating (min.)	Iodine value
0	164.1
7	160.2
14	154.0
21	150.6
28	146.8
35	143.0
42	140.6

calculated by

$$\eta_{sp} = \frac{\eta_s - \eta_0}{\eta_0} = K_0 C + K_1 C^2 \qquad (2),$$

where η_{sp} denotes the specific viscosity, η_0 the viscosity of the solvent, η_s that of the solution, C the concentration, and K_0 and K_1 are constants. The author has already(16) discussed the meaning of K_0. For bodied linseed oil K_0 is approximately proportional to molecular weight.

Assuming K_0 to be a constant relating to the molecular weight of the solute, the relative molecular weight, i.e. the ratio of K_0 of bodied oil to that of raw oil, was calculated from the viscosity data and are shown in Fig. 2.

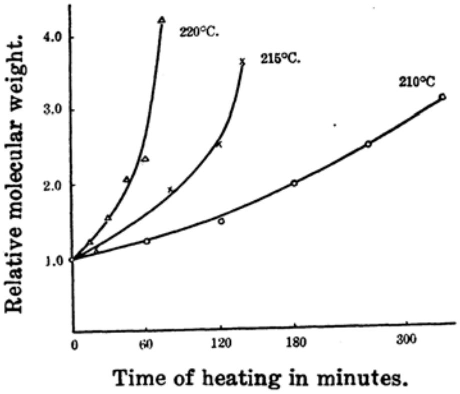


Fig. 2.

Decrease in refractive index. Refractive index was measured by an Abbe refractometer at 20°C. The results are shown in Tables 5–10. The total amount of decrease in refractive index up to gelation is ca. 0.0081 in agreement with the J. Rinse's result.

IV. **Kinetics of Polymerisation.** *Theoretical consideration.* The molecule of tung oil is composed of three fatty acids, each of which having one active center of polymerisation. Therefore two types of polymerisation are possible, intramolecular polymerisation and extramolecular poly-

---

(16) M. Tatimori, *J. Soc. Chem. Ind., Japan,* **40** (1937), Suppl. binding, 19B.

merisation, and it is known⁽¹⁷⁾ that both occur. In this case polymerisation velocity is given by the superposition of the first order and the second order reaction.

From the study of quantities such as iodine value and refractive index, we obtain the concentration of active radicals instead of that of molecules. In this case the concentration of active radicals should be taken into consideration, so that the polymerisation velocity can be expressed by a second order reaction formula,

$$\frac{dx}{dt} = K_2(a-x)^2 \qquad (3),$$

where x denotes the concentration of polymerised active radicals at time t, a the initial concentration of unpolymerised radicals, and K_2 is a reaction constant.

Then we have

$$K_2 t = \frac{x}{a(a-x)} \qquad (4).$$

If we denote by n the refractive index at time t, by n_0 that for $t = 0$, and by n_∞ that for $t=\infty$, then $x = K'(n_0 - n)$ and $a = K'(n_0 - n_\infty)$. By inserting these to equation (4), and putting $K = K_2K'$, we have

$$Kt = \frac{n_0-n}{(n_0-n_\infty)(n-n_\infty)} \qquad (5).$$

Generally the reaction constant can be calculated from equation (5). In reactions such as saponification of esters, n_∞ or the quantity corresponding to it can be obtained by raising the temperature or by prolonging the time of reaction. In this case, the gelation occurs before the polymerisation proceeds to the end, so that the measurement of n_∞ is impossible. This is the difficulty in the kinetical treatment of the reaction. Therefore n_∞ must be calculated. A glance at equation (5) shows that, unknown n_∞ being contained in a quadratic form, it is difficult to calculate the most probable value of n_∞ from the experimental data.

By taking reciprocals of both sides, equation (4) can be transformed as follows,

---

(17) As for intramolecular polymerisation see E. Fonrobert and F. Pallauf, *Chem. Umschau Fette, Öle, Wachse Harze*, **33** (1926), 41; E. Rossmann, *Fette u. Seifen*, **44** (1937), 187. For extramolecular polymerisation see Rhodes and Welz, *Ind. Eng. Chem.*, **19** (1927), 68; Nagel and Grüss, *Wiss. Veröffentl. Siemens-Konzern*, **4** (1925), 284.

$$\frac{1}{aK_2t} = \frac{b}{t} = \frac{a}{x} - 1 \qquad (6),$$

in which a and b are constants.

The relation between $1/t$ and $1/x$ is linear, so that in a graph a straight line should be obtained. This is a conventional method to determine whether a reaction proceeds in the schema (1) or not. a and b can be obtained from the relation of $1/t$ versus $1/x$, and K_2 can be calculated by equation (6).

As an illustration of bimolecular reaction, the decrease of iodine value (at 215°C.) and that of refractive index (at 206°C.) are given in Tables 4–5 and Figures 3–4.

Table 4.

Time of heating (min.)	Iodine value	$\frac{1}{t} \times 10^2$	$\frac{1}{x} \times 10^2$
0	162.6	—	—
20	157.4	5.000	19.23
40	153.0	2.500	10.42
60	149.2	1.666	7.462
80	146.7	1.250	6.289
100	144.9	1.000	5.650
120	142.6	0.833	5.000
140	141.3	0.714	4.695

Table 5. (206°C.)

t	n_D^{20}	$\frac{1}{x} \times 10^{-2}$	$\frac{1}{t} \times 10^3$	K
0	1.5183	—	—	—
30	1.5169	7.14	33.33	0.203
60	1.51575	3.92	16.67	0.201
90	1.51465	2.74	11.11	0.209
120	1.5138	2.22	8.33	0.208
150	1.5130	1.89	6.67	0.210
180	1.5123	1.67	5.56	0.212
210	1.51175	1.53	4.76	0.211
240	1.51115	1.40	4.17	0.215
270	1.5110	1.37	3.70	0.198
				Mean 0.2074

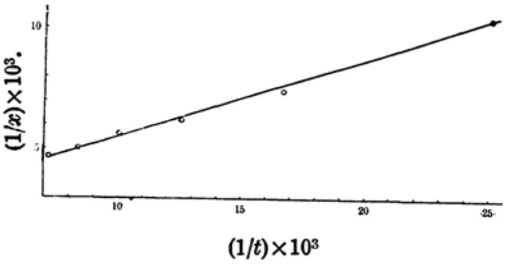


Fig. 3. Relation between reciprocals of iodine value and polymerisation time.

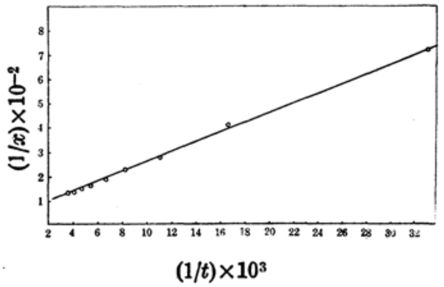


Fig. 4. Relation between reciprocals of refractive index and polymerisation time.

As the accurate measurements of iodine value of polymerised oil are difficult, refractive index is better for the study of the kinetics.

Reaction constants. The changes in refractive index of oils with time at various temperatures can exactly be expressed by equation (6).

Reaction constants were calculated from the refractive index and are given in Tables 5–10.

Table 6. (215°C.)

t	n_D^{20}	$\frac{1}{x}\times 10^{-2}$	$\frac{1}{t}\times 10^3$	K
0	1.5159	—	—	—
20	1.5149	10.00	50.00	0.297
40	1.51395	5.13	25.00	0.314
60	1.5131	3.57	16.67	0.324
80	1.5125	2.94	12.50	0.313
100	1.5118	2.44	10.00	0.324
120	1.51125	2.15	8.33	0.326
140	1.5111	2.08	7.14	0.293
				Mean 0.3130

Table 7. (224°C.)

t	n_D^{20}	$\frac{1}{x}\times 10^{-2}$	$\frac{1}{t}\times 10^3$	K
0	1.51695	—	—	—
15	1.5157	8.00	66.67	0.432
30	1.5146	4.26	33.33	0.453
46	1.5136	2.99	21.47	0.448
60	1.51275	2.38	16.67	0.466
75	1.5119	1.98	13.33	0.489
91	1.5113	1.77	10.99	0.481
				Mean 0.4614

Table 8. (229.5°C.)

t	n_D^{20}	$\frac{1}{x} \times 10^{-2}$	$\frac{1}{t} \times 10^3$	K
0	1.51595	—	—	—
8	1.51505	11.11	125.00	0.658
16	1.51425	5.88	62.50	0.664
24	1.5136	4.26	41.67	0.647
32	1.5130	3.39	31.25	0.644
41	1.5124	2.82	24.39	0.641
45	1.5121	2.60	22.22	0.653
50	1.5119	2.47	20.00	0.632
56	1.5116	2.30	17.86	0.625
64	1.5113	2.15	15.63	(0.605)
				Mean 0.6455

Table 9. (240°C.)

t	n_D^{20}	$\frac{1}{x} \times 10^{-2}$	$\frac{1}{t} \times 10^3$	K
0	1.5151	—	—	—
7.5	1.5140	9.09	133.3	0.999
15.0	1.5129	4.55	66.67	1.10
22.5	1.5121	3.33	44.45	1.09
30.25	1.51155	2.78	30.06	1.03
37.5	1.51045	2.41	26.67	1.02
45.0	1.51035	2.11	2.22	1.05
				Mean 1.049

Table 10. (245°C.)

t	n_D^{20}	$\frac{1}{x} \times 10^{-2}$	$\frac{1}{t} \times 10^3$	K
0	1.51555	—	—	—
7	1.5142	7.41	142.8	1.26
14	1.51295	3.85	71.43	1.44
21	1.5119	2.74	47.62	1.47
28	1.51115	2.27	35.71	1.41
35	1.5104	1.94	28.57	1.44
4	1.5100	1.80	23.81	1.34
				Mean 1.444

n_∞, n_G, and K are summarised in Table 11, where n_G is the refractive index just before the gelation.

Table 11.

Polymerisation temperature (°C.)	n_∞	n_G	K
245.0	1.5034	1.5100	1.444
240.0	1.5024	1.5104	1.049
229.5	1.5041	1.5113	0.6455
224.0	1.5034	1.5109	0.4505
215.5	1.5026	1.5111	0.3130
210.0	1.5026	1.5111	0.2447
206.0	1.5011	1.5110	0.2074
	Mean 1.5024		

Effect of temperature. The rate of polymerisation was determined at temperatures between 206 and 245°C.

In all cases the whole elapses can be expressed by a bimolecular reaction formula. The relation between reaction constant and temperature is shown in Fig. 5.

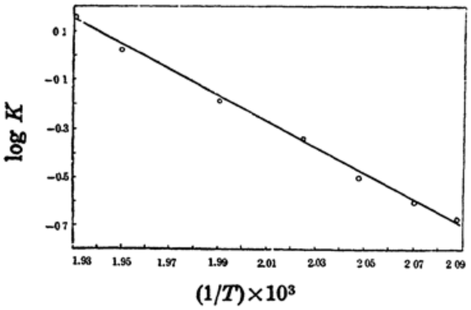


Fig. 5.

Table 12.

t°C.	K	K_1/K_2
240	1.065	1.67
230	0.635	1.62
220	0.392	1.55
210	0.250	

From Fig. 5 it will be seen that a linear relation exists between the logarithm of velocity coefficient and the reciprocal of polymerisation temperature, as can be expressed by the Arrehnius formula,

$$\ln K = C - \frac{Q}{RT} \qquad (7).$$

The values of C and Q were determined as: $C = 5.335$, $Q = 24{,}300$ cal. Temperature coefficient per ten degrees, which has a practical significance, was calculated in the temperature range from 240 to 210°C. and is shown in Table 12.

Summary.

(1) Tung oil was polymerised up to gelation at various temperatures from 206 to 245°C. In the course of cooking, density, iodine value, relative viscosity, and refractive index were measured.

(2) Density, iodine value, and refractive index change rather quickly at the beginning but slowly towards the end of polymerisation. The viscosity changes, however, in opposite sense.

(3) The constants of raw oil and of polymerised oil just before the gelation are as follows.

	Raw oil	Polymerised oil
Density	0.9418	0.9631
Iodine value	166.8	140.5
K_0	3.36	13.4
Refractive index	1.5191	1.5109

(4) A new method to obtain the reaction constant is proposed for reactions of the type $A + A \rightarrow A_2$.

(5) This method was applied to the polymerisation of tung oil and the following conclusions were obtained.

(6) The polymerisation is a second order reaction as determined by both refractive index and iodine value.

(7) The polymerisation velocity was calculated between 206 and 245°C.

(8) The heat of activation was found to be ca. 24,000 cal.

(9) The temperature coefficients of the reaction per ten degrees is 1.55–1.67, in the temperature range from 210 to 240°C.

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

Laboratory of Hitachi Works, Hitachi Ltd.,
Sukegawa, Ibaraki Prefecture.