Polymerisation of Tung Oil. X. Gelation of Tung Oil at High Temperature (Summarized Report).

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In the previous reports⁽¹⁾ the author informed about the gelation preventing effects of various materials, such as fatty oils, fatty acids, fatty alcohols, several organic and inorganic reagents, bitumens, cooked drying oils, brominated fatty oils, and natural and synthetic resins etc., and interesting results were obtained. In this paper the summarised conclusions are reported.

I. Classification by the Type of Relation of $1/t-x$. The gelation times of the samples were measured by the method of test tube similar to that of A.S.T.M. and the numerical results were reported in the previous reports.

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(1) M. Tatimori, *J. Soc. Chem. Ind.*, Japan, Supptl. Bd., **41** (1938) 39–41B; 100–102B; **42** (1939) 162–163B; **43** (1940) 102–104B; **43** (1940) 136–140B; 161–162B; 194–196B; This Bulletin, **13** (1938) 142; **15** (1940) 315, 474; **16** (1941) 16, 45, 51, 75, 82, 114.

The various types of relation of $1/t-x$ are shown in Fig. 1 and these could be classified in the next 8 classes:

(1) *Substances whose relations of* $1/t-x$ *are linear.* Greater part of the samples are included in this class. This class is noteworthy both from theoretical and industrial view point and the further discussion shall be given later.

Example: fatty oils, oxidised and polymerised linseed oil, oxidised perilla oil, fatty acids, fatty alcohols, paraffines, coumarone resin.

(2) *Substances which have no effect.*

Example: neutral salts and oxides, e.g. $BaCl_2$, NaCl, KCl, ZnO.

(3) *Substances of which gelation times increase more rapidely than the linear relation.* It is supposed that these materials have special actions upon tung oil, of which reaction products have gelation retarding action. At higher temperature than 300°C. many substances belonging to class (1) convert to this class.

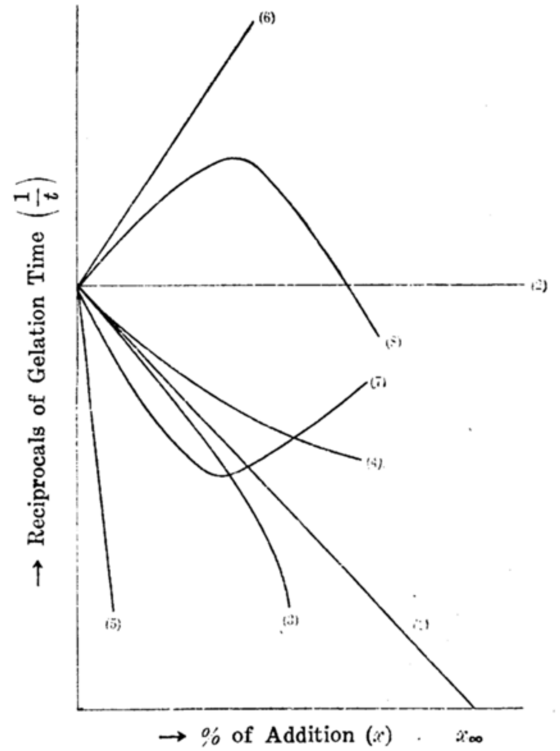

Fig. 1.

Example: glycerine, oleic acid monoglyceride, rosin.

(4) *Reverse of class (3).* The gelation retarding action of the substance decreases with the lapse of heating time, by the decomposion or vaporisation.

Example: β-naphthol, camphor, naphthalene.

(5) *Substances having very strong gelation retarding actions.* These substances act catalytically upon tung oil.

Example: sulphur, selenium, brominated fatty oils.

(6) *Substances having gelation accelerating actions.* These substances act catalytically upon tung oil.

Example: benzoyl peroxyde, tannic acid, gallic acid, pyrogallol, tartaric acid, metallic sodium.

(7) *Substances which act gelation retarding at little addition, but convert to gelation accelerating at increased addition.*

Example: succinic acid, citric acid.

(8) *Reverse of class (7).*

Example: α-naphthol, various bitumens.

II. General Consideration. Of the retarding nature of all substances the next could be concluded in common.

(1) *Effect of unsaturation.* In the addition of fatty oils and fatty acids, the values of x_∞ increase as the degree of unsaturation increases. This is anticipated from the fact that the unsaturated compound has the tendency to polymerise itself, and co-polymerise with the tung oil.

(2) *Effect of cooking degree.* Similarly the values of x_∞ of cooked drying oils increase according to the degree of cooking. This coincides with the fact when drying oils were cooked, they turned into gelatinous state at last. From this fact the gelation tendency of cooked drying oil could be estimated and these have wide application in industrial field.

(3) *Effect of secondary reaction at high temperature.* It is supposed that at higher temperature than 300°C. the secondary reactions occur during the measurement, because the relation of $1/t-x$ becomes irregular at high temperature. The gelation time shows a minimum value above 300 °C. and further it increases.

From the next experiment it is concluded that the cracking of glycerine radical occurs. The increased of acid value is shown in Table 1, when the mixture of 100 g. of tung oil and 100 g. of linseed oil was heated in a glass bottle at 310 °C. Acid value increased as proportion to the heating time.

Table 1.

Time of polymerisation (min.)	Acid value
0	4.56
5	6.21
10	6.93
15	7.32
20	7.93
25	8.34

The cracking products have gelation preventing action, therefore the gelation time of the system increases.

When fatty acids and alcohols were added, the minimum of gelation time was found at lower temperature than in the case of addition of fatty oils, and the temperature of minimum gelation time becomes lower as the amount of addition increases.

When fatty oils were heated at temperature higher than 200 °C. with fatty alcohols, fatty acids and esters the exchange of ester part occurred.⁽²⁾ Thus the strong gelation preventing action of glycerine and oleic acid monoglyceride can be explained.

Beside these reactions the isomerisation of α-eleostearic acid by S, Se and brominated fatty oils is considered as the cause of strong gelation retarding action of the substances.

(4) *Solubility.* The irregularlity of relation of $1/t-x$ was observed when tung oil was heated by addition of less soluble substances such as polybasic acids. At the limiting case the added reagent often crystalysed out when the polymerisation of tung oil proceeded considerably.

III. Effect of Molecular Weight. The values of x_∞ of several substances which was considered not to react with tung oil are shown in Table 2.

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(2) Norman, *Chem. Umschau*, **30** (1923) 250; Krumbhaar, "The Chemistry of Synthetic Coating Materials;" R. Oda, *J. Soc. Chem. Ind. Japan*, Supptl. Bd., **36** (1938) 755, 945.

Table 2.

Substances	Molecular weight	x_∞ (weight %)	x_∞ (mol %)
Tristearin	890	61.0	60.5
Camellia oil (triolein)	884	59.0	58.5
Stearic acid	284	33.0	59.2
Oleic acid	282	34.5	62.2
Olein alcohol	266	32.5	61.4
Cetyl alcohol	242	31.0	61.6
Oleic acid monoglycol	326	35.0	59.3
Oleic acid monoglyceride	356	24.0	40.8
Glycerine	92	10.5	52.5
Perilla oil	(878)	75.5	75.5

The values of x_∞ of first group, substances from tristearin to oleic acid monoglycol, are about 60%. The cause of gelation preventing action of these substances are considered as mechanical dilution.

Hitherto the special degelating actiton was considered as the nature of strong gelation preventing action of fatty acid, but from the author's opinion there is no special difference observed between fatty acid and oil, except their molecular weight. The molecular weight of fatty acid was 1/3 of that of fatty oil, therefore the gelation preventing action of fatty acid apparently is great when expressed by weight percentage.

Substance such as glycerine, whose value of x_∞ is less than 60%, has special chemical action, of which the reaction products have strong gelation preventing action; on the other hand substances whose value of x_∞ are greater than 60%, promote the gelation of tung oil due to co-polymerisation.

IV. Examination of Measured Gelation Time. As the gelation times of tung oil were measured by heating the sample taken in test tubes, they are affected by the conditions of measurement such as the dimensions of the apparatus, the volume of sample taken etc. The fatty oil itself is a complex mixture of glycerides of various fatty acids, therefore the absolute values obtained have no important meaning, but the results obtained in the same conditions can be used for the comparison of gelation preventing or accelerating actions of various substances.

As remarked above, in the case where the neutral substances soluble in tung oil were added to the oil, the relation between the reciprocals of gelation time and the amount of addition are linear. The value of x_∞ extrapolated, was experimentally shown to be a characteristic constant of the added substance and it is not affected by the measuring conditions. In order to ascertain this fact the measurements were carried out at 270°C. in the case of addition of linseed oil, by using two test tubes, one being the ordinary, with length of 15.5 cm., diameter of 4.0 cm., the other being the specially made, its length 13.9 cm. and its diameter 0.8 cm. (this is very small as compared to the ordinary one), and the linear relations were observed and the values of x_∞ were 67%, in the both measurements.

But strictly speaking the gelation time thus observed contains some errors apparently; that is, it takes about two minutes for the sample taken in the measuring apparatus to attain the measuring temperature.

The temperature of the sample was measured by inserting the pyrometer junction in the sample and it was observed that within the first one minute the temperature rose rapidly above 200°C., but after this time the elevation of temperature became very slow. Strictly, the gelation time must be measured at constant temperature, therefore the correction term (α minutes), the ineffectual time during the rise of the temperature of the sample to the measuring temperature, should be subtracted from the apparent gelation time.

Now denoting the apparent gelation times of tung oil and of that added with other gelation preventing substance as t_0 and t_0', it was established from the observations that the next equation holds.

$$\frac{1}{t'}=\frac{1}{t_0'}-\frac{x}{C} \tag{1}$$

As C equals $t_0'\times x_\infty$, so it can be expressed as follows.

$$\frac{1}{t'}=\frac{1}{t_0'}\left(1-\frac{x}{x_\infty}\right) \tag{2}$$

Taking t_0 and t, as the theoretical gelation time then $t_0'=t_0+\alpha$, $t'=t+\alpha$ and

$$\frac{1}{t+\alpha}=\frac{1}{t_0+\alpha}\left(1-\frac{x}{x_\infty}\right) \tag{3}$$

That is.

$$\frac{1}{t}\left(1-\frac{\alpha}{t}\right)=\frac{1}{t_0}\left(1-\frac{\alpha}{t_0}\right)\left(1-\frac{x}{x_\infty}\right).$$

$$\frac{1}{t}=\frac{1}{t_0}\left\{1+\alpha\left(\frac{1}{t}-\frac{1}{t_0}\right)\right\}\left(1-\frac{x}{x_\infty}\right)$$

$$=\frac{1}{t_0}\left(1-\frac{\alpha x}{t_0 x_\infty}\right)\left(1-\frac{x}{x_\infty}\right) \tag{4}$$

If we neglect the term $\frac{\alpha}{t}\frac{x}{x_\infty}$, the both equations (4) and (2) coincide.

Assuming $t_0=15$, $\alpha=1$, $x_\infty=0.5$, then the value of $\frac{\alpha}{t_0}\frac{x}{x_\infty}$ becomes as follows. The error increases as x increases, but the maximum value is about 5%. The term $\alpha x/t_0 x_\infty$ can be neglected, and by

Table 3.

x	$\alpha x/t_0 x_\infty$	**Error (%)**
0	0	0
0.1	1/75	1.3
0.2	2/75	2.6
0.3	3/75	4.0
0.4	4/75	5.3
0.5	0	—

using the theoretical gelation times we obtain the next formula.

$$\frac{1}{t}=\frac{1}{t_0}\left(1-\frac{x}{x_\infty}\right) \tag{5}$$

Thus it is noticed that the above formula should have theoretical meaning.

V. Theoretical Deduction of Linear Relation of $1/t$ and x. For this purpose the content of polymerides in the tung oil gel should be known. From the result of Bolton⁽³⁾ the next relation was obtained, $G=G_0\,(1-\alpha x)$, where G denotes the content of polymerised tung oil in the gel, G_0, that of 100% tung oil gel, x is the percent. of added substance, α is a constant.

From the study of the author⁽⁴⁾ the polymerisation of tung oil proceeds as a bimolecular reaction.

$$\frac{dx}{dt}=K(a-x)^2$$

Now integrating the above formula, we have

$$\frac{G}{a(a-G)}=Kt \tag{6}$$

Generally, when other substances were added to tung oil, then the value of a, K, G were changed, and consequently it results in various types of relation of $1/t$ and x.

Now we consider the case where the neutral substance was added. Assuming the amount of addition to be x, then $a=1-x$, and $G=G_0(1-\alpha x)$, $K=K_0(1-\beta x)$, then

$$\begin{aligned}\frac{1}{t}=\frac{K_0}{G_0}\Big[&(1-G_0)-\big\{A-\alpha+(1+\beta)(1-G_0)\big\}x+\big\{(1+\beta)(1-\alpha)\\&-\alpha(1-G_0\alpha)+(1-G_0)\beta\big\}\Big]x^2+\cdots\cdots\end{aligned} \tag{7}$$

By neglecting the higher term of x, we have

$$\frac{1}{t}=\frac{1}{t_0}-\frac{K_0}{G_0}\big\{2+\beta-\alpha-G_0(1+\beta)\big\}x \tag{8}$$

Thus the linear relation of (5) can be deduced theoretically.

VI. Polymeric Functionality and Gelation of Tung Oil. Carothers⁽⁵⁾ and Bradley⁽⁶⁾ classified the chemical reactions in the types of (m, n), from the number of reactive radicals of interacting molecules (functionality). In the reaction of (1, 1), (1, 2) and (2, 2) no gelation

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(3) Bolton, *Analyst*, **51** (1926) 335.
(4) M. Tatimori, this Bulletin, **13** (1938) 142.
(5) Carothers, *Trans. Faraday Soc.*, **32** (1936) 39.
(6) Bradley, *Ind. Eng. Chem.*, **30** (1938) 689.

occurs, and the gelation occurs only in the reactions of (2, 3) or higher order reaction.

According to Carothers a general equation relating degrees of reaction (P), average degree of polymerisation (x) and functionality can be developed.

Let f=degree of functionality
N_0=number of monomer molecules initially present
Then N_0f=number of functions initially present
N=number of molecules after reaction has occurred.
$2(N_0-N)$=number of functions lost
$\frac{2(N_0-N)}{N_0f}$=fraction of functions lost =P= extent of reaction
obviously, N_0/N=average degree of polymerisation=x.

Hence,

$$P=\frac{2}{f}\left(1-\frac{1}{x}\right) \tag{9}$$

This equation has interesting application in the gelation of tung oil.

Referring again to formula (9), if x is very large the second term disappears, and we have $P_\infty=2/f$, which tells us at what degree of reaction the molecular weight will become infinite (gelation occur), or where, in polyfunctional reactions, gelation will occur and inter molecular reaction cease.

It is supposed that the number of functionality f of α-eleostearic acid triglyceride is 6, but in the case of tung oil f=5.1 (6×0.85), then the value of P_∞ equals 0.40. That is, when tung oil turns to gelatinous state, at least 40% of the oil must be polymerised.(7) This fact coincides with the above experimental results which require for preventing the gelation of tung oil, 60% of other neutral substance should be added.

Summary.

(1) The summarized conclusions about the gelation of tung oil at elevated temperature are reported.

(2) The various types of relation of $1/t\sim x$ of added substances can be classified into 8 classes and the general consideration of gelation-retarding nature are given.

(3) The measuring method of gelation time are discussed and the formula of $1/t=1/t_0-ax$ is deduced from the polymerisation mechanism.

(4) The gelation phenomena of tung oil are considered from the theory of polyfunctionality and the value of x_∞ can be obtained from the formula $x_\infty=(1-p_\infty)=\left\{1-\lim_{x\to\infty}\frac{2}{f}\left(1-\frac{1}{x}\right)\right\}$ as 60%. This value coincides with the experimental fact.

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(7) P_∞ can be obtained also by the following method,

$$\frac{5.1\,(100-x_\infty)+0\times x_\infty}{100}=2$$

In conclusions, the author wishes to expresses his sincere thanks to Prof. J. Samesima of the Tokyo Imperial University and to Dr. K. Baba, Dr. T. Yosioka and Mr. K. Yokota of this Works for their kind guidance.

Tung oil is one of the most important product of Chinese continent and hitherto was exported about 65,000 tons per year. Tung oil is the most unsaturated and quick drying fatty oils in the world, and the varnishes made from it have many excellent properties such as water proofness, acid and alkali proofness, and used for the important maschines, such as arms, motor-cars and electric maschines.

The Japanese industry nowaday has a tendency to mass production with the development of the Japanese economical block from the standpoint of "autalkie" of the East Asia, and the demand of the quick-drying varnishes increases more and more.

Therefore the study of tung oil will be increased in its importance.

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