

Yellowing of Oil Films^{1,2}

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Results of studies of the effects of various factors on film yellowing, the mechanism of yellowing, its inhibition, and isolation and characterization of the yellow constituents are reported.

Yellowing appears to be a side reaction unrelated to the drying process, but colorless precursors of the yellow compounds are formed as a result of an oxidative process.

The formation of the yellow compound was postulated as taking place by the interreaction of the colorless precursors in some type of condensation. Low-molecular-weight aldehydes prevented yellowing, possibly by acting as substitutes for some reactant in the condensation reaction.

ALTHOUGH THE PROBLEM of yellowing in dried films of linseed and other drying oils is very important from a practical standpoint, relatively little is known about the chemical nature of the problem. Studies by Johnston and Fitzgerald (4,5) and Hess and O'Hare (3) showed that the higher unsaturated fatty acids are the main starting materials in the phenomenon. The formation of compounds containing carbonyl structures is generally believed to be involved in yellowing although Johnston and Fitzgerald (4,5) suggest that polyunsaturated, conjugated structures formed by aldehyde condensation also may be involved.

The association of yellowing with carbonyl structures was based mainly on the observation that appreciable amounts of carbonyl, particularly 1,2-diketones, are formed in the oxidation of films of drying oils (9) and that many compounds which contain carbonyl structures, such as $R(CH=CH)_4COCOOH$, are highly colored (2). It has been suggested (4) that possibly compounds of this type are, in fact, the major source of yellow color in drying oil films.

From the studies of ultraviolet absorption spectra of oxidized films (8) McAdie and Nicholls concluded that compounds containing benzoquinone structures were formed during the oxidation of films of pure esters of linoleic and linolenic acids through cyclization of some such structure as a conjugated ethenoid diketone. Since compounds of this type also are highly colored, the formation of quinonoid structures was suggested by these investigators as being responsible for yellowing.

The present investigation of yellowing involved several phases, including studies of some aspects of mechanism, inhibition of yellowing, isolation of the yellow compounds, and factors affecting the yellowing reactions.

Materials

Methyl Linolenate Concentrate. Linseed oil was interesterified with methanol and, after removing the catalyst and other water-soluble material, the esters were dried and vacuum-distilled to give a colorless product. The methyl linolenate then was concentrated to 86% by urea fractionation (15). Iodine value (Wijs) of the preparation was 240.

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Methyl Linolenate. This was obtained from purified hexabromostearic acid (m.p. 185.2), prepared from linseed oil acids; iodine value 259.4 (theory 260.4).

Methyl Linoleate. It was prepared by a combination of urea fractionation and low-temperature fractional crystallization of safflower seed acids, followed by fractional distillation of the methyl esters; iodine value 173.0 (theory 172.4).

Linolenyl Alcohol. This was prepared from methyl linolenate by reduction with lithium aluminum hydride according to the method of Lighthelm *et al.* (7); iodine value 288.0 (theory 288.0).

Octadecatriene. It was prepared from linolenyl alcohol, following the procedure used by Deatherage *et al.* (1) for the preparation of octadecene from oleyl alcohol. The final product had an iodine value of 300.0 (theory 306.5).

Pentaerythritol Tetralinolenate. This was prepared by transesterification of methyl linolenate and pentaerythritol tetraacetate, using sodium methoxide as the catalyst. Purification was effected by continuous extraction of Skellysolve F solution with ethanol. Only minor amounts of impurities could be detected in this preparation by silicic acid chromatography.

Linseed Oil Methyl Esters. Linseed oil was interesterified with methanol, using sodium methoxide as a catalyst. The crude methyl esters were extracted into petroleum ether and washed with distilled water until neutral, dried over sodium sulphate, filtered, and distilled under high vacuum. The final product was colorless and had an iodine value of 185.0.

Methyl cis-9,trans-11-Linoleate. It was prepared from dehydrated castor oil. The castor oil was dehydrated under vacuum by using 2% $KHSO_4$ as a catalyst. The dehydrated oil was interesterified with methanol and distilled through a Podbielniak Hyper-Cal column at 1 mm. of pressure. A concentrate of methyl cis-9,trans-11-linoleate was separated. Purification of this fraction was effected by low temperature crystallization from acetone. The final product had the following characteristics: iodine value (hydrogenation) 174.0; n_{D}^{30} , 1.4704; specific extinction coefficient (k_{233}) 92.1.

Methyl Docosaheptaenoate Concentrate. This material was obtained from tuna oil (12). It was colorless, had an iodine value of 432, and was 90% pure by gas-liquid chromatographic analysis.

Methods

Peroxide Value. This was determined iodimetrically at 35°C., with the reactants protected from oxygen by an atmosphere of nitrogen (10).

Infrared Spectra. These were determined with a Perkin-Elmer model 21 double-beam spectrophotometer, using liquid film, mulls in mineral oil or hexachlorobutadiene or 10% solution of the sample in carbon disulphide or carbon tetrachloride, depending on the nature of the sample and the region of the spectrum being measured.

Ultraviolet Spectra. These were determined with

a Beckman DU model spectrophotometer, using 95% ethanol as the solvent.

Aldehyde. It was determined by the Schiff reaction, using rosaniline hydrochloride (14). The general procedure was similar to one used for the determination of acetaldehyde (13) except that the sample was dissolved in acetone and adjusted to volume such that a 1-cc. aliquot contained 0.01–0.03 milliequivalents of the aldehyde. This aliquot was mixed with 2 ml. of the reagent and allowed to stand for 30 min. at room temperature. The mixture then was diluted to a volume of 10 ml. with acetone containing 10% of a 4% aqueous HCl solution, and its absorptivity at 551 $m\mu$ was determined in a Bausch and Lomb Spectronic 20 colorimeter. Pelargonyl aldehyde was used for the preparation of the standard curve and, over the range of concentrations employed, conformed to Beer's law.

Film Preparation. This involved the use of filter paper as substrate. The sample was placed by drops on the center of the paper. The amount of sample and the size of the filter paper were varied somewhat, depending on the nature of the experiment. Usually about 3 mg. of oil/cm.² were used.

Experimental

Effect of Various Factors on Yellowing. Johnston and Fitzgerald (5) showed that the amount and type of unsaturation, also illumination, exerted pronounced effects on the rate of yellowing. They also found that simple glyceryl esters yellowed more than alkyds. The effect of certain factors in our study is shown in the results of yellowing tests (11) summarized in Table I.

TABLE I
The Effect of Various Factors on Rate of Yellowing
[Yellowing Test at 50°C. (11)]

Sample	Time of onset
	<i>hrs.</i>
Octadecatriene.....	40
Linolenyl alcohol.....	16
Methyl linoleate.....	70
Methyl linolenate.....	30
Methyl docosahexaenoate.....	6
Pentaerythritol tetralinolenate.....	15
<i>cis-9-trans-11</i> Methyl linolenate.....	105
Methyl esters of linseed oil (I. V. 185).....	68
+ about 0.5% copper-stearate.....	35
+ about 0.5% linolenate peroxide.....	35
+ NH ₃	10
Methyl linolenate + butyraldehyde*	+30 days

* Test conducted at 25°C.

The markedly different rates for methyl linoleate, linolenate, and docosahexaenoate demonstrated the pronounced effect of unsaturation. The type of unsaturation also is a factor, as seen in comparing the results with methyl linoleate and methyl *cis-9,trans-11*-octadecadienoate. There appears also to be some difference between octadecatriene and methyl linolenate.

In general, compounds that catalyze oxidation also accelerate yellowing. This was demonstrated by the effect of copper stearate and linolenate peroxides.

Although yellowing occurs rapidly in the presence of vapors of amines and ammonia, this is believed to be caused primarily by the formation of colored adducts by reaction of these compounds with various components, probably carbonyl compounds, formed during the oxidation of the film. Support for this view was provided by the following experiment. Several films of linseed methyl esters, aged under non-

yellowing conditions until they were highly oxidized, were yellowed by exposure to aniline for about 3 hrs. at room temperature. Then the films were dissolved in ethyl ether and extracted with distilled water until all the free aniline was removed. Infrared spectral analysis of the recovered material showed that some aniline had combined chemically with the film.

Prevention of Yellowing. The yellowing tests (Table I) also showed that butyraldehyde retarded yellowing of linseed oil methyl esters exposed at room temperature. This inhibition was first discovered when it was observed that films of linseed methyl esters did not yellow when they were allowed to age in a desiccator. After investigating such factors as agitation of the atmosphere above the sample, oxygen supply, humidity, and illumination with ultraviolet light, none of which induced yellowing under these conditions, it was concluded that volatile products formed during oxidation of the film were responsible for the prevention of yellowing.

In order to learn more of the nature of the inhibition of yellowing, tests were made on the effect of the addition to films of a large number of model compounds similar to those that might be found among the products of the oxidation of drying oils, such as various esters, acids, ketones, hydrocarbons, and aldehydes. The only products which seemed to inhibit yellowing were the low molecular-weight aldehydes, but these could not be tested satisfactorily by simply adding them to the films because they were too volatile. Therefore a special test was devised to demonstrate the inhibitory action of these compounds. This test was based on the observation that yellowing was induced in a relatively short time in films aged under nonyellowing conditions (*i.e.*, in a closed system) by heating them *in vacuo* or in an atmosphere of nitrogen at 50°C. Details of the test are as follows.

About 0.1 ml. of aldehyde is placed in a 200-ml. round-bottom flask with a filter paper film aged under nonyellowing conditions. The flask is alternately filled with nitrogen and evacuated to remove atmospheric oxygen. Finally it is sealed under a slightly reduced pressure of nitrogen and placed in an oven at 50°C. A control sample (without aldehyde) is prepared in the same manner. Whether or not the yellowing is significantly inhibited is determined qualitatively by visual observation, or quantitatively by spectrophotometry (11).

The curves in Figure 1 are representative results given by the test. The height of the plateau in the curve measures the extent of yellowing and is dependent on the quantity of intermediates that have formed, which in turn are related to the age of the film. The amount of yellowing in the film containing hexaldehyde (Figure 1) is scarcely detectable by the naked eye.

Since the amount of yellowing under the conditions of this test reaches a plateau, an inhibition of yellowing may be observed readily by visual means. Thus inhibition was usually determined by visual comparison after allowing the test to continue until the plateau stage was reached in the control film.

In qualitative tests it was found that the low-molecular-weight aliphatic aldehydes such as propionaldehyde, butyraldehyde, hexaldehyde, and heptaldehyde prevented yellowing. Pelargonyl aldehyde was only slightly effective, and compounds such as chloral, benzaldehyde, and *p*-nitrobenzaldehyde, which con-

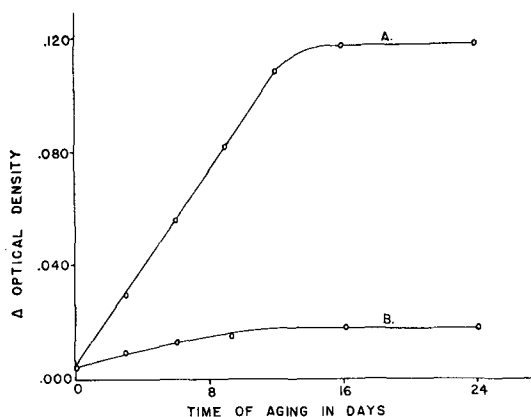


Fig. 1. Prevention of yellowing in aged nonyellowed films of methyl linolenate. A. Control film. B. Control film + hexaldehyde.

tain highly reactive aldehyde groups but no adjacent methylene group, were ineffective in preventing yellowing. Butyric acid was also ineffective.

Chemical and Spectral Changes in Films. In order to gain a further insight into the yellowing phenomenon, a study was made of the physical and chemical changes in films aged under open (yellowing) and enclosed (nonyellowing) atmospheres. Figure 2 compares the formation of peroxides and the nonvolatile aldehyde in films of linseed oil methyl esters aged under these conditions. More volatile aldehydes were believed to be more or less completely removed in the process of recovering the film material.

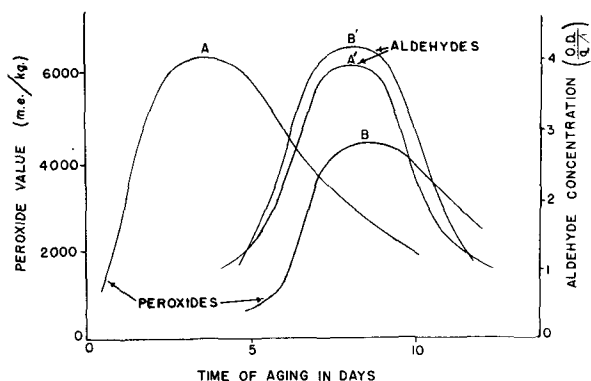


Fig. 2. Role of formation of nonvolatile aldehydes and peroxides in films of linseed oil methyl esters aged under yellowing (A) and nonyellowing (B) conditions.

There was no difference in the general nature of the curves (Figure 2), but for films dried in an open atmosphere the peaks of the curves for nonvolatile aldehyde and peroxide were well separated whereas with films dried in a closed atmosphere, they occurred at the same time. There is no direct indication of what relationship exists, if any, between this difference and the yellowing phenomenon. The difference shows up only in the relatively early stages of the aging of the film. As the aging proceeds beyond about 15 days, the aldehyde and peroxide values decrease and the differences disappear.

The results also show however that even though no yellowing occurred in a closed atmosphere, extensive oxidation (as well as polymerization) had occurred. Thus, from a quantitative standpoint, yellowing appears to be a minor side-reaction.

The only detectable difference in the ultraviolet spectra of films aged under open and closed atmospheres was the occurrence of a broad maximum at about $270\text{ m}\mu$ in the former (Figure 3). This band was produced by heating nonyellowed films *in vacuo*, a treatment that also produced yellowing. However a similar absorption maximum was produced by *in vacuo* thermal decomposition of methyl linoleate hydroperoxides (Figure 4), and neither the hydroperoxides nor their decomposition products were colored. As the peroxides decomposed, the absorption band at $270\text{ m}\mu$ increased and the absorption at $233\text{ m}\mu$ decreased. Thus it cannot be stated that the absorption at $270\text{ m}\mu$ in yellowed films is related specifically to the formation of the yellow compounds.

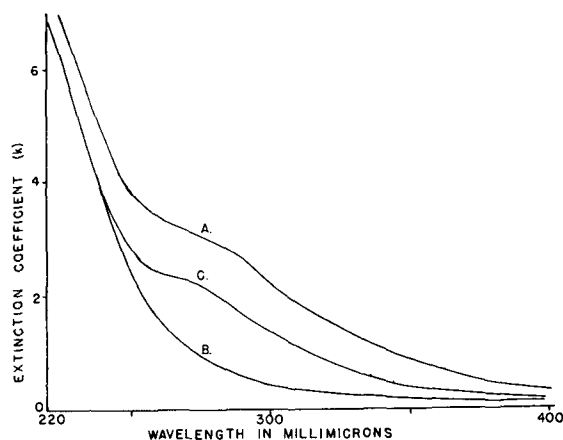


Fig. 3. Ultraviolet spectra of films of methyl linolenate. A. Aged under yellowing conditions. B. Aged under nonyellowing conditions. C. Aged under nonyellowing conditions and heated *in vacuo* at 50°C . for 20 hrs.

Infrared spectra were also obtained for films aged under open and closed atmospheres. No differences could be detected in films of methyl linolenate, but since one might expect the main differences to be

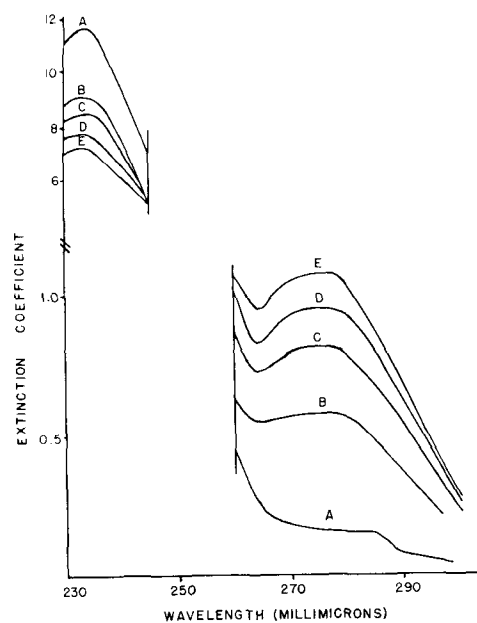


Fig. 4. Ultraviolet spectra of autoxidized methyl linoleate heated *in vacuo* for various periods at 80°C . A. Peroxide value (m.e./kg.), = 940. B = 695. C = 500. D = 367. E = 257.

found in the carbonyl region of the spectrum, this finding was not unexpected because of the large ester carbonyl absorption. In order to examine the carbonyl region in more detail, films of octadecatriene were studied. The spectra of these films (Figure 5) showed that large amounts of carbonyl formed in both open and closed atmospheres. Two bands can be distinguished, one at 5.8–5.82 μ and the other at about 5.86 μ . The band at 5.8 μ was more prominent than the band at 5.86 μ in films aged in the open. However because both carbonyl absorptions were complex, no bands in the infrared could be related specifically to the yellow compounds.

Polarographic analysis (6) of autoxidized films of methyl linolenate (Figure 6) showed the presence of four reducible structures, but none could be associated specifically with yellowing. Curve A, which exhibited a half-wave potential of -0.3 volt may be associated with the formation of dialkyl peroxide

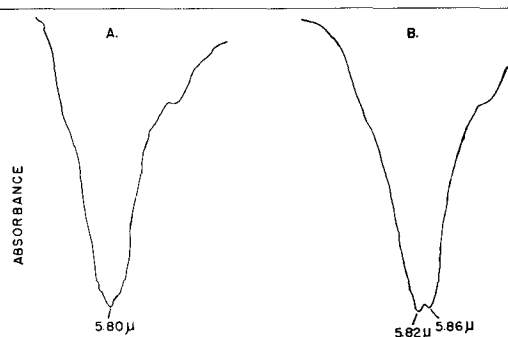


FIG. 5. Infrared spectra of films of octadecatriene. A. Aged in open conditions. B. Aged in enclosed conditions.

structures (6). Curves B and C, with half-wave potentials of -0.7 and -1.10 volts, respectively, are given by hydroperoxides. The total B and C (Curve F) correspond well with the chemically determined peroxides (Curve E). With the Curve D, which is characterized by a half-wave potential of -1.6 volts, may be due to the presence of unsaturated carbonyl compounds.

Isolation of the Yellow Compounds. Soon after this phase of the investigation was started, it became apparent that the yellow color was due not to one but

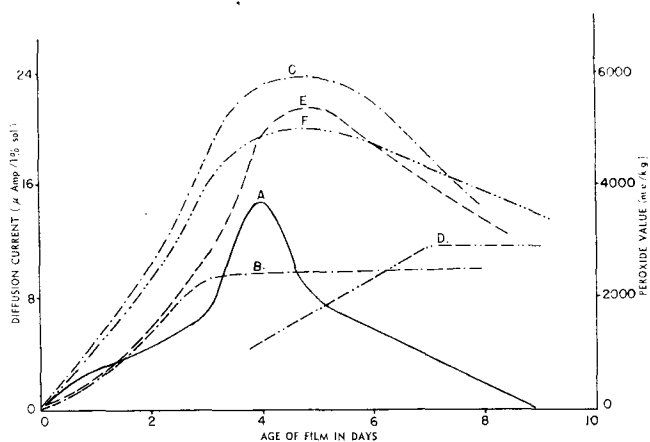


FIG. 6. Polarographic analysis of films of methyl linolenate aged for various periods. E = $E_{1/2} -0.3$ volts, B = $E_{1/2} -0.7$, C = $E_{1/2} -1.1$, D = $E_{1/2} -1.6$, F = the total diffusion current of B and C, E = peroxide value m.e./kg., KI reduction. (Diffusion current values for curves B and C should be multiplied by 2.5, and F by 5).

to a number of related compounds with varying degrees of structural complexity.

It was found that the more complex yellow compounds were soluble in 0.5% aqueous KOH or 10% Na_2CO_3 and could be extracted from ethyl ether solutions with these reagents. The extracted material was recovered by acidification with dilute HCl and re-extracted with fresh ethyl ether. When such a fraction was placed in a separatory funnel with ethyl ether and distilled water, it distributed itself entirely in the ether phase or the aqueous phase, depending on whether the aqueous phase was made acidic or alkaline.

A similar fraction was obtained from nonyellowed films. Treatment with alkali however increased the color of the material isolated from both yellow and nonyellowed films over and above what would be expected by merely effecting a concentration of these substances, and spectral analysis showed a strong new absorption band in the infrared spectra at about 3.8 μ . Thus it was evident that the alkali promoted some structural alterations in the extracted material. Treatment with HCl only partially reversed the color change and made this fraction preferentially soluble in ethyl ether, a behavior characteristic of indicators of the quinonoid type. Although some structural changes are caused by this treatment, it appears that the colored compounds and their precursors can be characterized by their solubility in dilute alkali.

The yellow chromophores, as well as their precursors, were found to have a high affinity for calcium chloride; hence this property also was used as a means of concentrating these compounds. In contrast to the action of alkali, adsorption on calcium chloride did not appear to cause any structural alterations of the yellow compounds. The general procedure in applying this method of fractionation was to slurry about 10 g. of calcium chloride (that had first been treated by exposure for a few minutes to dry HCl, followed by removal of the excess HCl under reduced pressure), with about 10 ml. of ethyl ether containing 1 g. of aged film. The calcium chloride was separated by filtration through filter paper and washed with fresh anhydrous ether. Sometimes the film solution was treated with CaCl_2 a second time, but all of the yellow chromophores could not be removed no matter how many treatments were used. The more highly colored, and possibly more complex, compounds were adsorbed more readily on the calcium chloride.

The adsorbed material was further fractionated by extracting the calcium chloride complex with generous amounts of chloroform. A portion of the adsorbed material was extracted into the chloroform by this treatment. Thus the yellow chromophores were divided into three fractions: a) a fraction which was not adsorbed by calcium chloride from ethyl ether solution ("nonadsorbed fraction"); b) a fraction which was adsorbed from ethyl ether but extracted with chloroform ("chloroform eluate"); and c) a final fraction which remained adsorbed on the calcium chloride after treatment with both ethyl ether and chloroform ("strongly adsorbed fraction"). The last fraction was recovered by dissolving the calcium chloride in distilled water and extracting the aqueous phase with ethyl ether. The total and relative amounts of material in the three fractions depended on age of the film. Table II shows results of the fractionation of a number of films of linseed oil methyl esters aged

TABLE II
Calcium Chloride Fractionation of Yellowed and Nonyellowed Films of
Methyl Linolenate Concentrate at Room Temperature

Fraction	Age of film	Yellowing conditions	Nonyellowing conditions	
		Wt. distribution	Wt. distribution	Yellowing test at 50°C.
	<i>days</i>	%	%	$\Delta O.D.$ <i>g./cm.²</i>
Nonadsorbed CHCl ₃ eluate Adsorbed	16	57.4	84.9	8.3
		34.1	15.1	49.5
		8.3	0
Nonadsorbed CHCl ₃ eluate Adsorbed	24	55.8	82.8	9.0
		35.5	14.4	47.9
		8.7	2.8 ^b
Nonadsorbed CHCl ₃ eluate Adsorbed	34	50.7 ^a	81.6	8.5
		38.1	14.4	31.0
		11.2	4.0	23.7
Nonadsorbed CHCl ₃ eluate Adsorbed	59	48.6	78.6	8.3
		41.8	15.9	26.4
		9.6	5.5	36.0

^a This group of films was aged for 42 days.

^b Not enough material.

for various periods of time under open (yellowing) as well as closed (nonyellowing) atmospheres.

The yellowing tendency of the fractions obtained from the nonyellowed films (Table II) was determined by heating films of these fractions for 72 hrs. at 50°C. *in vacuo* in a manner similar to that used for testing the inhibition of yellowing. The values represent the difference between the initial color and that obtained after heating for 72 hrs. A value of less than 10 was scarcely detectable by the naked eye and was not considered significant.

The adsorbed materials probably were fractionated on the basis of their polarities since more material was adsorbed from the older films. Since the yellow components as well as their precursors were distributed throughout all the fractions, it appeared that they existed in varying degrees of structural complexity. In the older films, in which significant amounts of material separated in the "adsorbed fraction," the "chloroform eluate fraction" contained less precursor. This may be an indication that only one major series of yellow compounds is involved and that eventually (in extremely old films) the major colored compounds would be found almost entirely in the "adsorbed fraction." The ultraviolet and infrared spectra of these fractions were little different from that of the parent films and were characterized by strong hydroxyl and complex carbonyl bands. The fractions with the yellow compounds and their precursors consisted of 15 to 20% in the nonyellowed films and up to about 50% in the yellowed films and obviously contained a large amount of other film constituents in addition to the yellow compounds and their precursors.

Further fractionation of the chloroform eluate, which had the bulk of the yellow compounds and their precursors, was effected by virtue of the wide differences in the solubilities of some of their constituents in ethyl ether and acetone. The first step in the procedure was to extract the residue from the chloroform eluate with ethyl ether. This gave an ethyl ether-soluble fraction. The residue from this extraction was then extracted with acetone to give acetone-soluble and -insoluble fractions. The ether-soluble and acetone-soluble fractions were viscous oils. The acetone-insoluble fraction was a light yellow crystalline solid which melted with decomposition at about 150°C. The major portion of the yellow compounds (obtained from yellowed films) and their precursors

(obtained from nonyellowed films) was concentrated in the acetone-soluble fraction although both the ether-soluble and the acetone-insoluble fraction also contained appreciable amounts of these substances.

The infrared spectra (Figure 7) of the fractions isolated from the nonyellowed films were virtually identical with those from the yellowed films, indicating that the acetone-insoluble fractions contained material with fairly similar structure. It also was evident that much of the hydroxyl and nonester absorption of the parent chloroform eluate was due to material separated in this fraction. This is significant because this fraction contained only minor amounts of yellow compounds or their precursors (depending on the film from which the material was isolated). Comparison of the infrared spectra in Figure 7 indicated that the separation of material between the acetone-soluble and -insoluble fractions was not sharp, and at least some of the hydroxyl and carbonyl absorption of the acetone soluble fraction resulted from this factor.

The ultraviolet spectra of these fractions showed only the same broad maxima at 270 m μ that had been observed previously. Thus although the yellow compounds and their precursors were concentrated by a factor of 50, no specific spectral properties could be associated with them. Further the strong hydroxyl and carbonyl absorption, which one might suspect of being associated with the yellow substances, was concentrated in a fraction which represented only a small part of the total yellow color.

Although the solid material does not appear to bear any principal relationship to the yellow compounds or their precursors, it is interesting since it makes a major contribution to the carbonyl formed in the oxidation of oil films. The strong hydroxyl, coupled with the relatively weak CH₂ band, suggests a highly hydroxylated cyclic structure. The strong band at 6.3 microns may be attributed mainly to chelated ketones and apparently is related to the strong hydroxyl absorption. The bands at 5.8 and 5.7 microns also are caused by ketones, probably cyclic. The presence of quinonoid structures could not be detected however. At present efforts are being made further to purify this material so as to define more clearly its structure and to learn something of its significance

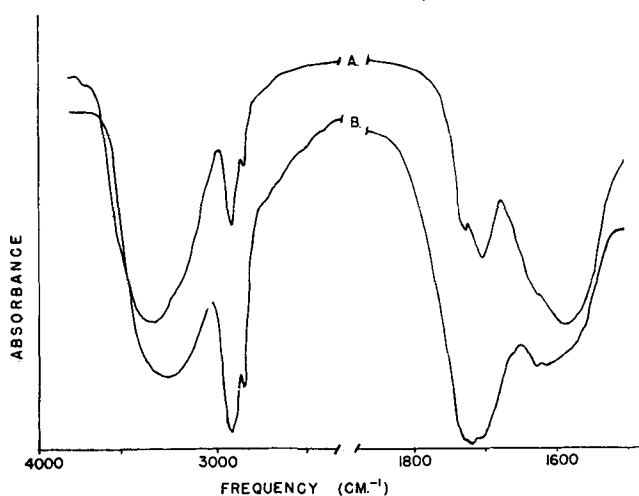


FIG. 7. Infrared spectra. A, acetone-insoluble fraction. B, acetone-soluble fraction isolated from material fractionated by calcium chloride adsorption (see text).

as a product of the oxidation of unsaturated fatty acid esters.

Discussion

The yellowing of drying oil films seems to involve two distinct steps, the formation of colorless precursors by an oxidative mechanism, followed by a further reaction of the precursors to give the yellow compounds. Only subtle differences were found between the yellow compounds and their precursors. The yellowing probably involves a reaction of active centers in the precursor molecules in some type of condensation. Two observations support this view: a) yellowing can be induced by heating aged, non-yellowed films *in vacuo* (nonoxidative process), and b) low-molecular-weight aldehydes containing an active methylene group are effective inhibitors of yellowing.

No specific physical or chemical property could be related quantitatively to the yellow compounds or their precursors. Two problems were responsible: the inhomogeneity of the colored compounds and the difficulty of concentrating them free from noncolored substances. If the yellow compounds are highly colored, only a few tenths or hundredths of 1% may be all that is necessary to produce the color normally observed in aged films. The strong hydroxyl and carbonyl absorption that characterizes the infrared spectra of aged films of drying oils is not associated directly with yellowing. This does not preclude the possibility that the yellow compounds and their precursors are carbonyl compounds. In fact, since they are soluble in dilute alkali, one might suspect that they are related to hydroxy quinones. However no quinonoid structures could be detected by ultraviolet spectral analysis. This contrasts sharply with the results of McAdie and Nicholls (8), who found that a strong absorption band at 250 $m\mu$ was formed on the aging of films of methyl linoleate and linolenate. This observation formed the basis of their theory that benzoquinone structures which have an absorption band at 245 $m\mu$ are produced in oxidized films, and led to the suggestion that quinonoid structures are responsible for the color of yellowed films. Failure to observe any strong absorption at 250 $m\mu$, since absorption at this wavelength occurred about equally in films of linoleate and linolenate esters (8), indi-

cates that yellowing in film must be largely explained in some other way.

The observed inhibition of yellowing by chemical additives is significant because it portends the possible development of inhibitors suitable for practical application. The function of the inhibitor seems to be different from that of an antioxidant in retarding autoxidation. In yellowing, the function of the inhibitor appears to be to substitute for some reactant in a way that will yield nonyellowed adducts with the colorless precursors. Thus a sufficient amount of inhibitor is required to form adducts with all of the precursor molecules. Nevertheless if, as suspected, the major yellowing compounds are formed in only minute amounts, only small amounts of inhibitor should be required to prevent yellowing, provided that sufficiently reactive inhibitors can be found.

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An Accelerated Test of the Yellowing Tendency of Drying Oils¹

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An accelerated test for the determination of the yellowing tendency of oils is described.

The test is demonstrated on purified esters as well as on a number of common oils used as vehicles in paints and varnishes.

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BECAUSE the yellowing of oils is influenced by many factors (1,2) and the colored bodies formed in the reaction have not been well characterized in terms of chemical and physical properties, it is not possible to predict the susceptibility of paint and varnish vehicles to this phenomenon on the basis of chemical examination of the vehicle.