

Long-Term Behavior of Oil-Based Varnishes and Paints. Photo- and Thermooxidation of Cured Linseed Oil

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ABSTRACT: Thermooxidation at 100°C and photooxidation at wavelengths above 300 nm of dried oil films were evaluated. The chemical modifications of the networks were determined by infrared analysis coupled with gaseous treatments (NO, SF₄, and NH₃). The dried films are rather stable in thermooxidation, whereas in photooxidation, important degradation of the network occurs with many chain scissions. This photoinstability results from the presence of crosslinks that are sensitive to radical attack because of the lability of the hydrogen atom on the tertiary carbons. The photooxidation reactions are fully described in this paper. Yellowing of the cured samples, observed with ultraviolet-visible and fluorescence spectrometries, rapidly is decreased by irradiation because the oil contaminants that are mainly responsible for the yellowness are photooxidized. On the contrary, yellowing slowly but continuously increases during thermooxidation at 100°C.

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Vegetable oils with important proportions of polyunsaturated fatty acids (PUFA) are called drying oils. Their high drying index (1) allows their use in the manufacture of oil-based paints and varnishes and especially for the creation of works of art. In this last field, oil-based paints and varnishes generate some problems, mainly a tendency to yellowing or cracking.

Analysis of the literature concerning the applications of oil-based paints and varnishes shows that most of the research has been focused on the identification of binding media (2–4). The results obtained allow selection of appropriate materials for cleaning paintings and give information to the art historian about artists' techniques (5). To our knowledge, only two valuable studies dealing with the photo-aging of dried oil films have been published, more than 40 yr ago (6,7). No studies of the reactions involved in photooxidation of these oils have been published. However, it is of great interest to understand the mechanisms of the chemical evolution that occurs during long-term aging with light exposure. This is the aim of this paper.

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The PUFA chains can oxidize quite readily, *via* a radical chain reaction (8,9). The thermooxidation mechanism of drying oils has been largely reviewed in the literature (10,11). Many oxidation products formed from the decomposition of hydroperoxides have been identified: they consist in alcohols, ketones, aldehydes, or epoxides (12). Oxidation of the PUFA chains leads to crosslinks by formation of C–C, ether, or peroxy linkages (13,14). The curing step, considered as an “oxidative polymerization,” leads to a three-dimensional network, and when the curing is complete, a stable state is reached (15). Determination of the peroxide value (PV) appears to be the best way to measure the extent of curing (16). When samples are totally dried, the antioxidants in the oil film have been consumed, but the contaminants initially present in the vegetable oil still remain in the film.

In the first part of our research (16), we used Fourier transform infrared (FTIR) spectroscopy to characterize oxidation products and to elucidate the drying mechanism of drying oils. We found that the addition of peroxy radicals on conjugated double bonds was responsible for the fast disappearance of conjugated double bonds, with the formation of epoxides as intermediate products. The properties of the hydroperoxides formed have been studied in the second part (17). Our results have permitted a complete understanding of the drying mechanism on the basis of an induced hydroperoxide decomposition reaction. We have also shown that only low concentrations of peroxy bridges were formed in the dried oil films.

Among drying oils, linseed oil is one of the most commonly used in paintings. In this paper, we focus on the identification of the various oxidation products formed during photo- and thermooxidation of dried linseed oil films. The products have been identified and quantified by FTIR spectrometry, sometimes coupled with gaseous treatments. Ultraviolet (UV)-visible spectroscopy and microfluorescence spectroscopy have been used as complementary methods, mainly to study decomposition of the various contaminants that can contribute to the yellowness of dried film.

EXPERIMENTAL PROCEDURES

Materials. Analyzed samples were prepared by spreading out linseed oil (Pebeo, Gemenos, France) (linolenic 54%, linoleic

13%, oleic 22%, and saturated 11%) on KBr or CaF₂ windows with a thickness of about 25 micrometers. IR spectra were recorded with a Nicolet 510 spectrometer (Madison, WI) (resolution 4 cm⁻¹, 20-scan summation), and UV spectra were recorded on a PerkinElmer Lambda 5 spectrophotometer (Courtabœuf, France), equipped with an integrating sphere. Fluorescence spectroscopy was performed with a Hitachi U6000 microspectrofluorimeter (based on an Olympus BHT2 microscope). The excitation wavelength was 395 nm.

Photooxidation, photolysis and thermooxidation experiments. Curing of linseed oil was carried out in a ventilated oven at 60°C in the dark for 25 d, on two series of samples on KBr or CaF₂ windows. Dried oil samples were then exposed in a SEPAP 12/24 unit for irradiation at wavelengths longer than 300 nm (temperature 60°C). This apparatus has been described in numerous articles (18,19). For photolysis, the samples were individually introduced into Pyrex tubes before being sealed in vacuum (5·10⁻⁶ torr). The tubes containing oxidized samples were exposed in the SEPAP 12/24 unit similar to the photooxidation experiment. Some dried samples were also placed in an oven at 100°C to study the influence of temperature.

Gaseous treatments. Nitrogen monoxide (NO) treatment and sulfur tetrafluoride (SF₄) treatment permit identification of alcohols and carboxylic acids, respectively. The nitrite band at 777 cm⁻¹ is characteristic of the presence of alcohol (20,21). In the same manner, after SF₄ treatment, the acid fluoride bands at 1843 and 1810 cm⁻¹ allow the determination of the carboxylic acid concentration (21). Treatment with gaseous ammonia (NH₃) was also performed on the oxidized film. Lactones, esters, and peresters, nonreactive to SF₄, are susceptible to reaction with ammonia. Lactones may be converted into lactams (22). Esters and peresters can form amides with a characteristic IR absorption band in the range 1660–1680 cm⁻¹ (23). Carboxylic acids are converted into ammonium carboxylates with IR absorption band in the range 1560–1580 cm⁻¹. NO and NH₃ treatments were carried out for 6 and 24 h, respectively, in a Pyrex container in darkness after a nitrogen purge. SF₄ treatment was carried out in an all-Teflon reactor for 6 h, the oil samples being on CaF₂ windows.

PV. PV of the 60°C samples was determined by iodometric titration (17): refluxing oxidized samples in acetic acid/propan-2-ol with excess sodium iodide and measuring the I₃⁻ liberated by spectrophotometry (Shimadzu UV-2101 PC) (Columbia, MD) at 357 nm.

RESULTS AND DISCUSSION

Photooxidation experiments. Linseed oil samples, oxidized at 60°C for 25 d, were considered as “dried” samples because, after this time, oxidative cross-linking is almost complete. The PV of these samples, determined by iodometry, was around 100 mmol·kg⁻¹. The 60°C-oxidized samples were placed in a SEPAP 12/24 device for irradiation. After various irradiation times, samples were analyzed by FTIR, UV-visible, and fluorescence spectroscopies, and their PV were de-

termined. IR spectra of irradiated linseed oil after different exposure durations are represented in Figure 1. The assignment of vibration bands for the sample dried at 60°C has been described in a previous article (16). Many changes can be observed in the spectrum in Figure 1, such as a decrease in the intensity of the alkyl bands between 3000 and 2820 cm⁻¹ and a marked modification of the ν(O–H) band, due to the formation of bonded carboxylic acids that have a broad absorption band from 3300 to 2500 cm⁻¹.

In the IR region from 2200 to 400 cm⁻¹ (not represented), important modifications are also observed. The vibration band at 975 cm⁻¹, assigned to residual unsaturation after curing (24), disappears within 13 h, and the vibrations of alkyl groups at 1464 and 725 cm⁻¹ decrease with irradiation time. Modifications in the range 1300–1100 cm⁻¹ and in the range 1900–1500 cm⁻¹ result from changes in the oxidized product concentrations. The mechanisms of the curing of drying oils were detailed in our previous publications (16,17). For the 60°C-dried linseed oil samples, residual unsaturation at 975 cm⁻¹ can be attributed to monounsaturated fatty acid chains with low reactivity or in-chain oxidation products, such as unsaturated ketones. The residual double bonds may be considered as preferential oxidation sites for photooxidation, which is confirmed by the fact that they disappear fast in the first hours of irradiation.

In parallel, the variation of PV in Figure 2 shows that many reactions occur during the first hours of irradiation. The fast increase in the hydroperoxide concentration may be partly attributed to reactivity of the sites mentioned above. There are great differences between the maximum PV in the curing step (17) and in the photooxidation step. During irradiation, the hydroperoxides formed are quickly decomposed into oxidation products (25).

The ν(C=O) vibration band of carboxylic acids cannot be observed in the broad band centered about 1745 cm⁻¹, including vibration band of ester bonds of triglycerides at 1744 cm⁻¹. The absorption of saturated and unsaturated ketones at 1720

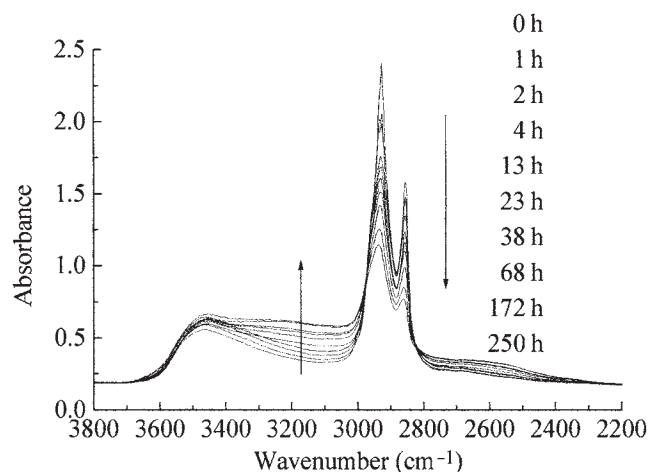


FIG. 1. Evolution of the infrared spectra of linseed oil after irradiation for various times.

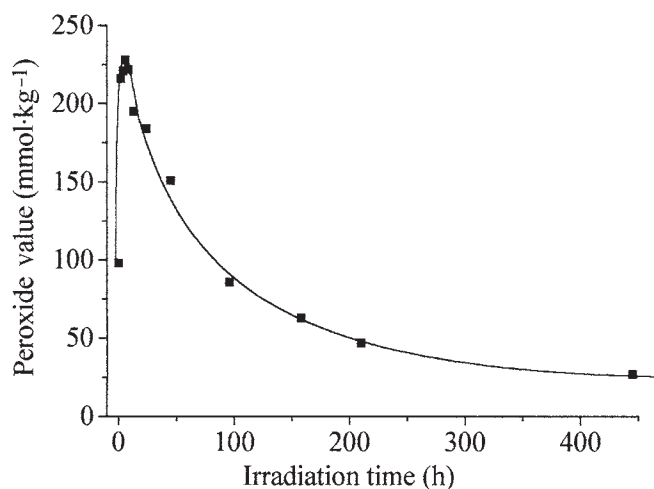


FIG. 2. Evolution of the peroxide value vs. irradiation time.

and 1696 cm^{-1} does not permit evaluation of the acid band around 1710 cm^{-1} . For this reason, the irradiated samples were treated with SF_4 to observe the presence of carboxylic acids.

As shown in Figure 3, SF_4 treatment is informative. In the unexposed oil spectrum, one can observe the decrease of the $\nu(\text{C}=\text{O})$ band of carboxylic acid at 1710 cm^{-1} and the appearance of the $\nu(\text{C}=\text{O})$ fluoride acid bands at 1843 and 1810 cm^{-1} , which reveals that saturated and unsaturated acids were produced. The disappearance of unsaturated carboxylic acids is not clearly observed in the spectra, because they could absorb near 1695 cm^{-1} , as a shoulder of the 1710 cm^{-1} band. When irradiation time increases, many changes occur. The fluoride acid band at 1843 cm^{-1} on the SF_4 -treated samples increases, showing that carboxylic acids accumulate in photo-oxidation. An important band around 1775 cm^{-1} also increases, which indicates the formation of γ -lactones and peresters. With increasing irradiation time, the decrease in the carboxylic acid band at 1710 cm^{-1} is masked because of the concomitant formation, during photooxidation, of products absorbing near

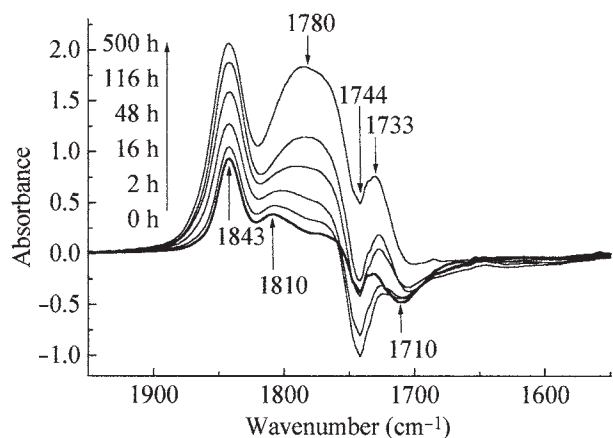
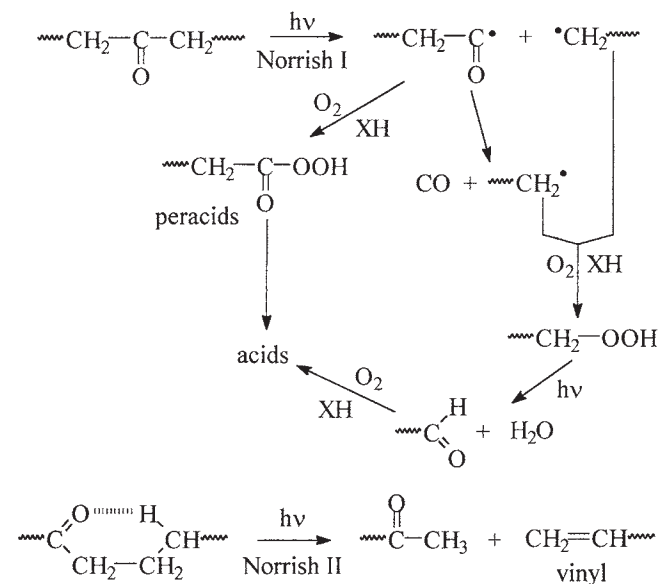


FIG. 3. Subtraction spectra: (dried linseed oil after various irradiation durations and SF_4 treatment) minus (60°C -dried linseed oil).

1735 cm^{-1} (band visible on the 500 h-irradiated spectrum). As proposed for the thermooxidation mechanism (16), hydroperoxides can be decomposed into alkoxy and hydroxyl radicals. These alkoxy radicals may then evolve to give ketones or aldehydes, rapidly oxidize into acids, or decompose into small molecules, such as carbon dioxide.

The IR spectrum of the gas phase was recorded for an oxidized sample placed in a gas cell in the SEPAP 12/24 for 40-h irradiation. The gas-phase spectrum of dried linseed oil after irradiation evidences the formation of CO_2 , as mentioned in the literature (6,26).

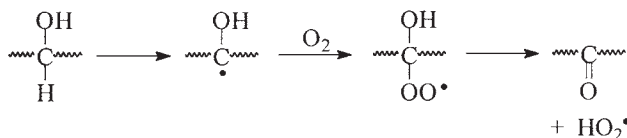
The ketones formed during the thermal curing step are photo-unstable and can decompose by Norrish I or II mechanisms (27) (Scheme 1). In the presence of oxygen, carboxylic acids are formed.



The IR spectra of photooxidized products do not show any vinyl vibration band at 909 cm^{-1} . This result suggests that the Norrish II mechanism is only a minor route for the decomposition of ketones, if it exists at all.

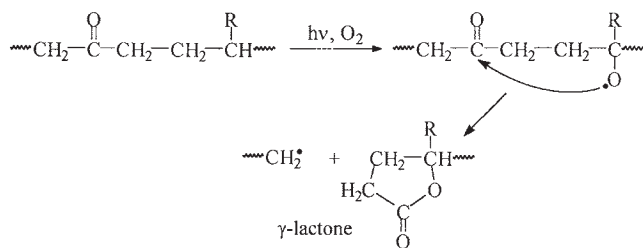
NO treatment permits quantitation of alcohols in irradiated samples. The decrease in the nitrite band at 777 cm^{-1} in exposed and NO -treated samples shows that, during irradiation, alcohols disappear. Usually, tertiary alcohols are considered as quite stable oxidation products. However, secondary alcohols can be oxidized when irradiated because of their labile hydrogen atom. The autoxidation mechanism proposed for the fatty acid chains (9) underwent formation of secondary alcohols. The disappearance of alcohols may be explained by the mechanism proposed in Scheme 2.

NH_3 treatment carried out on an oxidized sample leads to an important decrease in the 1775 cm^{-1} absorbance band. This could confirm the presence of peresters. In parallel, appearance of a new band at 1680 cm^{-1} indicates that amide groups are formed by NH_3 reaction in the photooxidized sam-

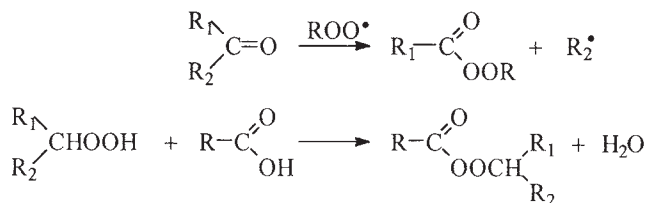


SCHEME 2

ple. A carboxylate vibration band is also visible at 1570 cm^{-1} . Residual absorption at 1775 cm^{-1} after NH_3 treatment may be attributed to γ -lactones, which do not react under our experimental conditions (28) or perhaps it indicates an incomplete reaction of peresters with NH_3 . γ -Lactones have been previously identified as oxidation products in lipids (29) and may be formed by a mechanism analogous to that proposed in Scheme 3 (30). Peresters could be obtained by one of the two reactions shown in Scheme 4 (28).



SCHEME 3



SCHEME 4

Modifications of the carbonyl band of oxidation products are more easily observed with spectra subtractions shown in Figure 3. The difference between samples before and after SF_4 treatment allows determination of the absorbances at 1843 and 1810 cm^{-1} . By subtracting the initial spectrum of linseed oil from those of the irradiated samples, one can measure the variations of absorbance at 1775 cm^{-1} . Moreover, subtraction of the spectrum of the unexposed and SF_4 -treated sample from those of irradiated and SF_4 -treated samples permits observing variations of the 1730 cm^{-1} band. Figure 4 summarizes variations of the oxidation product concentrations for irradiated samples.

The β -scission reactions mentioned above lead to a decrease of the alkyl groups concentration. However, these reactions cannot justify the notable disappearance of the alkyl chains induced by photooxidation. This decrease has been observed by Crecelius *et al.* (7) and is probably the result of chain breaking after oxidation in the α -position of the reac-

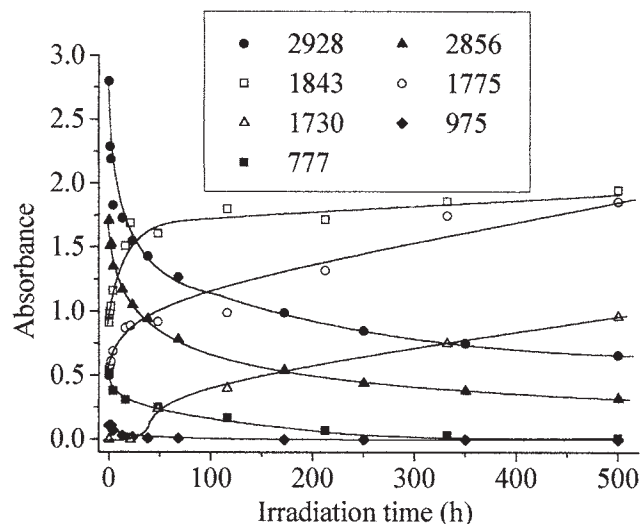
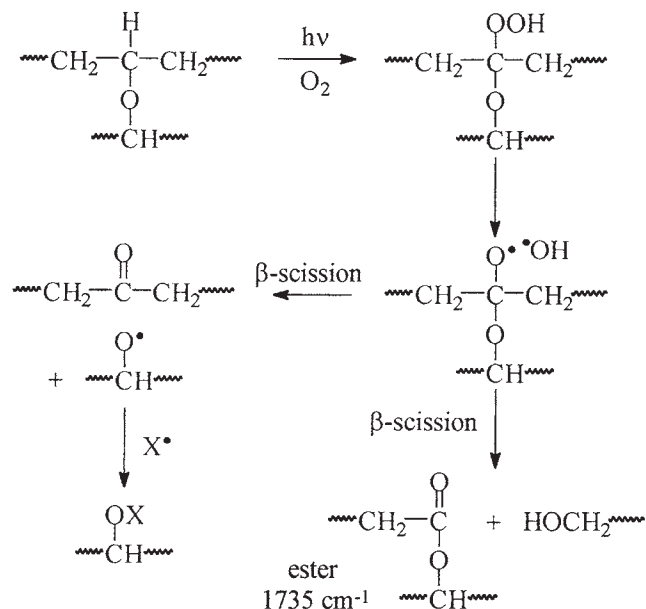


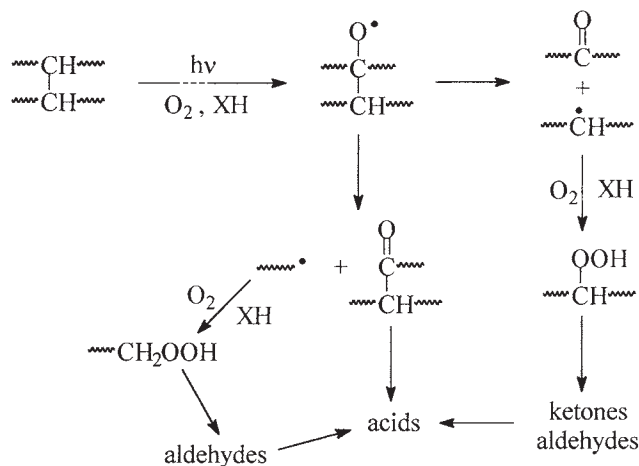
FIG. 4. Absorbance of oxidation product bands (cm^{-1}) as a function of irradiation time.

tive sites of the cross-linked oil. After all, the solid film is formed by cross-linking between fatty acid chains that can be of three types: C-C, ether, or peroxy (14). When the films are highly dried, the peroxy bridge concentration should be much lower than the ether concentration (17). The residual peroxy bonds quickly decompose upon irradiation. Homolytic breakdown of the O-O bond of peroxy bridges may occur (31), leading to two alkoxy radicals. These radicals may evolve to give ketones, alcohols, or aldehydes. Many studies on the photooxidation of polyethers with a tertiary carbon in the α -position are reported in the literature (32-34). Ethers are easily photooxidized and can lead to esters, following the reactions shown in Scheme 5. The formation of esters can also ex-



SCHEME 5

plain the growth of the band at 1735 cm^{-1} (35). The C–C linkages are also preferential sites of oxidation because of the presence of tertiary carbon. The radical attack occurs quite readily on these sites (36) (Scheme 6). For this reason one can postulate that cross-linking has two opposite consequences. On one hand, it allows curing and hardening of an oil film. On the other hand, it generates some structures that act as “fragile” sites in terms of durability of the material.

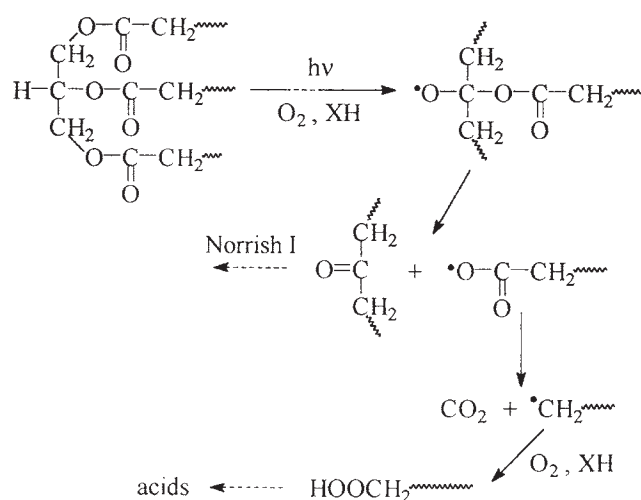


SCHEME 6

The decomposition of ether, C–C, or peroxy bonds justifies the global modification that occurs in the range $1000\text{--}1300\text{ cm}^{-1}$. Moreover, the breakdown reactions mentioned above can explain the formation of most low-molecular-weight oxidation products that have been identified by analysis of old oil-based paintings media (37,38). In the linolenate chain, for instance, they mainly consist of carboxylic acids that result from scission near the three double bonds (39).

The carbonyl group vibration of ester bonds of triglycerides at 1744 cm^{-1} probably decreases during photooxidation. However, the increase in acid bands and in the lactone and perester bands undoubtedly compensate for the disappearance of this ester band. The photodegradation of triglycerides can be described by the mechanism shown in Scheme 7. The ester bonds in aliphatic polyesters are quite stable in photooxidation at $\lambda > 300\text{ nm}$ (40). However, in the triglycerides constituting the oil, there is a site with a tertiary carbon atom in the α -position of the oxygen atom. As is true for the majority of previous reactions, a radical attack is then likely to occur.

Irradiated samples were also analyzed by UV-visible spectrometry (Fig. 5A). In photooxidation, the shift of UV absorption of dried oil to short wavelengths, which is characteristic for bleaching of the samples, is fast in the first hours of reaction. This result indicates rapid decomposition by oxidation of the linseed oil contaminants, as a result of their high photosensitivity. In parallel, the fluorescent products present in the thermooxidized samples disappear on photooxidation (Fig. 5B).



SCHEME 7

Photolysis experiments. To study the direct influence of exposure to UV on dried oil films, photolysis (irradiation in vacuum) experiments were carried out. Analyses were made on the photolyzed samples as described before.

The IR spectra show the disappearance of the compounds absorbing between $1500\text{ and }1700\text{ cm}^{-1}$. These absorption

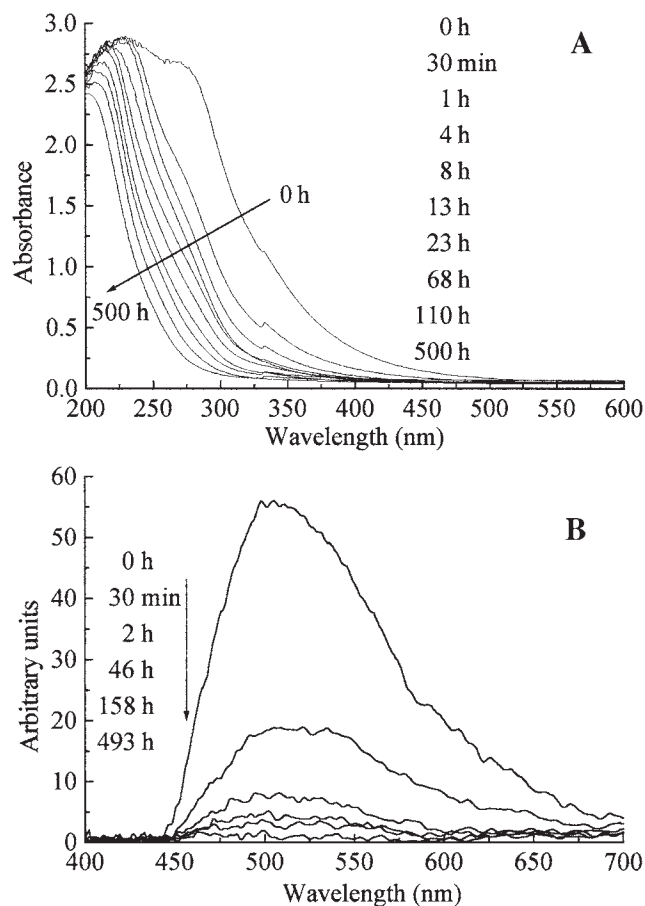


FIG. 5. Evolution of ultraviolet-visible spectra (A) and fluorescence spectra (B) as a function of irradiation time.

bands indicate the presence of contaminants of linseed oil, which contribute to yellowness and fluorescence of the samples. The ketonic absorption at 1720 cm^{-1} decreases and, in the hydroxyl range, one can also observe a decrease in the contribution of alcohols and acids. NO and SF₄ treatments on photolyzed samples have confirmed this result. Photolysis also leads to a fast decrease (in 3 h) in UV-visible absorption of the samples between 400 and 300 nm. Subsequent disappearance of the products absorbing below 300 nm is slow. However, products decomposed during irradiation are not fluorescent, and no notable variation of the fluorescence intensity is observed.

The results obtained in photolysis experiments that show only "minor" modifications of the sample structure confirm the proposed mechanisms that are involved in the degradation of linseed oil. In all experiments, the reactions include the fixation of oxygen molecules on radicals.

Thermooxidation experiments. Thermooxidation of a 60°C-dried sample of linseed oil has been carried out at 100°C. Modifications of the IR spectrum are not important compared to those after photooxidation. In the hydroxyl range, one observes the decrease of the broad band mainly attributed to bonded carboxylic acids between 3600 and 2300 cm^{-1} . This may be due to the formation of esters or anhydrides by reaction of acids and alcohols. Water that is produced by this reaction is lost by migration from the solid sample. This phenomenon is not visible in a linseed oil sample dried directly at 100°C. This suggests that, at low temperatures, the curing step provokes the formation of some hydroxylic compounds, such as alcohols or carboxylic acids. After 1,000 h at 100°C, the alkyl bands at 2928, 2856, and 725 cm^{-1} slightly decrease, and in the carbonyl zone there is a weak increase in the bands at 1775 cm^{-1} and about 1720 cm^{-1} . These variations could be attributed to the formation of γ -lactones or peresters and ketones, respectively. However, there is a decrease in absorbance in the range 1690–1620 cm^{-1} , owing to the disappearance of residual unsaturation. This is confirmed by the slight decrease in the 975 cm^{-1} band. It indicates that increasing the temperature allows partial curing to finish. This leads to the formation of hydroperoxides in the α -position of the double bonds, such as in a classical low-temperature oxidation of monounsaturated fatty acid chains.

In thermooxidation at 100°C, the increase in absorption in UV spectra is slow but continuous. The fluorescence spectrum exhibits minor changes, starting with a slight decrease in the fluorescence, and after 10 h, a new continuous increase. We expected an increase in the fluorescence intensity of linseed oil with time because the fluorescence results from the degradation process (41).

In this study, the thermostability of drying oils has been clearly demonstrated. In thermooxidation there is no notable evolution of the chemical structure of the dried oil film. This result is not surprising if one considers the state of conservation of paintings that are more than five centuries old. However, these paintings must not be exposed to sunlight [with the aim of reversing their yellowing (42)]; otherwise the re-

sult would be rapid degradation because of the numerous chain-breaking reactions that are likely to occur in photooxidation.

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