Two molecules of alcohol condense in a similar way to form ether:

$$2C_3H_8O \longrightarrow (C_3H_7)_2O + H_2O$$
$$2 \times 207.7° \text{ K.} = 272.3° \text{ K.} + 143.1° \text{ K.}$$

A molecule of alcohol and of acid unite to form an ester:

$$C_2H_5COOH + C_3H_7OH \longrightarrow C_2H_5COOC_3H_7 + H_2O$$
$$232.2° \text{ K.} + 207.7° \text{ K.} = 296.8° \text{ K.} + 143.1° \text{ K.}$$

In the first case the temperature is not $2 \times 232.2 = 464.4°$ K., but 321.3° K. which is 143.1° K. lower than this, 143.1 being the temperature value for water. In the case of propyl alcohol, two associated molecules would require a temperature of 415.4° K., but owing to the elimination of water the temperature is again 143.1° K. lower, or 272.3° K. In the third case the temperature required is not 232.2 + 207.7 = 439.9° K., but 296.8° K., which is again 143.1° K. below the value calculated on the basis of union by association.

The case is somewhat different in the formation of [illegible] tones:

$$CH_3.CHOH.CH_2.CH_2.COOH \longrightarrow CH_3.CH\begin{matrix}O.CO\\CH_2.CH_2\end{matrix} + [illegible]$$
$$299.8° \text{ K.} \qquad 275.3° \text{ K.} \qquad 143.1°$$

The ring formation in this case makes up for the loss of [illegible] hydrogens, so that the temperature required to produce [illegible] fluidity of 200 rhes is not 143.1° K. lower but simply 24.5° K. corresponding to one oxygen atom.

Elsewhere there will be given examples of the practical application of the method.

Literature Cited

(1) Bingham and Darrall, *J. Rheology*, **1**, 174 (1930).
(2) Bingham and Fornwalt, *Ibid.*, **1**, 372 (1930).
(3) Bingham and Harrison, *Z. physik. Chem.*, **66**, 1 (1909).

Studies in the Drying Oils

XV—Some Aspects of the Oxidation of Linseed Oil up to Gelation[1]

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This work is a continuation of the work of Long and Chataway (2) designed to test the original work and to extend it to a study of the effect of the following factors on the rate of oxidation up to the point of gelation: temperature, driers, inhibitors, degree of unsaturation, degree of complexity of the molecule, and acid value.

Free fatty acids unite with linseed oil during oxidation at 160° C., thus increasing the complexity of the molecule and playing a role of primary importance in facilitating gelation.

Linolenic triglyceride takes up nearly twice as much oxygen as its isomer, eleostearic triglyceride, before gelation. Gelation is a colloidal association process and depends on the size, complexity, polarity, and free energy of the molecules. Oxidation is a contributory cause.

Sodium oleate and selenium lower the rate of oxidation and thus delay gelation.

Metallic driers increase the rate of oxidation and decrease the time required for gelation. The presence of lead materially decreases the weight of oxygen required for gelation and also the percentage of the original oil in volatile oxidation products. Lead therefore has a specific action in promoting formation of groups that associate.

From 50 to 85 per cent of the oxygen absorbed up to the point of gelation remains in the oil gel. The other 15 to 50 per cent appears in volatile oxidation products which contain 3.5 to 5 per cent of the carbon and hydrogen of the original oil.

IT WAS at first thought that the transition of liquid drying oils into solid film was entirely a matter of oxidation. Later work introduced the concept of polymerization and classified at least the latter stages of the process as colloidal phenomena, the solid film being regarded as an association colloid gel. A recent survey and résumé of existing ideas is given by Eibner (*1*).

The words "polymerization," "association," "gelation," and "resinification" define processes that are closely related, often confused, and in some respects identical. No attempt will be made here to differentiate these terms, but it may be well to set down certain criteria of the phenomenon as applied to oils, although no sharp dividing line is drawn between oils and resins or the combination products thereof with oils. The phenomenon of thickening or bodying which results in gelation or resinification is influenced by the following considerations:

(1) Contrary to similar phenomena in the case of gases or of many liquids, polymerization of oils is greatly facilitated by elevation of temperature. However, it can be accomplished at room temperature by action of stannic, ferric, aluminum and other metallic chlorides.

(2) Polymerization is accelerated by heat, light, and electrical energy, and this absorption of energy can be greatly influenced by the presence of intermediate sensitizers such as halogens.

(3) Polymerization takes place at room temperature under the influence of very high pressure.

These factors can be considered together. Inasmuch as energy change is a universal characteristic of chemical reaction, even the polymerization caused by the presence and reaction of other chemical substances can be considered on the basis that these substances serve as reservoirs of energy to supply the oil with the energy quanta necessary for the polymerization or association process. Therefore, the major considerations are free-energy changes. Incidentally, this guiding principle is broad enough to cover most, if not all, of the varied phenomena and data that come under the heading of polymerization.

Polymerization or association can be likened in some respects to crystallization; i. e., there are forces which tend to orient the molecules into at least multiple units. The resultant product has not yet vielded fundamental evidence of

[1] Received April 9, 1931.

x-ray patterns of oils in various stages of transformation from liquid to solid are substantially the same as that of the original oil. With increasing improvements in x-ray technic it may be possible soon to detect some differences, but it seems evident that the polymerization forces are not very great.

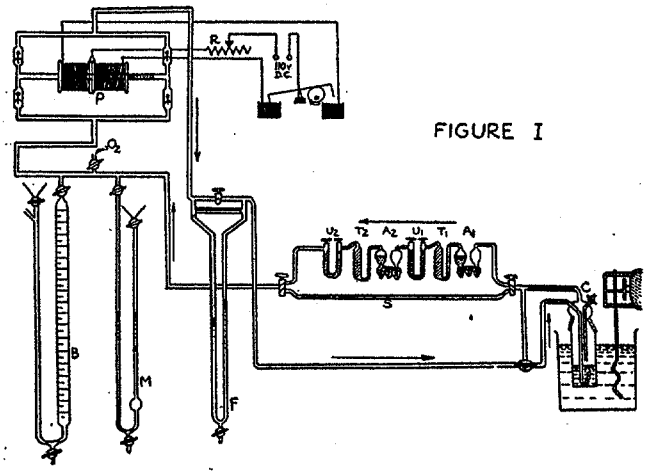


FIGURE I

The published figures for heats of polymerization of oils are few. The reaction needs stimulation and can be reversed to a considerable extent, thus:

(4) Gels and films are dispersed by solvents.

(5) Oxygen can and does break the bonds of association, with the result that bodied oils oxidize to nearly the same ultimate analysis that raw oil does. This fact is brought out by some recent, as yet unpublished, data obtained in this laboratory.

(6) Polymerization is greatly influenced by oxidation or other chemical reactions in the earlier stages preceding the polymerization itself. It is certain that peroxides form at the double bonds and also that they rearrange to some extent. One school of thought believes that these peroxides or other oxy bodies catalyze further oxidation and thus hasten the process of molecule building which leads to gelation. Certainly gelation is influenced by certain groups. This is also true of resinification and some workers ascribe resinification to the presence of "resinogenetic groups." However, this is not the whole story. The rest of the molecule must be considered. Orthodox, formal organic chemistry portrays a process by showing, say, an OH group of one molecule uniting with an H of another molecule—i. e., H_2O is eliminated and the residues unite. The process is called "condensation." Similarly, an SH group of one molecule unites with H of another, eliminating H_2S and uniting the residues. The second reaction is not so vigorous, however. The formal reaction correctly indicates the final products, but it does not put much emphasis on the energy relationships. Actually the molecule possesses reactivity at certain spots and this reactivity is influenced by the whole molecule.

(7) Metallic driers seem to function as association or polymerization catalysts. Our knowledge of the mechanism of drier action is not yet complete.

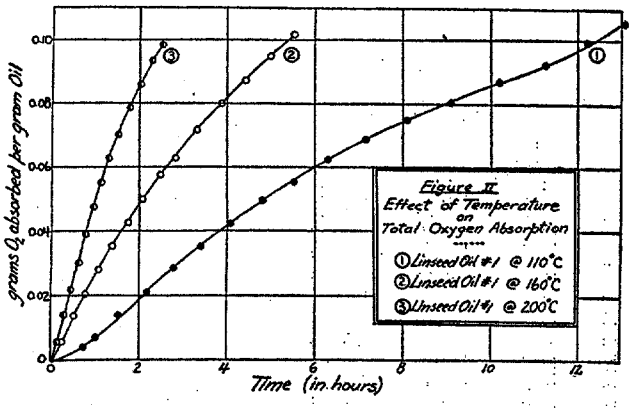
(8) Some consideration is being given to the idea that it is unnecessary to premise the association type of reaction which involves secondary valence effects. On this basis the molecules build up by reactions of the orthodox type involving primary valence effects. It is quite possible that in such large, long molecules the union by primary valence is so weak that it can be disrupted by solvents, oxygen, or other means. Furthermore, the reactions do not seem to be strongly exothermic. It may therefore well be that we should consider the entire process of heat-bodying down to gel on the basis of molecule building by regular primary valence effects. New data bearing on the subject of oxidation are presented in this paper.

Apparatus and Method

The apparatus used in this investigation was essentially that used and described by Long and Chataway (*2*). It was, however, partially redesigned and entirely rebuilt. The difference lies in the absorption train used to remove volatile oxidation products. The original train consisted of concentrated sulfuric acid, a glowing platinum wire, and ascarite, and the results gave a value for oxygen absorption higher than the true value by an amount equal to the oxygen necessary to burn a small fraction of the volatile product to carbon dioxide and water. In order to eliminate this error, a train consisting of concentrated sodium hydroxide solution, anhydrous calcium chloride, concentrated sulfuric acid, and ascarite was employed. The sodium hydroxide removes the volatile acids by forming the sodium soap. Some aldehydes and ketones are polymerized at the same time. The calcium chloride removes all water, both that given off by oxidation and that evaporated from the sodium hydroxide solution. The sulfuric acid is used to remove those compounds that are not absorbed by the sodium hydroxide. The ascarite takes care of any acid oxides, such as carbon dioxide or sulfur dioxide.

Figure I shows the complete apparatus. Briefly, circulation of oxygen through the closed system is effected by the electromagnetic pump *P*. The rate of oxygen circulation is kept constant for all runs, as indicated by the flowmeter, *F*, by adjusting the resistance, *R*. After passing through the absorption cell, *C*, containing the oil being studied, the oxygen and volatile products pass to the absorption train. A_1 and A_2 are Geissler bulbs containing sodium hydroxide and sulfuric acid, respectively. T_1 and T_2 are traps filled with glass wool. U_1 and U_2 are U-tubes containing calcium chloride and ascarite, respectively. *M* is a manometer containing sulfuric acid, and *B* is a 50-cc. buret.

The absorption train is well swept out with oxygen prior to use. The two three-way stopcocks are then turned, closing off the absorption train and opening the by-pass *S*. The apparatus is then ready for alternate evacuation and flooding with oxygen. The absorption train is again admitted to the system before the circulation is started. The function of the various parts of the apparatus and the experimental procedure have been described previously (*2*).



For the supplementary study of total carbon and hydrogen volatilized, a simple train was constructed. The oxygen is conditioned by passing through a wash bottle containing concentrated sulfuric acid and then through a trap containing glass wool to remove any entrained sulfuric acid. A constant rate of oxygen flow, as indicated by a flowmeter, is maintained throughout the experiment. This flow is the same as that employed in measuring the total oxygen absorption. A bubbling cell, identical with that used in connection with the main apparatus, contains the oil being studied. The volatile products emerging from this cell pass directly through a silica tube containing copper oxide which is maintained at a red heat by means of a muffle furnace. The combustion products, carbon dioxide and water, are absorbed by calcium chloride and ascarite and determined as carbon and hydrogen.

Materials

Linseed oil 1 is a commercial alkali-refined varnish oil; iodine number 180.5, acid value 0.3.

Linseed oil 2 is a raw oil treated to remove the break; iodine number 185.6, acid value 2.25.

The various esters were synthesized by the method previously described (*3*).

Results

The data are given in Tables I to III. The oxygen absorption is plotted against time in Figures II to V.

Table I—Total Oxygen Absorption up to Gelation

Run	Material	Gelling Time		Oxygen Absorbed per Gram Oil
		Hours	*Min.*	*Gram*
	TEMPERATURE VARIABLE			
1	Linseed oil 1, 110° C.	13	02	0.1080
2	Linseed oil 1, 160° C.	5	44	0.1035
3	Linseed oil 1, 200° C.	2	28	0.0980
	ACID VALUE VARIABLE			
4	Linseed oil acids, acid number 200	6	43	0.1350
5	Linseed oil 1 + acids, acid number 100	4	40	0.0985
6	Linseed oil 1 + acids, acid number 50	4	44	0.0866
	COMPLEXITY			
7	Methyl ester of linseed oil acids	(no gel)		
		5	16	0.1340
8	Glycol ester of linseed oil acids	3	47	0.0570
9	Pentaerythritol ester of linseed oil acids	1	45	0.0308
10	Linseed oil 1, 3-hour heat-body	3	45	0.0434
11	Linseed oil 1, 6-hour heat-body	2	11	0.0282
	UNSATURATION			
12	Oleic triglyceride	12	08	0.1510
13	Linolenic triglyceride	3	39	0.1030
14	α-Eleostearic triglyceride	2	16	0.0534
	DRIER			
15	Linseed oil 1 + 1.00% Pb[a]	3	32	0.0843
16	Linseed oil 1 + 0.29% Co[a]	1	59	0.1070
17	Linseed oil 1 + 0.27% Fe[b]	4	35	0.1031
	INHIBITOR			
18	Linseed oil 2	5	31	0.1015
19	Linseed oil 1 + 0.39% Se[c]	(no gel)		
		8	50	0.0603
20	Linseed oil 1 + 0.11% Na[d]	7	27	0.1010

[a] As resinates.
[b] As ferric oxide.
[c] As powdered selenium.
[d] As sodium oleate.

Table II—Partition of Oxygen between Gel and Volatile Products

Run	O_2 in Gel	Total O_2 Absorbed per Gram Oil	O_2 Retained by 1 Gram Original Oil	O_2 in Volatile Products from 1 Gram Original Oil (by diff.)	O_2 Remaining in Oil
	%	*Gram*	*Gram*	*Gram*	*% of total*
1	17.8	0.1080	0.0763	0.0317	70.7
2	17.1	0.1035	0.0737	0.0298	71.2
3	16.8	0.0980	0.0698	0.0282	71.4
4	17.5	0.1350	0.0740	0.0610	54.8
5	11.2	0.0985	0.0534	0.0451	54.3
6	11.1	0.0866	0.0470	0.0396	54.3
8	15.1	0.0570	0.0483	0.0087	84.8
10	14.1	0.0434	0.0361	0.0073	83.2
11	12.7	0.0282	0.0195	0.0148	69.2
12	19.4	0.1510	0.1041	0.0469	68.9
13	16.8	0.1030	0.0698	0.0332	67.7
14	13.6	0.0534	0.0301	0.0233	56.4
15	14.6	0.0843	0.0422	0.0421	50.1
17	17.6	0.1031	0.0802	0.0229	77.7
18	17.0	0.1015	0.0723	0.0292	71.2
20	16.2	0.1010	0.0620	0.0390	61.5

Table III—Volatile Oxidation Products

Run	Carbon per Gram Oil	Hydrogen per Gram Oil	Total C + H in Volatile Products	Ratio Atoms H to Atoms C	Original Oil in Volatile Products
	Gram	*Gram*	*Gram*		%
1	0.0274	0.0243	0.0517	10.65	5.17
2	0.0297	0.0151	0.0448	6.12	4.48
3	0.0879	0.0101	0.0480	3.20	4.80
4	0.0526	0.0257	0.0783	5.88	7.88
6	0.0320	0.0140	0.0460	5.25	4.60
15	0.0258	0.0094	0.0352	4.36	3.52
16	0.0290	0.0088	0.0378	3.63	3.78
20	0.0279	0.0153	0.0432	6.60	4.32

The data for linseed oil alone and for linolenic triglyceride check those obtained by Long and Chataway very closely, thus showing that results on the rebuilt apparatus may be used to extend the ideas previously developed.

Ultimate analyses were run on the original oils and on the final gels. Obviously, the analysis of the gel gives a value for the oxygen retained by the liquid phase on the basis of the final gel—i. e., as grams of oxygen per gram of gel. This value must then be translated to the basis of original oil in order to obtain the partition of oxygen between gel and volatile products. This is accomplished by a simple calculation, as shown by the following example, which is for run 2.

The computation resolves itself into determining how many grams of oxygen, x, are required to change 1 gram of oil containing 11 per cent of oxygen into a gel containing 17 per cent oxygen. It must be remembered that x is not the total oxygen absorbed, but only that part retained by the oil to form a gel; hence the volatile products do not appear in the calculation algebraically.

$$1 \text{ gram oil} + x \text{ grams oxygen} = (1 + x) \text{ grams gel}$$

Since this expression is an identity, we may equate the total weight of oxygen of the reactants to that appearing in the corresponding amount of product, thus:

$$0.11\ (1) + x = 0.171\ (1 + x)$$
$$x = 0.0737 \text{ gram oxygen per gram original oil}$$

Measurements show that the total amount of oxygen absorbed per gram of oil (run 2) is 0.01035 gram. Thus,

$$\frac{0.0737}{0.1035} \times 100 = 71.2 \text{ per cent of total oxygen absorbed is retained by liquid phase}$$

The percentage of oxygen in the gels as determined by ultimate analysis is in line with the weight of oxygen absorbed up to the gel point. This correspondence is only possible because the volatile products are not a large percentage based on either the carbon and hydrogen of the oil or the oxygen used.

No attempt was made to isolate and determine individual volatile products. Considerable work has already been done on this phase of the subject and a number of acids, aldehydes, etc., have been identified. In this investigation it was considered sufficient to obtain carbon, hydrogen, and oxygen balances. In Table II, column 5, appear values for the amounts of oxygen going to form volatile oxidation products; in Table III, column 4, values for total weight of carbon plus hydrogen in volatile products are listed. From these data it is possible to calculate the oxygen content of the volatile products.

In run 2 at 160° C., 0.0448 gram of carbon plus hydrogen per gram of linseed oil is given off. At the same temperature 0.0298 gram of oxygen appears in the volatile products. From this we compute the oxygen content of the volatile products as 40 per cent by weight. Propionic acid contains about 43 per cent oxygen and valeric acid contains about 36 per cent oxygen by weight. Thus the products obtained would represent a mixture of these two acids. However, it is recognized that compounds of much higher and much lower oxygen content are also present. Other investigators have pointed out that propionic and valeric acids are formed in reasonably large quantities.

Effect of Temperature

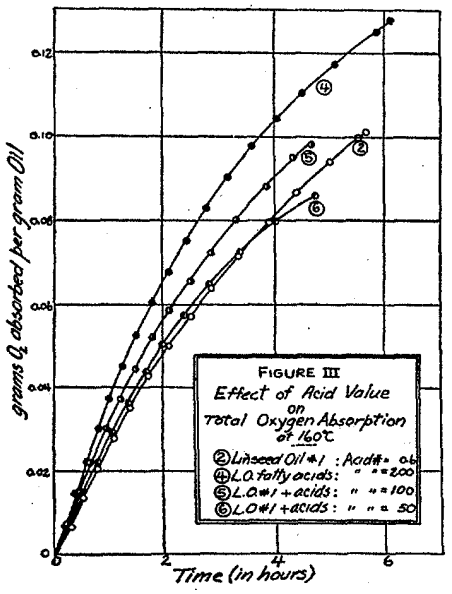
Runs 1, 2, and 3 show clearly that elevation of temperature increases the velocity of the reactions that lead to gelation and thus brings about gelation in shorter time. The number of grams of oxygen absorbed per gram of oil up to the point of gelation or setting is greatest at 110° C. and least at 200° C. There is a regular gradation, but the differences are small, especially in view of the great differences in time. Table III shows that the lower the temperature the greater is the amount of volatile products obtained. There appears to be

more opportunity for the splitting off of volatile oxidation products when the time for gelation is long.

The ratio of carbon to hydrogen decreases as the temperature decreases, indicating that the reactions by which the volatile products are split off are different. There are not sufficient data, however, to state wherein this difference lies.

Effect of Acid Value

During the process of oxidation or heat-bodying of drying oil the acid value of the oil increases. This seems to be due, at least in part, to cleavage at the fifteen or twelve double bonds. Aldehydes, acids both mono and dibasic, and alcohols with 3, 4, and 6 carbon atoms have been found in the volatile products by various investigators.



Inspection of runs 2, 4, 5, and 6 brings out interesting ideas. The fatty acids themselves oxidize faster than the glyceride (oil). Since they are smaller and less complicated molecules, they require greater oxygen absorption and longer time to gel. However, mixtures of fatty acids and glycerides gel not only quicker than oil alone but with less absorption of oxygen up to the gel point. As shown in Table II, less of this oxygen remained in the oil and more escaped in volatile products. It is significant that the presence of fatty acids should thus affect the oxygen absorption. This raises the question of the mechanism of their action—do they react?

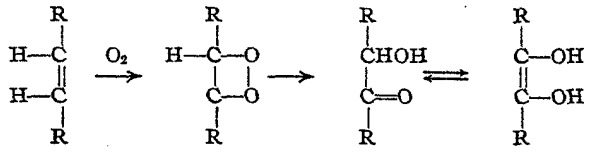
Determination of the acid values of the gels obtained at once throws light on the situation, as shown by the following tabulation:

Run	Acid Value at Start of Run	Acid Value after Gelation
2	0.6	7.58
4	200	125.8
5	100	56.9
6	50	29.0

It would be expected that the constant circulation of oxygen through the hot oil for several hours would carry away to the absorption train some of the free acids liberated by cleavage at the double bonds and also some of the larger 18-carbon acids introduced as such. However, the net result of the two influences, cleavage and vaporization loss, is an increase in acid value from 0.6 to 7.58 in the case of oil alone. On the other hand, the pure fatty acids and mixtures of glyceride (oil) and fatty acid all showed great reductions in acid value—i. e., carboxyl groups have disappeared. This fact coupled with the more rapid gelation of the oil and the smaller oxygen absorption up to the gel point, indicates rather definitely that the fatty acids have united with the glyceride molecules and also that this union is a primary factor leading to gelation.

Similar effects are observed during heat-bodying. Thus the acid value often increases to a maximum and then decreases more than would be expected on the basis of loss of volatile products. However, the effects are so much more pronounced when the oil is being oxidized that it is suggested that the acids adding are either oxidized or else react more easily with peroxide or other oxy linkages on the double bonds than with the double bonds themselves, or perhaps oxy acids react at oxy groups on the double bonds.

During oxidation peroxide groups form at the double bonds. This is well established by the work of Morrell and Marks (4). Various rearrangements, such as the following, are postulated and seem probable, though some doubt still exists as to the exact changes that occur:



It is quite possible for fatty acids, either oxidized or not, to react with compounds of this type, particularly at elevated temperatures. Condensation reactions involving elimination of water are possible among others. The hydrogen in volatile products, however, is no greater in run 6 than in run 4. This very vital detail of the mechanism therefore needs further study.

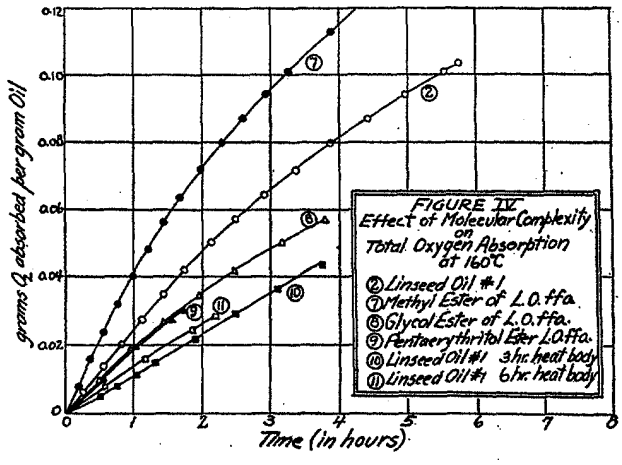


Figure III shows that the free acids oxidize more rapidly than the oil. If the acids adding to the oil have been previously partially oxidized, these polar oxy spots on their chains will have additional effect in attracting other molecules and leading to association, thus facilitating gelation as observed.

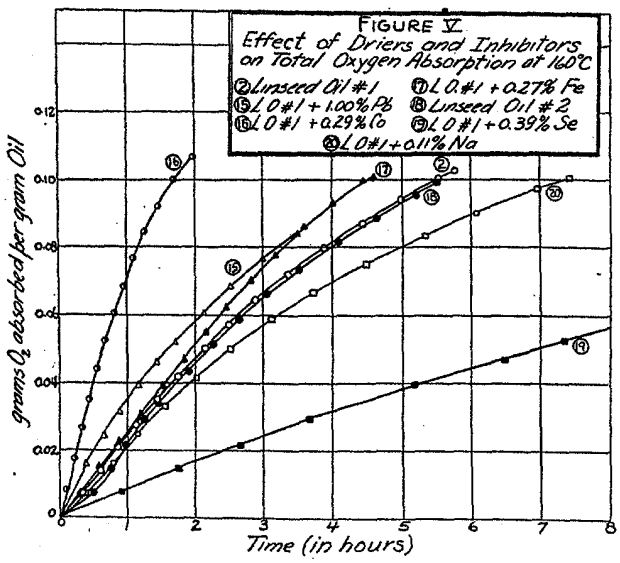
Effect of Complexity of Molecule

Runs 7 to 11, inclusive, together with 2 and 4, confirm more definitely the conclusion reached in the previous paper (2), that gelation ensues when the molecules have been built up to a sufficient size or degree of complexity, or perhaps polarity.

The methyl ester absorbed 30 per cent more oxygen, without gelling, than was required to gel the glycerol ester

(oil). The pentaerythritol ester, which has four fatty acid chains attached to a central carbon atom, gelled in the shortest time and absorbed only 29 per cent as much oxygen as the oil.

The glycol ester seems out of line, but was somewhat bodied during its preparation. Oils can be gelled by heat-bodying entirely in inert gas or *in vacuo*. The oils previously heat-bodied 3 and 6 hours, respectively, were well along toward gelation and required much less oxygen and shorter periods of time to complete the gelation. In general, as the complexity of the molecule increases, the rate of oxygen absorption decreases and less oxygen is required for gelation.



The rate of absorption of oxygen by the methyl ester was much greater than that of the glycerol ester (oil), but it did not gel after absorbing 30 per cent more oxygen. At the same time the methyl ester absorbed oxygen faster than the free fatty acids, although both methyl ester and fatty acids are represented by a single 19- and 18-carbon chain, respectively. Obviously, then, since the rate of oxygen absorption for fatty acids falls between that of methyl ester and oil, the unprotected carboxyl group permits association between two acid chains.

Effect of Degree of Unsaturation

The linolenic and α-eleostearic triglycerides are isomers which differ simply in the position and arrangement of the double bonds. If gelation were purely a matter of oxygen absorption, these molecules would absorb the same weight of oxygen before gelling. The great difference observed indicates that gelation is not simply a matter of oxidation, but that association or polymerization reactions are going on coincident with the oxidation reactions. It should be noted, however, that the velocity of the association reaction may be, and probably is, greater for oxidized than for unoxidized molecules. The two types of reactions are therefore interdependent.

Heating the oil in an inert gas leads to a thickening and final gelation which seems to be largely a matter of association of the molecules. The resulting gel can be disassociated by solvents or oxidized by oxygen.

At room temperature the velocity of the association reaction is very slow, but at 160° C. it is rapid enough to exert an appreciable influence.

It is interesting that two linseed oils with appreciably different iodine numbers and linolenic triglyceride with considerably higher degree of unsaturation all absorbed nearly the same weight of oxygen up to the gel point. This indicates that gelation does not correspond to complete oxidation but that it occurs when a certain size and degree of complexity or polarity of the molecules are reached. Since all three of these substances are glycerides, they should require approximately the same oxygen absorption to reach this condition, although the residual double bonds would be expected to have some positive gelling influence. As shown by Table II, the linolenic triglyceride gel contains, as expected, a little less oxygen than those from the oils, but in general the oxygen required to gel the glycerides is substantially the same. Table I shows that for seven different runs the oxygen absorption is nearly the same—a little over 10 per cent. The other figures which depart widely from 10 per cent would be expected on the basis of the composition involved.

Effect of Driers

The mechanism of the action of metallic driers is still subject to question. In line with the discussion in the previous section, it may well be asked whether driers accelerate the oxidation or association type of reaction.

In the presence of 0.29 per cent cobalt resinate, linseed oil was oxidized at 160° C. at a much greater rate and gelled in 2 hours as against 5 hours and 44 minutes for the oil alone. The oxygen absorbed was a little greater than when no drier was present. Cobalt therefore seems to favor and accelerate the oxidation type of reaction and is accordingly an oxidation catalyst.

In runs 15, 16, and 17 the weights of metal present are in the ratio of their atomic weights.

Lead resinate increases the rate of oxygen absorption and decreases the time required for gelation. The percentage of oxygen absorbed is, however, 18.5 per cent less than in the case of oil alone. Lead, therefore, also facilitates the association reaction.

Iron hastens the gelation by a little over an hour without affecting the percentage of oxygen absorbed.

The characteristics exhibited by the various driers at 160° C. should be magnified at higher or lower temperatures. Thus it would be expected that at 293° C., at which temperature much heat-bodying is done, the effect of lead in promoting the association type of reaction would be more strongly accentuated, whereas at room temperature any small associating tendency of the oil would be minimized by the strongly oxidizing tendency of cobalt.

Effect of Inhibitors

In previous work the writers had found that the presence of sodium oleate accelerated oxidation at 30° C. The contrary effect observed at 160° C. probably indicates that at this higher temperature the sodium oleate was dehydrated and rendered insoluble, thus changing the surface tension at the bubble interface and therefore the rate of oxygen absorption. It was observed that in this run the oil contained an insoluble suspended material. The oxygen absorbed up to gelation is nearly the same as for oil alone, but the rate is slower.

The fact that the oil retained only a slightly smaller fraction of the total oxygen absorbed and gave off practically the same amount of volatile products (also with the same ratio of carbon to hydrogen), as shown by Tables II and III, indicates that the sodium oleate serves merely to retard oxidation and unlike driers has no specific effect.

Acknowledgment

The writers wish to acknowledge the help of R. D. Jones and Francis Scofield in securing the data for Table III, and also the kindness of the Archer-Daniels-Midland and Wm. O. Goodrich companies for permission to publish these results.

Literature Cited

(1) Eibner, "Das Oeltrocken," Berlin, 1931.
(2) Long and Chataway, IND. ENG. CHEM., 23, 53 (1931).
(3) Long, Kittelberger, Scott, and Egge, *Ibid.*, 21, 950 (1929).
(4) Morrell and Marks, *J. Oil Colour Chem. Assocn.*, 12, 183 (1929).

Viscosity Increase and Gelation in Phenolic Resin Varnish Cooking[1]

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THE changes that occur in the physical properties of China wood oil when it is heated alone or with various resins are of great importance in varnish making. However, published numerical data on which to base the choice of proper temperatures and times for securing desired results have been rather meager.

It is common practice to determine the rates of gelation of different lots of China wood oil by the Brown or Worstall tests (*3*), after which the variations in treatment which will probably be necessary are found by experience, final determination of the end point being made by drip, string, or pill formation of a sample withdrawn during the heating.

The advent of synthetic resins has brought many surprises to the varnish maker because of the suggested departures from old practices during cooking. Therefore, methods of determining by experiment the optimum conditions of treatment of tung oil with natural and synthetic resins are desirable.

For the purpose of showing these effects on the oil bodying, the following two methods were developed in separate laboratories and are presented here, together with discussion of the two sets of data:

(1) A development of the Brown test (*3*), which gives comparative numerical values to the restraining or accelerating effects of the resin on the final gelation of tung oil. Variations produced at various temperatures and concentrations are shown.

(2) Use of the DeVilbiss viscometer (*2*) for recording the increase in viscosity of tung oil with natural and synthetic resins during heating at a constant temperature by placing the viscometer in the kettle during cooking. The numerical data were plotted for comparison and later gas check tests (*4*) were made upon the varnishes at different stages in the cooking.

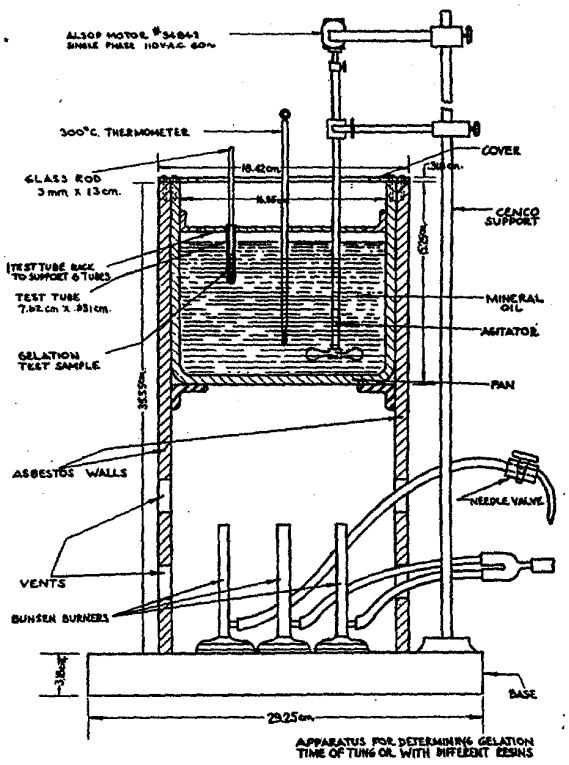
Gelation Tests

APPARATUS—The apparatus is a modification of that commonly used for the Brown test. The following changes are made: A bath of mineral oil is used in place of cottonseed or soy-bean oil, the total volume of mineral oil is increased, the bath is fitted with a stirrer, and the unit is insulated with asbestos. The size of the test tube is reduced from 15 cm. × 16 mm. to 7.62 cm. × 9.51 mm., and the sample from a volume of 5 cc. to 1.5 grams. These changes are made in order to obtain a more uniform temperature of the oil bath and sample. With this modified apparatus it is easily possible to attain the desired temperature quickly and to hold this temperature constant within ±1° C.

PREPARATION OF SAMPLE—A sample of approximately 100 grams is prepared by weighing in a 250-cc. Erlenmeyer flask the resin and the tung oil; it is heated to 180° C. in 15 minutes and then cooled to room temperature and stoppered. The temperature and time are arbitrarily chosen as being sufficient to effect solution of high-melting resins in the tung oil.

[1] Received April 9, 1931.

METHOD OF TESTING—The oil bath is heated to the required temperature, which is then adjusted and held constant by means of a pilot burner fitted with a needle valve. The test tube containing 1.5 grams of the sample, with a glass rod inserted in the tube, is then immersed in the oil bath and allowed to remain there until the tung oil forms a gel strong enough for the test tube to be lifted out of the apparatus with the glass rod. The time required is determined by raising the glass rod at short intervals after thickening has commenced. At 200° C. there is a gradual thickening, for about 15 minutes, before the gel structure is strong enough to support the test tube, but at 225° C. and above the gel structure forms rapidly. A thin film of oxidized oil forms on the surface of the oil and this can be easily broken by a slight movement of the glass rod.



APPARATUS FOR DETERMINING GELATION TIME OF TUNG OIL WITH DIFFERENT RESINS

DATA—The curves were plotted from the average of two or more determinations made with each sample. The results agreed within 1 minute at temperatures to 250° C., and within 30 seconds or less at higher temperatures. Table I