dry more rapidly and give films harder than those from the original oils. The same types of acids, such as β-furylacrylic or sorbic acid (*41*) when used as partial replacements for linseed acid in alkyd resins also gave harder films. The α,β-unsaturated acids have an active double bond which can react readily with conjugated dienes by a Diels-Alder type of reaction, and this may largely account for the rapid drying qualities of these oils. In the case of the alkyd resins, the presence of a portion of β-(2-furyl)-acrylic acid gave increased hardness and print resistance as compared with the corresponding alkyd containing a like proportion of sorbic acid. The fact that double bonds of the furyl group are conjugated with the other two double bonds in the molecule was regarded as the cause for these advantages.

Activation of isolated double bonds is usually desirable to promote the reaction with conjugated dienes. However, even ethylene has been found to react with dienes such as butadiene when heated at 200° C. and 200 to 400 atmospheres pressure for about 20 hours (*34*).

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Deterioration of Dried Oil Films

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Failure of a clear or pigmented oil film—that is, interruption or termination of its ability to perform its protective or decorative function, does not occur suddenly and without warning. In most practical cases, it is the final stage of a slow process of deterioration which passes through several more or less well defined intermediate stages before outwardly visible signs develop. The hypotheses advanced from time to time to explain the underlying reactions responsible for deterioration parallel the hypotheses of film formation. While oil film drying was explained on the basis of oxidation, oxidative decomposition was believed to be responsible for deterioration, and chemists searched diligently to unravel the composition of oxidized films and to discover the nature of the final oxidation products. With the advent of the colloid-chemical approach to oil drying, colloidal considerations predominated in explanations of deterioration. More recently high polymer chemistry has begun to influence the thinking and will probably point the way toward a more plausible explanation of oil film deterioration. According to high polymer chemistry, oil films consist of a three-dimensional network of polymer chains held together by primary linkages and terminated by certain characteristic end groups. The end groups and the bridge linkages are suspected of playing important roles in deterioration film.

THE ability of oil films, especially pigmented oil films, to resist deterioration is of the greatest technical importance. This resistance to deterioration, commonly termed durability, determines the length of time an oil or paint film performs its intended functions as a protective or decorative coating. It is difficult, if not impossible, to define the practical usefulness of oil films in general, since that definition must of necessity vary with the nature of the exposure as well as with the specific demands made by the particular user. It may be safe, however, to say that a coating has deteriorated to the point of failure when it is no

longer able to protect the substratum against decay or to satisfy the esthetic requirements of the user.

Considerable progress has been made during the last 20 or 30 years in improving the durability of coatings based on drying oils. Most of this progress, however, resulted from an empirical approach to the problems raised by the practical use of clear and pigmented drying oil films. The science of drying oil film deterioration continues to lag far behind. It is obvious to those familiar with this situation that a thorough understanding of the chemistry and mechanics of drying oil deterioration is essential to future progress toward more durable oil coatings. It is hoped that this review of the existing knowledge will not only stimulate the scientific study of this branch of drying oil chemistry but also will point the direction in which such a study might be undertaken profitably.

Failure, a Gradual Process of Deterioration

Ordinarily, failure of clear or pigmented oil films does not occur suddenly and without warning. In most practical cases, it is the end state of a slow process of deterioration which goes through several more or less well defined intermediate stages before complete failure becomes evident or outwardly visible. Such stages of deterioration in the case of protective coatings comprise the phenomena known as chalking, checking, cracking, blistering, peeling, flaking, etc., and in the case of decorative coatings hazing and other forms of loss of gloss, staining, yellowing, fading, wrinkling, blistering, softening, etc.

Some of these types of deterioration are definitely associated with specific pigmented systems and are not observed with clear or unpigmented oil films. By rights they belong in a discussion of pigments and will not be dealt with here. This discussion will strictly be limited to the deterioration of oil films. Moreover, within the scope of this symposium, the various outward manifestations of the deterioration of oil films are not of particular concern but interests are centered mainly in the chemical reactions responsible for such changes.

The hypotheses advanced from time to time to explain the underlying reactions responsible for deterioration parallel the hypotheses of drying or film formation. While the emphasis was on oxidation as the basis of oil drying or film formation, oxidative decomposition was believed to be responsible for the aging and deterioration of oil and oil paint films. With the advent of the colloid-chemical approach to oil drying, colloidal considerations predominated in explanations of oil film deterioration. The recent advances of high polymer chemistry have exerted their unmistakable influence on the hypotheses of film formation, and the hypotheses of film deterioration are bound to be affected fruitfully by modern concepts of the structure and properties of high polymeric organic compounds.

Era of Oxidation Theories

The first experimental investigations of the processes of film formation by Cloez (*3*) uncovered the fact that drying oil films, on exposure to the atmosphere, absorb oxygen and give off carbon dioxide and water. It was rather early in the development of the hypotheses of the autoxidation of drying oils that it was pointed out that drying and film decomposition are not two entirely separate reactions chronologically but occur side by side from the moment the first traces of oxygen have been absorbed. It was claimed that the rate of film decomposition was so much slower than the rate of film formation that it did not become a factor of importance until the film had been formed and aged for some time and the rate of film formation had decreased to a low value. Numerous attempts were made to unravel the complex reactions of oxidative decomposition by determining the chemical composition of aged drying oil films, and especially by identifying the compounds of relatively low molecular weight. Perhaps the most outstanding of these investigators were D'Ans and Merzbacher (*4*) who analyzed oxidized linseed oil and films several months old. In one experiment oil and oxygen were sealed into a round flask which was rotated to distribute the oil uniformly over the wall. Duplicate experiments were made with and without simultaneous exposure of the sample to sunlight. At the conclusion of the exposures the pressure in the flask, the composition of the atmosphere and of the oil were determined. The amount of carbon dioxide found was 1.9% in the absence and 10.25% in the presence of direct sunlight. The corresponding values for carbon monoxide were 0.36 and 1.06%, respectively. Additional gaseous products were given off when the oxidized oil was heated to 130° C. The total quantity of gaseous products obtained was 36% of the original oil. One mole of linseed oil had reacted with 21.5 moles of oxygen; of this, 9 moles appeared in the volatile carbon dioxide, carbon monoxide, water and low molecular weight acids, about 6 moles appeared in the water given off at 130° C., and the residue dried at 130° C. still contained about 6.5 moles. The volatile products obtained by heating the oxidized oil to 130° C. in a nitrogen atmosphere consisted of 12.3% water, 10.4% volatile acids calculated as formic acid, 1.5% carbon dioxide, and 0.8% aldehyde calculated as formaldehyde. Of the volatile acids 69.2% were formic acid. It was proved that the formic acid, as well as the other volatile acids, did not originate with the glycerol.

Somewhat more detailed information was obtained by Merzbacher in the analysis of a linseed oil film. The film was prepared by spreading linseed oil containing some manganese drier on glass plates, allowing it to dry under room conditions for a period of 3 weeks; scraping the dry film off the glass plates; and storing it in a closed glass vial for 9 months. This material was saponified with cold alcoholic potassium hydroxide solution. The acids were liberated after evaporation of the alcohol in vacuo. The film had the following composition:

	Per Cent
Ash	0.4
Moisture	9.0
Glycerol	9.0
Formic acid	1.0
Propionic acid	1.0
Caproic acid	0.3
Pelargonic acid	1.6
Azelaic acid	9.0
Saturated higher fatty acids	9.5
Unsaturated higher fatty acids (soluble in petroleum ether)	9.6
Water-insoluble oxidized acids	26.0
Water-soluble oxidized acids	8.0
Water-soluble organic material not identified	?.0
Loss (including CO_2)	12.6
Total	100.0

Some formic acid could be extracted from the film by leaching with water, and it is assumed that the formic acid was present in the film in the free state. The other acids, however, were probably liberated in the course of the analysis of the film especially during the saponification step. Therefore, it is not possible to draw any really reliable conclusions from these data, except perhaps that the decomposition of a linseed oil film in sunlight follows a different course than the decomposition in diffuse light or in the dark. This possibility has not received adequate consideration in past attempts to explain the chemistry of film deterioration; this fact probably contributed considerably to the confusion existing in this branch of drying oil chemistry. For the same reason, paint chemists have not been able to utilize the results of the rather extensive work that has been done by food chemists on the rancidity and spoilage of fats and oils. The paint chemist is interested in the deterioration of paint films whereas the food chemists are interested in the chemistry of the oxidative spoilage of oils and fats in bulk. The conditions of storage of the latter differ so markedly from the conditions of exposure to which paint films are subjected that it is not difficult to understand why there may be little if any connection between the two reaction mechanisms. It would seem advisable, therefore, not to complicate an already complex problem by trying to

develop an explanation or theory which will satisfy the observations made under widely differing conditions.

Era of Colloid-Chemical Theories

With the advent of the colloid-chemical viewpoint of drying and film formation, attempts were made to explain film deterioration on the basis of colloid-chemical concepts (*1*, *6*, *15*, *17*). The dry oil film was assumed to be a gel subject on aging to shrinkage and syneresis. While shrinkage might serve as the underlying colloidal reaction responsible for such film failures as chalking, checking, and cracking observed during exterior exposure, syneresis was believed to be responsible for the softening and reliquification of oil films stored in complete darkness in closed containers or under conditions preventing free access of air.

The colloid-chemical theories of film deterioration, however, were not satisfying largely because they failed to furnish a readily understandable picture of the chemical reactions which were believed to be the cause of the phenomena in question and because they failed to give the paint formulator any real clues as to how to improve the durability of his products. Nevertheless, the colloid chemists who advanced and developed these theories deserve considerable credit for having called the attention of the paint chemists to the fact that the chemistry of large molecules may differ materially from that of small molecules and that the concepts of classical chemistry must be modified in many essential respects if they are to serve as a basis for the explanation of the phenomena observed in the field of films.

Era of High Polymer Chemistry

When paint chemists began to realize that neither the old oxidation nor the colloidal theories would provide an entirely satisfactory basis for the explanation of the phenomena of film formation, workers in the field of synthetic resins and plastics had succeeded in developing highly useful concepts and working hypotheses: the concepts of functionality, and condensation and addition polymerization. There is now little doubt that a logical application of the theoretical concepts of the formation and properties of high polymeric compounds to the problems of oil film formation will contribute materially to their solution. It is easily understandable also that this newly developed branch of chemistry will exert a beneficial influence on the hypotheses to be advanced in an effort to explain the chemistry and mechanism of film deterioration.

The composition of drying oils and their structure before drying is known quite accurately, but the structure of the film is not known with equal certainty. Nevertheless several general principles appear to be well enough established to serve as guide posts.

High polymer chemistry has taught that a film which is insoluble and infusible must consist of a polymer comprising a cross-linked network of monomer units held together by primary linkages. Since drying oil films are insoluble and infusible within the limits of this specification, it must be assumed that they consist of such a network structure. It is known that this structure is not present in the liquid oil before drying and therefore it must be formed during the drying process. Assume that an oil film—that is, a linseed oil film, for instance—consists of a three-dimensional network of glyceride molecules held together by C—C, C—O—C, and C—OO—C linkages. Whether the bridge carbons are those associated with the double linkage systems of the original drying oil or with the methylene groups between or adjacent to these double linkage systems does not matter as far as this discussion is concerned. They differ only in that the bridge linkages are in conjugation with double linkages in one case while in the other case they are not.

INFLUENCE OF END GROUPS

Recent drying oil research indicates that the drying process consists of chain reactions initiated by the addition of oxygen to an active center of the drying oil molecule. The activated molecules join together to yield the three-dimensional network previously referred to.

High polymer chemistry has taught that in polymerizations of the chain reaction type, the reaction chains are broken sooner or later by the conversion to relatively nonreactive end groups of the reaction centers directly responsible for the bridges between the monomer units. Such chain termination reactions may involve: the addition of a proton to the active center; the addition of other ions originating with the catalyst or impurities; or a molecular rearrangement. The end groups thus created exert an important influence on the properties of the polymer when they are relatively plentiful—that is, when the degree of polymerization is relatively low. Their concentration and hence their influence decreases as the degree of polymerization increases.

The end groups present in drying oil films are derived from the active groups formed by the addition of oxygen to the oil molecule in the course of the reaction chains leading to film formation. Since the active groups present during the drying process appear to be of a peroxidic nature it seems reasonable to assume that the more important end groups present in the final film derive from these peroxides. Therefore, it is logical to suppose that the predominant end groups in an oil film are the hydroperoxide (—C—OO—H), the hydroxyl (—C—OH), and the keto (=C=O) groups.

Hydroxy and keto end groups are relatively stable and under the conditions under consideration would hardly be subject to change. Therefore, they are not expected to exert a significant direct influence on the durability of the structure represented by the oil or paint film. However, if their concentration is high enough they may exert a definite influence on the mechanical properties of the film and in this way indirectly affect its durability.

Hydroxyl groups impart to the film a definite affinity for water. For example, while stearic acid is insoluble in water, tetrahydroxystearic acid is soluble in hot water and may be crystallized from this solvent. In other words, if in an organic molecule the ratio of hydroxy groups to carbon atoms becomes high enough, water solubility is imparted. Although it is not likely that the concentration of hydroxy end groups in an oil or paint film formed under normal conditions is great enough to make it water soluble, it is to be anticipated that conditions which favor the formation of hydroxy end groups during the film formation stage will yield a film of impaired water resistance properties. Such films, when exposed to high humidity or immersed in water may exhibit lowered resistance to blistering and swelling and may fail sooner and perhaps in a different manner than corresponding films formed under more normal drying conditions.

Keto end groups, like the hydroxyl end groups, would not exert a direct influence on the film integrity although if present in a sufficiently high concentration, they may significantly alter the properties of the film. An accumulation of keto groups might soften the film and reduce its solvent resistance. These effects, however, will be of minor importance as compared with the possible effect of accumulated keto groups on yellowing.

Ketones are susceptible to autoxidation. Acetone, for example, forms the dimeric or trimeric acetone peroxide (*2*, *9*) which, like other peroxides, are highly reactive and may readily enter into polymerization or decomposition reactions. The properties of these peroxides are extremely difficult to determine because of their great instability, and because not much is known concerning their mode of decomposition and the nature of the fragments formed. It seems plausible, however, to assume that any ketones formed during the autoxidation of drying oils would be capable of undergoing further autoxidation similar to that of simpler ketones and in this manner would open the attack of atmospheric oxygen on dry oil films; this eventually would lead to oxidative decomposition and disintegration.

The third type of end groups mentioned, the hydroperoxide

groups, may affect the film properties to the extent to which they are converted to hydroxyl or keto groups.

$$>CH—OOH \xrightarrow{-O} >CH.OH$$

$$>CH—OOH \xrightarrow{-H_2O} >C=O$$

The conversion of a hydroperoxide group to a hydroxyl group may be the result of the reaction of the hydroperoxide with an oxidizable substance whereas the conversion of the peroxide to the ketocompound results from a dehydration of the peroxide. To what extent these two reactions take place in a film and under what conditions is still a guess. Experimental data on which an estimate might be based are lacking although some investigators have uncovered evidence that hydroxyl and keto groups are present in oil films.

Even allowing that the influence of the end groups on the properties of oil and paint films is greater than it would seem, any reaction they might undergo could hardly be expected to cause ruptures in the primary bonds responsible for the network structure of a film. Therefore, it seems logical to assume that end group reactions do not result in the disruption of the film and do not contribute significantly to its disintegration. An explanation for this phenomenon, therefore, must be sought in changes in other functional groups of the polymer molecule.

INFLUENCE OF BRIDGE LINKAGE

The single carbon-carbon and carbon-hydrogen linkages may be eliminated from consideration. They are the same as those existing in such durable materials as paraffin wax, etc. Experience and experiments have shown also that the ester linkages are retained intact under normal service conditions. Their susceptibility to saponification contributes materially to the lack of alkali resistance of oil films. Their influence on moisture resistance, however, has been greatly overemphasized. Some evidence obtained in the course of researches conducted in the laboratories of the New Jersey Zinc Company during recent years indicates that the ester linkage is not subject to hydrolysis under conditions of normal indoor or outdoor exposure, not even during prolonged immersion in fresh or salt water. The conclusion is that it contributes significantly less to the lack of moisture resistance of oil films than do other oxygen containing groups formed in the course of normal or abnormal autoxidation reactions.

Residual Double Linkages. The residual double linkage, like the double linkage in the original oil, is subject to oxidation; either it adds oxygen itself or it promotes the peroxidation of adjacent methylene groups. These reactions are merely a continuation of the first stages of the drying process. They may lead to further cross linking of the structural units; thus they cause further densification of the film with its consequent increase in hardness and brittleness. This then may reduce the elasticity and distensibility of the film matrix to such a degree that it is no longer able to withstand the expansion and contraction which the substrate undergoes as a result of normal fluctuations of temperature and humidity. Thus the film may become subject to mechanical destruction as the result of the normal chemical reactions which are responsible for drying and do not stop abruptly after the film has been formed and has reached its optimum of mechanical stability.

If these reactions continued at the rate at which they started during the drying stage, the life of an oil film would be short indeed. There are two factors, however, which greatly reduce the rate of oxidation during the stages following film formation and may even and probably do alter its course. The rate of continued oxidation is dependent on the rate with which oxygen from the atmosphere is able to get to the active centers in the oil molecules comprising the film. This in turn depends on the solubility of oxygen in the film substance and its diffusion through it. There are no experimental data which would permit making an estimate of the solubility of oxygen in an oxidized oil film—whether it is greater or smaller than the oxygen solubility in the unoxidized drying oil. However, the rate of diffusion of oxygen through the film is probably appreciably smaller than its rate of diffusion through the unoxidized oil. Added to this retarding effect is the second factor—namely, the mobility of the oil molecule in the film. There seems to be little doubt that this is greatly reduced as compared with the mobility of the oil molecule in the drying oil before it has set to a solid film. Both of these factors combine to greatly reduce the rate of oxidation of unsaturated centers in the oil film after it has reached what is generally known as the dry point.

The reduced mobility of oil molecules in the dry film also exerts a retarding influence on further polymerization. It is obvious that two activated monomer or polymer units must be brought into the proper relative position before they can combine to form a new polymer and, all other factors being equal, the rate of polymerization is controlled by the mobility of the activated oil molecules. Since the chances for the activated molecules to enter into polymerization reactions are so greatly reduced after the film has solidified, it is likely that the peroxidic groups which characterize the activated oil molecules will be available for other reactions.

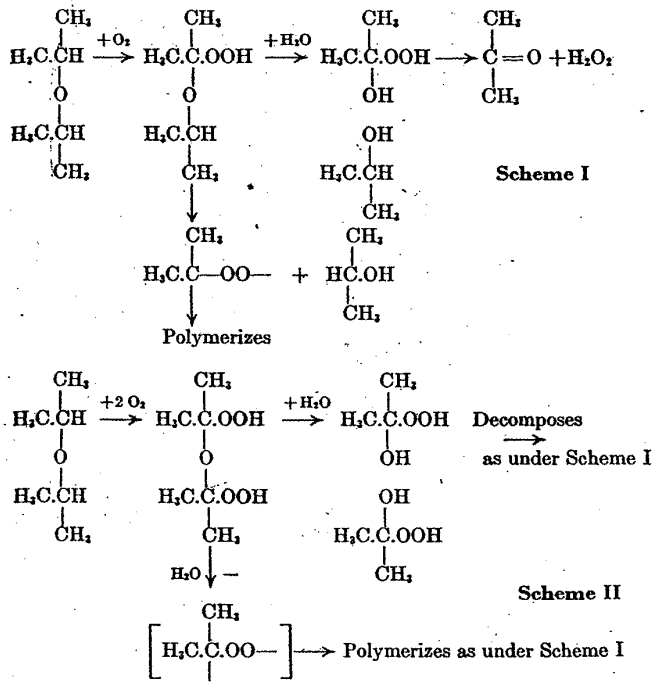
Two of these possible reactions already have been discussed. Both of these reactions presuppose that the activated molecule possesses a hydroperoxide structure. Although much has been written against it, the four-membered ring structure of the peroxide cannot be ignored in this discussion. Even though it may not be correct in all details, it does serve excellently to illustrate a possible reaction mechanism which might result in the formation of some compounds whose presence in dry oil films has been reported by several investigators. The reaction referred to is as follows:

$$\begin{matrix} R—CH—O \\ | \\ R—CH—O \end{matrix} \longrightarrow \begin{matrix} R—CH=O \\ | \\ R—CH=O \end{matrix}$$

This reaction leads to the rupture of the oil molecule at the place of the original double linkage and yields two molecules of aldehyde. It takes on considerable importance owing to the fact that it causes the rupture of a bond within the network structure of the film; this rupture results in the division of a polymer molecule into two parts. Thus, in contrast with the first two reactions this third reaction contributes directly to the disintegration of the film. That this reaction is possible is suggested by the fact that aldehydic decomposition products have been detected in aged oil films by several investigators. The exact mechanism of this reaction, however, and the conditions under which it can and does take place have not been established.

Bridge Ether Linkage (CH—O—CH). That ethers are subject to autoxidation has been known for many years. The autoxidation products of ethers are peroxides, but little is known about their exact structure and their mode of decomposition. The ethers that conceivably could occur in dry oil films are of the secondary dialkyl type; the simplest representative is diisopropyl ether. According to Rieche and Koch (*13*) diisopropyl ether may absorb 1 or 2 moles of oxygen and form the mono- or dihydroperoxide. These peroxides may decompose according to schemes I and II.

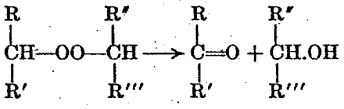
If ethers present in dry oil films entered into similar reaction schemes, the major products would be ketones, hydrogen peroxide, and polymeric peroxides. The amount of hydroxy compounds formed would be relatively small since, according to Rieche and Koch, scheme II predominates. The formation of the polymeric peroxides would result in an increase in the number of cross linkages and hence in the hardness and brittleness of the film. It could conceivably continue to a point wher the film would no longer possess the necessary distensibility an



would lose its ability to withstand normal stresses and strains. The effect of the ketones on the film properties has been discussed already. The formation of hydrogen peroxide in this series of reactions is of interest as it has been reported (*16*) that drying oil films give off hydrogen peroxide under certain conditions of exposure, and a plausible explanation for its formation has not been offered heretofore.

According to Milas (*10*) the rate with which molecular oxygen combines with ethers seems to be influenced largely by the nature of the groups to which the ether oxygen is attached. Aromatic groups impart a rather high stability whereas aliphatic groups, especially when the two groups are unlike, impart to it a high instability towards molecular oxygen. With the majority of ethers studied, the total peroxide formed increased, for long periods of time, proportionately with the time of ultraviolet light exposure. These observations seem to support the assumption that autoxidation of the bridge ether linkages might be an important factor in the oxidative decomposition of drying oil films. In any case these reactions would lead to a rupture of structurally important linkages and thus contribute to the disintegration of the oil film network.

Peroxide Bridge Linkage. The peroxidic bridge linkage also has not been studied sufficiently to permit us to advance any reasonably plausible hypotheses. The experiences gained with normal dialkyl peroxides are hardly applicable in this case because the susceptibility to further autoxidation and molecular rearrangement in branched dialkyl peroxides no doubt differs in essential respects from that of normal dialkyl peroxides. However, there might be a tendency to break the O—O bond. This again would lead to the formation of ketonic and alcoholic decomposition products:



This reaction would also result in the rupture of network bonds and therefore could well be a contributing factor in film disintegration.

Thus it is seen that regardless of the scission reaction involved the fragmentary end products are aldehydes (and perhaps their oxidation products, acids), ketones, and hydroxyl compounds. The effect of the scission on the mechanical properties of a film varies greatly with the point of scission in the molecule. When the polymer bridge connects two near—that is, with respect to the ester linkage—active centers, the remaining points of oxidative attack are outside of that part of the fatty acid chain which is between the ester linkage and the polymer bridge. This then means that any scission will cut off a relatively short-chain appendix without very seriously reducing the size and weight of the main polymer body. On the other hand, when the polymer bridge connects two remote—with respect to the ester linkage—centers of activity and scission takes place at a near center of activity the size and weight of the polymer unit and hence the mechanical properties of the film may be affected materially. It may be well to keep these considerations in mind when formulating a chemical explanation for any observed deterioration phenomena.

These scission reactions might feasibly take place under exposure to sunlight. This guess is based not on any experimental evidence or specific scientific knowledge but merely on the fact that the phenomena of film deterioration observed under prolonged exposure to sunlight might be expected to result from scission reactions. Since indoor exposure, especially in the dark, usually leads to a reversion of the film to a tacky state accompanied by yellow and orange discoloration, it appears reasonable to assume a different set of chemical reactions for these phenomena.

YELLOWING

One of the more important phenomena of oil film deterioration is yellowing which, because of its practical importance, has received considerable attention from paint chemists.

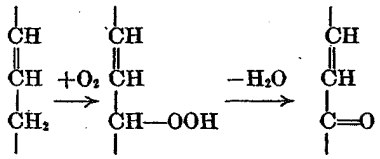
Yellowing occurs when a clear or pigmented oil film is exposed to the atmosphere either in diffuse daylight or in total darkness. It is accelerated and perhaps intensified by high temperatures and humidity. A yellowed oil film frequently may be bleached by exposure to a strong light source especially to ultraviolet light. There is little doubt that the yellowing is due to the formation of yellow or orange-colored bodies in the film matrix. Yellowing increases as the degree of unsaturation in a drying oil increases. Opinions are still divided as to the effect of conjugation on yellowing.

The yellowing of oil films has been ascribed to the formation of chromophoric groups by the oxidation or rearrangement of oxidized oil molecules. There is considerable difference of opinion as regards the structure of these chromophoric groups. While Eibner (*5*) and his pupils are inclined to accept ketohydroxy compounds as the cause of yellowing, Scheiber (*14*) and Nauroy (*12*) ascribe it to the presence of di- and triketones. Although di- and triketones are pale yellow, their color intensity is so low that it is doubtful that they constitute the major coloring factor. More recently Morrell and Marks (*11*) came to the conclusion that yellowing is caused by the keto-enol tautomerism of keto hydroxy compounds formed from the oil peroxides by simple intramolecular rearrangement. This viewpoint, however, was criticized by Elm and Standen (*7*) who showed that ketohydroxy derivatives of fatty acids are not visibly colored.

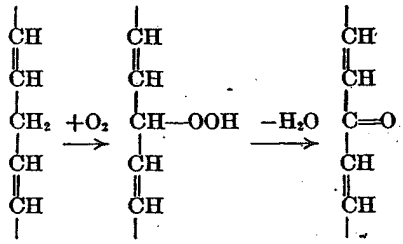
After an interruption of several years, work on the yellowing oil films has been resumed from the following viewpoint. As previously pointed out, a relatively large number of double linkages is left intact in a drying oil film after it has dried and solidified. These residual double linkages either are subject to oxidation themselves or could induce oxidation of neighboring groups. If Farmer's proposal (*8*) that autoxidation occurs at methylene groups adjacent to or between double linkages with the forma-

of hydroperoxides is accepted, there would be little difficulty in postulating a series of reactions which might produce the phenomenon under discussion.

The hydroperoxides might dehydrate to keto groups and the following structural units would result:



The particular keto olefin pictured in this example might result from the autoxidation of oleic acid or its esters. This grouping is not visibly colored, although it possesses a fairly well defined absorption band in the ultraviolet region (at 2220 Å.). When a linoleic acid radical undergoes the same series of reactions a compound possessing an absorption band in the blue region of the spectrum and therefore exhibiting visible yellow color results:



A related compound, phoron $(CH_3)_2C{=}CH.CO.CH{=}C(CH_3)_2$, is yellow. A still deeper yellow to orange color would be produced from linolenic acid or its esters; this could yield the following chromophore: —CH=CH—CO—CH=CH—CO—CH=CH—.

Compounds containing these chromophores are being prepared and their absorption characteristics will be studied.

A set of reactions of this sort could explain the observation that the tendency of oil films to yellow increases as their degree of unsaturation increases. It also would contribute materially to an explanation for the observation that a film which yellows badly usually possesses good gloss retention and *vice versa*, or that conditions which are conducive to yellowing seldom cause serious loss of gloss or extensive film disintegration. The reactions described to explain yellowing do not attack the bonds responsible for linking the monomer units together in the polymer structure and therefore do not tend to destroy film continuity. The other reactions previously described which cause film disintegration and chalking tend to break up the film and hence interfere with the proper specular reflection of light.

It is not implied here that these really are the reactions responsible for the specific deterioration phenomena discussed, but merely that they could be. No doubt it has become obvious by now that knowledge of the deterioration reactions is less complete than knowledge of film formation. Much of the literature on film deterioration is pure conjecture and frequently wild speculation. The only solution to this rather difficult and highly complex problem lies in painstaking experimental research with simple model compounds embodying the structural factors believed to be essential. Work of this sort has been undertaken recently by several investigators. This work is aimed at establishing the structure and properties of the peroxides formed in the course of the autoxidation and film formation of drying oils. There is no obvious reason why the results of these and similar researches should not be applied to the problem of film deterioration. If this discussion has accomplished no more than to emphasize that experimental work is absolutely necessary for progress in this field and to point out a possible line of approach, it will have served its purpose.

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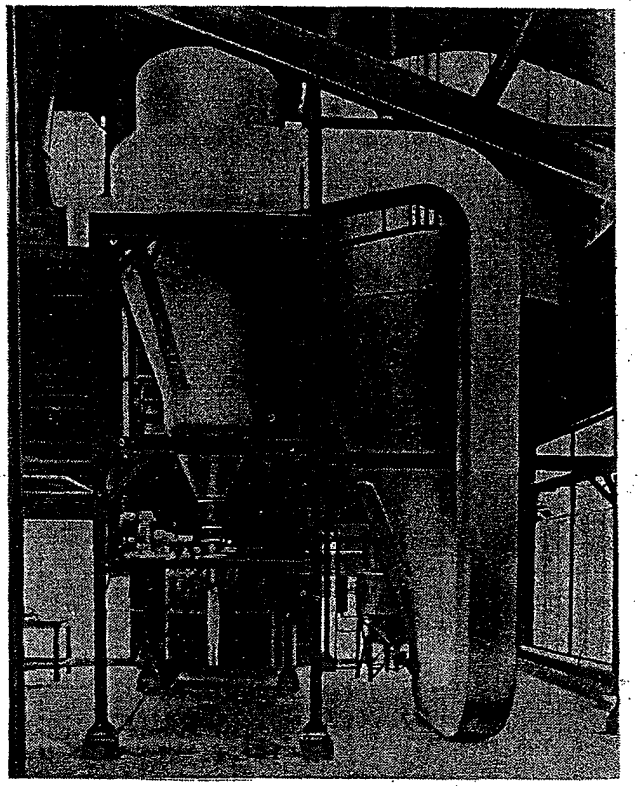

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(End of Symposium)