Long-Term Behavior of Oil-Based Varnishes and Paints. Fate of Hydroperoxides in Drying Oils

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ABSTRACT: The thermal stability of linseed oil and poppyseed oil hydroperoxides in a temperature range from ambient to 120°C has been investigated on the basis of iodometric titration. The peroxide value (PV) vs. oxidation time curves show similar developments at the six temperatures chosen for the experiments. These curves are characterized by a fast increase in the PV up to a maximal value, followed by a decrease in the PV at a lower rate. The maximal PV is higher when the curing temperature is lowered. This result indicates thermal decomposition of the hydroperoxides. The peroxy crosslink concentration in the dried oil film varies similarly to the hydroperoxide concentration. This indicates that, for dried films, the network is almost totally constituted of ether and C–C crosslinks. A comparison of the rates of peroxide decomposition under thermolytic and thermooxidative conditions has evidenced that the only homolytic scission of the O–O bonds cannot justify the decrease of the PV in thermooxidation. Another mechanism accounting for hydroperoxide decomposition, based on an induced decomposition of the hydroperoxides, has been proposed. These results have permitted completing the description of the curing mechanisms of drying oils.

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KEY WORDS: Curing mechanism, hydroperoxides, iodometry, linseed oil, peroxides, peroxy bridges, poppyseed oil, thermal stability.

The oxidation of polyunsaturated fatty acids (PUFA) has been extensively reviewed in the literature. The main interest was the study of oxidation of fatty acids contained in food products because even low levels of oxidation often imply a denaturation of the taste or odor of the product.

The aim of our research is to study the oxidation of drying oils in paints where the surface/volume ratio is much higher. In a previous article (1), we reported data that showed that the oxidation levels in the dried films were much more important than in the food industry. Mechanisms accounting for the oxidative polymerization of drying oils have been proposed. However, it is of great interest to investigate the influence of temperature on the fate of the hydroperoxide groups (ROOH) formed in the drying step, because secondary oxidation reactions (formation of oxidized by-products and crosslinking) can probably be influenced by the concentrations of alkoxyl and hydroxyl radicals obtained by decomposition of the hydroperoxides.

Thermal or photochemical oxidation of fatty acid chains contained in oils leads to the formation of ROOH as primary oxidation products (2,3). Their structures are those of secondary ROOH in α-position to a double bond (4,5). Although the structures of all these ROOH groups are well determined, only a few articles deal with the stability of these products in dried films. The photochemical degradation of ROOH is a well-known property (6), and their thermal instability at high temperatures up to 150°C has been used to determine their structure (7) and to study the structures of the volatile products formed in autoxidation (4,8–11). However, thermal stability of ROOH at lower temperatures (from ambient to 120°C) has received only little attention in thin layers of drying oils, that is, under realistic conditions of oxidation for paints or varnishes. The only important survey has been made by Privett (12), who examined autoxidative polymerization.

The present article reports on the influence of temperature on network construction, determined by quantification of ROOH and other oxidation products. Characterization of the chemical structure of the network is the key point for understanding the differences that could arise in further photooxidation, resulting from the exposure to real aging conditions of dried linseed and poppyseed oil films cured at temperatures varying from 25 to 120°C. Oxidation of these oils was measured by Fourier transform infrared spectroscopy, coupled with gaseous treatments to determine the relative importance of secondary oxidation products. The thermooxidative and thermolytic decomposition reactions of ROOH were characterized by iodometric titration.

EXPERIMENTAL PROCEDURES

Materials and reagents. Linseed and poppyseed oils were graciously supplied by Pebeo (Gemenos, France). Oils were placed on KBr windows or polyvinylidene difluoride (PVDF) films with an average thickness of about 20 microns. Isopropanol used for iodometry (99.5%, high-performance liquid chromatography grade) was supplied by Sigma-Aldrich (Gillingham, England). Acetic acid (99–100% for synthesis) was supplied by Merck (Schuchardt, Germany), and sodium

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iodide (99.5%) by Prolabo (Paris, France). The infrared (IR) spectra were recorded with a Nicolet 510 spectrometer (Madison, WI) (resolution 4 cm^{-1}, 20-scan summation).

Thermolysis. For thermolysis experiments, samples were placed in Pyrex tubes and sealed in vacuum ($5 \cdot 10^{-6}$ torr). Thermooxidation and thermolysis of samples occurred by placing the samples in an oven ventilated by natural convection.

Gaseous treatments. Gaseous treatments were carried out to quantify alcohols and carboxylic acids. Nitrogen monoxide (NO) treatments are carried out based on a 6-h reaction between gaseous NO and the sample, in the dark at room temperature. ROOH moieties are converted into nitrates, and alcohols into nitrites (13,14). The derived products present characteristic vibrations in IR spectroscopy, but only the nitrite band at 779 cm^{-1} can be used because unsaturated bonds can react with NO_2 present in small quantities in the reactor (15), and the bands of nitro compounds formed by this reaction interfere with those of nitrates. Sulfur tetrafluoride (SF_4) treatment was used to quantify the acids present in the samples. SF_4 reacts with the carboxylic acid group to form an acid fluoride, with a characteristic IR vibration around 1840 cm^{-1} (13).

Peroxide value (PV) determination. Few methods can be used (16–19) for the peroxide titration (including alkyl peroxides, ROOR, and hydroperoxides, ROOH), but the iodometric method was chosen because the literature mentions its accuracy and its great reliability. It is based on the reduction of peroxides with iodide and the subsequent reaction of iodine with excess iodide (Scheme 1).

$$
\begin{aligned}
&\mathrm{ROOH} + 2\,\mathrm{I}^- + 2\,\mathrm{H}^+ \longrightarrow \mathrm{I}_2 + \mathrm{H_2O} + \mathrm{ROH}\\
&\mathrm{ROOR} + 2\,\mathrm{I}^- + 2\,\mathrm{H}^+ \longrightarrow \mathrm{I}_2 + 2\,\mathrm{ROH}\\
&\mathrm{I}_2 + \mathrm{I}^- \rightleftarrows \mathrm{I}_3^-
\end{aligned}
$$

SCHEME 1

The AOCS method (Cd 8-53) cannot be applied here because large oil quantities are required. Various modified methods for iodometric titrations have been proposed (20,21), varying in the choice of the solvents (22–24) and/or the acid concentration (25,26). The experimental procedure used in the present work is derived from that proposed by Wagner *et al.* (27). It has been successfully used in peroxide titrations in polymers (28,29), attempting to eliminate certain interferences, such as reaction of iodine with ethylenic linkages of the substrate, volatility of iodine, or sensitivity to oxygen (16,20).

Oil samples were dried at different temperatures on PVDF films to obtain a thickness of about 20 μm. At different oxidation times, samples (oil + PVDF film) were cut up to obtain small parts whose surface areas would be ~3 cm^2. After precise weighing (W_1) on a Mettler-Toledo balance (type AG 204), the sample was introduced in a 50-mL balloon flask with 7 mL of 10:1 isopropanol/acetic acid solution. The solution was heated to reflux, and 2 mL isopropanol, saturated at room temperature with sodium iodide, was added through the condenser. This operation limits the dissolved oxygen interaction. After 5 min of refluxing, the balloon was ice-cooled, and 1 mL distilled water was added. The liberated I_3^- was determined by spectrophotometry (Shimadzu UV-2101 PC) (Columbia, MD) at 357 nm ($\varepsilon = 25000\ \mathrm{mol^{-1} \cdot L \cdot cm^{-1}}$) in a 1-mm quartz cell. A blank determination was made with PVDF film alone to ensure that PVDF was inert under the thermal conditions used. The PVDF film was then retrieved and rinsed with ethanol before drying in a 60°C oven until constant weight (W_2). The difference ($W_1 - W_2$) indicated the oil quantity involved in the titration. The oil weight was about 6 mg. PV was calculated as follows:

$$\mathrm{PV}\ (\mathrm{mmol \cdot kg^{-1}}) = 4000\,\frac{\Delta \mathrm{DO}_{357}}{(W_1 - W_2)\ (\mathrm{mg})} \qquad [1]$$

The use of excess iodide in the reaction causes the iodine-triiodide equilibrium to be shifted to the formation of triiodide. Therefore, the almost complete conversion of iodine to the nonvolatile triiodide species ensures that the loss of iodine from the system is minimized. Because the refluxing solution is heated to around 80°C, it could seem important to check the stability of oil peroxides at this temperature (29), but the loss of peroxide during 5 min of refluxing is generally considered negligible.

The PV determined by iodometric titrations is the sum of the ROOH and ROOR contributions, although the conditions used in this work are considered as mild (25). According to the results of the literature, all ROOH groups are supposed to react but not dialkyl peroxides, which usually only react with a strong acidic medium (25) or a small amount of metal ion (30). Evidence of the reaction of ROOR in our experimental conditions is given by the results of iodometric titration of samples treated with SF_4. SF_4 reacts with all hydroxylic groups (acids, alcohols, and ROOH) (31), and the PV found for the SF_4-treated samples then represents the contribution of only the peroxide ROOR.

RESULTS AND DISCUSSION

Curing of the two drying oils has been investigated at various temperatures (25, 40, 60, 80, 100, and 120°C). Only the modifications of linseed oil IR at 25 and 120°C are shown here (Figs. 1A and 1B).

Only a few differences in the shapes of the spectra are observed. At 120°C, the *trans* epoxide vibration band at 885 cm^{-1} is much more important than at 25°C, and the intensity of the hydroxyl band is less important at 120°C than at 25°C. There is no other marked difference between the IR spectra at the two temperatures. IR spectroscopy is not adapted to the quantitative determination of ROOH concentrations because ROOH groups have their characteristic ν(O–H) band between 3000 and 3600 cm^{-1}, in the same range as alcohols and carboxylic acids. For this reason, ROOH concentration as a function of oxidation time was determined by iodometric titration. Figures 2A and 2B represent evolution of PV of the two dry-

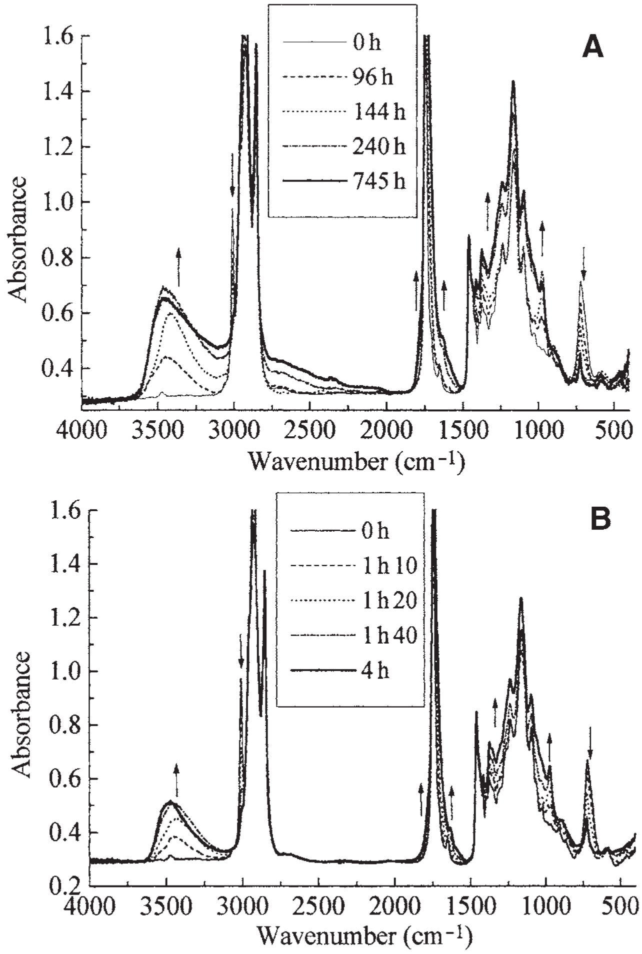


FIG. 1. (A) Evolution of the infrared spectra of linseed oil oxidized at 25°C. (B) Evolution of the infrared spectra of linseed oil oxidized at 120°C.

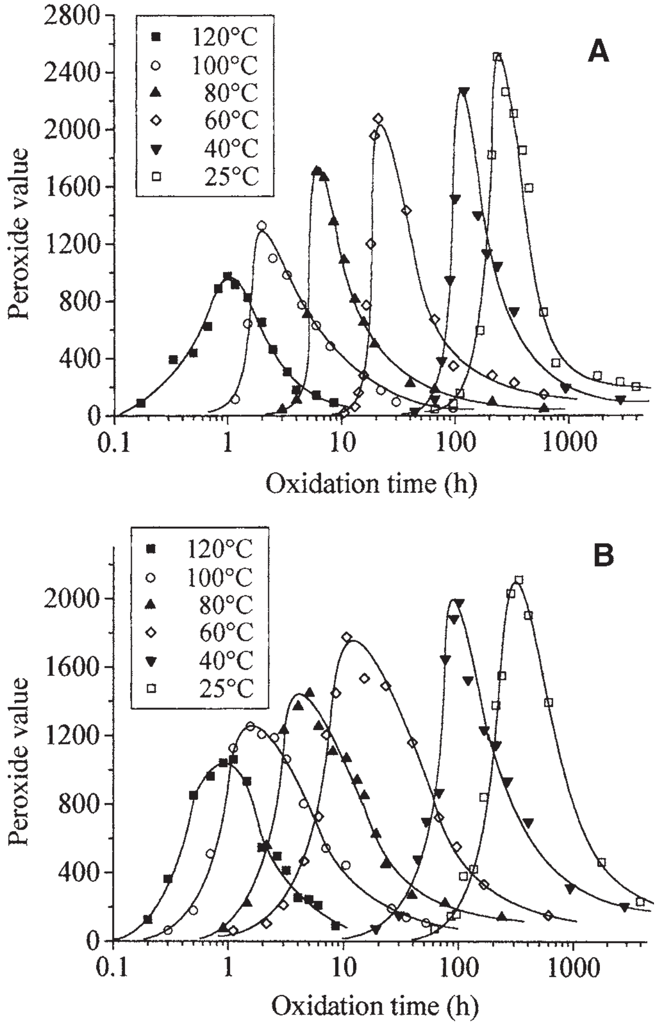


FIG. 2. (A) Peroxide value (PV) vs. oxidation time at 25, 40, 60, 80, 100, and 120°C for linseed oil. (B) PV vs. oxidation time at 25, 40, 60, 80, 100, and 120°C for poppyseed oil.

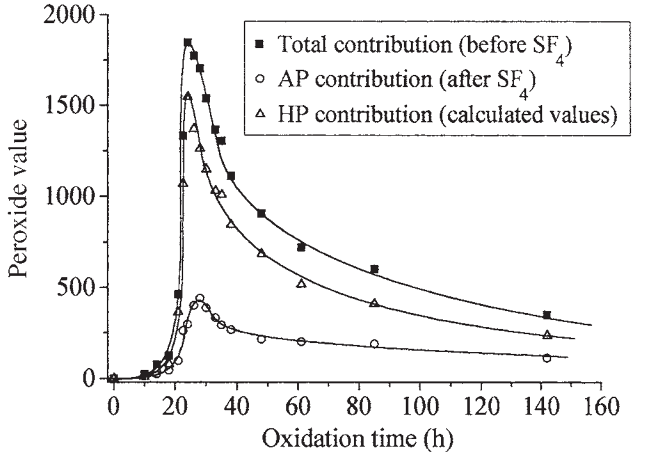


FIG. 3. PV vs. oxidation time for linseed oil oxidized at 60°C before sulfur tetrafluoride (SF_4) treatment [hydroperoxide (ROOH) + alkyl peroxide (ROOR) contributions] and after SF_4 treatment (only ROOR contribution). By subtraction, the ROOH contribution is obtained. AP, alkyl peroxides; HP, hydroperoxides. See Figure 2 for other abbreviation.

ing oils for the six oxidation temperatures. Figure 3 shows the contribution of ROOR and ROOH in PV of linseed oil dried at 60°C, calculated on the basis of iodometric titration coupled with SF_4 treatments.

These figures show that PV always reaches a maximum before decreasing slowly (a logarithmic scale is used for the abscissa axes in Figs. 2A and 2B). This behavior of the ROOH concentration has been previously suggested by Gardner (31), and the ROOR concentration varies similarly.

Figures 1A and 2A show that, despite no marked evolution of the IR spectra of linseed oil after 500 h at 25°C, the total peroxide content reached a value around 700 mmol·kg^{-1}. The curves shown in Figs. 2A and 2B are useful to estimate the curing step of a sample. These results indicate that, at ambient temperature the curing step is probably much longer than 3 mon, even for thin samples. These curves allow a comparison of the curing at different temperatures and give evidence of the dependence of the maximal PV on the drying temperature. The literature reports similar observations in a study of a reaction involving 500 g of oil, with temperature varying from 84 to 200°C (32). As anticipated, this indicates that the extent of cross-linking is closely related to the curing temperature. Increasing the temperature favors network formation.

Figure 3 shows that, for the 60°C-dried oil film, the ROOR concentration remains below the ROOH concentration. This is the first quantitative approach to the peroxide bridges in a dried oil film. To our knowledge, only Muizebelt *et al.* (33) had given some information on the relative proportions in C–C, ether, and peroxy bridges in ethyl linoleate dried at ambient temperature by using ^{13}C nuclear magnetic resonance (with POMMIE technique). However, a steady state was obtained for the peroxy bonds concentration, due to the fact that ROOR groups are quite stable at ambient temperature. Figures 2A and 2B show that the PV at 25°C remains quite important after 165 d of drying. This result indicates the contribution of ROOR to the total PV. The new result is that the peroxide bridges can be considered as almost totally destroyed when curing at 60°C is achieved. No conclusion concerning the lowest temperatures of curing can be given, but the ROOR concentration is probably expected to reach a maximal value, giving a PV curve similar to that shown in Figure 3. In parallel, concentrations of C–C and ether bridges are enhanced by the radicals produced by peroxide decomposition.

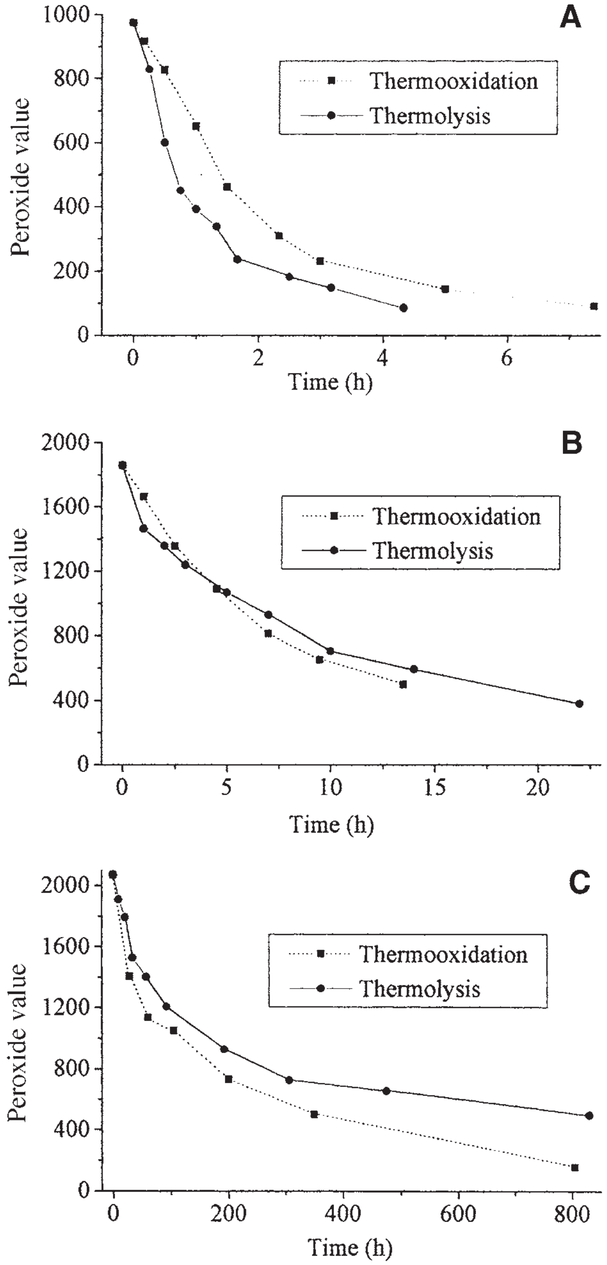


FIG. 4. PV curves: comparison of the decomposition of ROOH in thermooxidation and in thermolysis for linseed oil at (A) 120°C, (B) 80°C, and (C) 40°C. See Figures 2 and 3 for abbreviations.

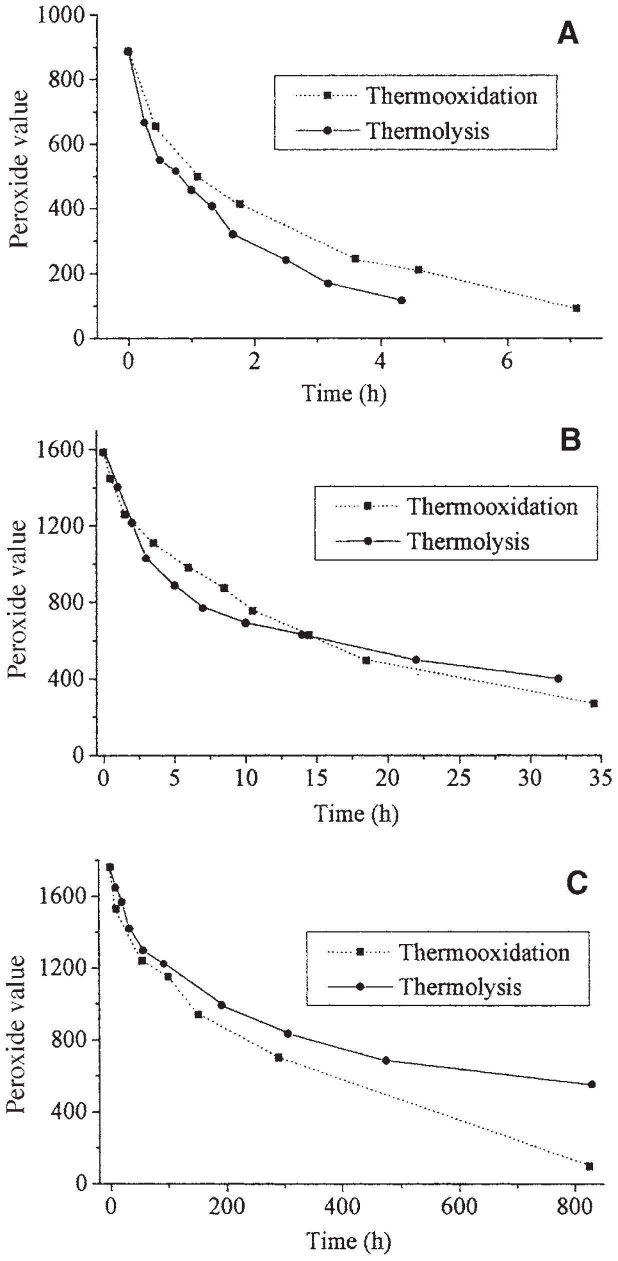


FIG. 5. PV curves: Comparison of the decomposition of ROOH in thermooxidation and in thermolysis for poppyseed oil at (A) 120°C, (B) 80°C, and (C) 40°C. See Figures 2 and 3 for abbreviations.

TABLE 1
Comparison of the Absorbances of Various Oxidation Products as a Function of Temperature for Dried Linseed Oil and Dried Poppyseed Oil[a]

	Temperature (°C)	Acids (1843 cm^{-1})	Lactones (1772 cm^{-1})	Ketones (1720 cm^{-1})	Alcohols (779 cm^{-1})
Linseed oil	25	1.28	0.54	0.77	0.40
	40	1.20	0.56	0.85	0.48
	60	1.04	0.61	1.02	0.46
	80	0.94	0.56	0.98	0.50
	100	0.98	0.58	0.97	0.54
	120	0.95	0.59	1.07	0.50
Poppyseed oil	25	1.25	0.35	0.62	0.23
	40	1.32	0.44	0.74	0.25
	60	1.17	0.48	0.80	0.29
	80	1.13	0.47	0.82	0.33
	100	1.09	0.47	0.74	0.38
	120	1.09	0.46	0.86	0.30

[a] Values are corrected by using the alkyl band at 1462 cm^{-1} as reference.

Differences observed in the ROOH maximal concentrations for the different temperatures suggest that the study of thermal stability of ROOH could be indicative. Oil samples were oxidized at 120, 80, and 40°C for durations chosen to obtain a PV just after the maximal value. Samples were then thermolyzed at the same temperature (120, 80, and 40°C, respectively), and the decomposition curves of peroxides under these conditions were compared to those determined under thermooxidative conditions (Figs. 4A–C and 5A–C)

The curves obtained for linseed oil and poppyseed oil prompt similar comments. At 120°C, the PV under thermolytic conditions decreased faster than during thermooxidation. At 80°C, the decrease under thermolytic conditions was more important than in thermooxidation in the first period, but the curves crossed and the phenomenon was inverted. Finally, at 40°C, the thermooxidation curve was always below the thermolysis curve.

Variations observed in decomposition kinetics of ROOH under thermolytic and thermooxidative conditions at the three temperatures investigated could probably lead to differences in concentrations of secondary oxidation products. IR spectra were recorded to confirm this hypothesis, and NO and SF_4 treatments were carried out on oxidized samples at the six temperatures chosen. Oil samples were dried for various durations, depending on the temperature used, to obtain the same oxidation level. The PV reached was about 220 $mmol \cdot kg^{-1}$ for all cured poppyseed oil samples and 180 $mmol \cdot kg^{-1}$ for all cured linseed oil samples.

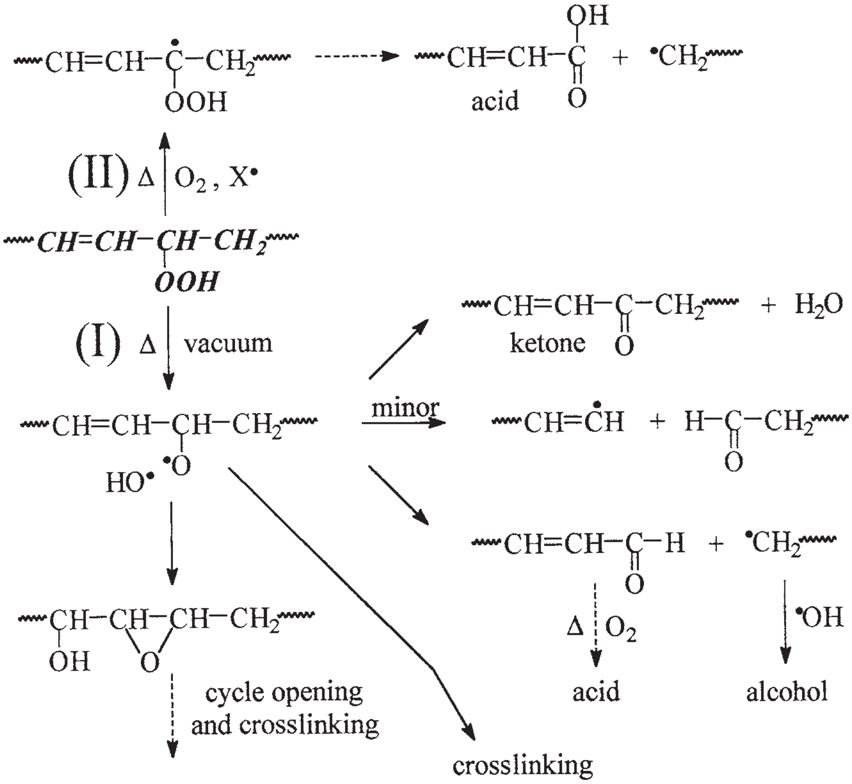
The gaseous treatments permitted quantifying four oxidation products. Alcohols were identified by the nitrite band at 779 cm^{-1} after NO treatment. Subtraction of the initial IR spectrum of nonoxidized linseed oil from that of the oxidized linseed oil after SF_4 treatment revealed the presence of a broad band between 1730 and 1670 cm^{-1}. This band indicates the formation of saturated and unsaturated ketones at 1720 and 1698 cm^{-1}. The band at 1772 cm^{-1} was attributed to the formation of γ-lactones and peresters. Unsaturated and saturated acid fluorides identified after SF_4 treatment at 1810 and 1843 cm^{-1}, respectively, revealed the presence of carboxylic acids. Absorbances corresponding to the various products are reported in Table 1.

The relative proportions of the oxidized products reported in Table 1 vary slightly with the curing temperature. Precise quantitation is, however, quite difficult because concentrations of the detected oxidation products are largely dependent on the oxidation extent that is reached (mainly the PV), and also on the thickness of the sample. However, trends can be observed: formation of saturated carboxylic acids is more important at lower temperatures; intensity of the saturated ketone band at 1720 cm^{-1} seems to increase with increasing temperature and so does the nitrite band at 779 cm^{-1} (this indicates an increase of alcohol concentrations); concentration of the oxidation products near 1772 cm^{-1} seems to be constant, independent of the drying temperature. Moreover, the only products present in larger concentrations in poppyseed oil are the carboxylic acids.

Comparison between the curves of thermooxidation and thermolysis of the two drying oils brought an important result. Figures 4 and 5 show that peroxides are rapidly decomposed upon thermolysis at 120°C. Because some residual oxidation sites exist, new peroxides are produced by thermooxidation, and as a consequence, the PV under thermooxidative conditions is higher than in thermolysis. On the contrary, Figures 4 and 5 indicate that the PV in thermooxidation is lower than in thermolysis at 25°C. This result suggests that another mechanism also exists, which is different from that occurring in thermolysis. The occurrence of this mechanism may be attributed to kinetic factors. At low temperatures, the thermolytic reaction rates are slow, which allow oxidation of the residual unsaturation, leading to different products. The results in Table 1 suggest that, at low temperatures, formation of acids is more important than at 120°C. Carboxylic acids are known to be the final products in oxidation reactions.

Our results permit the proposal of mechanisms involved in thermooxidation and thermolysis. These mechanisms are given in Scheme 2.

The aim of this paper is not to discuss the occurrence of unimolecular or bimolecular decomposition of ROOH. The



SCHEME 2

two types of reaction lead to alkoxyl radicals that are the species of interest in the determination of a mechanism.

The homolytic decomposition of the ROOH generates an alkoxyl radical that can lead to an alkyl radical or vinyl radical by β-scission reactions. The formation of intermediate vinylic (34) is not favored because the C–C bonds of the alkyl groups are weaker. The secondary oxidation products formed by reaction I (Scheme 2) consist of epoxides, ketones, alcohols, and aldehydes, which are oxidized into acids. The formation of epoxides can easily be observed at 885 cm^{-1} when drying is carried out at temperatures above 60°C. At lower temperatures, epoxides are formed slowly and do not accumulate. Because epoxides are unstable under oxidative conditions, their concentration within the last stages of the curing can be neglected (see Table 1). The alkoxyl radicals formed by decomposition of ROOR may evolve by the same mechanism as that proposed for ROOH.

At their maximal concentration, most of the hydroperoxides are conjugated. The relative concentrations of compounds formed by decomposition of ROOH have been mentioned to be dependent on the temperature. However, this observation has always been obtained for substrates in solution (2,35–37). H-abstraction of the ROOH group leads to an equilibrium with the peroxy radical, which is in equilibrium with alkyl radical and oxygen. Isomerization of the pentadienyl radical obtained may potentially lead to eight isomers (31). However, all these isomers are of the ROOH type, and this reaction, if existing in pure oil, may be neglected in our mechanistic considerations.

At low temperatures, a different mechanism (II) may be proposed. This mechanism is based on the ability of H-abstraction on the tertiary carbon of the hydroperoxidic groups by radical attack (38). Reaction II could lead to the formation of higher concentrations of carboxylic acids and also to peresters. Figures 4C and 5C show that the decomposition of peroxides at 40°C in thermolysis is slow, and reaction II could be an important way of decomposition for peroxides at ambient temperature.

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