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Mechanism of the Oxidation of Drying Oils

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The steps encountered in the oxidation of drying oils by air are peroxide formation, decomposition of peroxides, polymerization, and degradative oxidation. An induction period occurs prior to uptake of oxygen and this has been shown to be due to the presence of inhibitors. Recent work has shown the presence of hydroperoxides, particularly when oxidation is conducted under mild conditions, but there is also considerable evidence for the presence of cyclic peroxides. Peroxides apparently decompose by dehydration and by reduction. It seems possible that peroxide decomposition and polymerization are intimately associated. Polymerization inevitably occurs subsequent to oxidation but it has not been established clearly whether the polymer chains are formed through either ether or peroxide linkages or through carbon-to-carbon bonds. Considerable evidence for the latter structure has been accumulated.

DURING recent years a careful study has been made of the oxidation of animal and vegetable oils; still, the statement of Milas (*24*) made in 1932, " . . . the mechanism of the oxidation of unsaturated oils is still relatively obscure owing to the complexity of the oxidation products and the uncertainty of their structure," remains an accurate estimate of our present knowledge. Progress has been apparent in the intervening 15 years and much valuable work has been done by university, government, and industrial laboratories both here and abroad. In spite of all this activity, it must be admitted that an entirely satisfactory explanation of all the phenomena observed in the oxidation of drying oils has not been achieved.

This failure often has been attributed to the complexity of the drying oils themselves, and it is only in recent years that an accurate analysis of the composition of linseed oil was possible. However, our knowledge of the composition of the common drying oils is now on a quantitative basis, and the accuracy of the methods of analysis has been greatly improved. A great deal of progress has been made in the separation of the pure fatty acids. Methyl esters of these acids serve as useful methods of interpreting the behavior of the drying oils on oxidation. The study of the behavior of mixtures of esters does not always parallel the behavior of the pure ester since the oxidation of oleate esters is greatly increased (*18*) in the presence of a small amount of a linoleic acid ester. Rate of oxidation is increased, however, with the unsaturation (*33*), and when mixtures of trienoic and dienoic esters (*15*) are present, the trienoic esters are oxidized first. Also, when dienoic and oleic esters are present, the dienoic esters are oxidized first.

In one respect the methyl esters are not complete models for the drying oils. They do not dry and thus remain susceptible to oxidation to a greater degree than do the glycerides. Thus, greater amounts of oxygen may be absorbed than will be absorbed by the corresponding glyceride (*33*). Such information may be applicable to the study of deterioration but is a further stage of oxidation than usually is encountered in the drying process.

The complexity of the products of oxidation of the drying oils is well known and is the principal reason for the difficulties en-

countered in studying the mechanism of oxidation. The reactions occurring are often consecutive and apparently in some instances are competitive. It has been found (*26*) that conditions can be controlled to favor oxidation rather than polymerization. In many oxidation reactions there seems to be a preliminary phase where oxidation alone occurs; subsequently polymerization takes place with little oxidation. Whether this behavior is more apparent than real remains to be established. One factor that may explain in part the lack of a satisfactory mechanism of the oxidation process is the divergent aims of groups of investigators. Much of the investigation of the oxidation process has been conducted with the purpose of preventing oxidation completely. Other workers are interested in completing the oxidation as quickly as possible and are primarily interested in accomplishing polymerization of the oils.

Methods of Research

It is becoming increasingly apparent that no one method of attack will reveal the whole mechanism of oxidation of the drying oils. Chemical methods of analysis in many cases are limited severely by the instability of the oxidized products. Also, the insolubility of the gels resulting from oxidation severely restricts such methods of attack. Physical methods offer promise of supplementing chemical analysis. Spectroscopic information is proving especially helpful in this direction, particularly the ultraviolet absorption spectra. The effect of the carbonyl group is recognized, but a complete quantitative measure of its presence in conjugated structure is not established yet. Infrared spectra of oxidized oils have been measured but further work with model substances will be required before the results will give more than speculative information on the structure of the oxidized oils. The temperature of oxidation (*37*), exposure to light, presence of driers, access to oxygen, film thickness, and other factors influence the course of oxidation. Volatile products which are evolved in the course of the oxidation, particularly water, may yield useful clues on the course of the oxidation. Information on the nature and amount of these products and of the stage of oxidation when they are evolved is still incomplete. The dielectric constant of blown oils (*26*) has been measured at various stages of oxidation. The Grignard reagent has been employed recently (*39*) and gives promise in establishing the function of the oxygen in the oxidized oils.

Oxidation Process

The stages in the oxidation of drying oils by air may be broken down into inhibition, peroxide formation, peroxide decomposition, and polymerization. In Figure 1, the changes encountered are plotted to illustrate the behavior at each stage of the oxidation. The scale is purely arbitrary and may vary greatly according to conditions or materials employed. In the inhibition step, the end of the phase is quite apparent, and at early stages of the oxidation, peroxides are the only products formed. Beyond this point, separation of phases of the various steps is largely artificial. Peroxidation does not cease necessarily when rearrangement begins. Polymerization may well begin with the decomposition of peroxides. These steps, however, do represent a period in the oxidation when a given process appears to predominate.

The induction period ends when oxygen absorption begins, and the peroxidation step may be considered to continue to the maximum peroxide value. Peroxides subsequently largely disappear although oxygen may continue to add to the oil. The polymerization phase is marked by the rapid increase in viscosity. Oxidation continues long after the polymerization phase is apparently complete.

INHIBITION

However, such effects may be caused by physical conditions which limit the rate of oxygen uptake. The induction period now is considered generally to be caused by the presence of inhibitors. It has been found (*18*) that synthetic unsaturated esters do not show an induction period. Also, the induction period can be extended by the addition of inhibitors; the inhibition period is prolonged with each successive increment of antioxidant. The induction period is shorter as the temperature is increased and is often negligible at 100° C. in the presence of the amounts of inhibitors naturally present in drying oils.

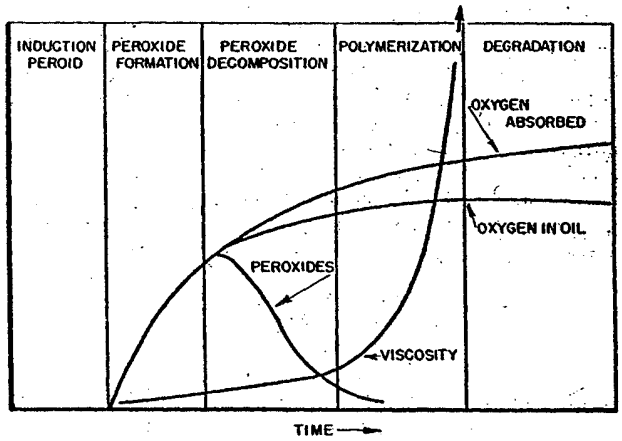


Figure 1

Materials which can be oxidized to quinones are among the most effective antioxidants although many other phenols and aromatic amines show some antioxidant effect (*11*, *27*). Of the dihydric phenols, catechol and hydroquinone have pronounced antioxidant power whereas resorcin is less effective. The ethers or esters of hydroquinone are much less active inhibitors. Aminophenols and substituted aminophenols are often active antioxidants, as are phenylenediamines and other aromatic diamines. Of the more highly substituted phenols, pyrogallol and gallic acid and its esters have been found to possess pronounced antioxidant power. α-Naphthol is more effective than β-naphthol (*27*).

Many of the natural oils exhibit a definite induction period and all of the nonlipid components of the oil have been suspected of being responsible for the effect. It has been established that the inhibition is due to the presence of the tocopherols. On removal of these sterols, the oils dry more rapidly, and by addition of tocopherol concentrates obtained by molecular distillation, the stability of oils to oxidation is increased.

The effectiveness of antioxidants often is found to be increased by the presence of acids. Phosphoric acid has been found to be especially effective although citric and ascorbic acid also exhibit synergistic properties. It has been found that the amount of phosphoric acid which is soluble in an oil (0.0002%) is not effective (*8*) in promoting the antioxidant action. Oxalic acid is active as an antioxidant in addition to any synergistic effect (*23*).

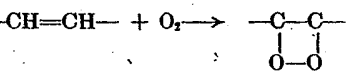
In vinyl polymerization it is found that a small amount of antioxidant can prevent the polymerization of a large amount of vinyl compound because the chains are long. In the case of the oxidation of drying oils, the length of the chains has been estimated as rather short (*32*). If oxidation is autocatalytic, however, a small amount of antioxidant should be effective.

FORMATION OF PEROXIDES

There is general agreement that oxygen first adds to drying oils with the formation of peroxides; their structure and position in the oil molecule has not been entirely clarified. The method of Wheeler for determination of peroxides usually is employed. Determination of peroxides by oxidation of the ferrous ion has been employed often to determine peroxides from the hydrocarbons, but this apparently gives unexpectedly high values when

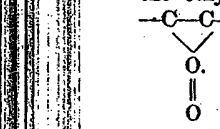
applied to fatty acid peroxides (*4*). There is indication that peroxides of varying stability occur, since, on heating, the peroxide value drops to a constant value which decreases but slowly on further heating (*29*).

Types of Peroxides. Until recently, the cyclic peroxide formed by the addition of a molecule of oxygen to the double bond has been generally accepted. This view has been reinforced by the almost generally observed drop of the iodine value corresponding to the disappearance of one double bond with the addition of one molecule of oxygen.



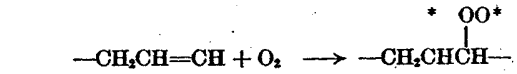
The rupture of the carbon chain at the double bond by decomposition of the peroxides also is indicative of addition of oxygen at the double bond. This structure, however, has been considered (*12*) sterically so unstable as to eliminate any but momentary occurrence.

A modification of this structure may be considered also—the ethylene oxide type structure proposed by Paquot (*12*)

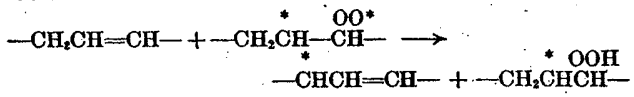


the four-membered ring peroxide. In addition, it suggests the possibility of rupture of the O=O bond to yield an ethylene oxide derivative. The high content of esters (*9, 28*) formed in oxidized oils and particularly oxidized unsaturated acids suggests such a structure, as does the isolation (*28*) of a dihydroxystearic acid by hydrolysis.

The hydroperoxide theory proposed by Farmer (*12*) has many points in its favor. In the case of the drying oils, Farmer (*12*) believes the initial addition of oxygen is at the double bond. Addition to the α-methylenic carbon atom is regarded as improbable because of the high energy of activation required to break the C—H bond. The oxygen is believed to add to the double bond to form a biradical:



This combines with another unsaturated group to yield two radicals:



These radicals continue the chain reaction and lead to the formation of α-methylenic hydroperoxides. Thus, a small amount of addition at the double bond will lead to the formation of a large amount of hydroperoxide if the chains are long.

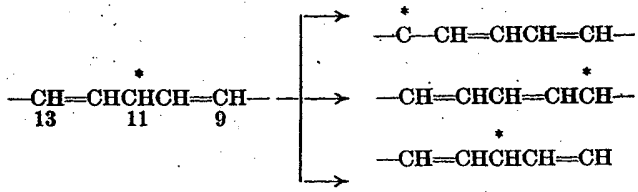
One piece of evidence that does not fit smoothly into the hydroperoxide structure is the drop in iodine value on oxidation; this would not be expected if the peroxide added at the α-methylene carbon atom. This decrease in iodine value may in part be explained by the formation of conjugated structures which are known to add less than the theoretical amount of iodine. The other questionable point is the failure to find (*41*) active hydrogen in air-dried films. The expected amount of active hydrogen, however, has been found (*4*) in blown ethyl linoleate. Investigation of this field is active and further work undoubtedly will be done to clarify these points.

Since the behavior of the oleate esters, the unconjugated polyene esters, and the conjugated unsaturated esters each exhibit their own peculiar behavior pattern on oxidation, they will be considered separately.

Oleate Esters. Relatively pure hydroperoxides have been obtained only from methyl oleate. A methyl oleate hydroperoxide apparently of over 90% content has been isolated; it consists of two oleate hydroperoxides differing in the position of the hydroperoxide group. The hydroperoxide has been concentrated by molecular distillation from methyl oleate slightly oxidized at moderate temperatures. The further separation from unoxidized methyl oleate is accomplished by chromatographic separation (*14*) or by low temperature crystallization from acetone (*35*). This hydroperoxide apparently is quite stable and failed to decompose α-tocopherol after several weeks' exposure. It has an iodine value corresponding to one double bond. On oxidation with potassium permanganate, azelaic and suberic acid were formed as were caprylic and pelargonic acids (*35*). These acids were formed apparently in approximately equivalent amounts, indicating that the hydroperoxide groups are at the 8 and 11 positions, the methylenic groups alpha to the double bond. It has been found that when methyl oleate is oxidized at 120° C., no indication was found of the presence of the 8 hydroperoxide ester (*2*) although the same investigators found evidence of its presence in sunlight at 20° C.

Since methyl oleate hydroperoxide exhibits an iodine value and a conjugated structure is not present, the iodine value of methyl oleate should give an index to the extent of hydroperoxide formation. It is found that while the iodine value does not decrease to the extent expected if the peroxide group added to the double bond there is a considerable drop in iodine value on peroxidation which is apparently 70% of the expected drop (*2*).

Unconjugated Polyene Acid Esters. Considerable study has been made recently of the peroxidation of methyl linoleate. However, hydroperoxides have not been isolated. It has been found that the ultraviolet absorption at 2325 Å. increased with the absorption of oxygen. At moderate temperatures all of the absorbed oxygen is present in the form of peroxides and 70% of these peroxides are conjugated (*22*). This is in agreement with the mechanism proposed for the formation of the hydroperoxides (*6, 13*). The 11 carbon atom becomes the center of a radical formed in the oxidation process. This may rearrange to radicals having their center at the 9 or 13 carbon. The hydroperoxide then can add at either the 9, 11, or 13 carbon atom; the probability is assumed to be equal for each position. Since the 9 and 13 hydroperoxides are conjugated a value of two thirds of the peroxides containing a conjugated structure is in agreement with these assumptions. However, by hydrogenation of methyl linoleate hydroperoxide, 9 and 13 hydroxystearic acid were identified (*3*) but no proof of the presence of the 11 hydroxy compound could be obtained.



It has been shown that the diene conjugation (*17*) increases parallel to the rise of the peroxide value, but a sharp drop in diene conjugation occurs just before the decrease in peroxide content which occurs as oxidation proceeds. This is in contradiction to the observation (*17*) that the diene content is not changed when peroxides are decomposed by heating in vacuum.

The methyl esters of soybean acids on oxidation at five temperatures from 15° to 100° C. show (*29*) that during the early stages of oxidation the iodine value drop is less than the expected value for the disappearance of one double bond at low temperatures. As the temperature is raised, the iodine value approaches the expected value and coincides at 100° C. The iodine number drop exceeds the peroxide value as the oxidation is carried further. This condition occurs at progressively lower peroxide values as the temperature is raised. In this connection, it has

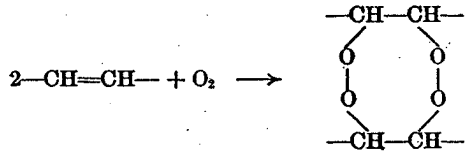
been found (*22*) that at low stages of oxidation, the conjugation is measured by the peroxide value at several oxidation temperatures ranging from 40° to 100° C. This evidence points to a cyclic peroxide possessing a conjugated structure. The ultraviolet spectrum of methyl oleate hydroperoxide (*35*) shows no evidence of diene structure.

The behavior of methyl linolenate parallels that of methyl linoleate. Diene conjugation increases with peroxide content. Triene conjugation also is found but the amounts are rather smaller than the diene content, usually less than 20% of the diene content.

The kinetics (*4*) of the oxidation of ethyl linoleate has been studied recently. The oxidation is autocatalytic since the rate of oxygen pickup is proportional to the peroxide content. When benzoyl peroxide is added to ethyl linoleate, the rate of oxygen uptake is proportional to the square root of the peroxide content. Since the radicals liberated by benzoyl peroxide are well recognized, examination of products from benzoyl peroxide promoted oxidation might afford information on the mechanism of the oxidation. The heats of oxidation of ethyl linoleate and linolenate have been measured (*5*). The value of each ester was substantially the same (*5*), 52 kg-cal. per mole of peroxide. A value of about 66 kg-cal. was estimated as the bond energy of the O—O bond in the hydroperoxide, an estimate considerably greater than earlier values.

Conjugated Esters. In the case of the conjugated esters, the evidence seems clear that the addition is at the double bond. There is no evidence of active hydrogen during the early stages of the oxidation (*39*). Although there is a notable increase in conjugation on oxidation of unconjugated systems, there is every evidence of disappearance of conjugation on oxidizing conjugated systems. It has been suggested that the addition of oxygen in conjugated systems is 1–4. However, there is evidence that conjugation is still present in methyl oleostearate after the addition of 1 mole of oxygen; this is suggestive of 1–2 addition. The formation of polymeric peroxides has been suggested frequently as occurring in conjugated systems. Evidence to this effect is shown by the lower content of polymers obtained in dilute solution oxidation. However, the same effect would be expected whatever the mechanism of the polymerization reaction.

The reaction for the formation of cyclic peroxides is often written as occurring in one step. The presence of two molecules of oxygen and two fatty acid segments in an active state at the same time is too remote for serious consideration.



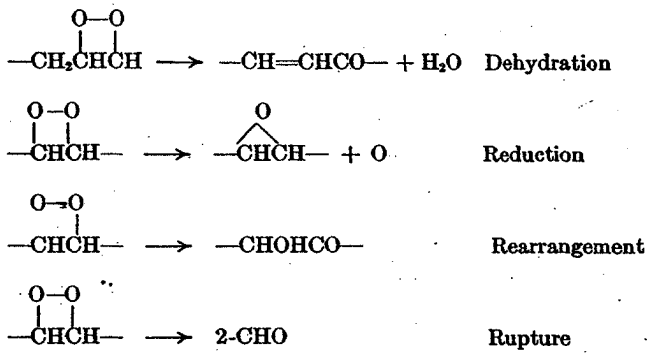
If the reaction is considered to occur in steps, it is surprising that two links between segments are required. One peroxide link between chains would be sufficient to form a cross link and it might be expected that the second oxygen molecule would add at another double bond in the molecule or to an unoxidized molecule.

DECOMPOSITION OF PEROXIDES

In the oxidation of drying oils the peroxide value accounts for practically all the oxygen added during early stages of oxidation. At low temperatures this may be the case until 0.5 mole of oxygen has been added (*29*). At higher temperatures and under more severe conditions other oxygenated products besides peroxides are formed earlier in the oxidation. It is apparent that the oxygen first adds as peroxide and other oxygen compounds are their decomposition products. In addition to temperature, light driers, acids, and bases accelerate the decomposition of peroxides.

In the case of peroxidized petroleum oils (*41*), three modes of decomposition are recognized; dehydration with the liberation of a molecule of water; reduction with the liberation of a molecule of active oxygen; or by further oxidation with the splitting of at least one C—C bond. Aldehydes, ketones, and acids are among the principal products formed. The same type of reactions are observed in the case of the drying oils and polymerization reactions induced by oxidation also occur.

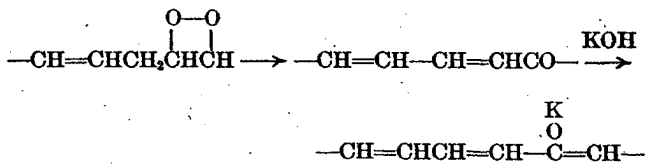
Type reactions by which peroxides decompose may be indicated as follows:



These reactions are expressed in terms of the cyclic peroxide structure, which has been used generally to explain the products formed. Each of these reactions will be considered separately.

Dehydration. Water is evolved in the drying of oil films; as much as 6% has been measured (*16*). It is well known that high humidity retards the drying of oil films. It apparently does not greatly affect the pickup of oxygen, hence dehydration may be involved in the polymerization step. The increase in conjugation found in oxidized oils has been ascribed (*20, 25*) to the formation of unsaturation by the dehydration step. It has been found that methyl linoleate evolves 1 molecule of water on exposure to air in thin films and methyl linolenate evolves between 1 and 2 moles per mole of ester (*39*). The glycerides evolve the same amount of water on drying (*40*). This water is evolved after considerable oxygen has been added to the esters.

Increase in triene conjugation when oxidized oils are treated with alkali is often quite large (*19, 20, 22*); this suggests the enolization of carbonyl groups adjacent to a double bond. Such a structure would be anticipated from the dehydration of a peroxide:



Reduction of Peroxides. The evolution of active forms of oxygen has been postulated and evidence (*34*) has been presented for the evolution of hydrogen from drying oils. It is to be expected that active oxygen if evolved would be absorbed readily by the drying oils. The increase in ester number encountered in oxidized oils and the isolation of dihydroxystearic acid (*9*) are suggestive of this type of decomposition of peroxides.

Rearrangement of Peroxides. This reaction has been suggested to explain the disappearance of peroxides. However, there is little quantitative evidence in its favor. If peroxides in drying oils decomposed largely in this manner, a much higher content of hydroxyl groups would be found. Oxidized oils often contain less than 2% hydroxyl (*28*).

Chain Rupture. The final reaction suggested for the decomposition of peroxide results in breaking of the carbon chain. This undoubtedly occurs in the oxidation of drying oils. However,

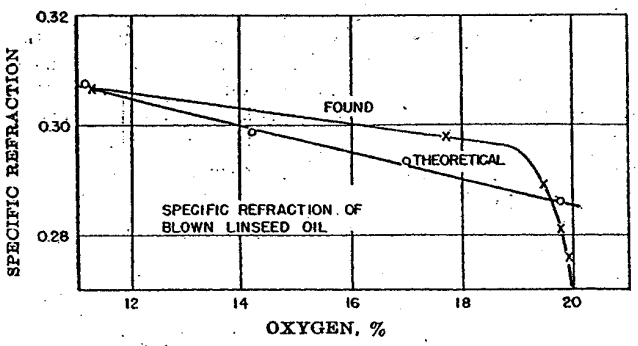


Figure 2

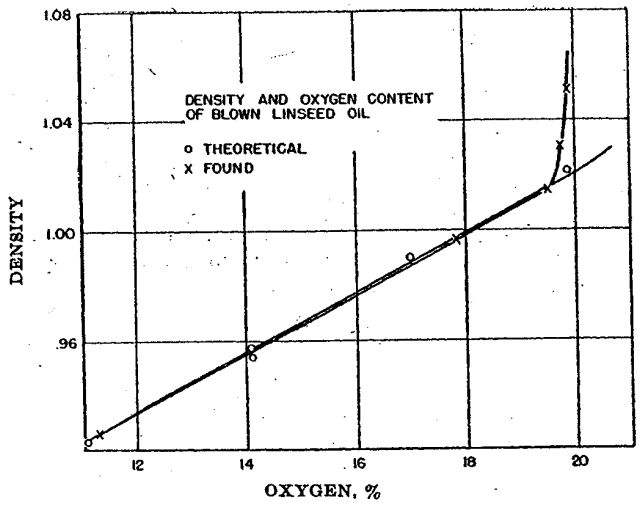


Figure 3

in the drying of films it does not occur to any great extent. It may be an important factor in the eventual destruction of the films. Dicarbonyl groups also have been found present in drying oils (*31*). Their content in oxidized oil is not large, however. They could be formed by the dehydration of a peroxide adjacent to a carbonyl group.

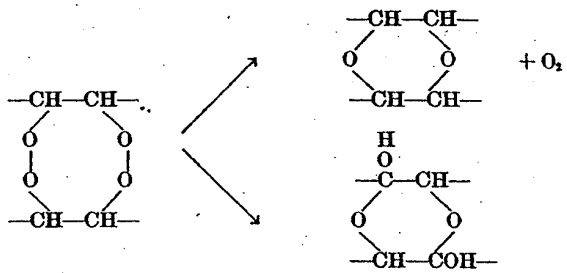
Change in hydroxyl content and iodine value has been measured when peroxides are decomposed (*29*) by heating 190 hours at 55° C. The hydroxyl value did not change appreciably even with a decrease of 2000 in the peroxide value. The iodine value also showed no appreciable decrease. This indicates some other mechanism than rearrangement, and is not in agreement with the dehydration reaction unless the unsaturation formed is saturated by some attendant reaction, such as polymerization.

POLYMERIZATION OF DRYING OILS

The polymerization of oils induced by oxidation is now recognized as the process responsible for the drying of oil films. The concepts of high polymer chemistry have thrown considerable light on this process. The background of this interpretation was outlined by Bradley (*7*) in 1936. It was not recognized then that three fatty acid segments could combine in a single chain. In the case of heat bodied oils, the presence of such trimers is now well substantiated. In the case of the air dried materials, evidence for trimer formation exists in the observation of Elm (*28*) that glycol linoleate forms a gel while glycol linolenate dries to a hard film. This may be interpreted as an indication that linoleic acid shows a slight tendency to form trimers while the tendency is much greater in the case of linolenic acid. This is in agreement with the behavior of the esters of the two acids on heat bodying. However, in neither case is there quantitative evidence of the extent of dimer or trimer formation on oxidation. An analysis (*1*) of the polymer structure on polymerizing unsaturated glycerides has been developed. This analysis was developed to interpret the behavior of heat bodied oils but is equally applicable to oxygen induced polymerization.

Oxygen Linked Polymers. While the air dried oil films give clear evidence of a cross linked polymeric system, our knowledge of the bonds between the chains is still fragmentary and has been arrived at largely by inference and as yet no rigorous determination of structure has been made.

The view held for years and recently supported by Treibs (*39*, *40*), is that a dioxane link joins the fatty acid segments. This ring has been assumed to be formed by the rearrangement or decomposition of a perdioxane ring:



There are several serious objections to this mechanism. There has never been any explanation offered of why it does not operate in the case of oleic acid esters which show a negligible tendency to polymerize under usual conditions. The mechanism of such a reaction would be exceedingly complex to the point of being improbable. A peroxide formed at the double bond would have to combine with an unsaturated group on another fatty acid segment, the second mole of oxygen would then add and complete the ring. The reaction often is written as comprising a single step. The probability of two molecules of oxygen and two unsaturated groups arriving at the required arrangement in space at the same time is too remote for serious consideration.

Other objections to this theory include the fact that the presence of the dioxane ring has never been established in oxidized oils (*10*). Also the only evidences for the presence of the necessary amount of ether oxygen are indirect and inconclusive.

Carbon-Carbon Linked Polymers. A more reasonable bond between segments is by a carbon-carbon linkage. This might result from an aldol condensation between a carbonyl group in one chain and a methylene group in a second chain. This type of bond has been suggested (*20*) as the cause of chromophores developed in oxidized oils. Changes in physical and chemical

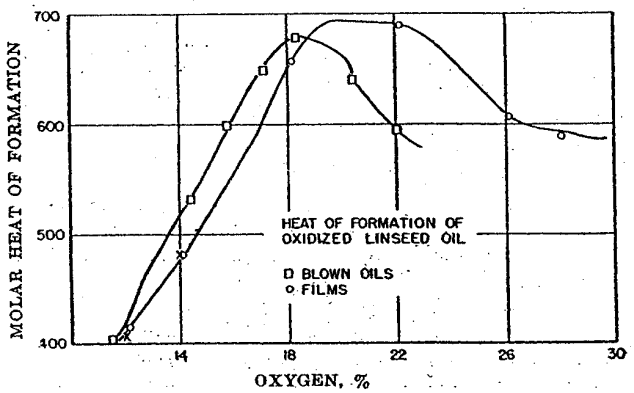


Figure 4

properties accompanying the polymerization step indicate that aldol formation is not the principal step responsible for the polymerization of drying oils.

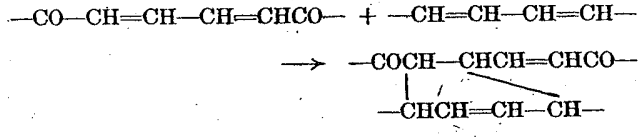
It has been proposed (*30*) that two of the unsaturated groups in adjacent fatty acid segments combine by vinyl polymerization. The pronounced changes in density, decrease in iodine value, and decrease in refractivity accompanying the drying of films with little change in oxygen content are indicative of such a mechanism. It was shown that linoleic esters show these changes to a more pronounced degree than do linolenic esters. This might be expected since two double bonds are sufficient to give air-drying properties. With linolenic acid the third double bond affords a site for further oxidation which partially masks the effect of the polymerization reaction.

To determine if blown oils show the same behavior as do films, linseed oil was blown at 80° C. and samples taken at intervals. Density and refractivity were determined, also the carbon and hydrogen content. The curves (Figures 2 and 3) show that the blown oils do indeed show the same behavior as the films on drying. It should be noted that the blown oils were carried only to the gel stage while films become hard. Therefore, the trend exhibited at the end of the blowing might well be expected to continue as drying is completed.

In an attempt to throw additional light on the mechanism of polymerization, the heat of formation of blown oils and oil films at various stages of oxidation was calculated from data in the literature (*21*, *36*). This work was supplemented by determination of the heat of combustion of samples of linseed oil blown under conditions stated above. The results were in general comparable for all the data obtained (Figure 4). The heat of formation increased up to the point where about two molecules of oxygen were added by the glyceride. Beyond this point, the heat of formation decreases.

No definite conclusions have been drawn. It was felt that since volatile products, including carbon dioxide, were lost from the system, the analysis of the process was not accurate until the effect of these materials was included in an analysis of the whole system. However, all values were reduced to an oxidized triglyceride and should be roughly comparable. The polymerization reaction would be expected to give a greater heat of formation and such a result was expected. A possible explanation is the formation of unsaturated groups in the oxidation process. It has been suggested above that the liberation of water from the oxidized oils may lead to unsaturation. Such groups would give a lower heat of formation.

It has been shown (*30*) that the loss of unsaturation, increase in density, and drop in molecular refractivity accompanying the drying of unsaturated ester films might equally well be interpreted as reflecting bonding between the chains by a Diels reaction.



The weight of evidence accumulated on the behavior of oxidized oils now seems to favor this view above the possibility of vinyl polymerization. Spectroscopic evidence points to the presence of carbonyl groups adjacent to carbon-carbon double bonds, and possibly such carbon-carbon double bonds with carbonyl groups alpha to both carbon atoms and also a considerable content of conjugated dienes. Such systems might readily be expected to enter into a Diels reaction. The changes in density and specific refraction with little change in oxygen content are in agreement with this type of reaction and the decrease in iodine value is more nearly in agreement with this type of reaction than is vinyl polymerization.

The results of the study of the decomposition of peroxides cited above suggest that the dehydration and polymerization steps may be closely associated and occur in immediate sequence. Such a mechanism would explain the failure to observe a drop in iodine value on decomposition of the peroxides (*29*), the double bond formed in each chain becoming saturated in the formation of the six-membered ring. The evolution of water, associated with the drying of oils, is suggestive of such a reaction.

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