Long-Term Behavior of Oil-Based Varnishes and Paints
I. Spectroscopic Analysis of Curing Drying Oils

Jacky Mallégol, Jean-Luc Gardette*, and Jacques Lemaire

Laboratoire de Photochimie Moléculaire et Macromoléculaire,UMR CNRS 6505, Centre National d'Evaluation
de Photoprotection, Université Blaise Pascal (Clermont-Fd), F-63177 Aubière Cedex, France

ABSTRACT: The curing of drying oils at 60°C has been investigated by Fourier transform infrared spectroscopy and Fourier transform Raman analysis of linseed oil and poppyseed oil. In the first step, hydroperoxides are formed (broad vibration band centered around 3425 cm^{-1}) with concomitant conjugation and *cis-trans* isomerization of the double bonds (disappearance of *cis* bands at 3011 and 716 cm^{-1}, appearance of *trans* conjugated and *trans* nonconjugated bands at 987 and 970 cm^{-1}). The subsequent decomposition of hydroperoxides in the presence of oxygen leads to the formation of alcohols (nitrite band at 779 cm^{-1} after nitrogen monoxide treatment), aldehydes (bands at 2810 and 2717 cm^{-1} in gas phase), ketones (saturated and unsaturated at 1720 and 1698 cm^{-1}, respectively), carboxylic acids (saturated and unsaturated acid fluorides identified at 1843 and 1810 cm^{-1} after SF_4 treatment), and peresters or γ-lactones (near 1770 cm^{-1}). A rapid decrease in the double-bond concentration is recorded when curing continues, and the formation of epoxides, characterized by a vibration band at 885 cm^{-1}, is observed. Thermolysis experiments have suggested the proposal of a reaction of addition of peroxyl radicals on the conjugated double bonds as a probable mechanism. This mechanism explains both the rapid disappearance of conjugated double bonds and the formation of epoxides as intermediate products observed in the initial step of curing.

Paper no J9119 in *JAOCS 76*, 967–976 (August 1999).

KEY WORDS: Alcohol, carboxylic acid, curing mechanism, epoxide, hydroperoxide, infrared spectroscopy, Raman spectroscopy, thermooxidation.

The objective of this work on drying oils used in paints was to determine the influence of the curing step on the long-term durability of the cross-linked material.

The reactions that are involved in the many steps of formation of the network and further processing are crucial for determining the long-term durability of the material. These reactions control the chemical structure of the network and can result in the introduction of various types of structural defects that are likely to influence the stability of the polymerized material regarding oxidative aging.

Modification of the chemical structure of drying oils resulting from oxidative curing cannot be considered as fully understood. Considering the impact of formation of the cured film on the long-term durability of the material, two basic questions arise: What is the intimate chemical structure of the cured material, and what is the influence of the several parameters that are involved in the curing operations? Answering both these questions is the first step required before the long-term durability of these materials can be studied.

The problems of oil oxidation have attracted much attention, and many papers report on the mechanisms of autoxidation of unsaturated fatty acids (oleic, linoleic, and linolenic). The aim of most published results was clarification of the source of undesirable flavors resulting from oxidation. Major volatile products were identified, and reaction mechanisms were proposed (1–5). However, these results cannot easily be extended to drying oils used in paints and varnishes because oxidation conditions are different (6), and these results concern only the first steps of oxidation (7). Studies dealing with the oxidation of drying oils do not explain clearly the various reactions occurring within the curing process that lead to the formation of a solid film (8–10). Only recent studies have brought information about the oxidative cross-linking (11–13).

Autoxidation can be explained in terms of two main steps: the formation of hydroperoxides and the decomposition of these hydroperoxides to generate oxidation products and cross-linking between the chains. Oxidation leads to some increased saturation of the substrate, as observed by the notable decrease of the iodine index (14). The mechanism by which the double bonds disappear is quite complex. The disappearance of unsaturation cannot only be attributed to the formation of cyclic structures. The departure of unsaturated oxidation products resulting from chain breaking is also a minor reaction at 60°C (3). Actually, these reactions only concern small proportions of the fatty acid chains (15,16).

The aim of the study presented in this article was to demonstrate the suitability of spectroscopic methods for determining modifications of the chemical structure of drying oils under the thermooxidative conditions that are required for curing these materials. Identification of the products obtained and the mechanisms of their formation were investigated by analyzing the modifications of drying oils by Fourier transform infrared (FTIR) and Fourier transform Raman (FT-Raman) spectroscopies. We focused on the oxidation of drying oils (linseed oil and poppyseed oil) under conditions rep-

---

*To whom correspondence should be addressed.
E-mail: gardettejl@cicsun.univ-bpclermont.fr

resentative of real conditions for drying of paints, i.e., thin films with a high surface/volume ratio.

EXPERIMENTAL PROCEDURES

The drying oils used in the study (linseed oil, poppyseed oil, heat-bodied linseed oil) were supplied by PEBEO (Gemenos, France). The fatty acid contents determined by ^{1}H nuclear magnetic resonance (NMR) (17) are given in Table 1. Heat-bodied linseed oil is usually obtained by heating linseed oil in vacuum or under N_2 between 250 and 300°C. This treatment results in nonoxidative polymerization involving Diels-Alder cyclization (18). Six-membered unsaturated rings are formed by reaction involving the double bonds of two fatty acid chains. Approximately 66% of the unsaturation implicated in the Diels-Alder mechanism disappears during this process.

A thin film of oil was spread out on a KBr window in which a little furrow was plowed. This allows control of the thickness of the sample and avoids spreading of the oil that can occur so long as the curing has not started. The infrared spectra were recorded with a Nicolet 510 spectrometer (Madison, WI) (resolution 4 cm^{-1}, 20-scan summation).

For the Raman analysis, samples were obtained by spreading out the oil film on glass windows and then introducing oxidized oils into quartz tubes. The Raman spectra were recorded with an FT-Raman Nicolet 910 spectrometer, equipped with an infrared Nd-YAG laser (excitation 1064 nm) (resolution 4 cm^{-1}, 100-scan summation).

The samples were oxidized in a ventilated oven at 60°C in the dark. For the photolysis and thermolysis experiments, the samples were introduced into Pyrex tubes and sealed in vacuum (5×10^{-6} torr). Thermolysis was carried out at 60°C. For the photolysis experiments, the samples were irradiated in a SEPAP 12-24 unit working at 60°C (MPC, Paris, France). This device has been described in many articles (19,20). The SEPAP unit is used to produce accelerated artificial aging of polymeric materials. It is equipped with four medium-pressure mercury lamps, filtered with a borosilicate envelope to eliminate the shortest wavelengths ($\lambda < 300$ nm).

The volatile products were analyzed by introducing a sample of oil in a gas cell with KBr windows and then heating at 60°C. The gas phase was identified by FTIR spectroscopy.

Nitrogen monoxide (NO) treatment has often been used for the identification (21,22) of hydroperoxide and alcohol functions. Alcohols are converted into nitrites (characteristic bands at 1248 and 779 cm^{-1}), and hydroperoxides are converted into nitrates (characteristic bands at 1650, 1260, and 860 cm^{-1}). NO treatment was carried out in a Pyrex container in the dark, after a nitrogen purge. Reaction time was fixed at 6 h. Treatment with sulfur tetrafluoride is used to identify carboxylic acids (23). SF_4 transforms the carboxylic acids into acid fluorides. Reaction with SF_4 induces the complete loss of the carbonyl band of the acid and the formation of a C=O band of the acid fluoride, which is largely shifted toward the higher frequencies. The saturated and α,β-unsaturated acid fluorides have a carbonyl absorption near 1843 and 1811 cm^{-1}, respectively (24). The treatments by SF_4 were carried out in an all-Teflon® container for 6 h, the oil samples being placed on CaF_2 windows.

TABLE 1
Fatty Acid Composition of Linseed Oil and Poppyseed Oil (mol%)

Acid	Linseed oil	Poppyseed oil
Linoleic	54	1
Linoleic	13	64
Oleic	22	24
Saturated	11	11

RESULTS

Figure 1 shows modifications of the infrared spectrum of linseed oil as a function of the heating time at 60°C.

The various absorption bands in the infrared spectrum of linseed oil can be assigned on the basis of data given in the literature (25–27). Figure 1 shows that, after an induction period that is characterized by a low rate of oxidation, hydroxyl groups are formed. This induction period probably results from the presence of natural antioxidants in the linseed oil. The antioxidants scavenge the radicals formed in the organic substrate, which leads in turn to their disappearance and creates an induction period.

The absorption band in the OH vibration range with a maximum at 3425 cm^{-1} can be attributed to the formation of hydroperoxides (after 22 h). Evolution of the spectrum also reveals notable modifications of the absorption bands attributed to unsaturation. One observes a progressive decrease in the ν=C-H) absorbance at 3011 cm^{-1} and the γ(C-H) absorbance at 716 cm^{-1}, which indicate the disappearance of the double bonds in the *cis* conformation. On the other hand, in Figure 2, one observes during the first 24 h the appearance of two absorption bands at 970 and 987 cm^{-1}, which can be attributed to the formation of *trans* isomers (nonconjugated *trans* and conjugated *trans,* respectively). A weak band appears as a shoulder at 950 cm^{-1}. This absorption maximum may be at-

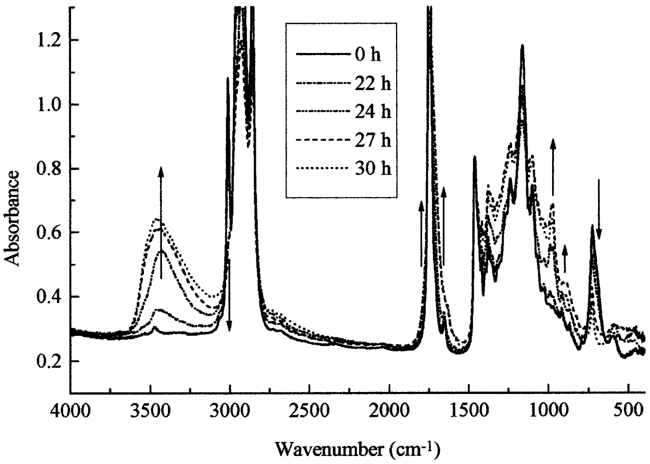


FIG. 1. Evolution of the linseed oil Fourier transform infrared spectrum in the range 4000–400 cm^{-1} during oxidation at 60°C.

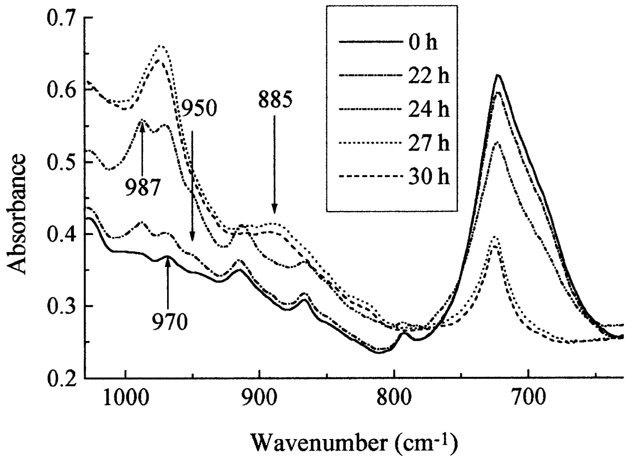


FIG. 2. Evolution of the linseed oil Fourier transform infrared spectrum in the range 1030–630 cm^{-1} during oxidation at 60°C.

tributed to the formation of conjugated *cis* isomers. After 30 h of oxidation, a decrease in the *trans* isomer bands evidenced the saturation of the fatty acid double bonds. The infrared spectra of oxidized linseed oil also show a weak band at 885 cm^{-1}. This band reveals the formation of epoxides. The formation of epoxy groups with an absorption at 885 cm^{-1} has been reported in the thermal decomposition of methyl oleate hydroperoxides (28) and is attributed to *trans* epoxides (29).

Similar results were obtained for poppyseed oil, despite a slower rate of oxidation. The intensity of the conjugated *trans* band, compared to the nonconjugated *trans* band, is more important, but this band disappears during oxidation in the same way as in linseed oil. The OH stretching vibration of alcohols lies around 3470 cm^{-1} and cannot be separated from that of the hydroperoxides, which are postulated to be the major products responsible for the broad band in the OH range when oxidation starts. The OH absorption of carboxylic acids also participates in this absorption band. Treatment with NO is useful to detect the formation of alcohols and hydroperoxides. However, the double bonds in our substrates readily react with NO (in fact, with the NO_2 present at low levels in NO gas) and lead to nitro compounds that have absorption bands close to those of nitrates. Thus, NO treatment permits quantitative determination of only alcohols. The formation of alcohols is evidenced in Figure 3B, with the nitrite band at 779 cm^{-1} increasing with oxidation time.

Modifications of the spectrum in the C=O range are more easily observed on the subtraction spectra. Figure 4 shows the evolution of the spectra between 1900 and 1500 cm^{-1}. The initial spectrum of the sample before thermal oxidation is subtracted.

A notable decrease of the initial C=O band of the esters is observed in Figure 4. This evolution may be attributed to the physical changes of the oil film during drying. These changes induce a continuous loss of resolution at the maximum of the most intense bands (mainly the carbonyl bands at 1745 cm^{-1} and the alkyl bands between 2800 and 2950 cm^{-1}). The negative absorption could also be explained by oxygen uptake

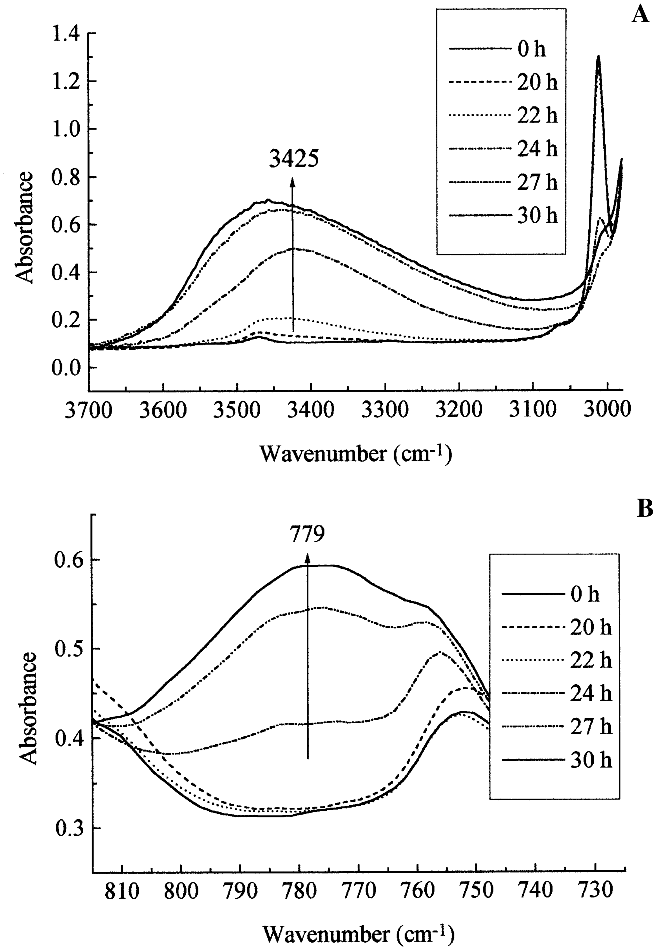


FIG. 3. Infrared spectra of oxidized linseed oil before (A) and after (B) nitrogen monoxide treatment.

(27). Formation of a broad carbonyl band with absorption maxima at 1772, 1720, 1698 and 1633 cm^{-1} is observed during oxidation. The absorption band at 1772 cm^{-1} can be assigned to peracids, peresters or γ-lactones (30,31). The maxima at 1720 and 1698 cm^{-1} can be partly attributed to the

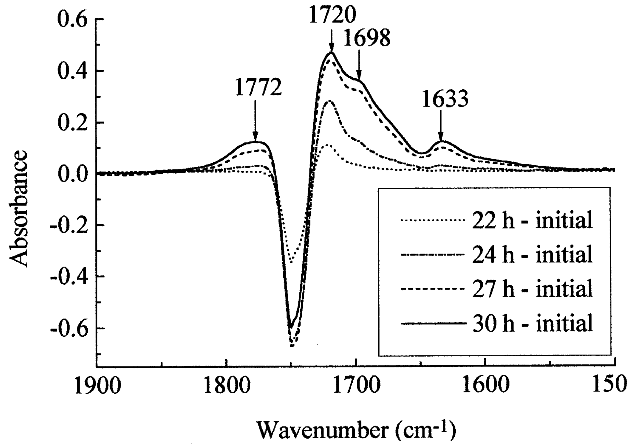


FIG. 4. Subtraction spectra for linseed oil dried at 60°C (carbonyl group range).

formation of saturated and α,β-unsaturated ketones, respectively. The band at 1633 cm^{-1} reflects the formation of C=C bonds, conjugated with the C=O bond of the ketone.

The formation of carboxylic acids can be anticipated on the basis of knowledge about the oxidation of organic substrates. Depending on their structures, the C=O stretching vibration of carboxylic acids lies between 1695 and 1720 cm^{-1}. For the drying oils studied here, modifications of the spectrum in the carbonyl range reported above prevent the observation of an absorption band that could reflect the formation of carboxylic acids. As mentioned before, the hydroxyl vibration of carboxylic acids also cannot be identified. For that reason, the derivatization reaction with SF_4 is potentially much more informative. Treatment with SF_4, carried out on a sample heated for 30 h at 60°C, shows the formation of two absorption bands at 1810 and 1843 cm^{-1} (Fig. 5A).

The absorption maxima at 1843 and 1810 cm^{-1} have to be attributed to the acid fluorides derived from saturated and unsaturated acids, respectively. A decrease in the absorbance of the shoulder on the ester C=O band is observed. A similar treatment on a control sample (0 h of drying) also gives absorption at 1843 cm^{-1} and a slight decrease of absorbance at 1711 cm^{-1} (Fig. 5B). This result indicates that a few free fatty acids are initially present in the linseed oil samples. Similar results were obtained for poppyseed oil.

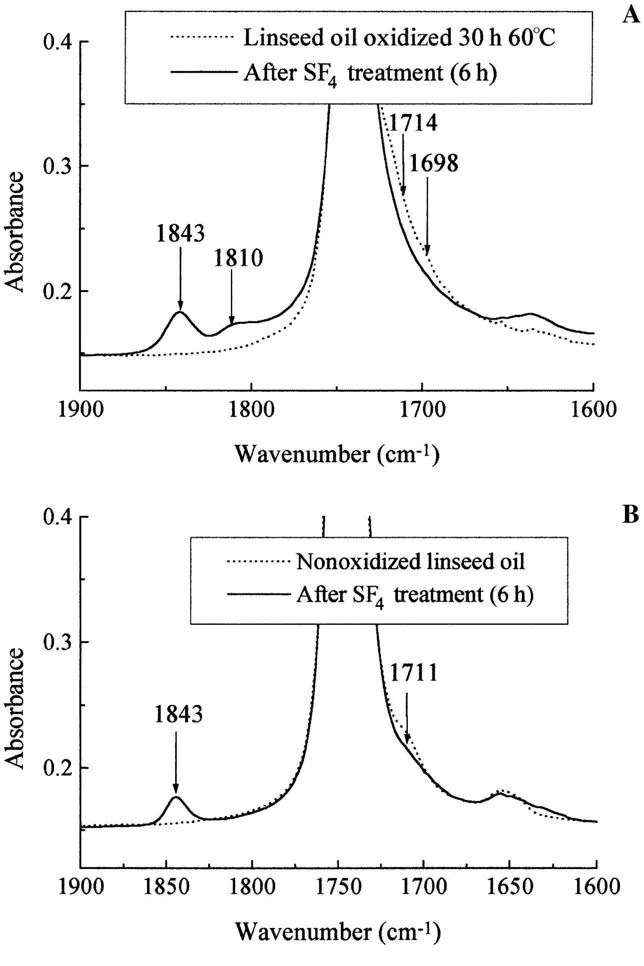


FIG. 5. SF_4 treatment on (A) oxidized linseed oil and (B) nonoxidized linseed oil.

One can observe on the spectra of the oxidized samples a global absorbance increase in the region 1300–1000 cm^{-1}. This modification of the spectra can be tentatively attributed to the formation of alcohols and hydroperoxides [ν(C–C–O) between 1210 and 1100 cm^{-1}], of ethers [ν(C–O–C) between 1150 and 1060 cm^{-1}], or carboxylic acids [ν(C–O) between 1315 and 1200 cm^{-1}] (30). Vibrations of C–C or peroxy cross-links may also be present in this range. So, to identify peroxy bonds, we have studied the oxidation of linseed oil by Raman spectrometry. It is known that the ν(O–O) vibration of peroxides gives a notable absorption between 900 and 700 cm^{-1} (32). The behavior of the Raman spectrum of a linseed oil film heated at 60°C up to 50 h is shown in Figure 6.

The spectrum of the control sample (0 h) shows a narrow band at 866 cm^{-1}. This absorption maximum is observed for linseed oil but not for poppyseed oil. This band, which can be attributed to skeletal vibrations of linolenic acid, reflects the presence of important concentrations of this acid in linseed oil. The intensity of the band at 866 cm^{-1} decreases with heating time. The initial band at 1270 cm^{-1}, which is assigned to the in-plane deformation (=C–H) of the nonconjugated *cis* double bonds, also decreases. In contrast, the growth of a broad band with an absorption maximum around 850 cm^{-1} may be assumed to result from the formation of hydroperoxides [ν(O–O) vibration] (33). However, this band does not disappear after drying times (more than 100 h), whereas the concentration of hydroperoxides decreases notably. This behavior probably evinces the formation of peroxy cross-links.

Hydroperoxides are intermediate products in the oxidation of oils (34). Determining the characteristics of these products, and in particular their stability, is of great interest. Linseed oil samples oxidized at 60°C for 25 h were submitted to photolysis and to thermolysis in vacuum at 60°C. Figures 7A and 7B show the modifications of the spectrum of linseed oil oxidized for 25 h at 60°C and then photolyzed for 2 h. A 25-h duration was chosen because this time corresponded to extensive oxi-

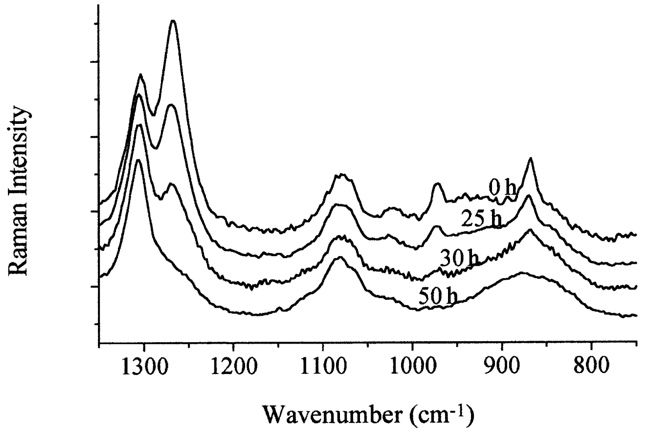


FIG. 6. Modification of Raman spectra of linseed oil with oxidation time.

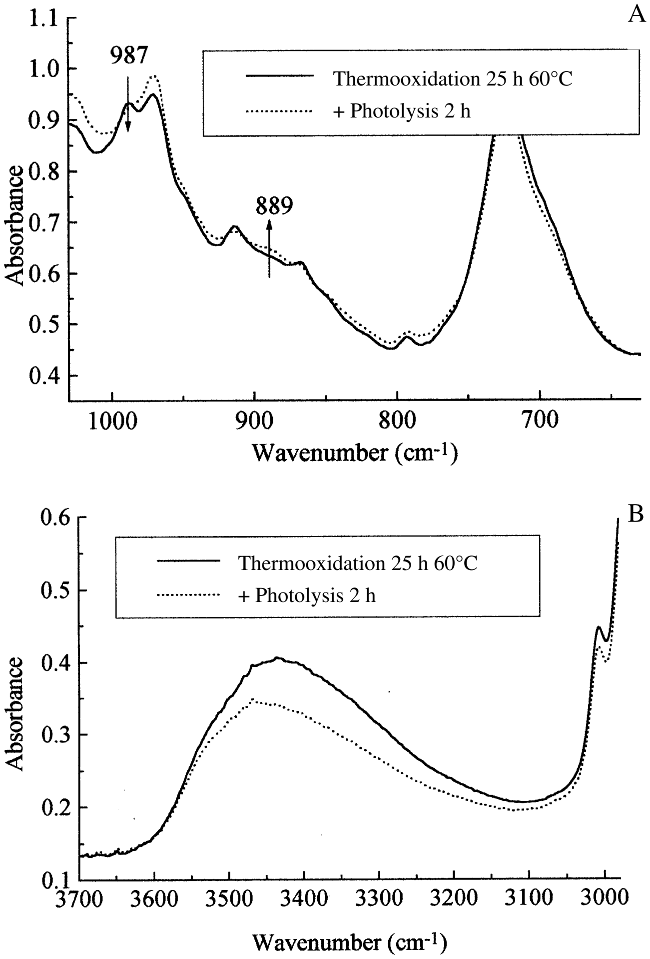


FIG. 7. Photolysis of oxidized linseed oil: (A) *trans* double bonds region. (B) OH band region.

dation with notable concentrations of hydroperoxides and conjugated *trans* double bonds being formed (see Figs. 2 and 3B). Figure 7A shows that the photolysis of the hydroperoxides leads to the disappearance of the conjugated *trans* double bonds, observed through the decrease of the 987 cm^{-1} band, whereas *trans* epoxides are formed (a weak absorption appears at 885 cm^{-1}). Photolysis of the hydroperoxides leads to a decrease of the OH band at 3425 cm^{-1} (Fig. 7B). This behavior confirms that hydroperoxides are decomposed when submitted to irradiation (35) and can generate epoxides.

For the sample thermolyzed at 60°C, a marked decrease in the OH absorption between 3200 and 3500 cm^{-1} could also be observed after 7 h, but no significant modifications of the bands attributed to *trans* conjugated double bonds or epoxides could be noticed. Thermooxidation at 60°C of photolyzed or thermolyzed samples permits the observation of a weak band at 663 cm^{-1} because the contribution of the *cis* double bonds at 716 cm^{-1} almost completely disappears (Fig. 8). The residual band, visible at 725 cm^{-1}, is due to a skeletal vibration of the fatty acid chains. The new band at 663 cm^{-1}, also present in the spectrum of heat-bodied linseed oil, may be attributed to the formation of small quantities of unsaturated cycles occurring when heated in vacuum.

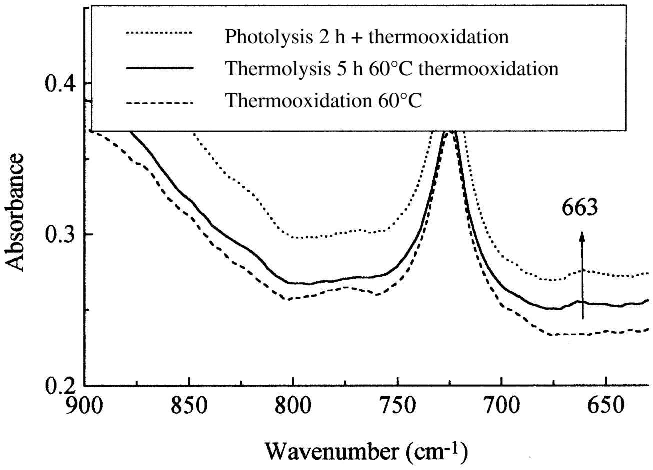


FIG. 8. Oxidation at 60°C of thermolyzed and photolyzed samples.

Analysis of the volatile compounds formed during thermooxidation at 60°C was carried out by infrared spectrometry. Several oxidation products were identified in the spectrum of the gas phase (Fig. 9).

The two bands at 2717 and 2810 cm^{-1} suggest the formation of aldehydes (27). A comparison with the spectra of pentanal and nonanal (36) indicates that the ratio between the number of alkyl groups and the number of carbonyl groups was around 4–5. The spectrum in Figure 9 shows that water and carbon dioxide were also obtained.

DISCUSSION

It is well agreed that the oxidation of unsaturated compounds is initiated by abstraction of a hydrogen atom on the methylene group in α-position to the double bonds, followed by an addition of oxygen (15). Hydrogen abstraction by the peroxy radicals generates hydroperoxides, which are observed at 3425 cm^{-1}. Modifications of the infrared spectra of oxidized linseed oil (Fig. 2) can be interpreted by *cis-trans* isomerization and conjugation

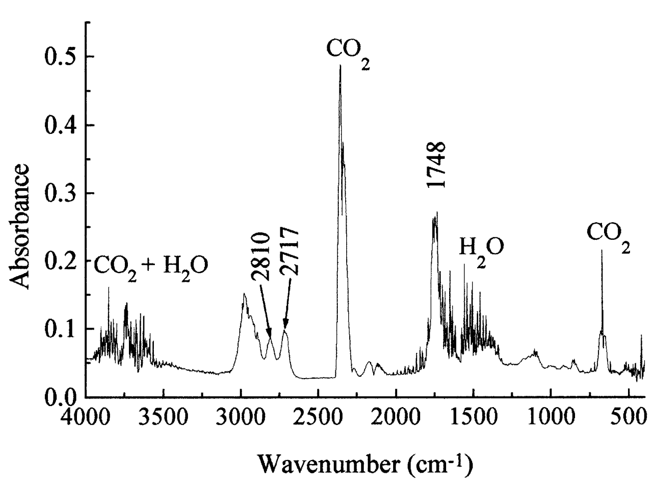
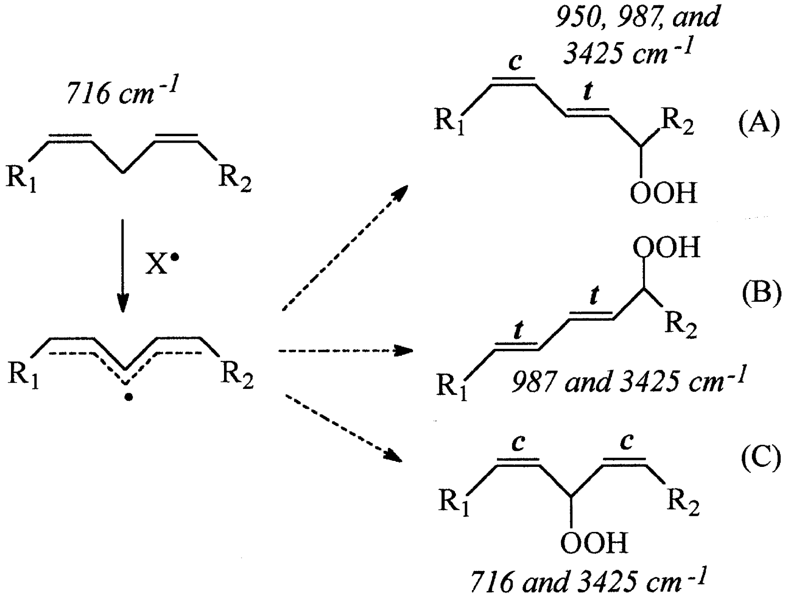


FIG. 9. Infrared spectrum of the gas phase obtained during oxidation of linseed oil.



SCHEME 1

of polyunsaturated fatty acids (37). Three hydroperoxides, A, B, and C, can potentially be formed (Scheme 1).

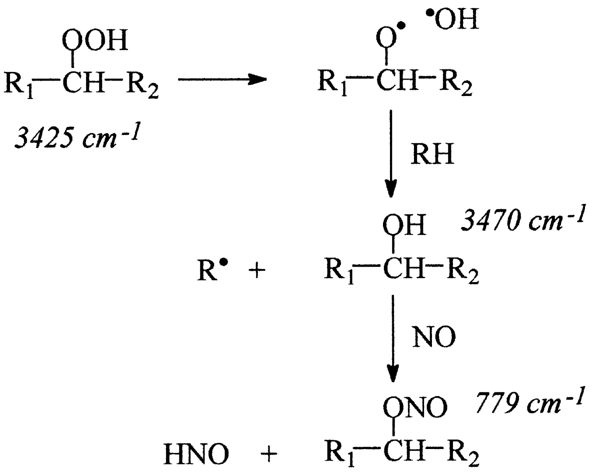
The disappearance of the *cis* band at 716 cm^{-1} implies that the formation of nonconjugated hydroperoxide C is not favored. This result has been previously reported from high-performance liquid chromatography and ^{1}H NMR data (38,39). It is well known that secondary hydroperoxides can be decomposed by heat (1,40). Homolysis of the peroxy bond gives a hydroxyl radical and an alkoxyl radical, which can generate alcohols, ketones, or aldehydes. NO treatment is useful to differentiate alcohols and hydroperoxides. To our knowledge, this is the first time that alcohols have been characterized in a dried oil film. By observing Figure 2A and 2B, it appears clearly that alcohols are secondary products formed after hydroperoxides are created (Scheme 2).

In the carbonyl range, one can observe the formation of conjugated and nonconjugated carbonyl products. The carbonyl groups can be assumed to result from a cage reaction involving the alkoxyl and hydroxyl radicals obtained by decomposition of the hydroperoxides (15) (Scheme 3). A termination reaction has been proposed to produce ketone, alcohol, and oxygen (41) (Scheme 4).

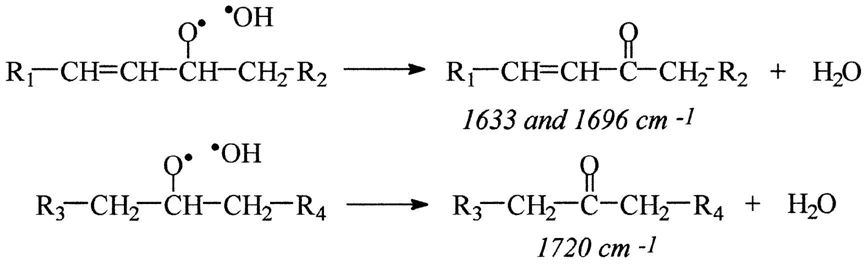
From the alkoxyl radicals, a β-scission reaction is possible and aldehydes can be formed. Aldehydes have a carbonyl absorption band near 1745 cm^{-1}, but these compounds are anticipated to be quite oxidizable and probably do not accumulate in the sample. In our experiments we have observed aldehydes only in the gas phase (Fig. 9). Considering the temperature of the experiments, the ratio of alkyl/carbonyl groups is in good agreement with the results published in the literature that report the formation of ethane and propanal as the major volatile oxidation products of methyl linolenate (1). Aldehydes with higher molecular weight are not volatile at 60°C and as a consequence are not observed in the gas phase. The formation of ethane and propanal could result from the β-scissions of the alkoxyl radical obtained by decomposition of the hydroperoxides formed on the linolenic chains (Scheme 5). Only weak concentrations of volatile products are formed. The decrease in the alkyl bands of the fatty acid chains in infrared spectra is not important when observed.

The presence of water in the gas phase is easily explained by a hydrogen abstraction by the hydroxyl radical HO$^•$ (Scheme 3). CO_2 is assumed to be formed by decarboxylation of the α-β unsaturated carboxylic acids (42) or that of the β-ketoacids (43). An alternative proposal is the oxidation of aldehydes to give peracids (2).

There are only a few results in the literature concerning the formation of carboxylic acids in oils. Nonetheless, the formation of carboxylic acids in the curing step evinces chain scission reactions that can weaken the dried film. Carboxylic



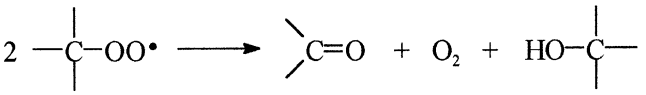
SCHEME 2



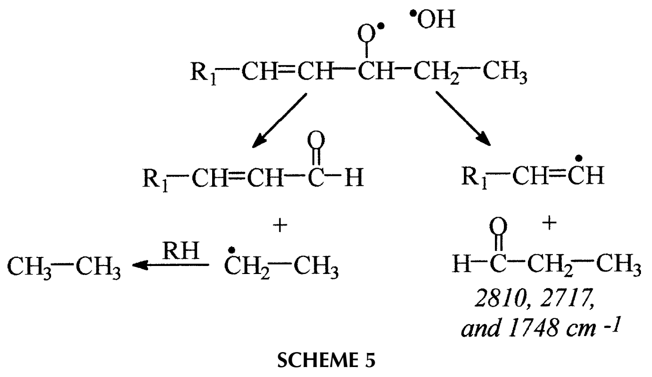
SCHEME 3

acids, characterized by infrared spectrometry after SF_4 treatment, are probably formed by oxidation of aldehydes (Scheme 6) (44). Another reaction proposes that the formation of carboxylic acids can result from a hydrogen atom abstraction on the tertiary carbon atom with a hydroperoxide function (Scheme 7) (45). Then, acid formation is due to β-scissions reactions after hydroperoxide decomposition. This result is important because one can assume that SF_4 treatment could be used to quantify the scission reactions occurring when curing under different conditions.

During oxidation, various radicals are formed. Recombination reactions between alkyl, alkoxyl, and peroxyl radicals are responsible for an increase in viscosity, in molecular weight, and in refractive index (14). The C–C, ether, and peroxy bonds formed by these reactions have been identified by ^{13}C NMR analysis (11) and by mass spectrometry (12,46). Infrared spectroscopy is not appropriate to their detection because many vibration bands are present in the same range. The Raman spectra of Figure 6 indicate that not only the ν(O–O) vibration of the hydroperoxides but also that of peroxides contribute to the absorption at 850 cm^{-1}. This interpretation has been given in the literature (33). The accurate assignment of this band remains difficult to assess because skeletal vibrations also produce an absorption in this region (47), as well as peracids and peresters that may be formed by oxidation of the fatty acid chains. Moreover, the formation of ethers could also account for this absorption.



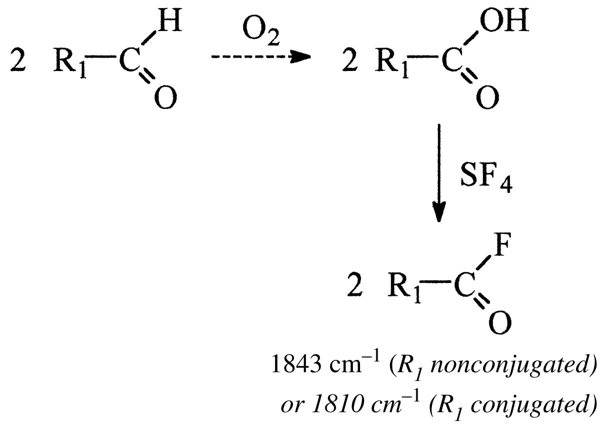
SCHEME 4



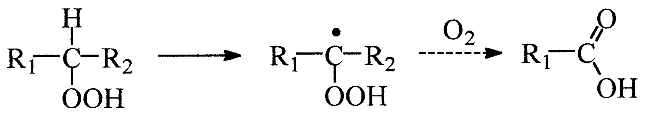
SCHEME 5

As mentioned above, the explanation of the fast decrease in the unsaturation concentration observed during the first step of oxidation is still not clear. A first mechanism involves a cyclization reaction, but this reaction occurs only at high temperatures (250°C) on one fatty acid chain (48,49) or between two fatty acid chains (16,50). This reaction is not favored at 60°C. No absorption band at 664 cm^{-1}, characteristic of the formation of cyclohexene (48), is observed in the spectrum of 60°C-oxidized linseed oil. A weak band at 663 cm^{-1} is present nevertheless, after photolysis and thermolysis at 60°C of oxidized linseed oil. The rings are probably formed *via* a radical mechanism as mentioned in Scheme 8. A Diels-Alder mechanism cannot be reasonably proposed because such a reaction would be photochemically disadvantaged (51). In thermooxidation at 60°C, alkyl radicals can react quickly with oxygen. The above reaction is unlikely, and no notable concentration of cyclohexenic rings can be observed in the spectra of thermooxidized samples.

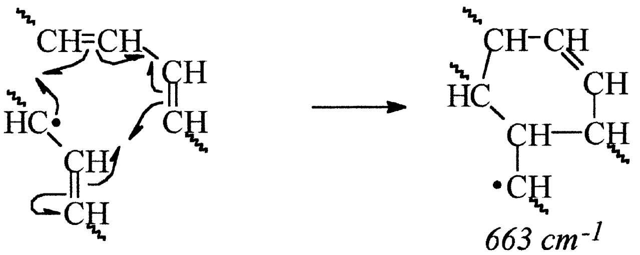
The decrease of unsaturations could also be explained by the formation of epoxides (52) or epidioxides (53–56). The weak concentrations of epidioxides found by various authors do not permit considering these products as responsible for the disappearance of the double bonds. Epoxides can be ob-



SCHEME 6



SCHEME 7



SCHEME 8

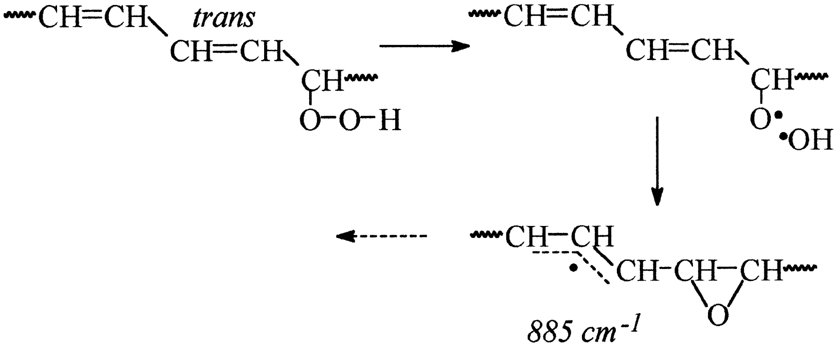
tained by reaction of hydroperoxides with the double bonds (57) (Scheme 9).

Other reaction mechanisms accounting for the formation of epoxides may be proposed (58,59) (Schemes 10 and 11). The results published by Mayo (60) have shown that the addition reaction of peroxy radicals on unsaturation involves the conjugated double bonds. This addition would be partly responsible for the curing of a drying oil. The results obtained by Muizebelt and Nielden (12) confirm this hypothesis: it is shown that the radical formed by addition on a conjugated double bond is stabilized by delocalization.

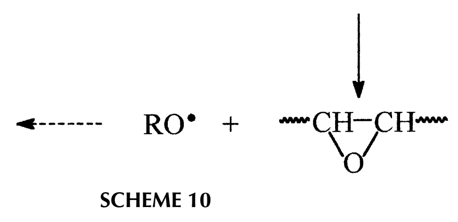
The formation of epoxy groups at 885 cm^{-1} can be observed in the infrared spectra of oxidized samples (Fig. 2) only after important concentrations of conjugated double bonds and hydroperoxides have been obtained. This result suggests that the epoxy groups could be formed by decomposition of the hydroperoxides in α-position of a double bond, as presented in Scheme 9 or by radical addition on unsaturation as shown in Scheme 10. The formation of epoxides is not observed after thermolysis at 60°C of oxidized linseed oil. On this basis, it can be postulated that, under conditions of thermooxidation at 60°C, the formation of epoxy groups and the disappearance of unsaturation mainly involve the addition of peroxy radicals to the double bonds. This reaction produces alkoxyl radicals $RO^{\bullet}$ that can lead to the formation of aldehydes by β-scission and the oxidation of aldehydes can be a possible epoxidation route (Scheme 11). Both these mechanisms most probably account for the observed results.

The epoxy groups are not stable, and their stationary concentration reaches only a low value (Fig. 2). Epoxide rings can be opened by addition of various radicals and may be partly responsible for the curing of drying oils. It may be postulated that the slow formation of epoxides and the slow disappearance of unsaturation in the second step of curing (when conjugated double bonds have disappeared) are due to homolytic decomposition of O–O bonds of hydroperoxides. The rate of formation of the epoxy groups considerably decreases when the residual unsaturation is not conjugated.

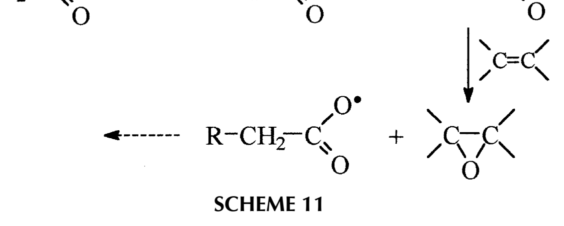
Under conditions of thermal oxidation at 60°C, the radical oxidation of fatty acid chains of linseed oil or poppyseed oil involves the sequence (methylene-interrupted *cis* → *trans* conjugated → *trans* nonconjugated → saturated). Hydroperoxides, decomposed by homolytic cleavage of their peroxy bond, can lead to a complex mixture of ketones, aldehydes, alcohols, acids, etc. by subsequent reactions. The decrease in the concentration of unsaturation is explained by easy addition of peroxy radicals on the conjugated double bond, which produces epoxy groups. The several radical species that are formed by the various reaction mechanisms can recombine and lead to the formation of a three-dimensional network, which is responsible for the curing of a drying oil.



SCHEME 9



SCHEME 10



SCHEME 11

REFERENCES

1. Frankel, E.N., W.E. Neff, and E. Selke, Analysis of Autoxidized Fats by Gas Chromatography–Mass Spectrometry: VII. Volatile Thermal Decomposition Products of Pure Hydroperoxides from Autoxidized and Photosensitized Oxidized Methyl Oleate, Linoleate, and Linolenate, *Lipids 16*:279–285 (1981).
2. Schieberle, P., and W. Grosch, Model Experiments About the Formation of Volatile Carbonyl Compounds, *J. Am. Oil Chem. Soc. 58*:602–607 (1981).
3. Hancock, R.A., and N.J. Leeves, Studies in Autoxidation. Part I. The Volatile By-Products Resulting from the Autoxidation of Unsaturated Fatty Acid Methyl Esters, *Prog. Org. Coat. 17*:321–336 (1989).
4. Neff, W.E., and E. Selke, Volatile Compounds from the Triacylglycerol of *cis,cis*-9,15-Linoleic Acid, *J. Am. Oil Chem. Soc. 70*:157–161 (1993).
5. Mahungu, S.M., S.L. Hansen, and W.E. Artz, Quantitation of Volatile Compounds in Heated Triolein by Static Headspace Capillary Gas Chromatography/Infrared Spectroscopy–Mass Spectrometry, *Ibid. 71*:453–455 (1994).
6. Elm, A.C., Deterioration of Dried Oil Films, *Ind. Eng. Chem. 41*:319–324 (1949).
7. Gladovic, N., L. Zupancic-Kralj, and J. Plavec, Determination of Primary Oxidation Products of Linoleic Acid and Triacylglycerols, *J. Chromatogr. A 767*:63–68 (1997).
8. Wexler, H., Polymerization of Drying Oils, *Chem. Rev. 64*:591–611 (1964).
9. Hutchinson, G.H., Some Aspects of Drying Oils Technology, *J. Oil Colour Chem. Assoc. 56*:44–53 (1973).
10. Baer, N.S., and N. Indicator, Linseed Oil–Metal Acetylacetonate Systems. III. Infrared Spectroscopic Observations of the Drying Film, *J. Coat. Technol. 48*:58–62 (1976).
11. Muizebelt, W.J., J.C. Hubert, and R.A.M. Venderbosch, Mechanistic Study of Drying of Alkyd Resins Using Ethyl Linoleate as a Model Substance, *Prog. Org. Coat. 24*:263–279 (1994).
12. Muizebelt, W.J., and M.W.F. Nielden, Oxidative Crosslinking of Unsaturated Fatty Acids Studied with Mass Spectrometry, *J. Mass Spectrom. 31*:545–554 (1996).
13. Muizebelt, W.J., Oxidative Crosslinking of Alkyd Resins Studied with Mass Spectrometry and NMR Using Model Compounds, *J. Coat. Technol. 70*:83–93 (1998).
14. Hess, P.S., and G.A. O'Hare, Oxidation of Linseed Oil. Temperature Effects, *Ind. Eng. Chem. 42*:1424–1431 (1950).
15. Frankel, E.N., Lipid Oxidation, *Prog. Lipid Res. 19*:1–22 (1980).
16. Cristopoulou, C.N., and E.G. Perkins, Isolation and Characterization of Dimers Formed in Used Soybean Oil, *J. Am. Oil Chem. Soc. 66*:1360–1370 (1989).
17. Wollenberg, K., Quantitative Triglycerol Analysis of Whole Vegetable Seeds by ^{1}H and ^{13}C Magic Angle Sample Spinning NMR Spectroscopy, *Ibid. 68*:391–400 (1991).
18. Clingman, A.L., D.E.A. Rivett, and D.A. Sutton, The Chemistry of Polymerised Oils. Part IV. Thermal Polymerisation of Some Long-Chain Unsaturated Fatty Esters, *J. Chem. Soc. 1*:1088–1090 (1954).
19. Arnaud, R., and J. Lemaire, Photocatalytic Oxidation of Polypropylenes and Polyundecanoamides, in *Developments in Polymer Photochemistry-2*, edited by N.S. Allen, Applied Science Publishers, England, 1981, pp. 135–164.
20. Tang, L., D. Sallet, and J. Lemaire, Photochemistry of Polyundecanamides. 1. Mechanisms of Photooxidation at Short and Long Wavelengths, *Macromolecules 15*:1432–1437 (1982).
21. Carlsson, D.J., R. Brousseau, C. Zhang, and D.M. Wiles, Polyolefin Oxidation: Quantification of Alcohol and Hydroperoxide Products by Nitric Oxide Reactions, *Polym. Deg. Stab. 17*:303–318 (1987).
22. Carlsson, D.J., and J. Lacoste, A Critical Comparison of Methods for Hydroperoxide Measurement in Oxidized Polyolefins, *Ibid. 32*:377–386 (1991).
23. Wilhelm, C., and J.L. Gardette, Infrared Identification of Carboxylic Acids Formed in Polymer Photooxidation, *J. Appl. Polym. Sci. 51*:1411–1420 (1994).
24. Lacoste, J., D. Vaillant, and D.J. Carlsson, Gamma-, Photo-, and Thermally-Initiated Oxidation of Isotactic Polypropylene, *J. Polym. Sci.*: *Part A*: *Polym. Chem. 31*:715–722 (1993).
25. Shreve, O.D., M.R. Heether, H.B. Knight, and D. Swern, Infrared Absorption Spectra. Some Long-Chain Fatty Acids, Esters and Alcohols, *Anal. Chem. 22*:1498–1501 (1950).
26. Sinclair, R.G., A.F. McKay, G.S. Myers, and R. Norman Jones, The Infrared Absorption Spectra of Unsaturated Fatty Acids and Esters, *J. Am. Chem. Soc. 74*:2578–2585 (1952).
27. Van de Voort, F.R., A.A. Ismail, J. Sedman, and G. Emo, Monitoring the Oxidation of Edible Oils by Fourier Transform Infrared Spectroscopy, *J. Am. Oil Chem. Soc. 71*:243–253 (1994).
28. Lercker, G., P. Capella, L.S. Conte, and U. Pallota, Sur certains produits de transformation thermique des hydroperoxydes de l'oléate de méthyle, *Rev. Fr. Corps Gras 25*:227–237 (1978).
29. Shreve, O.D., M.R. Heether, H.B. Knight, and D. Swern, Infrared Absorption Spectra of Some Epoxy Compounds, *Anal. Chem. 23*:277–282 (1951).
30. Lin-Vien, D., N.B. Colthup, W.G. Fateley, and J.G. Grasselli, *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, Academic Press, San Diego, 1991.
31. Avram, M., and G.D. Mateescu, *Spectroscopie Infrarouge*, Dunod, Paris, 1970.
32. Jacob, P., B. Wehling, W. Hill, and D. Klockow, Feasibility Study of Raman Spectroscopy as a Tool to Investigate the Liquid-Phase Chemistry of Aliphatic Organic Peroxides, *Appl. Spectrosc. 51*: 74–80 (1997).
33. Higuchi, S., T. Hamada, and Y. Gohshi, Examination of the Photochemical Curing and Degradation of Oil Paints by Laser Raman Spectroscopy, *Ibid. 51*:1218–1223 (1997).
34. Ho, C.-T., and Q. Chen, Lipids in Food Flavors—An Overview, in *ACS Symposium Series 558,* American Chemical Society, Washington, 1994, pp. 1–14.
35. Schieberle, P., W. Grosch, and J. Firl, Photolysis of Unsaturated Fatty Acid Hydroperoxides, in *Oxygen Radicals in Chemistry and Biology*, Walter de Gruyter & Co., Berlin, 1984, pp. 257–265.
36. *Aldrich Vapor Phase Sample Library*, OMNIC 3.0 software, Nicolet Instrument Corp., 1990.
37. Frankel, E.N., Lipid Oxidation: Mechanisms, Products and Biological Significance, *J. Am. Oil Chem. Soc. 61*:1908–1917 (1984).
38. Hall, G.E., and D.G. Roberts, A Study by Infrared and Proton Magnetic Resonance Spectroscopy of the Monohydroperoxides of Oleate and Linoleate Esters, *J. Chem. Soc. B*:1109–1112 (1966).
39. Haslbeck, F., W. Grosch, and J. Firl, Formation of Hydroperoxides with Unconjugated Diene Systems During Autoxidation and Enzymatic Oxygenation of Linoleic Acid, *Biochim. Biophys. Acta 750*:185–193 (1983).
40. Gardner, H.W., Reactions of Hydroperoxides—Products of High Molecular Weight, in *Autoxidation of Unsaturated Lipids*, Academic Press, London, 1987, pp. 51–93.
41. Russel, G.A., Fundamental Processes of Autoxidation, *J. Chem. Educ. 36*:111–118 (1959).
42. Bigley, D.B., and J.C. Thurman, On the Transition State for Decarboxylation of β-Keto Acids and βγ-Unsaturated Acids, *Tetrahedron Lett. 25*:2377–2380 (1967).
43. Huang, C.L., C.C. Wu, and M.H. Lien, *Ab Initio* Studies of Decarboxylations of the β-Keto Carboxylic Acids $XCOCH_2COOH$ (X = H, OH, and CH_3), *J. Phys. Chem. A 101*:7867–7873 (1997).
44. March, J., *Advanced Organic Chemistry—Reactions, Mechanisms and Structure,* 4th edn., John Wiley & Sons, New York, 1992, p. 701.

45. Teissedre, G., J.F. Pilichowski, S. Schmela, and J. Lacoste, Aging of EPDM-I: Photo and Thermal Stability of EPDM Hydroperoxides, *Polym. Deg. Stab. 53*:207–215 (1996).
46. Miyashita, K., N. Hara, K. Fujimoto, and T. Kaneda, Dimers Formed in Oxygenated Methyl Linoleate Hydroperoxides, *Lipids 20*:578–587 (1985).
47. Budinger, P.A., J.R. Mooney, J.G. Grasselli, P.S. Fay, and A.T. Guttman, Spectra-Structure Correlation of Alkyl Peroxides, *Anal. Chem. 53*:884–889 (1981).
48. McInnes, A.G., F.P. Cooper, and J.A. McDonald, Further Evidence for Cyclic Monomers in Heated Linseed Oil, *Can. J. Chem. 39*:1906–1914 (1961).
49. Dobson, G., W.W. Christie, and J.L. Sebedio, The Nature of Cyclic Fatty Acids Formed in Heated Vegetable Oils, *Grasas Aceites 47*:26–33 (1996).
50. Wheeler, D.H., and J. White, Dimer Acid Structures. The Thermal Dimer of Normal Linoleate, Methyl 9-*cis*, 12-*cis* Octadecadienoate, *J. Am. Oil Chem. Soc. 44*:298–302 (1967).
51. Dewar, M.J.S., Aromaticity and Pericyclic Reactions, *Angew. Chem. Int. Ed. 10*:761–776 (1971).
52. Thums, R., and G. Spiteller, Epoxidation—A Consequence of Cell Damage, *Monatsh. Chem. 128*:411–420 (1997).
53. Chan, H.W.S., J.A. Matthew, and D.T. Coxon, A Hydroperoxy-epidioxide from the Autoxidation of a Hydroperoxide of Methyl Linolenate, *J. Chem. Soc. Chem. Commun.*:235–236 (1980).
54. Porter, N.A., L.S. Lehman, B.A.Weber, and K.J. Smith, Unified Mechanism for Polyunsaturated Fatty Acid Autoxidation. Competition of Peroxy Radical Hydrogen Atom Abstraction, β-Scission, and Cyclization, *J. Am. Chem. Soc. 103*:6447–6455 (1981).
55. Neff, W.E., E.N. Frankel, and K. Fujimoto, Autoxidative Dimerization of Methyl Linolenate and Its Monohydroperoxides, Hydroperoxy Epidioxides and Dihydroperoxides, *J. Am. Oil Chem. Soc. 65*:616–623 (1988).
56. Frankel, E.N., W.E. Neff, and K. Miyashita, Autoxidation of Polyunsaturated Triacylglycerols. II. Trilinolenoylglycerol, *Lipids 25*:40–47 (1990).
57. Walther, U., and G. Spiteller, Zur Bilbung von Ölsäureepoxid bei der Lagerung Technischer Ölsäure, *Fat Sci. Technol. 95*:472–474 (1993).
58. Mayo, F.R., The Oxidation of Unsaturated Compounds. VIII. The Oxidation of Aliphatic Unsaturated Compounds, *J. Am. Chem. Soc. 80*:2497–2500 (1958).
59. Van Sickle, D.E., F.R. Mayo, E.S. Gould, and R.M. Arluck, Effects of Experimental Variables in Oxidations of Alkenes, *Ibid. 89*:977–984 (1967).
60. Mayo, F.R., Free-Radical Autoxidations of Hydrocarbons, *Acc. Chem. Res. 1*:193–201 (1968).

[Received January 12, 1999; accepted April 8, 1999]