Polymerisation of Tung Oil. III. Molecular Weights of Tung Oil and its Polymerides.

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The determination of molecular weights of drying oils has the marked importance for the elucidation of polymerisation and oxidation mechanism. However, the results obtained are generally discrepant even with the standard methods. It has been generally known that the molecular weights of fatty oils determined by the cryoscopic method vary to a great extent with the solvent and concentration[1]. As solvent camphor, benzene, nitrobenzene and others are generally used.

The molecular weight to be determined cryoscopically is calculated by the formula: $M=KC/\Delta T$, where K is the calculated depression of the freezing point due to 1 gram molecule of any solute in 100 g. of solution, C the concentration of solute in gram per 100 g. of solution, and ΔT, the observed depression of the freezing point. The molecular weight (which will hereafter be denoted briefly as M) calculated from the above formula is a linear function of concentration (C) in the range of dilute solution.

The true molecular weight corresponding to zero concentration is obtained by extrapolation. But in the case of benzene solution the molecular weight of fatty oils is not a linear function of concentration and the extrapolation to zero concentration is practically impossible.

(1) Normann, *Chem. Ztg.*, **31** (1907), 211; H. J. Backer, *Chem. Weekblad.*, **12** (1915), 1034; Morrel, *J. Oil Colour Chem. Assoc.*, **7** (1924), 146; Seaton and Sawyer, *J. Ind. Eng. Chem.*, **8** (1916), 490; Rhodes and Welz, *ibid.*, **19** (1927), 68.

Nevertheless the cryoscopic method with benzene is usually preferred, because the operations are easily practicable. J. S. Long and J. G. Smull[(2)] reported about the oxidation and polymerisation mechanism of linseed oil, using the data of the apparent molecular weight of a constant concentration (molecular weight of 1 g. of oil in 25 c.c. of benzene).

In the study of polymerisation of tung oil, the author reported[(3)] that the molecular weights of polymerised tung oils calculated from the specific viscosity of benzene solution, when the molecular weight was assumed to be proportional to the specific viscosity, were too great as compared with that inferred from the chemical commonsense. Therefore it is very important to ascertain the relation of molecular weight of polymerised tung oil and the concentration of solution, and to obtain the molecular weight at zero concentration.

Experimentals. Tung oil used was characterized as follows: density (15/15°C.) 0.9409, iodine value (Wijs' method) 166.8, refractive index (n_D^{30}) 1.5164. The polymerised tung oils were obtained by polymerising the raw tung oil at 220°C. and had the following refractive index.

Table 1. Refractive index of polymerised tung oils.

Sample	Polymerisation time (m.)	n_D^{30}
No. 0	Raw oil	1.5164
No. 1	0	1.5122
No. 2	20	1.5109
No. 3	40	1.5097
No. 4	50	1.5090
No. 5	60	1.5082

(1) *Camphor method.* The determination of molecular weight by the melting point depression of camphor was carried out as in the usual method.

For the sake of comparison, the molecular weight of pure oleic acid was measured and the value 290 (calculated molecular weight 284) was obtained. The molecular weight of the polymerised tung oils are shown in table 2.

Table 2. Molecular weights of polymerised tung oils.

Sample	Concentration (%)	Depression of m.p. (ΔT °C.)	Calculated molecular weight
No. 0	4.11	2.25	906
	4.14	2.33	881
	5.01	2 67	931
	5.50	2.80	979
	5.66	3.30	852
	6.17	3.75	810
			893
No. 1	3.35	1.50	1111
	3.68	1.65	1110
	4.77	2.10	1130
	9.97	4.68	(1055)
			1110

(2) J. S. Long and J. G. Smull, *J. Ind. Eng. Chem.*, **17** (1925), 138, 905.
(3) M. Tatimori, this Bulletin, **13** (1938), 142.

Table 2.—(*Concluded*)

Sample	Concentration (%)	Depression of m.p. (ΔT °C.)	Calculated molecular weight
No. 2	4.29	1.68	1269
	4.94	2.00	1230
	5.33	2.50	(1060)
	6.26	2.83	1100
	6.30	2.70	1160
			1220
No. 3	4.42	1.60	1374
	5.28	2.10	1254
	6.50	2.60	1240
	6.63	2.70	(1201)
			1380
No. 4	3.82	1.20	1593
	4.35	1.50	1444
	5.82	1.90	1523
	6.21	2.40	1314
	7.32	3.30	(1140)
			1550

The apparent molecular weight by the camphor method decreases as the concentration increases, but within the range of dilute solution the constant molecular weight is obtained.

(2) *Benzene method.* The molecular weight of oleic acid was measured and the value 565 was obtained. This is twice as much as the theoretical value. The molecular weights of polymerised tung oils are shown in Table 3.

Table 3. Molecular weights of polymerised tung oils.

Sample	Solvent (g.)	Solute (g.)	Concentration (%)	ΔT (°C)	$\frac{\Delta T}{C}\times 10^2$	M
No. 0	17.862	1.145	6.02	0.362	6.01	852
		1.558	8.02	0.530	6.60	795
		1.890	9.57	0.680	7.10	721
No. 1	17.862	0.635	3.44	0.120	3.50	1465
		0.990	5.25	0.200	3.81	1344
		1.521	7.85	0.330	4.21	1217
		2.093	10.49	0.520	4.96	1033
	13.400	2.117	13.64	0.765	5.61	913
		2.368	15.02	0.893	5.95	949
		2.695	16.74	1.035	6.18	817
		3.044	18.52	1.260	6.81	752
No. 2	17.862	1.100	5.80	0.180	3.10	1650
		1.475	7.63	0.259	3.39	1508
		1.820	9.25	0.370	4.00	1280
		2.567	12.56	0.570	4.53	1128
	13.400	1.636	10.88	0.455	4.18	1225
		1.859	12.18	0.588	4.83	1061
		2.209	14.16	0.770	5.44	942
		2.361	14.98	0.840	5.61	913

Table 3.—(*Concluded*)

Sample	Solvent (g.)	Solute (g.)	Concentration (%)	ΔT (°C)	$\frac{\Delta T}{C} \times 10^2$	M
No. 3	17.862	1.202	4.84	0.150	3.10	2152
		1.699	6.67	0.265	3.98	1678
		1.957	7.58	0.320	4.23	1580
		2.500	9.42	0.450	4.78	1396
	13.400	1.812	11.91	0.440	3.69	1387
		2.154	13.85	0.555	4.01	1278
		2.374	15.05	0.645	4.29	1195
		2.528	15.87	0.705	4.44	1153
No. 4	13.400	0.989	6.87	0.148	2.15	2376
		1.415	9.55	0.255	2.67	1916
		1.717	11.36	0.330	2.91	1751
		1.888	12.35	0.385	3.12	1642
No. 5	17.862	1.078	5.69	0.128	2.25	2277
		1.720	8.78	0.203	2.31	2215
		2.203	10.98	0.330	3.01	1703
		2.468	12.14	0.440	3.30	1554
	13.400	2.344	14.89	0.585	3.93	1303
		2.651	16.52	0.710	4.30	1191
		2.743	16.99	0.750	4.41	1159
		2.910	17.88	0.835	4.67	1097

The relations between the apparent molecular weight and the concentration are shown in Fig. 1.

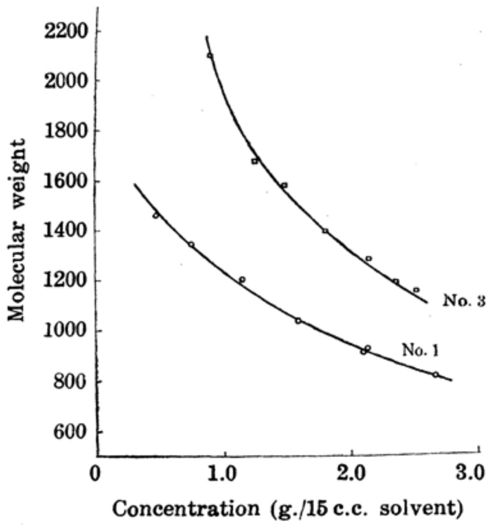

Fig. 1.

It is noticed that the apparent molecular weight decreases rapidly with increasing concentration. These values, obtained by the camphor method, may be accepted as probable molecular weights. But, for the data obtained in the benzene solution the linear relation does not hold between the apparent molecular weight and the concentration, therefore it is impossible to extrapolate to the zero concentration.

A fundamental difficulty in the determination of molecular weights of polymerised tung oil lies in the following fact: in order to increase the accuracy of the measurement, the concentration of the solution must be increased; for this purpose the concentration in weight percent becomes too high, nevertheless the concentration in mol percent remains small, because the molecular weight of polymerised tung oil is very great. This difficulty becomes more eminent as the molecular weight of the solute increases. An abnormally great value for the molecular weight of polymerised tung oil in benzene solution was noticed by Gay[4] and for which he obtained 4320.

This abnormality is probably due to an action between solute and solvent. In other solvents such great values are not obtained. The author carried out the molecular weight determination of another polymerised tung oil, using as solvent nitrobenzene, bromoform and ethylene-bromide. With these solvents the linear function is held between the molecular weight and the concentration, and the values extrapolated to zero concentration are shown in Table 4.

Table 4.

Samples	Heating time at 206 °C. (m.)	n_D^{20}	Nitro-benzene	Bromoform	Ethylene bromide
No. 0	Raw oil	1.5193	800	800	830
1	0	1.5192	820	810	970
2	60	1.5171	960	1120	1160
3	120	1.5149	1320	1360	1420
4	180	1.5139	2095	1785	1940

Thus, reasonable values were obtained.

Gay reported that cyclohexane is an ideal solvent which displays no specific action on the solute. The author determined the molecular weight of raw tung oil in a purified cyclohexane and obtained the results shown in Table 5.

Contrary to other solvents the apparent molecular weight in cyclohexane increases with the increasing concentration and the value at zero concentration amounts to 970. This is a reasonable value for the molecular weight of commercial tung oil.

Discrepancies found between the theoretical value and the observed one may be explained by the mechanism of association of solute, solvation of solvent, association of solvent etc.

Table 5.

Sample (g.)	Melting point depression (ΔT °C.)	Molecular weight
0.3683	0.35	942
0.7721	0.70	1003
1.2168	1.09	1017
1.7161	1.49	1049

Table 6.

Sample	$\lim_{C\to 0} \Delta T/C$	$M_{C\to 0}$	M'
No. 0	4.35	1145	893
1	2.70	1845	1110
2	1.60	3110	1220
3	1.20	4150	1380
4	0.94	5030	1550
5	0.60	8300	—

(4) Gay, *Chemistry and Industry*, **1933**, 70.

It is already known that some of high molecular compounds behave abnormally in the solution(5). G. V. Schulz and his co-workers(6) tried to obtain reasonable values for the molecular weight by the following formula, $M=RT/\lim_{C\to 0}(P/C)$, where P is the osmotic pressure and C the concentration.

In the case of benzene solution of polymerised tung oils the relation between $\Delta T/C$ and C may approximately be represented by a straight line. Thus the value of $\Delta T/C$ and molecular weight at zero concentration can be calculated as shown in Table 6.

In this table $M_{C\to 0}$ is the molecular weight calculated from $M_{C\to 0}=\frac{k}{100}\left(1/\lim_{C\to 0}\frac{\Delta T}{C}\right)$, and M' the molecular weight determined by the freezing point depression of camphor. Further it is noticed that at the end of cooking the molecular weight of tung oil in benzene solution becomes very great, which coincides with the viscosity data(7).

It is reasonable to think that this abnormality is due to the solvation of benzene. The relation between the molecular weight by camphor and benzene methods is shown in Fig. 2.

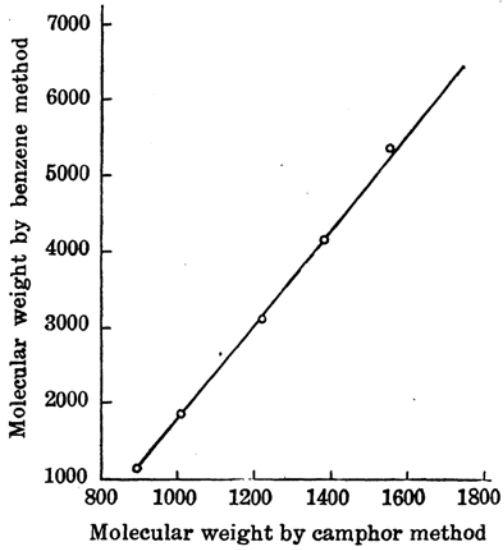

Fig. 2.

An approximate proportionality holds for them. The relations between the molecular weight by camphor method and refractive index, and also heating time of the oil are shown in Figs. 3 and 4.

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(5) P. Stamberger and C. M. Blow, *Kautschuk*, **6** (1930), 22.

(6) G. V. Schulz, *Z. Phys. Chem.* B, **196** (1936), 317; G. V. Schulz and H. Staudinger, *Ber.*, **68** (1935), 2320; G. V. Schulz, *Z. angew. Chem.*, **49** (1936), 549.

(7) M. Tatimori, this Bulletin, **13** (1938), 142.

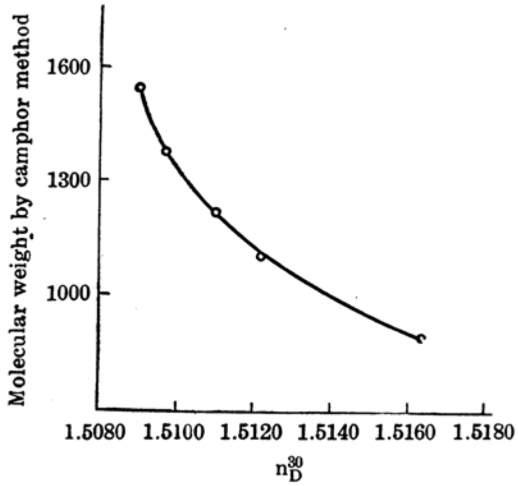

Fig. 3.

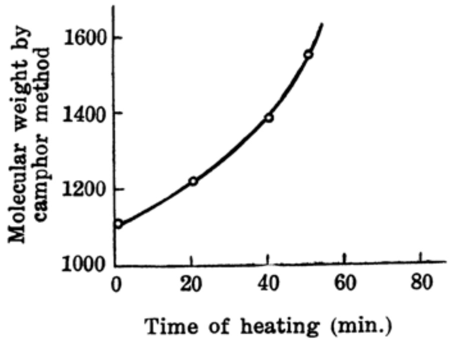

Fig. 4.

Summary.

The molecular weights of polymerised tung oils were measured in the solution of benezne, camphor, nitrobenzene, bromoform, ethylene bromide by the cryoscopic method.

By the camphor method reasonable molecular weights were obtained. But in benzene the molecular weight decreases rapidly with the increasing concentration. In nitrobenzene, ethylene bromide, bromoform the molecular weight behaves as linear function of concentration and the rate of decrease in molecular weight with increasing concentration is not so eminent as in benzene.

On the contrary in cyclohexane the molecular weight increases with the increasing concentration and reasonable values are obtained by extrapolation. The abnormality in benzene may be considered as the solvation action.

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

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