TABLE VII

Accelerated Weathering

	450 hrs.	575 hrs.	775 hrs.
Urethane oil A	ok	ok	ok
Urethane oil B	ok	ok	ok
Alkyd	ok	Slt. check whitening	Failed
Epoxy ester	Slt. check low gloss	Severe whitening	Failed
Spar varnish	Checking	Failed	....

in several areas in the coatings industry. For example, exterior durability together with water resistance has led to their use in spar varnishes. Speed of dry and wear resistance have suggested their evaluation and use in both clear and pigmented floor finishes. Similarly impact resistance, adhesion, solvent holdout, and salt spray-resistance have brought about the use of the urethanes in some metal primer applications. As new resin-formulating data become available, and, as more is learned about paint formulation techniques with these resins, it is likely that oil-modified urethanes will attain a significant use in the coatings industry.

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Autoxidation and Autoxidative Polymerization

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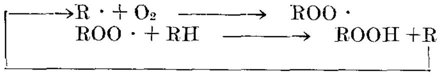
IN THE OXIDATION of drying oils, as in the preparation of blown oils and the formation of films, the reactions that lead to hydroperoxide formation are usually referred to as autoxidation. The subsequent reactions of the peroxides that give polymers are termed autoxidative polymerization. The over-all process is extremely complex because both reactions have many ramifications and go on simultaneously.

Autoxidation

Primary Reaction. Autoxidation has been studied most extensively with methyl oleate and linoleate at low temperature. Unsaturated hydroperoxides, the primary reaction products of these esters, are formed in an autocatalytic chain reaction in accordance with the following mechanism:



$$\begin{array}{lcl} R\cdot + O_2 & \longrightarrow & ROO\cdot \\ ROO\cdot + RH & \longrightarrow & ROOH + R\cdot \end{array} \qquad (2,6)$$

Triunsaturated hydroperoxides have been isolated in yields of about 60% from autoxidized methyl linolenate (27) and likewise are the primary products of the autoxidation of this ester.

Although the mechanism of the primary reaction is well defined, there are certain facets of the autoxidation of nonconjugated fatty acid esters that need further clarification, particularly the mode of initial attack by molecular oxygen or the initiation of the chain reaction, and the formation of products other than the simple hydroperoxides.

Chain Initiation. The reaction involved in the initiation of the chain reaction is difficult to analyze because theoretically only a single molecule need be involved. This eliminates product analysis as a means of examining this stage of the reaction. At the time of the development of the hydroperoxide theory of autoxidation (6, 12) it was postulated that the reaction involved an initial attack by molecular oxygen. There was considerable speculation whether the site of the initial attack was at the double bond or at the methylenic carbon atom adjacent to the double bond.

The theory of initiation by direct oxidative attack was based primarily on the observation that, on extrapolation of the plot of the rate of autoxidation *vs.* the extent of the reaction, the curve did not pass through the origin but gave a positive intercept of the rate of oxidation axis (6), indicating that a minor but significant reaction took place prior to the primary reaction. This was presumed to be the initiation reaction. However detailed studies by Bateman *et al.* (3, 4) showed that the relationship between the rate and extent of autoxidation deviated from linearity in the early stages of autoxidation and, in fact, intersected the origin; hence the extrapolation upon which this hypothesis was based was invalidated. These investigators demonstrated further that the deviation of this relationship from the linear in the initial stage of autoxidation resulted from a difference in the mode of peroxide decomposition at this stage of the reaction. At low peroxide concentrations the reaction was first order whereas at high peroxide concentrations it was bimolecular because of association of the hydroperoxides. This hypothesis was supported by infrared spectral data which showed that hydroperoxides became associated very easily. It was hypothesized that initiation of the chain reaction took place essentially as a result of peroxide decomposition. Formation of the initial hydroperoxides was not explained, but it was considered to be of such a small order as to be insignificant.

Uri (39) advanced the hypothesis that the initially formed hydroperoxides, as well as the first order decomposition of hydroperoxides leading to the initiation of the chain reaction, occurred as a result of metal catalysis. This view was based on extensive kinetic studies as well as the observation that even the purest fatty acid ester preparations contained traces of metal catalysts.

Formation of Nonhydroperoxidic Material During Autoxidation. There is some evidence that nonhydroperoxidic substances are formed concurrently with the primary reaction in the autoxidation of nonconjugated fatty acid esters. This has been demonstrated in the autoxidation of methyl oleate at various stages in the reaction from a comparison of the analysis for total peroxide, as measured by KI reduction, and that for hydroperoxides, as determined by polarography (19, 42) and specific chemical tests (16).

The autoxidation of methyl linoleate is generally assumed to give virtually quantitative yields of hydroperoxides, but infrared and ultraviolet spectral analyses indicate that the major products of the reaction (methyl *cis*-9, *trans*-11,13-hydroperoxy linoleate, and methyl *cis*-12, *trans*-10, 9-hydroperoxy linoleate) consist of only about 90% of the products of the reaction (8, 29, 35). Efforts to detect the 11-hydroperoxy isomer, which could account for the remaining 10%, have not been successful (35). Lundberg and Chipault (21) observed that not all the oxygen absorbed in the autoxidation of methyl linoleate could be accounted for as hydroperoxide. The proportion of oxygen containing nonhydroperoxidic substances increased with increasing temperature. By kinetic studies on the oxidation of methyl linoleate hydroperoxide, Privett and Nickell (32) obtained evidence that these products originated from secondary oxidation of the hydroperoxides.

Thus evidence appears to be accumulating that nonhydroperoxidic substances are formed in minor amounts even in the early stages of the autoxidation of nonconjugated fatty acid esters. However there is some question whether these are formed as a result of secondary oxidation of the hydroperoxides or form direct oxidative attack.

Autoxidative Polymerization

General Considerations

Greater progress has been made on the technological phases of oxidative polymerization of drying oils than on the chemistry of the reaction. However the physical and chemical changes that occur during the bodying of drying oils have been studied extensively and have yielded considerable information on the characteristics of the reaction. It is evident that the process occurs in two distinct stages. The first stage is known as the induction period. There is little change in the physical and chemical properties during this period, and its duration is related to the temperature of the reaction (17). In the preparation of blown oils this stage of the reaction is usually hastened by the use of a higher temperature than that of the main reaction. The existence of an induction period is believed to be caused mainly by the presence of antioxygenic compounds. It also may be considered as a period during which precursors for the reaction are accumulated.

After the induction period a rapid change in the chemical and physical properties heralds the onset of polymerization. The most apparent physical change is an increase in viscosity. Pronounced changes also occur in the refractive index, density, and ultraviolet and infrared spectral properties. These result from the formation of various specific chemical structures, such as peroxides, hydroxyl, carbonyl, isomerized double bonds, and polymers.

Influence of Various Factors on the Reaction

Because oxidative polymerization is the cumulative effect of a number of reactions, conditions which affect any one of these more than another, even in a quantitative sense, will alter the course of the reaction and the composition of the end-product.

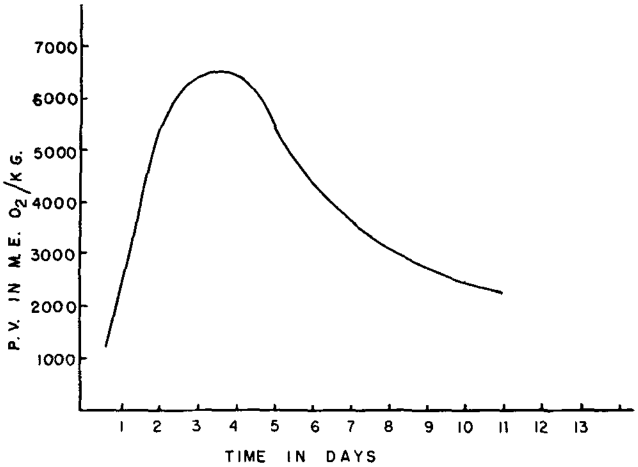


FIG. 1. The autoxidation of methyl linolenate in a thin film at room temperature.

Temperature. On the basis of studies on the rate of change in viscosity, Hess and O'Hare (17) demonstrated three temperature ranges in which marked differences in the course of the reaction could be expected. These were below 84°C., 84 to 130°C., and above 130°C. Others have observed similar effects. During the blowing of oils the rate of oxypolymerization, if not the course of the reaction, is also affected by air-flow and agitation (18).

Fatty Acid Composition. Since the double bonds are the active site of oxypolymerization, fatty acids vary in their reactivity according to their degree of unsaturation. For example, the rate of oxidation of films of triolein, linolein, and linolenin was in the ratio of 1:120:330 (10).

Functionality. In addition to the unsaturation *per se*, the amount and form in which the fatty acids are combined greatly influences the characteristics of the final product. This is attributed to the functionality of the molecules which may be defined broadly as the ability to polymerize. Oleates do not form set films even at high levels of oxidation and thus are considered to have a functionability of zero. Trilinolein, trilinolenin, and the corresponding pentaerythritol and dipentaerythritol esters are given functionalities of 3, 3, 4 and 6, respectively. Monofunctional molecules can only form dimers; bifunctional molecules form only linear polymers whereas molecules with tri- and greater functionality can form cross-linked polymers. In order to form solid films some trifunctional molecules must be present. Furthermore it is evident that the properties of the final product, be it a film or a blown oil, will depend on the relative proportions of zero-, mono-, di-, and polyfunctional molecules.

At first thought it may seem desirable to have the highest possible functionality. However Lundberg (20) reported that films prepared from linseed oil had more superior properties than those prepared from trilinolenin. Actually solid films may be formed with an average functionality of only about 2; 2.5 is perhaps ideal. With higher functionalities, unsaturated residues will be present and these may undergo secondary oxidative attack leading to early degradation of the film or other undesirable properties.

Other Factors. Many factors may exert an effect on the course of oxidative polymerization. Noteworthy in this regard are the effects that different conditions of temperature, humidity, light, and film thickness have on the properties of films (14). Oxidations in films and in bulk, for example, differ markedly in certain respects. Figure 1 shows that, in the oxidation of thin films, the peroxide value may go up to 6,000-7,000 m.e./kg. whereas in bulk oxidation the peroxide value may reach a maximum of about 3,500 m.e./kg. if the reaction is carried out under mild conditions. This, of course, demonstrates an effect of conditions on the relative rates of peroxide formation and decomposition. The effect of many other factors on various characteristics of the reaction may be similarly demonstrated.

Autoxidative Polymerization Reactions

Although many factors affect the course of oxidative polymerization, there are certain basic chemical reactions which are believed to be involved. These are as follows.

Chain Termination Reactions. As the autoxidation proceeds into the advanced stages, the concentration of free radicals increases and the chances of their interreacting become greater. Generally these reactions are visualized as follows:

$$\begin{aligned} R\cdot + R\cdot &\longrightarrow R\text{-}R \\ ROO\cdot + R\cdot &\longrightarrow ROOR \\ RO_2\cdot + RO_2\cdot &\longrightarrow \; ? \end{aligned}$$

R-R represents carbon-carbon linked polymers and ROOR represents peroxide-linked polymers.

Peroxide Decomposition. Both the uncatalyzed and catalyzed thermal decompositions of polyunsaturated fatty acid peroxides give rise to polymers (28, 24, 41). O'Neill (24) and Williamson (41) indicate that the primary reaction involves dehydropolymerization with the formation of carbon-carbon bonded polymers. The reaction may be represented as follows:

$$\begin{aligned} ROOH &\longrightarrow RO\cdot + OH\cdot \\ RO\cdot + RH &\longrightarrow ROH + R\cdot \\ OH + RH &\longrightarrow H_2O + R\cdot \\ R\cdot + R\cdot &\longrightarrow R\text{–}R \end{aligned}$$

This mechanism appears to be based mainly on the finding that the major products of the decomposition of linoleate and linolenate hydroperoxides consist of carbon-carbon bonded dimers which contain most of their original unsaturation.

This mechanism may be criticized on several points. First, although dehydropolymerization of fatty acid esters can be effected by ditertbutyl peroxide, peroxides of greater reactivity and conversely lesser stability are not particularly effective in this regard (13, 15, 37, 38). Hydroperoxides would also appear to fall in this category. This mechanism suggests that unreacted ester (RH) is dimerized. In our studies on the products of the decomposition of the hydroperoxides of autoxidized methyl linoleate (Table I), a large amount of polymer was found in the oxygenated fraction. This indicated that the hydroperoxide formed polymers as a major product of the reaction. The magnitude of the decrease of the diene conjugation likewise indicated that the reaction involved interreaction of hydroperoxides. These results do not preclude the possibility of a dehydropolymerization mechanism, but they cast considerable doubt on the above hypothesis. That the mechanism of the decomposition of hydroperoxides is complex is indicated by the kinetics of the reaction (Figures 2 and 3). Figure 2 showed that, at any single peroxide concentration, the reaction conformed to the kinetics of a first-order reaction in that the plot of the log of peroxide value was a linear function of time. However when the rate of reaction, expressed by the specific reaction velocity, was plotted against peroxide concentration (Figure 3), the reaction appeared to be first order only at low peroxide concentrations. The difference between the two curves in Figure 3 indicated that substances which catalyze peroxide decomposition (apart from a simple peroxide concentration effect) are produced as the autoxidation progresses. It was demonstrated that small amounts of free fatty acid catalyzed the decomposition. Since free acid is produced during peroxide decomposition, this is another factor which complicates the reaction.

TABLE I

Thermal Decomposition of Linoleate Peroxides (*in vacuo*) at 56.5°C.

Analysis	Original	Decomposed sample	
		A	B
Before countercurrent extraction			
Peroxide value (m.e./kg.)	875	333	108
k_{234} mμ	10.5	7.0	6.5
Decomposed peroxide (%)	0	62.3	87.6
After countercurrent extraction (oxygenated fraction)			
Oxygenated material (%)	14.5	13.2	11.0
k_{234}	75.0	38.8	31.6
Peroxide value (m.e./kg.)	6100	2680	1010
Acid value	nil	18.7	15.2
Polymer (%) (Mol. dist. after $SnCl_2$ reduction)	nil	35	43

Another feature of the decomposition of hydroperoxides is that the reaction is catalyzed by antioxidants of the phenolic type (31). This reaction seems to be akin to the observed catalytic effect of radical-forming compounds on the heat polymerization of nonconjugated fatty acid esters and may be visualized as follows:

$$\begin{aligned} AH + ROOH &\longrightarrow A\cdot + RO\cdot + H_2O \\ A\cdot + RH &\longrightarrow R\cdot + AH \end{aligned}$$

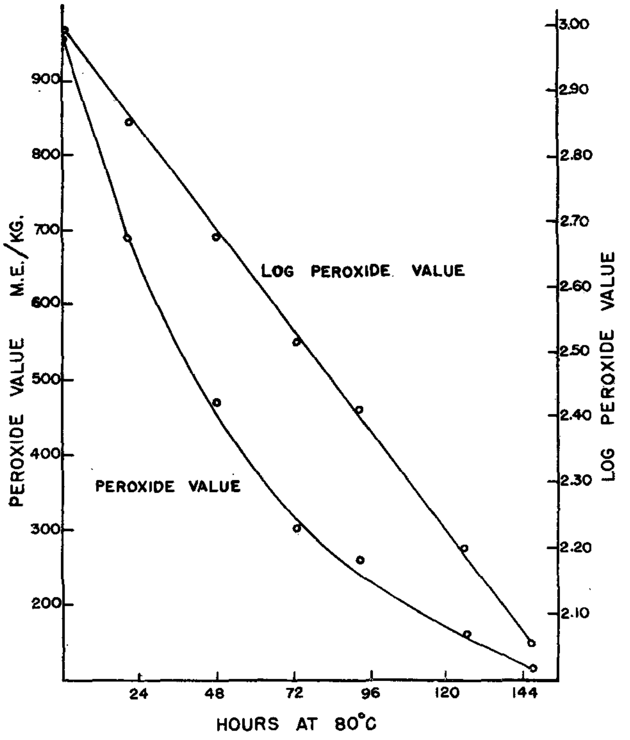


Fig. 2. The *in vacuo* thermal decomposition of methyl linoleate hydroperoxides.

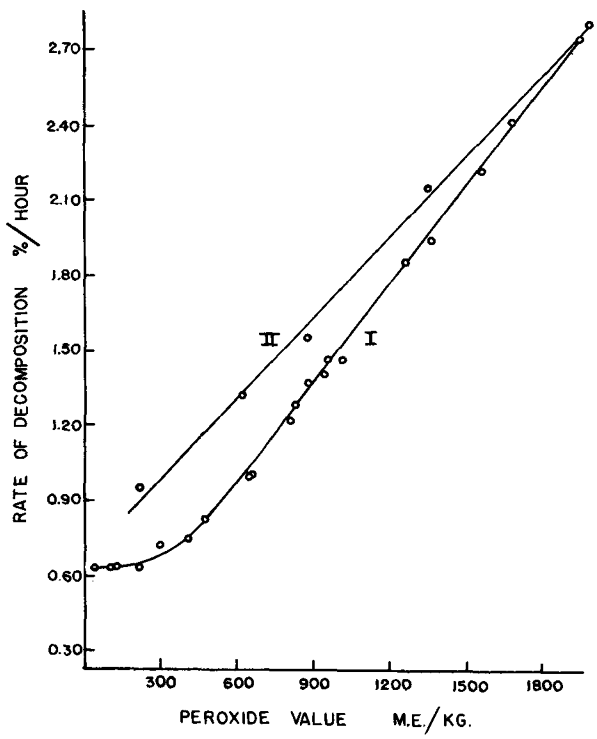


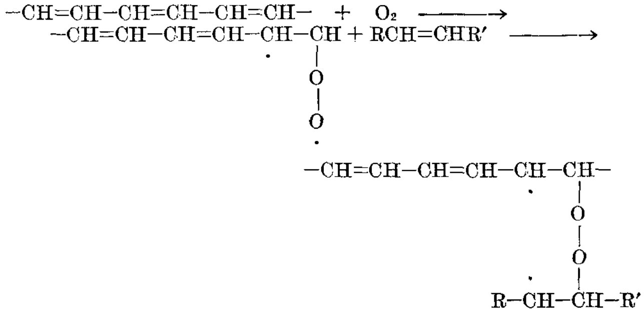
FIG. 3. The effect of initial peroxide concentration on the rate of the *in vacuo* thermal decomposition of methyl linoleate hydroperoxides. I. Autoxidized methyl linoleate. II. Autoxidized methyl linoleate diluted with methyl linoleate.

This reaction explains the pro-oxidant effect of antioxidants because the R · radical will react with molecular oxygen and initiate new reaction chains. In the absence of oxygen the R · radicals would be expected to interreact to form polymers. This, in effect, is the condition produced when the oxygen tension is reduced in autoxidation (2); under such conditions it is hypothesized that chain termination takes place predominantly by the union of R · radicals. That radicals formed from phenolic antioxidants (A ·) may react with an unreacted molecule is not unreasonable because of the demonstrated catalytic effect of anthraquinone (34) and diphenyldisulphide (37) on heat polymerization. It also is possible that the antioxidant radical may extract a hydrogen atom from a peroxide molecule. Further evidence in support of the above mechanism was the observation (31) that the antioxidants do not appear to be destroyed (after an initial partial destruction) during the *in vacuo* thermal decomposition of the peroxides. It would be interesting to determine if the products of the antioxidant-catalyzed decomposition of hydroperoxides differ from those of the uncatalyzed reaction. Presumably the products of chain termination in autoxidation are different under conditions of high and low oxygen pressures (2).

It is evident from a consideration of the foregoing that the mechanism of peroxide decomposition is far from settled. Nevertheless there is little doubt that peroxide decomposition is one of the most important polymer-forming reactions in oxidative polymerization.

Secondary Oxidative Reactions. Since hydroperoxide formation in polyunsaturated fatty acid esters involves a simultaneous conjugation of double bonds, it is believed that secondary oxidative reactions are similar to the autoxidation of simple conjugated fatty acid esters. This appears to be true, but a generally acceptable mechanism has yet to be defined and the structure of the products of the reaction are not known.

Allen and Kummerow (1) postulated the following mechanism for the oxidation of methyl eleostearate:



$$-CH{=}CH-CH{=}CH-CH{=}CH- + O_2 \longrightarrow$$

$$-CH{=}CH-CH{=}CH-\underset{\cdot}{C}H-\underset{\substack{|\\ O\\ |\\ O\\ \cdot}}{CH} + RCH{=}CHR' \longrightarrow$$

$$-CH{=}CH-CH{=}CH-\underset{\cdot}{C}H-\underset{\substack{|\\ O\\ |\\ O\\ |}}{CH}-$$
$$\overset{\cdot}{R-CH}-CH-R'$$

It was postulated that the dimeric radical could add more oxygen and thus build a polymer chain in which the reacting unit was CHR'–CHROO or cyclize to form a dimer. This mechanism was based primarily on evidence of 1:2, 1:4, and 1:6 addition of oxygen to the triene conjugation and other analytical data which showed that much of the original unsaturation was unattacked.

While this mechanism fits some of the facts, it does not provide for a facile mode of autocatalysism. Brauer and Steadman (7) and Myers *et al.* (23) obtained evidence for the autocatalytic mechanism of the oxidation of methyl eleostearate. Our studies (30) on the mode of autoxidation of methyl *cis*-9, *trans*-11-linoleate (Figure 4) likewise indicate that the oxidation of conjugated diene esters proceeds by an autocatalytic mechanism.

Although O'Neill (24) also concluded that oxidative attack involved the addition of oxygen at the double bond, he found only a relatively small amount of polymer among the products of the reaction, and it was believed to be carbon-carbon bonded. No evidence was obtained for the formation of oxygen-bonded polymers, as postulated by Allen and Kummerow (1). Most of the products of the reaction in this case were monomeric; from these a relatively pure cyclic peroxide was isolated.

Our studies on the products of the autoxidation of

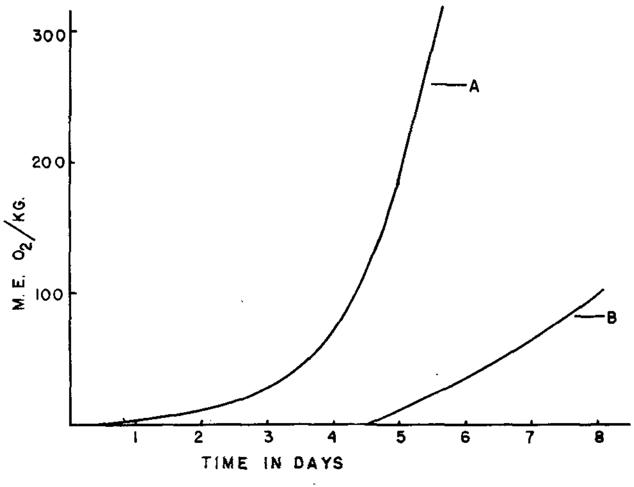


FIG. 4. The autoxidation of methyl *cis*-9, *trans*-11 linoleate at 30°C. A, no antioxidant; B, + 0.1% NDGA.

TABLE II

Autoxidation of Methyl *cis*-9, *trans*-11 Linoleate at 30°C.

	Before autoxidation	After autoxidation
Reaction time, hrs.	0	196
O_2 uptake (m.e./kg.)	0	1107
Peroxide value (m.e./kg.)	0	450
k_{233}	85.3	70.8
Polymer (%)		
(Mol. dist. after $SnCl_2$ reduction)	0	14.3
Monomer (%)		
(Mol. dist. after $SnCl_2$ reduction)	100	85.7
k_{233}, distilled monomer	......	82.7
Oxidized material in monomer (%)	......	3.0
Unoxidized ester (%)	100	83.0

methyl *cis*-9, *trans*-11 linoleate (Table II) likewise show that primary oxidative attack occurred at the double bonds. In this case about 84% of the products of the reaction were polymers which were not fissioned by stannous chloride. The remaining 16% were either monomeric or monomers produced by reaction with stannous chloride. (Stannous chloride was used to reduce the peroxide to avoid interference with the distillation analysis.) From a comparison of the amount of oxygen absorbed and the amount of material oxidized, it appeared that the primary reaction involved the addition of one mole of oxygen for each mole of monoester reacted. Infrared analysis showed that an appreciable amount of isolated *trans* unsaturated was formed during the course of the reaction. This resided almost entirely in the polymer in accordance with the above observation.

About one-third of the products of the reaction appeared to consist of easily reducible peroxide, as determined by KI reduction. These could not be identified as hydroperoxides and possibly are cyclic peroxides of the type isolated from oxidized methyl eleostearate by O'Neill (24).

Studies in our laboratory on the oxidation of methyl linoleate hydroperoxides (32) indicated that the autoxidation of these compounds resembled that of conjugated fatty acid isomers with certain notable points of difference in the kinetics of the two reactions.

Like the autoxidation of conjugated fatty acid esters, oxidative attack occurs in these compounds at the double bonds with the formation of polymers as the primary reaction product. Polymers however are not formed exclusively. Thus there is the possibility that some cyclic peroxides are formed in the autoxidation of these compounds also (5, 8, 22). The autoxidation also is inhibited by antioxidants (Figure 5) and therefore is fundamentally an autocatalytic reaction. Furthermore virtually all of the isolated *trans* unsaturation formed as the reaction proceeded resided in the polymer fraction. The peroxide value of the hydroperoxides changed very little even after an uptake of about 2,000 m.e. of oxygen per kilogram. In accord with the observations on the autoxidation of conjugated fatty acid esters, the amount of titratable peroxide (KI reduction) would not be expected to correspond with the amount of oxygen consumed. Obviously some titratable peroxide formed, in view of the change in weight caused by the oxygen that entered into the molecules. It appears therefore that there was no change in the measured peroxide value because of this compensation and there was probably a small amount of peroxide decomposition. Thus the autoxidation of the hydroperoxides may be considered to parallel that of the conjugated esters in this respect also.

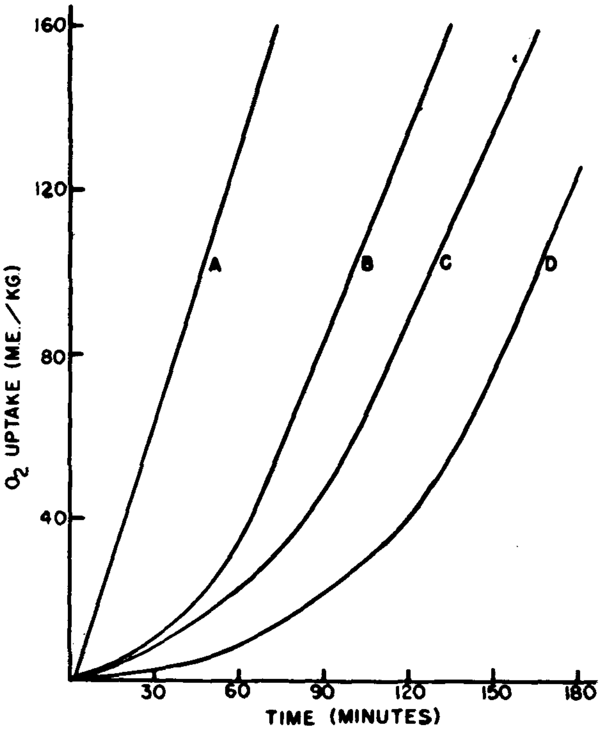


FIG. 5. The autoxidation of methyl linoleate hydroperoxide at 30°C. A, no antioxidant; B, + 0.05% hydroquinone; C, + 0.05% NDGA; D, + 0.05% propyl gallate.

Kinetically the hydroperoxides were autoxidized by a different pattern than conjugated fatty acid esters. Figure 5, curve A, showed that the amount of absorbed oxygen formed a linear relationship with the time of the reaction. However when the effect of initial peroxide concentration on the rate of autoxidation was determined, the relationship shown in Figure 6 was obtained. The nature of this relationship showed that the reaction was complex and of a high order. It is not unlikely however that the kinetics of the reaction can be explained at least in part on the basis that the hydroperoxide group functions as a "built-in" catalyst for the reaction and thus masks its autocatalytic characteristics.

Secondary oxidative attack undoubtedly is one of the more important polymer-forming reactions in many oxidation processes. This was indicated from the analyses of a thin film of aged methyl linolenate of a peroxide value of 5,600 m.e./kg. (near the peak of the peroxide value curve, Figure 1) shown in Table III. The oxygen uptake of this sample was estimated to be about 8,700 m.e./kg. on the basis of auxiliary experiments performed under similar conditions. In view of the magnitude of the peroxide value, most of the polymer was believed to have originated from multiple oxidative attack, probably not unlike that observed in the autoxidation of pure hydroperoxides.

Other Reactions. Ellis (11) and Skellon (36) suggested that dimerization, particularly of monoethenoic

TABLE III

Autoxidation of Methyl Linolenate
Thin film 25°C.

Peroxide value (m.e./kg.)	5600
Unoxidized ester (GLC)	13.0%
Polymer (mol. dist. after $SnCl_2$ reduction)	39.4%
Oxidized monomer (GLC on distilled monomer)	47.6%

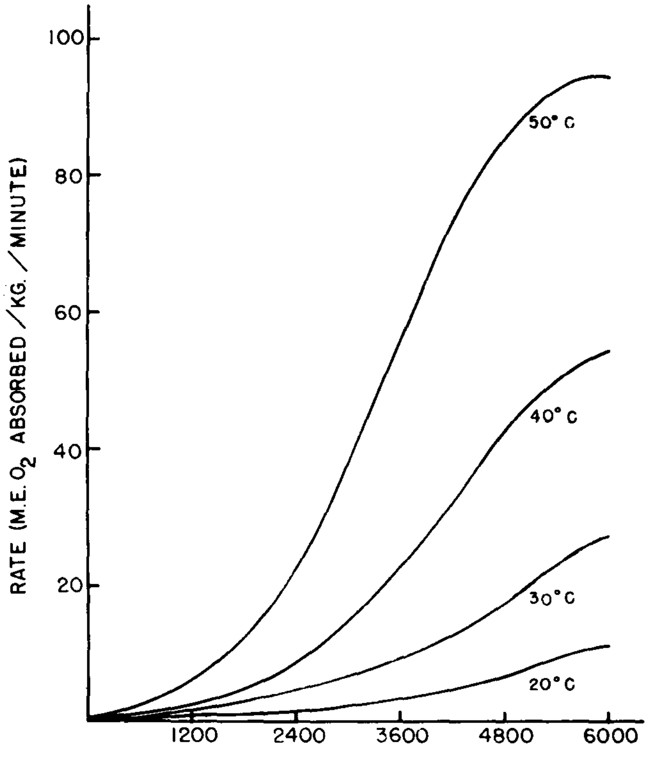


FIG. 6. The effect of initial concentration and temperature on the rate of autoxidation of methyl linoleate hydroperoxides.

esters, may occur by linkage through oxygen atoms, giving diether or dihydrofuran structures.

Reactions which characterize the thermal polymerization of polyunsaturated acids also may contribute to polymer formation, especially at the higher temperatures. These reactions may occur *via* a Diels-Alder mechanism in which polyunsaturated esters conjugated through the agency of heat condensed with unreacted molecules to form polymers containing substituted cyclohexene rings (25, 26), or by a free radical mechanism as suggested by Rushman and Simpson (33). In the latter hypothesis a preliminary conjugation of double bonds is not a prerequisite for polymer formation. The initial reaction is believed to involve the removal of a hydrogen atom from a linoleate molecule by a second linoleate molecule, giving rise to two radicals as follows:

$$2(-CH{=}CH-CH_2-CH{=}CH-) \xrightarrow{\qquad\qquad}$$
$$-CH{=}CH-CH-CH{=}CH- \qquad (R_1)$$
$$+$$
$$-\dot{C}H-CH_2-CH_2-CH{=}CH- \qquad (R_2)$$

Radical R_1 is a resonance hybrid with two conjugated forms and therefore accounts for the formation of conjugation during the reaction.

The polymer-forming reactions are visualized as taking place by the union of radicals R_1 and R_2. The extent of these reactions in oxidative polymerization would depend on the conditions, particularly the temperature of the reaction. However they do not appear to constitute a major reaction of polymerization under oxidative conditions.

Acknowledgments

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