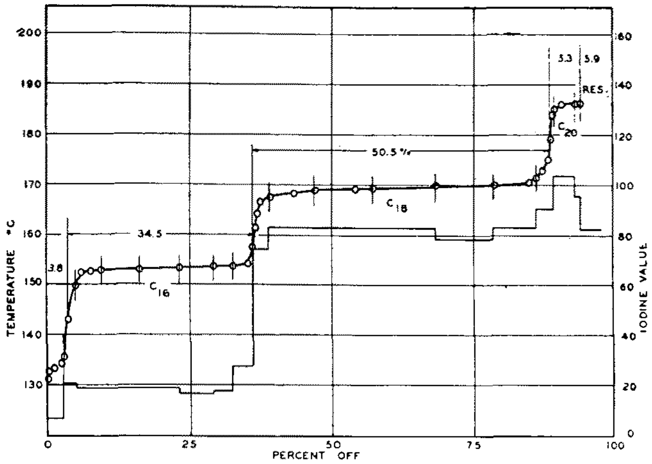


FIG

FRACTIONATION OF ALCOHOLS FROM SPERM OIL

ference in boiling points is not accurately known, but probably does not exceed 2-3° C. A plot of per cent methyl oleate in the distillate against per cent off shows appreciable concentration of the methyl oleate. A complete separation at reasonable distillation rates would require a much longer column.

(3) Fig. 4 illustrates the possibility of separation of the homologous fatty alcohols from sperm oil. Although numerous constituents have been identified, the literature contains little, if any, quantitative data on such mixtures. On the basis of the distillation and iodine value curves, the following approximate composition has been calculated:

Name of Alcohol	Carbon Atoms	Double Bonds	% Present
Myristyl	14	0	2.1
Physeteryl	14	1	Trace
Cetyl	16	0	21.1
Zoömaryl	16	1	7.4
Stearyl	18	0	5.0
Oleyl	18	1	49.7
Eicosenol	20	1	6.1
Eicosdienol (?)	20	2	2.1
Residue	—	—	6.5

Many more curves and tables of data could be shown, but we think the utility and efficiency of Stedman wire guaze packing for ester fractionation has been adequately demonstrated. Very little novelty can be claimed for the distillation equipment which has been described. It consists mainly of a combination of the best contributions of the pioneers in this field. The future will undoubtedly bring forth apparatus of even better design.

REFERENCES

(1) B. H. Lincoln, G. D. Byrkit, and E. W. Nelson, Oil and Soap, *17*, 73 (1940).
(2) H. E. Longenecker. Oil and Soap, *17*, 53 (1940).
(3) C. O. Tongberg, S. Lawroski, and M. R. Fenske, Ind. Eng. Chem., *29*, 957 (1937).
(4) M. R. Fenske, S. Lawroski, and C. O. Tongberg, Ind. Eng. Chem., *30*, 297 (1938).
(5) M. L. Selker, R. E. Burk, and H. P. Lankelma, Ind. Eng. Chem., Anal. Ed., *12*, 352 (1940).
(6) H. S. Lecky and R. H. Ewell, paper presented before the Division of Petroleum Chem., Am. Chem. Soc., Cincinnati, April. 1940.
(7) D. F. Stedman, Canadian Jr. of Research, *15*, 383 (1937).
(8) U. S. Patent 2,047,444 (1936).
(9) L. B. Bragg, Ind. & Eng. Chem., Anal. Ed., *11*, 283 (1939).
(10) H. M. Evans, R. E. Cornish, S. Lepkovsky, R. C. Archibald, and G. Feskov, Ind. Eng. Chem., Anal. Ed., *2*, 339 (1930).
(11) M. R. Fenske, D. Quiggle, and C. O. Tongberg, Ind. Eng. Chem., *24*, 408 (1932).
(12) J. B. Hill and S. W. Ferris, Ind. Eng. Chem., *19*, 379 (1927).
(13) J. H. Brunn and S. T. Skicktanz, Bur. of Stds. J. Res., *7*, 851 (1931).
(14) M. G. Marshall, Ind. Eng. Chem., *20*, 1379 (1928).

The Role of Oxidation in Drying Oils

By J. D. VON MIKUSCH and G. W. PRIEST
WOBURN DEGREASING COMPANY OF NEW JERSEY, HARRISON, N. J.

IN THE conventional classification of the fatty oils into non-drying and drying oils, the latter are characterized by their power to absorb oxygen from the air and to form "dry" or coherent films when exposed in thin layers. It is this ability to dry which makes these oils useful as the principal ingredients in paints, varnishes and numerous other commercial products. The role played by oxidation in this drying process has long been a subject of primary interest in the chemistry of drying oils.

Since oxidation plays a vital part in the process of film formation, it has a decidedly constructive role, which is, perhaps, a somewhat unusual aspect with fats and oils in general. At the same time, oxidation has its destructive aspects and the coatings formed by drying oils are themselves subject to further oxidation, leading to their deterioration and destruction.

Another important aspect of oxidation in drying oils is connected with color changes, i.e., the yellowing of oil films under certain conditions on one hand, and the bleaching which may occur in the oils as well as the films, on the other.

Finally, oxidation has an informative role and is employed in the laboratory for the identification of fatty acid components and for the characterization of the oils.

In order to limit the scope of this discussion, the main section will be devoted to the role of oxidation in film formation, while the other aspects will be briefly reviewed.

I

COMPOSITION AND CLASSIFICATION

Most of the natural oils are complicated systems of mixed glycerides which frequently contain half a dozen or more fatty acid components. Since both drying and non-drying fatty acids are found together not only in the same oils but in the same triglyceride molecule as well, their analysis and identification are both difficult and important. Although numerous contributions have been made to this branch of chemistry in the last few years, our knowledge on this subject is still in its infancy. It is only necessary to remember that even with the best methods now available it is still not possible to give the exact percentages of the various fatty acids and triglycerides in an oil such as linseed oil, without provoking discussion as to the validity of the methods employed.

However, the constitution of the various fatty acids occurring in the drying oils has, in general, been established beyond doubt. As a result, the drying oils may be subdivided according to the fatty acids occurring in them. Most classifications (11, 96, 99) recognize the differences in behavior of the fatty acids containing isolated double bonds and those containing conjugated double bonds or "dienes." Since the presence of the latter in any substantial proportion causes the oil to "frost," i.e., to form cracks and folds on air drying in the absence of driers, the drying oils may be divided into the frosting and the non-frosting type.

The non-frosting type includes such well-known oils as linseed, perilla and hempseed, various semi-drying oils, such as sunflower and soybean and some recently manufactured products derived from the latter or from fish oil by separating some of the non-drying constituents. They consist of varying proportions of linolenic, linoleic and oleic acids with some saturated fatty acids, usually stearic. The fish oils contain fatty acids with more than three double bonds, chiefly clupanodonic acid. These oils may be subdivided either according to the percentage of the various fatty acids present or according to their iodine value, which measures their total unsaturation.

The frosting type may be subdivided according to the quantity of conjugated double bonds present, into those predominantly conjugated, such as tung and oiticica oil, and those also containing a considerable portion of isolated double bonds, such as dehydrated castor oil. The fatty acids in the first two, i.e., eleostearic and licanic acid respectively, have three double bonds in the conjugated position, while the conjugated fatty acid in dehydrated castor oil, which amounts to about 25 per cent of the total fatty acids (114), has only two and is an isomer of linoleic acid. In the oils of the frosting type, the iodine value, when determined by the ordinary methods, is not very significant because conjugated double bonds react incompletely with the halogenating agents used.* Instead, the diene value, which indicates the quantity of conjugated systems present, is frequently used as a characterization of these oils.

II
INFORMATIVE ROLE OF OXIDATION

Both qualitative and quantitative oxidation procedures are employed in the analysis of drying oils. The former are principally concerned with the location of unsaturated linkages in the fatty acid chains by cleavage into fragments which are subsequently indentified.

Some of the quantitative methods are concerned with the determination of the percentage of certain fatty acid constituents. In the method of Bertram (6) the unsaturated components are oxidized with permanganate while the saturated acids remain unattacked and are isolated. Kaufmann and Fiedler (56) recently selected the proper conditions for the oxidation with the same agent which will convert the oleic acid quantitatively into dihydroxystearic acid. From the amount of the latter isolated, the percentage of oleic acid originally present is calculated.

The percentages of the more highly unsaturated components are not usually determined directly, but they may be calculated with the aid of various methods used to determine the degree of unsaturation or the iodine value of the oil or fatty acid. One method available for this purpose, which employs oxidation, is that of Smit (103-106) who studied the action of peracetic acid on unsaturated fatty acids and found that this reagent may be used to determine the unsaturation provided no conjugated double bonds are present. Permanganate in acetic acid was recently recommended (58) for a similar purpose and said to be of particular advantage for oils which are already partially oxidized and cause difficulties in the more familiar methods of determining iodine values with halogen compounds.

III
OXIDATION AND COLOR

White paint and enamel coatings all too frequently develop a yellow tinge, especially under conditions where light has little or no access. While this may be caused by certain pigments and resins, it is frequently due to the oil. Eibner and collaborators have shown (29, 30, 31, 34) that the triply unsaturated fatty acids, linolenic and eleostearic, are greater offenders in this respect than the doubly unsaturated acids. Therefore, tung, perilla and linseed oils yellow more than dehydrated castor oil or the semi-drying oils. While the exact mechanism leading to the formation of colored substances during oxidation is not fully understood, there is considerable agreement on the assumption that the yellowing is caused by the formation of diketo groups. Elm and collaborators (115, 43, 44) prepared diketo stearic acid and examined its absorption spectrum. It has the yellow color which is typical of compounds, such as diacetyl and thymoquinone, containing the —CO—CO— group, which dyestuff chemistry has long recognized as one of the important chromophores. They also were able to show that ketohydroxy stearic acid is colorless and thus disproved the belief held previously (70, 75) that the ketoxy group and its tautomerism is responsible for the yellow color. Elm also showed that yellowing is due to insufficient rather than excessive oxidation and that exposure of enamel films to ultraviolet light made them resistant to subsequent yellowing in the dark.

In the commercial process of blowing the drying oils with air, the product is usually lighter than the original oil, provided the process is carried out below 248°F. (120°C.) (67). This bleaching effect is believed to be due to the destruction of natural colored components, such as chlorophyll, by oxidation. When oils are bodied in the absence of air, a similar bleaching usually occurs; however, this takes place only at much higher temperatures, usually above 550°F. (287.8°C.).

IV
ROLE OF OXIDATION IN FILM FORMATION

The question as to what role oxidation plays in film formation is one of the most unsettled and controversial subjects of the chemistry of drying oils. The theories of film formation range all the way from strictly colloidal viewpoints to purely chemical concepts, with numerous intermediary theories, some of them referred to as colloidal-chemical, others as chemical-colloidal.

The controversy comprises not merely the deductions to be drawn from experimental results, but, unfortunately, in some cases also the experiments themselves. Some investigators who had unique and unheard of results in oil film experiments have preferred, in order to explain them, to add new theories to the already complicated picture rather than to recheck their experiments for possible errors. As a result, others have had to discuss and disprove these theories, even going to the trouble of carefully repeating the unorthodox experiments—but with different results—in order to undo the damage.

Much of the lack of agreement in this problem of film formation is due to the fact that many investigators have attempted to analyze the highly complex mixtures of oxidation products which are formed in the drying of natural oils, rather than to gather some information about the course of the oxidation reaction and the nature of the products obtained from the individual constituent acids of the drying oils. Frequently, such

---

* A method for determining total unsaturation in oils containing conjugated double bonds has been developed in this laboratory and will be reported on in the near future.

procedure seemed justified from a practical viewpoint, since it is the film of linseed oil, tung oil or dehydrated castor oil, etc., or the varnish or paint film in which we are eventually interested. However, here as in other fields, the strictly scientific approach through the isolated, pure compounds, such as trilinolenin or beta-eleostearin, has taught us more about the nature of the film and the film-forming processes than all attempts to gain such information from the complex oil films themselves.

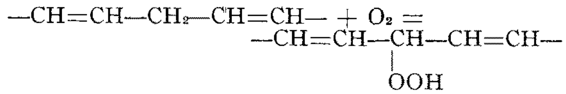
Examination of the experimental evidence on this subject, especially of some very recent investigations, leads us to the belief that we are perhaps not as far from a full understanding of the film-forming process as the extensive literature with its opposing views might make us believe. Since various able reviews of experimental findings and theories have been published (4, 19, 25, 29, 50, 75), we will confine ourselves to showing how some recent studies—which frequently have not become as thoroughly known as their merits deserve—have cleared away much of the earlier confusion and made possible an understanding of at least certain phases of the drying process.

These phases now emerging more clearly cover on the one hand the initial reactions taking place, when a drying oil film is exposed to air and, on the other, certain regularities involved in the formation of an insoluble and infusible oil film. Since only indirect conclusions can be drawn as to the exact nature of the reaction leading from the products of the initial oxidation to the final film system, a missing link still remains to be found before the entire film-forming process can be completely understood.

Autoxidation

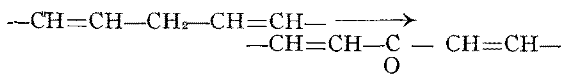
Autoxidation, although occasionally contested, has for a considerable time been recognized as one of the principal steps in the air drying of oils. Ample evidence of it is found in the fact that all drying oils take up oxygen from the air, when exposed to it, a phenomenon, which has been the subject of numerous quantitative and qualitative studies under varied conditions.

As the result of these studies and speculation, various conflicting theories have been advanced to describe the mechanism of the oxidation process. According to one of these, the oxygen attacks the activated CH_2 groups situated between two ethylene linkages as follows:



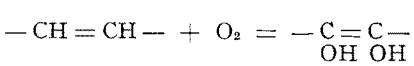
$$\mathrm{-CH{=}CH{-}CH_2{-}CH{=}CH{-}} + \mathrm{O_2} = \mathrm{-CH{=}CH{-}}\underset{\displaystyle \mathrm{OOH}}{\underset{|}{\mathrm{CH}}}\mathrm{{-}CH{=}CH{-}}$$

According to another (94, 96, 97), the same group is attacked with the formation of a keto group:



$$\mathrm{-CH{=}CH{-}CH_2{-}CH{=}CH{-}} \longrightarrow \mathrm{-CH{=}CH{-}}\underset{\mathrm{O}}{\mathrm{C}}\mathrm{{-}CH{=}CH{-}}$$

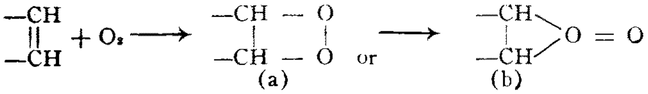
Finally, it has been suggested (41) that, similar to the oxidation mechanism of alcohol to aldehyde to acid, oxygen is introduced between carbon and hydrogen thus:



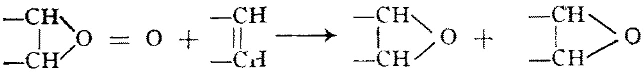
$$\mathrm{-CH{=}CH{-}} + \mathrm{O_2} = \mathrm{-}\underset{\mathrm{OH}}{\mathrm{C}}{=}\underset{\mathrm{OH}}{\mathrm{C}}\mathrm{-}$$

All these theories are similar in that the supposed oxidation products have the same number of double linkages as the original oil and should, therefore, have an iodine value which is decreased only in proportion to the increased molecular weight of the oxidized product. Aside from other considerations, which speak against either of these mechanisms, they are in discord with the experimental evidence that peroxides are formed in the exposed oils and that in the early stages of oxidation the iodine value of linseed oil and other non-frosting drying oils drops quantitatively with the formation of peroxide groups in a ratio of one equivalent iodine to one equivalent of active oxygen, or in other words, that one double bond disappears for each peroxide formed. This was observed by Fahrion (46) a generation ago and again by Coffey (21), Elm (43), and others (51, 49).

These observations can only be explained by the assumption that autoxidation in the early stage consists of an addition reaction of oxygen to the double linkages of the fatty acid chain with the formation of one peroxide for each double bond. Two ways in which this may occur have been suggested (46, 66, etc.):

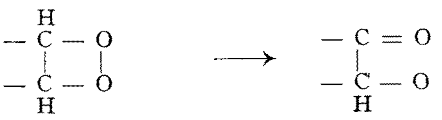


In (b) the outer oxygen would be held only loosely and could be expected—especially in statu nascendi—to react quickly with another double linkage leading to the formation of two monoxide rings:



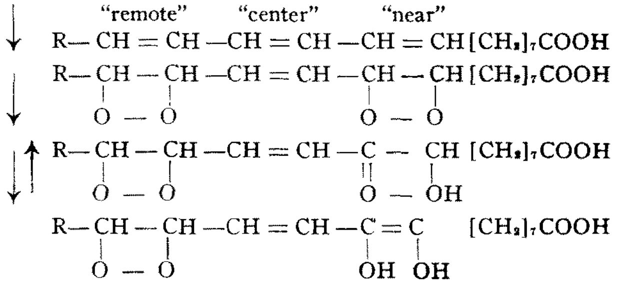
Although some investigators (84) believed that such monoxides are formed, Elm (43), as well as Morrell and collaborators, could find no evidence of such groups in air dried linolenic glyceride or beta-eleostearin respectively. Furthermore, the relationship of iodine value to oxygen absorbed does not support such a rearrangement into monoxides. Formula (a) must, therefore, be given preference with the more highly unsaturated fatty acids. In the case of oleic and elaidic acid, however, Ellis (41) found that oxido acids are formed on oxidation in the presence of cobalt driers. Deatherage and Mattill (26) found ethylene oxide rings among the autoxidation products of oleic acid and its compounds, which in the case of the free acid was believed to immediately form the half ester of dihydroxistearic acid.

While Goldschmidt and Freudenberg (51) found the quantitative relationship between iodine value decrease and peroxide value (determined with concentrated hydroiodic acid in acetic acid at 194°F. (90°C.) to hold strictly during the entire period of oxidation of linolenic acid and its esters, other workers (46, 21, 43) observed that after the initial stages of autoxidation the iodine value decreases more than the peroxide formation would account for. Also, the completely oxidized oils or linoxyns have been found to contain two atoms of oxygen (3, 38, 39, 64) for every double bond present, while their peroxide content is considerably smaller than would correspond to either iodine value or total oxygen absorbed. It has, therefore, been proposed tha some of the peroxide rearranges, possibly with the formation of a ketoxy group; a scheme first suggested by Fahrion (46).



$$\begin{array}{c}\mathrm{H}\\ \mathrm{-C-O}\\ |\quad\ |\\ \mathrm{-C-O}\\ \mathrm{H}\end{array} \longrightarrow \begin{array}{c}\mathrm{-C=O}\\ |\\ \mathrm{-C-O}\\ \mathrm{H}\end{array}$$

In the case of beta-eleostearin obtained from tung oil by irradiation and recrystallization, Morrell and collaborators (71 to 80) have, in the meantime, been able to identify the product obtained on oxidation in solutions as peroxy-ketoxy eleostearin. They were able to show by way of the maleic anhydride addition products that the three conjugated double bonds in eleostearic acid behave entirely differently toward oxidation. If, beginning at the carboxyl end of the chain, the double bonds are referred to in turn as the "near," "center," and "remote" one, both the near and the remote linkages form peroxides on autoxidation while the center one remains inactive. Only the peroxide on the remote double bond, however, is stable while the near peroxide immediately rearranges into the keto-hydroxy group. which in turn may exist in the dienol form:



$$\begin{array}{l}
\text{R—CH}=\text{CH—CH}=\text{CH—CH}=\text{CH}[\text{CH}_2]_7\text{COOH} \\
\downarrow \\
\text{R—}\underset{\text{O}\,—}{\text{CH}}\text{—}\underset{\text{O}}{\text{CH}}\text{—CH}=\text{CH—}\underset{\text{O}\,—}{\text{CH}}\text{—}\underset{\text{O}}{\text{CH}}[\text{CH}_2]_7\text{COOH} \\
\downarrow \\
\text{R—}\underset{\text{O}\,—}{\text{CH}}\text{—}\underset{\text{O}}{\text{CH}}\text{—CH}=\text{CH—}\underset{\overset{\|}{\text{O}}\,—}{\text{C}}\text{—}\underset{\text{OH}}{\text{CH}}[\text{CH}_2]_7\text{COOH} \\
\downarrow\uparrow \\
\text{R—}\underset{\text{O}\,—}{\text{CH}}\text{—}\underset{\text{O}}{\text{CH}}\text{—CH}=\text{CH—}\underset{\text{OH}}{\text{C}}=\underset{\text{OH}}{\text{C}}\;[\text{CH}_2]_7\text{COOH}
\end{array}$$

Some rearrangement of peroxides is also assumed to take place in the case of linolenic acid by Franke and Jerchel (49), who found a decrease of peroxide content of 30 per cent in 24 hours on an approximately two third oxidized product. They ascribe the contradictory result obtained by Goldschmidt and Freudenberg to the fact that the latter did not carry the oxidation far enough and used conditions for the peroxide value determination which are prone to give high results. After studying the kinetic relationship between peroxide value, oxygen consumption and iodine value, Franke and Jerchel were able to show that the autoxidation of linolenic and linoleic acids has great similarity with the course of the reaction found by Morrell for eleostearic acid. Thus, one double bond is again rapidly saturated with oxygen with the formation of a relatively stable peroxide. Subsequently, a second double bond is attacked with the formation of an unstable peroxide system, which rapidly rearranges without the participation of oxygen. Overlapping with this second reaction is a further slow decrease of double bonds. The third double bond in linolenic acid is attacked only very slowly, i.e., about as fast as oleic acid.

No clear evidence is, however, available as to which of the double bonds of linolenic and linoleic acid forms the more stable and which the more unstable peroxide. Nor has any evidence been presented in favor of the assumption that a ketoxy group is formed from the unstable peroxide, as in eleostearic acid.

In fact, it must be doubtful if the formation of ketoxy groups occurs at all during the drying process proper in any but negligible quantities because it has been shown by Eibner and Ried (36) and others, that the hydroxyl content of fresh linoxyn is small. Scheiber (96) found acetyl values of 11 to 14 on fresh films, which rose to 205 after 123 weeks, confirming the belief that the formation of hydroxyl values is due to secondary reactions occurring after the film formation rather than to an immediate rearrangement of the peroxide.

The question as to what other reaction is responsible for the decrease in peroxide value during and after the autoxidation and drying process leads to a consideration of what is necessary to change the oxidized oil to a dry film. The formation of peroxides and other primary oxidation products alone does not, of course, explain the change of liquid oil to a coherent solid film. That this film is not merely an amorphous solid which would eventually crystallize is well recognized (33). Its infusibility and insolubility leave no doubt that it is the product of some process of molecular growth into larger complexes either by polymerization, as some think, or by colloidal association as others believe. Before viewing the possible course which may lead from the oxidation products to the dry oil film, let us consider certain regularities involved in film formation and some of the properties of the film.

Functionality and Film Formation

We have seen that the formation of dry films at room temperature is always accompanied by oxidation. Only those fatty acids impart drying properties which are unsaturated and are, therefore, able to add oxygen spontaneously. Thus, oxidation appears as a prerequisite of film formation. It is, however, not the only requirement. Numerous compounds will autoxidize in much the same manner as the drying oils, without leading to dry films. Such compounds may be very similar to the drying oils in their constitution; this is true, for instance, for the fatty acids themselves (32) which do not form dry and hard films on exposure to air, although they absorb oxygen even faster than the corresponding triglycerides (21).

At one time it was thought that, since all known drying oils (at that time) contained glycerin, this compound itself undergoes oxidation and plays an important direct part in film formation. Later, when it had been found that the glycerin remains unchanged during the drying process and could be quantitatively recovered from the film, it was believed to be unimportant altogether and not required for film formation. Such conceptions were held up to quite recently and as late as 1931, leading authorities on the subject were surprised at the "anomalous behavior" of free linolenic acid when they found that it did not dry even as fast as linseed oil, although, "it ought to dry like a varnish." (32). Other authorities believed and still believe the glycerin to be merely contributory to drying in that the triglycerides on polymerization or association yield larger molecules than the fatty acids themselves, or, for example, the glycol esters. While this view may serve to explain some of the phenomena observed, such as the difference in viscosity increase and the gelation times of various polyhydric alcohol esters (62) on air-blowing or heat bodying, it is not strictly in agreement with the latest concepts and experimental evidence concerning polymerization and film formation. According to these, the true part played by the glycerin radical is defined by the concept of functionality. In order to understand it, it is necessary to briefly review the modern theories of polymerization which have been applied to the drying oils by Kienle (57), and more fully by Bradley (12, 13).

According to this theory, which is based on the work of Carothers (17, 18) and others, polymerization is defined as the occurrence of the ordinary reactions of organic chemistry in multiple fashion, due to multiplicity of reactive or functional groups present in the polymerizing substance. This so-called "general theory of polymerization" differs from older definitions in that the latter included only addition reactions, while the new theory includes condensation reactions as well. The course which a polymerization will take depends on the number of reactive groups available in the monomeric unit, or its so-called active functionality. If polymerization is to occur, the monomer must be at least bi-functional in the case of addition reactions, while in the case of condensation, each of the two reacting units must be at least bi-functional, i.e., the system must be bi-bi-functional. If this is the case, polymerization will lead to chain formation. Such a chain-like or two dimensional polymer will be either fusible or soluble or both. In order to form an insoluble and infusible polymer, a three-dimensional or cross-linked structure must be formed, which is possible only if the monomers are *more* than bi-functional in addition reactions or *more* than bi-bi-functional in case of condensation reactions.

The drying oil films are infusible and insoluble in the common sense of the word (some apparent exceptions in this respect will be discussed below). They, therefore, immediately suggest a three-dimensional or cross-linked polymer. According to the general polymerization theory it would then be expected that only such compounds can form true films which are more than bi-functional or more than bi-bi-functional. Glycerin has three hydroxyl groups which can be combined with fatty acid radicals and is, therefore, tri-functional. The drying fatty acids have one functionality available for esterification, that is, the carboxyl group and a number of further potential functionalities in their unsaturated systems. The latter, however, have been shown in the case of heat polymerization of oils to have an effective functionality of only one, that is, only one other fatty acid radical is added to it but no more, with the possible exception of eleostearic acid, the triple unsaturation in which may under certain conditions exhibit a functionality of two, or combine with two other fatty acid radicals.

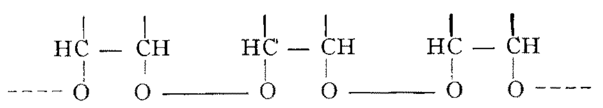
If similar conditions prevail with respect to the air-drying process, the combination of unsaturated fatty acids with glycerin would represent a tri-bi-functional system and, therefore, be expected to lead to insoluble and infusible, three-dimensional polymers, while the free fatty acids, and their mono-esters or di-esters, with the possible exception of eleostearic acid, should not have this power. Actually, while some of the free fatty acids or their mono or di-esters form soft and tacky films, these are not identical with true drying oil films because they are either fusible or soluble. Thus, the drying process is seen to be subject to the conditions of the general polymerization theory for cross-linkage or three-dimensional polymerization.

May we then not conclude that the drying oil film is a true three-dimensional polymer? On first sight, such a conclusion would appear justified, and the authorities of the polymerization theory, encouraged by the success of the new concepts in explaining heat polymerization and gelation of resins and oils, conclude that the drying of oil is "oxygen induced polymerization." However, if polymerization is to mean the multiplicity of "ordinary reactions of organic chemistry" as defined by the exponents of this theory), then a positive answer to the above question is not warranted. In fact, it would be a serious fallacy to draw conclusions from the gross-mathematical aspects of the process to the nature of the individual reaction concerned in the molecular growth. The basic reaction may or may not be one of the ordinary reactions of organic chemistry; it may or may not involve primary valence forces. All that we may safely conclude from the striking way in which the functionality aspects apply to the drying process is that:

1. The air-dried film has a three-dimensional or cross-linked structure which determines its insolubility and infusibility.
2. Ordinarily, the unsaturated systems of drying fatty acids, with the possible exception of the triply-unsaturated acids (it was not reported if trilinolenic glycol ester forms a converted film on air drying or not) exhibit an active functionality of but one, that is, on air drying they combine with only one other fatty acid radical.

We cannot, however, say if this combination of the fatty acid radicals, leading to a three-dimensional glyceride film, is due to an organic chemical reaction, i.e., either a condensation or an addition reaction, or if it is due to an association reaction which might be determined by secondary valence or colloidal forces. In the first case, the film would represent a true polymer, while in the second, it might be termed a psuedo-polymer.

The value of the application of active functionality concepts to the drying of oils is not made smaller by this limitation; in fact, we believe that it is one of the most important recent contributions to the understanding of this problem. Thus, it permits immediately narrowing down the possible film-forming processes to those which fulfill very specific conditions. Whatever the true nature of the process combining the fatty acid radicals or their oxidation products, this unit process must lead to the combination of two but no more than two radicals. If it is a chemical addition reaction, then it is *not* one which leads to a chain, such as has been frequently proposed, according to Staudinger's mechanism (107) of the polymerization of diphenyl ethylene peroxide:



$$\begin{array}{cccccc} | & | & | & | & | & | \\ HC - & CH & HC - & CH & HC - & CH \\ | & | & | & | & | & | \\ ----O & O\text{———} & O & O\text{———} & O & O---- \end{array}$$

In such a mechanism, one double bond forming one peroxide would have bi-functionality, which is in contradiction to the above evidence.

If, on the other hand, a secondary valence or association reaction is concerned, then again it is not one which would lead to vague colloidal clusters of fatty acid chains or their polar oxidation products but one in which specifically two such groups associate.

An attempt to understand the exact nature of this addition or association and to decide between the two alternatives of a primary or secondary valence combination must depend on other evidence.

Oxidation and Carbon to Carbon Polymerization

In the case of heat bodying, it has been possible on the basis of the general polymerization theory to calculate the drop of iodine value which should accompany increase in molecular weight with good agreement to actual observations (14). Allowing for difficulties in molecular weight determinations, it may be said that the belief that addition polymerization between the double linkages, with the formation of carbon to carbon rings, takes place in bodying is well born out by experiments. This has been further confirmed by molecular weight and iodine number determinations (15) on heat treated esters, which show these to be a mixture of monomeric and dimeric products in the same proportion as statistical considerations of the polymerization theory require.

Some authorities believe in view of the similarities between heat polymerization and gelation of oils in the absence of oxygen on the one hand, and the film formation in air on the other, that the same reaction between the unsaturated fatty acids take place in both cases. These similarities are undeniable, both physically and chemically. Both heat polymerization and air-drying lead to so-called converted, that is, infusible and insoluble products. Both processes, as has been shown, are subject to the requirements of the general polymerization theory. Furthermore, as a rule, oils that body and gel the fastest will also dry the fastest (some exceptions to this rule have recently been observed by the authors and will be reported on in the near future). The semi-drying oils which form only partially converted, soft and tacky films, do not gel on heat treatment until their composition has been materially changed by the evaporation and decomposition of some of the non-drying constituents (95). Linseed oil gels on heat treatment and dries well on exposure. Dehydrated castor oil bodies and gels in about one-fourth the time required for linseed oil under equal conditions (114); similarly its films set and dry in shorter time. Tung oil is the fastest in gelling and also in air-drying of the commonly used oils.

Does the peroxide or some other oxidation product then merely act as an accelerator for the carbon to carbon polymerization which has been found responsible for the heat polymerization of oils?

An interesting physical chemical aspect must here be considered. A certain class of chemical reactions are called chain reactions. They are characterized by the fact that, when one molecule or one pair or triplet or molecules in a system undergoes reaction, the energy given off is sufficient to activate another nearby molecule or group of molecules sufficiently to undergo reaction in turn; the latter after reacting will again be able to activate further molecules, etc., until a great number or chain of them has reacted which would otherwise not have had the necessary activation energy to do so. It was pointed out by Rhodes and Ling (89) and by Stephens (108) that certain aspects in the drying of oils are typical for such chain reactions. The action of anti-oxidants and traces of certain impurities (22, 65, 70, 112, 113) of greatly retarding film formation is characteristic for chain reactions, in which the chains are easily broken by minute quantities of inhibitors. Similar conditions prevailing in the heat polymerization of oils lead to the belief that the latter is also a chain reaction. If both oxidation and heat polymerization are chain reactions, Stephens points out, conditions may prevail which make it possible that the energy evolved in either one of these reactions may start a chain of the other one. Thus, if

$Eo + Qo = Ep$, where
Eo = activation energy necessary for oxidation
Qo = heat of oxidation
Ep = activation energy necessary for polymerization,

then oxidation in the exposed drying oil might set chains of carbon to carbon polymerization in motion. If this condition were fulfilled, the entire film-forming process might be nothing else but a heat polymerization and gelation, with the only difference, that the heat necessary for it is supplied by the internal combustion of some of the fatty acid radicals. The peroxide formation would then merely serve to replace the fire under the kettle of oil.

This would, indeed, be a simple interpretation of the drying process and would account for the similarities between bodying and air-drying; between gel and film. Unfortunately, however, the experimental evidence does not support this scheme of drying under ordinary conditions.

In the first place, in spite of the similarities between the drying oil gel and the dried film, there are essential dissimilarities. While uniformly high molecular weights have been found on heat bodied and geled oils (45, 66), the air dried oil films yield different values according to the method and solvent employed. In some solvents only unimolecular values are obtained (43). Similarly, the fatty acids obtained by saponification of the oxyns give monomeric molecular weights and, therefore, show no signs of carbon to carbon polymerization (34).

Furthermore, while a drying oil film does not dissolve in the common solvents under ordinary conditions, it is slowly dissolved by acetone under pressure (43). The viscous residue from these solutions gradually changes back to the "insoluble" or gelatinous form (84).

Finally, direct evidence that no reaction between the ethylene linkages occurs during oxidation of the non-frosting oils must be seen in the previously mentioned observation, that, during the early stages of drying, the drop in iodine value is equivalent to the peroxide formation at the ratio of one iodine to one active oxygen. If heat polymerization were induced by the formation of peroxides the iodine value would decrease faster than in this ratio. The assumption of any carbon to carbon polymerization induced by the heat of oxidation is, therefore, not feasible in the case of linseed oil or other drying oils of the non-frosting type. It appears that the hypothetical case suggested by Stephens, where the activation energies of both reactions, oxidation and polymerization, are within the same order of magnitude and either reaction could set in motion a chain of the other, is not realized under the normal drying conditions of such oils.

This is not surprising, for it should be expected that the activation energy necessary to cause polymerization is very much greater than the activation energy of oxidation (109). The oxidation of oil films proceeds with ease at room temperature or at zero weather, while polymerization of linseed oil requires temperatures of 550°F. or higher to proceed with satisfactory velocity. The speed of bodying of linseed oil decreases by a factor of 2 for every decrease in temperature of about 25°F. (114). Lowering the temperature from 570°F. (298.9°C.) to 70°F. (21.1°C.) will then retard the reaction by a factor of 2^{20} or approximately 1,000,000, provided the same relationship holds at the lower temperature ranges. If it requires 12 hours to bring linseed oil to a heavy body at 570°F. (298.9°C.) it would re-require about 12,000,000 hours, or 1,400 years to reach the same viscosity on standing at room temperature in the absence of oxidation.

On the other hand, it is conceivable that on oxidation at higher temperatures, i.e., in the baking of oil films, the two reactions, oxidation and heat polymerization, the latter activated and accelerated by the former, may overlap to some extent.

Thus, Long and McCarter (63) found that the gel obtained on blowing linseed oil with oxygen at 110°C. (230°F.), 160°C. (320°F.) and 200°C. (392°F.) contained 7.63 per cent, 7.37 per cent and 6.98 per cent respectively of oxygen, which might indicate that at the higher temperatures some heat bodying has contributed to gel formation and reduced the extent of oxidation required to lead to the same stage of molecular growth. However, "the differences are small, especially in view of the great differences in time," and may have been caused by other secondary factors. Payne (85) studied the differences in water resistance and permeability of raw and bodied oil films as well as air-dried and baked films. The bodied oil films were found to be less permeable than the raw oil films and, similarly, the baked films less than the air-dried films, which would tend to confirm the assumption that on baking some carbon to carbon polymerization participated in the film formation similar to that present in the heat-bodied oils (90). In bodied oils carbon to carbon polymerization has already taken place to some extent, with the result, that less oxygen is needed for film formation (89, 85, 59).

An overlapping of molecular growth by the air drying mechanism and by heat polymerization at elevated temperatures is evident when the oxygen present is reduced to low concentration, such as in a vacuum of about 2mm. This was demonstrated by recent findings of Ockrent (83) on a molecularly distilled linseed oil. The rate of absorption was found to be slower under these conditons for higher temperatures than for the lower, that is, the temperature coefficient of oxidation was found to be negative. At normal pressure the temperature coefficient for linseed oil oxidation had previously been found to be positive, the process proceeding faster at higher temperatures than at lower ones (63, 112). A negative coefficient, Ockrent concluded, indicates that the reaction involved is not a simple one, but a combination of different reactions with different temperature coefficients. At the higher temperatures, polymerization can take place with "oxygen poor" molecules. This was confirmed by the observation that at 128°C. (262.4°F.) film formation is completed after only a little more than one-half of the oxygen has been absorbed compared to the amount required at 82°C. (179.6°F.). At the same time, it was shown that no drying takes place if oxygen is absent altogether, as under nitrogen or in a vacuum of 10^{-3} cm. Thus, it is obvious that the temperatures used were too low to cause heat polymerization or gelation by itself and if, in spite of this, a considerable share of the film formation was due to a reaction not involving oxygen absorption, there seems to be a clear case for an oxygen induced polymerization which might be explained by Stephens' (108) mechanism of carbon to carbon polymerization chains, set in motion or activated by the energy of oxidation.

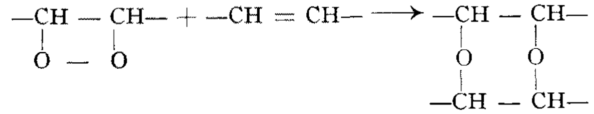
Similar conditions may prevail in the drying of the oils chiefly containing conjugated double bonds, such as tung and oiticica oil, or in the type containing both isolated and conjugated double bonds. Some of these gel in a number of minutes at temperatures where linseed oil requires many hours. Thus, tung oil at room temperature should have a tendency to polymerize comparable to that of linseed oil of 200-250°F. (93.3-121.1°C.), or an air-dried tung oil film should resemble a baked linseed oil film with respect to the amount of carbon to carbon polymerization involved. This would explain the greater resistance toward water and various chemicals of the frosting oils compared to the non-frosting. It has not been possible to investigate the change of unsaturation in tung oil to the same extent as was done on linseed oil because none of the customary iodine value procedures measures all of the double bonds in conjugation. There is, therefore, at present, no direct evidence as to whether and to what extent carbon to carbon polymerization is involved in the drying of tung oil or other oils of the frosting type.

This phenomenon of frosting itself, sometimes erroneously referred to as "crystallization," which is exhibited by these oils when air dried without the previous addition of driers, is an indication of decided differences between the drying process of these oils and those of the non-frosting type. Eibner and Rossmann (37) have examined this phenomenon microscopically on tung oil films and have come to the conclusion that cracks are first formed due to shrinkage while the film is still wet; later they are supplemented by small folds formed at right angles to these cracks simultaneous with oxygen absorption and an increase in volume. It is generally believed that polymerization is responsible for this behavior. Hyman and Greenfield (54) showed that no frosting takes place in air containing less than 4 parts in ten million of nitrogen dioxide, but no attempt has been made to explain the role played by traces of this gas in polymerization or oxidation of oil films.

However, polymerization between double linkages is not alone responsible for the drying of the conjugated oils since even in the case of tung oil a considerable percentage of oxygen is absorbed before film formation occurs (37, 89, 63). Carrick and collaborators (19) showed that the diene value of tung oil remains almost unchanged during the oxidation of the first double bond. If the oxidation of one of three double bonds of eleostearic acid would activate the remaining two conjugated linkages sufficiently to cause them to undergo polymerization, the diene value would be expected to drop simultaneously with the oxygen absorption.

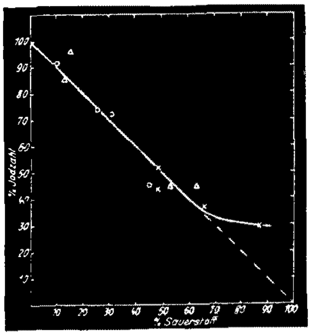
Polymerization Involving Peroxides

It has been suggested by Fahrion (46) and by Eibner and co-workers (29, 34), who have examined numerous drying oil films, and by others, that the peroxide groups react with an unattacked double linkage with the formation of a six-membered, so-called dioxan ring:

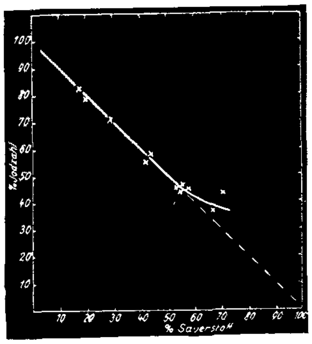


$$\begin{array}{c} -\mathrm{CH}-\mathrm{CH}- \\ |\qquad\ | \\ \mathrm{O}-\mathrm{O} \end{array} + -\mathrm{CH}=\mathrm{CH}- \longrightarrow \begin{array}{c} -\mathrm{CH}-\mathrm{CH}- \\ |\qquad\ | \\ \mathrm{O}\qquad\mathrm{O} \\ |\qquad\ | \\ -\mathrm{CH}-\mathrm{CH}- \end{array}$$

No proof of the existence of such a dioxan ring in the film has yet been found. This scheme seemed, however, supported by the observed relationship between peroxide and iodine value. As previously stated, the latter drops quantitatively with the formation of peroxides during the early stages of the drying process at a ratio of one iodine for each active oxygen. After oxidation has somewhat proceeded, however, the peroxide content tends to reach a maximum and decrease again, while the iodine value continues to decrease as before. In addition to the previously discussed rearrangement reactions of the peroxide which had been suggested to account for this decrease of the peroxide value, the formation of dioxan rings was held responsible. Franke and Jerchel (49), however, in their previously quoted paper, were able to show that, even after the initial phase of peroxide formation, the drop of iodine value in linoleic and linolenic acids corresponds exactly to the total oxygen absorbed until about 60 to 70 per cent of the oxidation has been completed. At this point the decrease of iodine value becomes smaller than the absorbed oxygen would require, but at no point does the iodine value decrease beyond the value calculated from the oxygen absorbed:



% Oxygen
Autoxidized Linoleic Acid

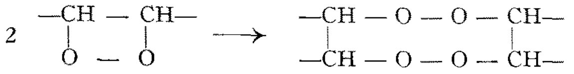


% Oxygen
Autoxidized Linolenic Acid

This result makes it impossible to uphold the dioxan ring polymerization theory or any other mechanism involving unoxidized double linkages because any such reaction would require an iodine value decrease beyond that calculated from the oxygen absorption.

The fact that toward the end of the oxidation the iodine value does not drop as fast as the oxygen is absorbed is ascribed to a more intense oxidation of the attacked double bonds or of other groups in the chain. Some investigators believe that new double bonds may be formed due to a dehydrogenating action of oxygen on the two carbon atoms next to the peroxide group (26, 50). Such a mechanism might explain the observation of some investigators that fully oxidized oil films contain somewhat more oxygen than that corresponding to the saturation of oil originally present double bonds with two oxygen atoms each (21, 19).

Others have suggested that two peroxides react together with the formation of an eight-membered ring (66):

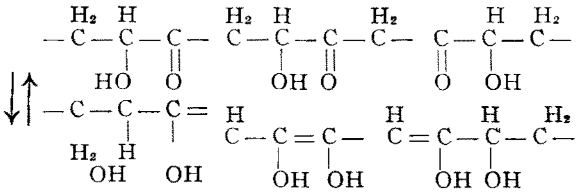


$$2\ \begin{array}{c}-CH-CH-\\ |\qquad | \\ O-O\end{array} \longrightarrow \begin{array}{c}-CH-O-O-CH-\\ |\qquad\qquad\qquad | \\ -CH-O-O-CH-\end{array}$$

While this scheme is in agreement with the observed oxygen-iodine value relationships, it must be remembered that eight-membered rings are formed very rarely and never with the spontaneous ease with which the drying oil sets to a film.

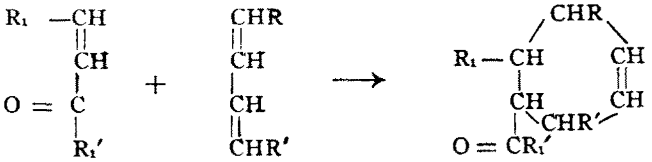
Other Polymerization Mechanisms

It has also been suggested that the drying of non-frosting oils is preceded by the rearrangement of the double bonds into the conjugated position, in which they would be able to undergo polymerization by the diene syntheses or some similar mechanism. Such a reaction is believed by some investigators to be involved in the heat bodying of non-conjugated oils (94). A mechanism by which such a rearrangement might occur on air drying was suggested by Rheineck (88). He pointed out that in fully oxidized linolenic acid conjugated double bonds may be formed by the enolization of ketoxy groups as follows:



As evidence of the formation of conjugated double bonds, a study by Taylor and Smull (110) is quoted in which it was shown that a linseed oil which had been air-blown for almost two months reacted with enough maleic anhydride at 120°C. (248°F.) to lower the iodine value by 9 points. While this might indicate that 5 to 10 per cent of the double bonds were present in the conjugated position, it must be remembered that the determination of these bonds with maleic anhydride is not considered reliable in the presence of peroxides or other oxidized groups. The possibility that the oxidation products of linoleic and linolenic acids may form conjugated double bonds via the enolization of keto-groups had previously been pointed out by Scheiber (96). That such a mechanism is responsible for air-drying, is made unlikely, however, by the previous observation (36, 97) that hydroxyl groups are not formed until after the film formation is complete.

Dean (25) pointed out that the structure of ketoxyperoxide of beta-eleostearin contains a keto group in conjugation with an ethylenic linkage. Such a C=C—C=O compound would be expected to react with a C=C—C=C group in a typical Diels-Alder condensation:



Considering the ease with which the corresponding reaction between maleic anhydride with conjugated fatty acids proceeds even at room temperature, such a reaction would, indeed, seem very likely. However, since in this case the polymerization would depend on the formation of the ketoxy group on the near double bond and directly involve the center double bond which is believed to be rather inactive (19, 71), this scheme does not have the evidence in its favor. Instead, the investigation of Morrell and others make it appear likely that in the oils of the frosting type, as well as the non-frosting, the more stable peroxide plays a very direct part in film formation and is probably itself the reactant or one of the reactants which combine the triglycerides into larger complexes.

Possible Nature of Film Forming Reaction

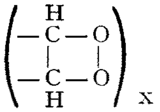
It has been shown, that many of the proposed mechanisms of film formation do not satisfy the latest experimental evidence. While they may have fitted the picture when they were first proposed and served to stimulate further research, they are now outdated. But even today, the exact nature of the reactions, or of the attractive forces which build the triglycerides into a coherent film, is not known. The possibilities have, however, been narrowed down and certain conditions are imposed by the sum of the evidence to date:

1. The mechanism in question must take into account the scheme of autoxidation which has been established for all major drying oil acids. Since this involves the formation of peroxides and since it was possible to show, at least in one case (74, 79, 80), that the most stable peroxide is principally responsible for the drying, these peroxides must themselves play some part in the mechanism.
2. It must proceed without the involvement of any unoxidized carbon to carbon double bonds in order to meet the observed relationship of iodine value and oxygen absorption during drying. It must, therefore, neither involve reactions between ethylenic linkages themselves nor between peroxide and ethylenic linkages.
3. It must lead to a product which is characterized by the functionality requirements of the general polymerization theory. It must be subject to the same mathematical aspects as the reaction occurring in heat polymerization. That is to say, while the individual reaction itself is not identical with that of heat polymerization, it must lead to an identical pattern of cross linkages. With the possible exception of triply unsaturated systems, the entire oxidized fatty acid radical must combine with only one other such system but no more. This condition, therefore, precludes any of the polymerization schemes which involve chain formations in which a double bond or its oxidation product has double functionality.
4. Finally, it must account for the fact that the film does not have the stability towards solvents of most

true polymers and that the union involved is, therefore, reversible.

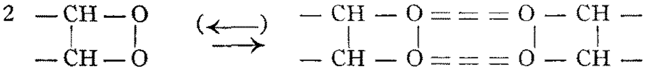
Conditions 1 and 2 would be best met by assuming that the peroxides react with each other. Condition 3 would then require that each peroxide react with only one other peroxide, for instance, in a ring formation. Condition 4 would be best met by a pseudo polymer in which the individual linkages are supplied by secondary rather than primary valences.

The belief that secondary valences or colloidal forces are involved has frequently been upheld. While some of the colloidal explanations advanced in the past, however, have been extremely vague, we may today assign a very specific function to any such attractive forces, as laid down by conditions 1, 2, and 3. All of the conditions seem to be best met if we assume, as Long and Chataway (62) and Elm (43) foresaw as an alternative, that secondary valences come into action



$$\left(\begin{array}{c} H \\ -C-O \\ |\quad\;| \\ -C-O \\ H \end{array}\right)_x$$

between the peroxides. Rather than describing the reaction with this general formula, condition 3 is met only if x equals 2. The combination might then be one of pseudo rings:



$$2\;\begin{array}{c}-CH-O\\ |\quad\;\;|\\ -CH-O\end{array} \;\rightleftarrows\; \begin{array}{c}-CH-O{=}{=}{=}O-CH-\\ |\qquad\quad|\qquad\quad|\qquad\quad|\\ -CH-O{=}{=}{=}O-CH-\end{array}$$

It is remembered that the tendency of oxygen to form tetravalent "oxonium" compounds is not a rare phenomenon but manifests itself in as every day a substance as water with its dimeric and trimeric molecules (116).

This scheme is not to be taken as a new theory of film formation but as a suggestion of how the various, frequently contradictory experimental findings of numerous investigators who have attacked the problem from different angles and contributed each to one particular phase of the process might be correlated, and how by elimination rather than by any direct evidence, a possible mechanism of film formation may be derived. However, since deductions by elimination are always subject to error and may be modified by new evidence, the controversy as to the processes which lead from autoxidation to the formation of a coherent film will not be settled until some direct proof of the nature of the reaction can be found.

V

OXIDATION IN THE DESTRUCTION OF FILMS

While oxidation plays a vital part in film formation, it is also one of the primary causes of its destruction. This role is best understood if it is kept in mind that while the drying of oil films involves molecular growth into a cross-linked structure, which determines its insolubility and infusibility, a certain portion of the oil remains unpolymerized or unassociated. This portion acts as a plasticizer for the film and is responsible for the highly important and vital property of flexibility and durability. A permanent balance between the cross-linked and the plasticizing portion is required to maintain the usefulness of the film and any factors which tend to upset this balance will lead to its destruction.

Some drying and semi-drying oils form films which, after assuming a certain hardness, become soft and tacky again. This phenomenon, called syneresis, is exhibited principally by oils containing a considerable proportion of oleic acid. This acid and probably some of the more highly unsaturated acids as well are broken at the double bonds by oxidation forming such fragments as pelargonic and other short-chain acids (2, 52, 69) which cause swelling, softness, and tackiness of the film. Eibner has determined the acid values of numerous air-dried oil films and found them especially high for the raw oils (29):

Raw poppyseed oil, after 127 days, acid value	221
Raw linseed oil, after 60 days, acid value	192
Bodied linseed oil, after 12 days, acid value	48
Raw tung oil, after 127 days, acid value	60

D'Ans lists the following causes of weathering and destruction of linseed oil films (2):

1. Natural oxidation.
2. Hydrolysis with participation of the oxidation products of the oil.
3. Destruction by molds.

The destruction of paint and varnish films is usually caused by a loss of flexibility, i.e., embrittlement, rather than softening of the oil films. The coating then loses its ability to withstand the daily cycle of expansion and contraction due to the temperature changes outdoors and thus cracks. This is especially true for the more powerful drying oils of the tung oil type, but also for linseed oil, and may be connected with the presence of the triply unsaturated acids. Long and associates (64) ascribe this behavior to colloidal changes consisting in the gradual transition of polar liquid phase in the film to the solid phase by association.

The desire to overcome failure in the oil films and thus to prolong their useful life has suggested the thought of preventing oxidation in the finished films. However, the most obvious method of accomplishing this, i.e., by addition of anti-oxidants to the paint or varnish, has been prevented by the fact that the drying process itself is extremely sensitive to anti-oxidants. Scheiber (97) exposed tung oil, linseed oil, and dehydrated castor oil to the air after adding small percentages of beta-naphthol and resorcin and found that the drying was delayed up to two years in the case of the latter. When drying finally occurred, it was believed to do so only after destruction of the anti-oxidant itself by oxidation. Stephens (108) believes the search for specific anti-oxidants which would retard the degradation of oil films without effecting the drying speed to be hopeless, because the latter, being a chain reaction, would always be more strongly effected than the former, which shows no evidence of belonging to that type of reaction.

On the other hand, it has been suggested to apply an anti-oxidant in solution as a final coat on top of the dried paint to preserve it (92). No evidence that this process is practiced in industry has come to the attention of the authors. Wagner and Brier (112, 113) found that certain aromatic amines have no anti-oxygenic influence at room temperature but develop such power at 100°C., probably as a consequence of decomposition reactions. They suggest that an ideal anti-oxidant might be found in some compound which similarly is not active in itself but changes into an anti-oxidant by some suitable spontaneous reaction occurring after thorough drying.

The answer may lie in another direction. While in the past most drying oils were natural products, although usually refined or heat treated, the present tendency is toward synthetic and "tailor-made" oils which are not bound to a certain composition by nature and may be made to have whatever composition is required to give them the properties desired in the final paint and varnish film. Dehydrated castor oil represents probably the first important step in this direction and its durability is considered superior to that of the older drying oils. Various other manufactured drying oils are now on the market and the future may bring new developments in this direction.

LITERATURE

1. Ans, J. D', Z. Angew. Chem. *41,* 1193-7 (1928).
2. Ans, J. D', Ibid. *42,* 997-9 (1929).
3. Ans. J. D', and Merzbacher, S. [Fett] Chem. Umschau *34,* 283-91, 295-6 (1927).
4. Bauer, K. H., "Die Trocknenden Oele," Stuttgart (1928).
5. Behrer, H., Farbe u. Lack 1937, 425-6.
6. Bertram, S. H., Z. Untersuch. Lebensm. *55,* 179 (1928).
7. Blom, A. V., Z. Angew. Chem. *40,* 146-7 (1927).
8. Blom, A. V., Kolloid Z. *75,* 223-35 (1936).
9. Blom, A. V., Ibid. *76,* 351-2 (1936).
10. Blom, A. V., [Fett] Chem. Umschau *43,* 33-6 (1936).
11. Blom, A. V., Paint Varn. Prod. Mgr. *15,* No. 4, 24, 26-30 (1936).
12. Bradley, T. F., Ind. Eng. Chem. *29,* 440-5 (1937).
13. Bradley, T. F., Ibid. *29,* 579-84 (1937).
14. Bradley, T. F., Ibid. *30,* 689-96 (1938).
15. Bradley, T. F. and Johnston, W. B., Ibid. *32,* 802-9 (1940).
16. Brambilla, M., Am. Chim. applicata *28,* 444-54 (1938).
17. Carothers, W. H., J. Am. Chem. Soc. *51,* 2548-59 (1929).
18. Carothers, W. H., and Arvin, J. A., Ibid. *51,* 2560-70 (1929).
19. Carrick, L. L., Knudson, G. E., Porter J. V., and Thompson, N. J., Am. Paint J. *23,* May 1 to Sept. 11, 1939.
20. Clewell, D. H., Paint Varn. Prod. Mgr. *17,* No. 1, 30 (July, 1937).
21. Coffey, S., J. Chem. Soc., *119,* 1152-60 (1921).
22. Cohen, H. C., Verfkronick *10,* 3-4 (1937); C.A. *31,* 5185^9.
23. Couture, E., Compt. rend. *190, 532-3* (1930); C.A. *24,* 2620.
24. Currier, A. J., and Kagarise, I. H., Ind. Eng. Chem. *29,* 467-9 (1937).
25. Dean, H. K., "Utilization of Fats," New York 1938, Chem. Pub. Co., page 228, etc.
26. Deatherage, F. E., and Mattill, H. A., Ind. Eng. Chem. *31,* 1425-31 (1939).
27. Eibner, A., Farben Ztg. *33,* 1222-4 (1928).
28. Eibner, A., Ibid. *33,* 2165-9 (1928).
29. Eibner, A., "Das Oeltrocknen, etc." Berlin, 1930, Allgem. Ind. Verl. Ges.
30. Eibner, A., Paint Varn. Prod. Mgr. *14,* 12, 14, 30-1 (March, 1936).
31. Eibner, A., and Greth, A., Farben Ztg. *33,* 1595-8 (1928).
32. Eibner, A., and Jung, K. [Fett] Chem. Umschau *38, 267-73* (1931)
33. Eibner, A., and Muenzing, E., Ibid. *32,* 153-62, 166-76 (1925).
34. Eibner, A., and Munzert, H., Ibid. *33,* 188-94, 201-8, 213-6 (1926).
35. Eibner, A., and Munzert, H., Ibid. *34,* 89-96, 101-8 (1927).
36. Eibner, A., and Ried G., Ibid. *32, 233*-49 (1925).
37. Eibner, A., and Rossmann, E., Ibid. *35,* 281-90 (1928).
38. Ellis, G. W., J. Soc. Chem. Ind. *44,* 401-8T (1925).
39. Ellis, G. W., Ibid. *44,* 463-8T (1925).
40. Ellis, G. W., Ibid. *44, 469-72,* 486T (1925).
41. Ellis, G. W., Ibid. *45,* 193-9T (1926).
42. Ellis, G. W., Biochemical J. *30,* 753-61 (1936).
43. Elm, A. C., Ind. Eng. Chem. *23,* 881-7 (1931).
44. Elm, A. C., and Standen, G. W., Ibid *24,* 1044-5 (1932).
45. Eloed, E., and Mach, V., Kolloid Z. *75,* 338- (1937).
46. Fahrion, W., Z. Angew. Chem. *16,* 665-80, 697-704 (1903); *22,* 2083-97 (1909); *23, 722-6* (1910).
47. Faucett, P. H., Drugs Oils Paints *54,* 13-14 (1939); C.A. *33,* 1970^6.
48. Faucett, P. H., Paint Oil Chem. Rev. *101,* No. 12, 9-11, No. 14, 7-10, 30, 32, 37, No. 16, 9-10, 12, 31-2, No. 18, 5-10 (1939).
49. Franke, W. and Jerchel, D., Liebig's Ann. Chem. *533,* 46-71 (1938).
50. Glimm, E., Fette u. Seifen *46,* 348-50 (1939).
51. Goldschmidt, S. and Freudenberg, K., Berichte *67,* 1589-94 (1934).
52. Hamilton, L. A., and Olcott, H. S., Ind. Eng. Chem. *29,* 217-23 (1937).
53. Hilditch, T. P., J. Oil a. Colour Chem. Ass'n. *13,* 209-19 (1930).
54. Hyman, J., and Greenfield, T., Ind. Eng. Chem. *28,* 238-41 (1936).
55. Kappelmeier, C. P. A., Chem. Weekblad *28,* 174-83 (1931); C.A. *25,* 3182^1.
56. Kaufmann, H. P. and Fiedler, H., Fette u. Seifen *46,* 569-72 (1939).
57. Kienle, Ind., Eng. Chem. *22,* 590 (1930).
58. Knowles, G., Lawson, J. C., and McQuillien, T., J. Oil a. Colour Chem. Ass'n *23,* 4-7 (1940).
59. *Laurie, A. P., Trans. Far. Soc. 33, 293-9 (1937).*
60. Lehrer, Farbe u. Lack 1937, 293.
61. Long, J. S., Am. Paint J. *14,* No. 10, 60ff (1929); Paint, Oil a. Chem. Rev. *89,* No. 1, 8ff. (1930).
62. Long, J. S., and Chataway, H. D., Ind. Eng. Chem. *23,* 53-7 (1931).
63. Long, J. S., and McCarter, W. S., Ibid. *23,* 786 ff (1931).
64. Long, J. S., Rheineck, A. E., and Ball, G. L., Ibid. *25,* 1086-91 (1933).
65. Marling, P. E., Can. Chem. Met. *11,* 63-6 (1927).
66. Marcusson, Angew. Chem. *38,* 148 (1925).
67. Mellan, I., Nat'l Paint Bull. 1, 12-13 (August, 1937); 8-9 (Sept., 1937).
68. Merzbacher, S. [Fett] Chem. Umschau *35,* 173-6 (1928).
69. Merzbacher, S., Ibid. *36,* 339-42 (1929).
70. *Morrell, R. S., J. Oil a. Colour Chem. Ass'n. 10, 278-89 (1927).*
71. Morrell, R. S., Chem. and Ind. *56,* 795-8 (1937).
72. Morrell, R. S., "Varnish Making," New York, 1940, Chem. Pub. Co., p. 141.
73. Morrell, R. S., and Davis, W. R., Trans. Faraday Soc. *32,* 209-19 (1936).
74. Morrell, R. S., and Davis, W. R., J. Soc. Chem. Ind. *55, 237*-46T, *261*-5T *(1936).*
75. Morrell, R. S., and Marks, S., J. Oil A. Color Chem. Ass'n. *12,* 183-205 (1929).
76. Morrell, R. S., and Marks, S., Paint Manuf. *3,* 10-13, 21-2 (1933).
77. Morrell, R. S., and Marks, S., and Samuels, H., Soc. Chem. Ind. *52,* 130-2T (1933).
78. Morrell, R. S., and Phillips, E. O., Ibid. *57,* 245-7 (1938).
79. Morrell, R. S., and Phillips, E. O., Ibid. *58,* 159-62 (1939).
80. Morrell, R. S., and Phillips, E. O., Fette u. Seifen *46,* 541-6 (in English) 546-51 (in German) (1939).
81. Morrell, R. S., and Wood, H. R., "The Chemistry of Drying Oils," London, 1925, Ernest Bem Lim., p. 84-111.
82. Nicholson, D. G., and Holley, C. E., Jr., Ind. Eng. Chem. *30,* 114-6 (1938).
83. Ockrent, C., Paper presented at Oil a. Color Chem. Ass'n conference, Harrogate, 1939.
84. Orloff, J., Russ. Phys. Chem. Soc. *42,* 658 (1910).
85. Payne, H. F., Ind. Eng. Chem. *32, 737-43* (1940).
86. Petrov, G., Kasterina, T., Masloboino Zhirovoe Delo 1931, No. 10, 30-7; C.A. *26,* 4484^3.
87. Popkov, S., Org. Chem. Ind. (U.S.S.R.) *5, 27-33* (1938); C.A. *32,* 6130^6.
88. Rheineck, A. E., Paint, Oil. a. Chem. Rev. *99,* No. 5, 9-12 (1937).
89. Rhodes, F. H., and Ling, T. T., Ind. Eng. Chem. *17,* 508 ff (1925).
90. Rinse, J., and Wiebols, W. H. G., Ibid. *29,* 1149-54 (1937).
91. Rogers, Wm., Jr., and Taylor, H. S., J. Phys. Chem. *30,* 1334-47 (1926).
92. Scheiber, J., Farbe u. Lack *32, 75-6,* 135-6 (1927).
93. Scheiber, J., Z. Angew, Chem. *40* 1279-85 (1927).
94. Scheiber, J., Farbe u. Lack *34, 477*-8 (1929).
95. Scheiber, J., Ibid. *34, 585-7* (1929).
96. Scheiber, J., Ibid. *35,* 51-3, 63-5 (1930).
97. Scheiber, J., Z. Angew. Chem. *46,* 643-58 (1933).
98. Scheifele, B., Farben-Ztg. *33,* 739-41 (1927).
99. Scheifele, B., Z. Angew. Chem. *42,* 787-90 (1929).
100. Scheifele, B. [Fett] Chem. Umschau *40,* 141-4 (1933).
101. Scheifele, B., Ibid. *43, 74* (1936).
102. Schmalfuss, H., and Werner, H., Kolloid-Z. *49, 323*-8 (1929).
103. Smit, W. C., Rec. Trav. Chim. *49,* 539-51 (1930); C.A. *24,* 4261.
104. Smit, W. C., Ibid. *49, 675-85* (1930); C.A. *24,* 4263.
105. Smit, W. C., Ibid. *49,* 686-90 (1930); C.A. *24,* 4261.
106. Smit, W. C., Ibid. *49,* 691-6 (1930); C.A. *24,* 4262.
107. Staudinger, Berichte *58B,* 1075-79 (1925); Annalen. *488,* (1931).
108. Stephens, H. N., Ind. Eng. Chem. *24, 918-20 (1932).*
109. Tatimori, M., Soc. Chem. Ind., Japan, J. Suppl. B. *39,* 395-6B (1936).
110. Taylor, R. S., and Smull, J. G., Ind. Eng. Chem. *28,* 193-5 (1936).
111. Thomas, C. A., and Marling, P. E., Ibid. *24,* 871-3 (1932).
112. Wagner, A. M., and Brier, J. C., Ibid. *23,* 40-9 (1931).
113. Wagner, A. M., and Brier, J. C., Ibid. *23,* 662-6 (1931).
114. von Mikusch, J. D., Ibid. *32, 1061-9 (1940).*
115. Werthan, S., Elm., A. C., and Wien, R. H., Ibid. *22, 772-6* (1930).
116. Williams R. J., "An Introduction to Organic Chemistry," New York, 1927, D. Van Nostrand Co., p. 168.