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Long-term behaviour of oil-based varnishes and paints 4. Influence of film thickness on the photooxidation

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Abstract

Photooxidation of dried linseed oil films with various thicknesses is analysed. Distributions of the photoproducts resulting from photooxidation are determined by photoacoustic IR spectrometry and by micro-IR spectrometry. Oxidation profiles are observed and it is shown that oxidation can extend up to 300 μm. This result is confirmed by micro-fluorescence analysis of the photo-oxidized sample. On the other hand, the cross-sectional analysis of the exposed films suggest that crosslinking occurs in the oxidized layers, which could prevent some of the low molecular weight products formed from migrating from the solid film towards the surrounding atmosphere.

Keywords: Linseed oil; Micro-infrared spectrometry; Photoacoustic; Fluorescene

1. Introduction

Oil-based paints and varnishes used for creating works of art are largely based on polyunsaturated fatty acids (PUFA) called drying oils. However their tendency to both yellowing and cracking is one of the major problems encountered in the use of these substrates.

The PUFA chains thermally oxidize to form a three-dimensional network consisting in cross-links formation, mainly by generation of C–C, C–O–C and C–O–O–C bonds. This oxidative "polymerisation", also called drying, involves radical chain reactions. The mechanisms of these reactions have been largely reviewed in the literature [1–4] and recently characterized by identification of the oxidation products by IR spectroscopy [5].

Our attention has also focussed on the photooxidation and thermooxidation of dried linseed oil films [6]. The various products that are formed have been identified and quantified by IR spectrometry coupled with derivatization chemical treatments, by UV-visible spectrometry and by fluorescence spectroscopy. It has been shown that, in photooxidative conditions, a shift of the UV absorption to the short wavelengths was observed in the first hours of the exposure to UV-light. This behaviour has been attributed to the oxidation of the contaminants present in the linseed oil. In parallel a fast disappearance of the fluorescent products present in the thermooxidized samples was observed. As recalled above, the various photoproducts formed by irradiation of linseed oil samples, previously "dried" by thermooxidation at 60°C for 25 days, were characterized. Mechanisms accounting for the formation of these products and the resulting modifications of the chemical structure of the samples were proposed. The ketonic compounds formed by thermooxidation decompose mainly by Norrish I reactions. The disappearance of the alkyl chains mainly results from oxidation of the tertiary carbon atoms in α-position to the oxygen atom of the ether linkages created by the drying step. Oxidation at the tertiary carbon atom resulting from the formation of C–C linkages is also involved, as well as the homolysis of the O–O bonds of the peroxy linkages. These reactions explain the modifications of the IR spectra of the dried films submitted to photooxidation, and the formation of various oxidation photoproducts including carboxylic acids and esters.

Many different parameters can influence the long-term behaviour of oil-based varnishes and paints in the conditions of ageing involving exposure to UV-light: the

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temperature, the extent of drying, the use of dryers [7], the spectral distribution of the UV-light and the thickness of the exposed samples.

In the present paper, we focus on the influence of this last parameter. Varnishes and paints are indeed used in the form of very thin films with thickness in the range of only a few microns, but these substances can also be used to form layers with quite important thicknesses of several hundreds of microns.

2. Experimental

2.1. Materials

Samples were prepared by spreading out linseed oil (PEBEO, France) (linolinic 54%, linoleic 13%, oleic 22% and saturated 11%) on KBr windows with thicknesses ranging from only a few microns (5 μm) up to 70 μm.

The thickest samples were prepared on metal plates. These samples were then dried and exposed to the conditions of photooxidation (see below) before being separated from the metal plate and microtomed.

2.2. Photooxidation experiments

Dried oil samples were exposed in a SEPAP 12-24 unit at a temperature of 60°C. This apparatus, which has been described in many previous papers (see for example [8,9]), allows irradiation at wavelengths longer than 300 nm.

2.3. Spectrometric analysis

Infrared analysis in "macroscopic" mode were carried out on a Nicolet 510 spectrometer (resolution 4 cm^{-1}, 20 scans summations).

The analyses by micro-FTIR spectroscopy were carried out on a Nicolet 800 spectrometer coupled to a Nicplan microscope (nominal resolution 4 cm^{-1}, 128 scans summation). The thickness of the microtomed slice was 20 μm. An image-masking aperture of 22 μm was used with an increment step of 11 μm. Therefore, the recorded signal is the average signal corresponding to the centre of the aperture, i.e. 11 μm (half of 22 μm). Thus, starting at 5 μm from the edge of the sample, the analysed intervals were 5–27, 16–38, 27–49 μm) and so on. This analytical technique has been reported in numerous papers (see for example [10]).

The photoacoustic IR spectra were recorded with a Nicolet 860 SS-FTIR spectrometer in a rapid-scanning mode with an MTEC Model 300 photoacoustic accessory. Before acquisition, the photoacoustic cell was purged with dry helium at 20 cm^3/s for 10 min. All sample spectra were recorded in the 4000–400 cm^{-1} region with a spectral resolution of 4 cm^{-1}. Eight different velocities of the moving mirror were employed to collect the data with the use of the above parameters (from $v = 0.6329$ to $v = 0.0158$ cm/s).

It has been shown [11] that the reproducibility of the signal measured is dependent not only on the position of the material in the sample holder but also on the pressure and volume of the vector gas used to purge the cell. The ease and repeatability of filling the PA sample holder as well as the sample uniformity are important factors for obtaining reproducible spectra. The sample holder has been sized in order to maintain the same cell filling factor above the sample. One purge was used to measure the spectra at different velocities in order to be in exactly the same operating conditions. Each spectrum was ratioed against a reference spectrum collected on a carbon black-filled elastomer at the same moving mirror velocity.

Analyses by PAS-IR spectrometry are currently used in our laboratory to monitor the distribution of oxidation photoproducts in the thickness of irradiated samples (see for example Refs. [12,13]).

The fluorescence spectra were recorded using a Hitachi U6000 micro-spectrofluorimeter (based on an Olympus BHTZ microscope). The excitation wavelength was 395 nm and the spectra were obtained in the following conditions: objective ×50, voltage 520 V, exposure time 1.8 s, 5 scans. The analysed area was a circle with a diameter around 6 μm.

3. Results and discussion

The effect of heterogeneous oxidation can be measured quite simply by monitoring the intensity of an oxidation band as a function of the thickness of the samples that are exposed.

Several films of linseed oil with different thicknesses (5–45 μm) were dried at 60°C in order to obtain similar oxidation levels, corresponding to a peroxide index around 100 mmol/kg [6]. The drying time increased with the film thickness and 45 days were required for the thickest samples. The films were then irradiated and the consequences of the photooxidation were measured as a function of the irradiation time. It is recalled that photooxidation of dried linseed oils leads to a decrease of the alkyl absorption bands, as evidenced by the modifications of the IR spectra in the range 3600–2200 or 1500–1420 cm^{-1} (Fig. 1).

Monitoring the decrease of the area of the alkyl bands at 2900 cm^{-1} can be used quite efficiently to evaluate the effect of oxidation. One obtains the set of curves presented in Fig. 2.

This figure shows clearly the influence of the film thickness on the photooxidative behaviour. A limited decrease is obtained for the various films after 2000 h approximately. In the case of the 5 μm film, the decrease

of the alkyl bands is approx. 85% whereas it reaches only 50% for the 45 μm film.

A thicker sample (70 μm) was also prepared and photooxidized. The results are not given on Fig. 2 because the absorbance was too high to be measured quantitatively ($A > 2.2$). However the result obtained for this sample indicated a loss of only a few percent.

These results indicate that oxidation is not homogeneously distributed in the sample. However the analytical method used does not permit distinguishing an oxygen diffusion effect from a limitation of the degradation by the attenuation of light absorbed either by an initial chromophore or by UV-absorbing photoproducts. For that reason, the measurements were completed by photoacoustic analysis and investigations by micro-IR spectrometry.

As indicated in the experimental section, the PAS spectra were obtained for six different mirror velocities varying from 0.0150 to 0.6329 cm/s. It is recalled that, according to the theory [14–16], the thermal diffusion

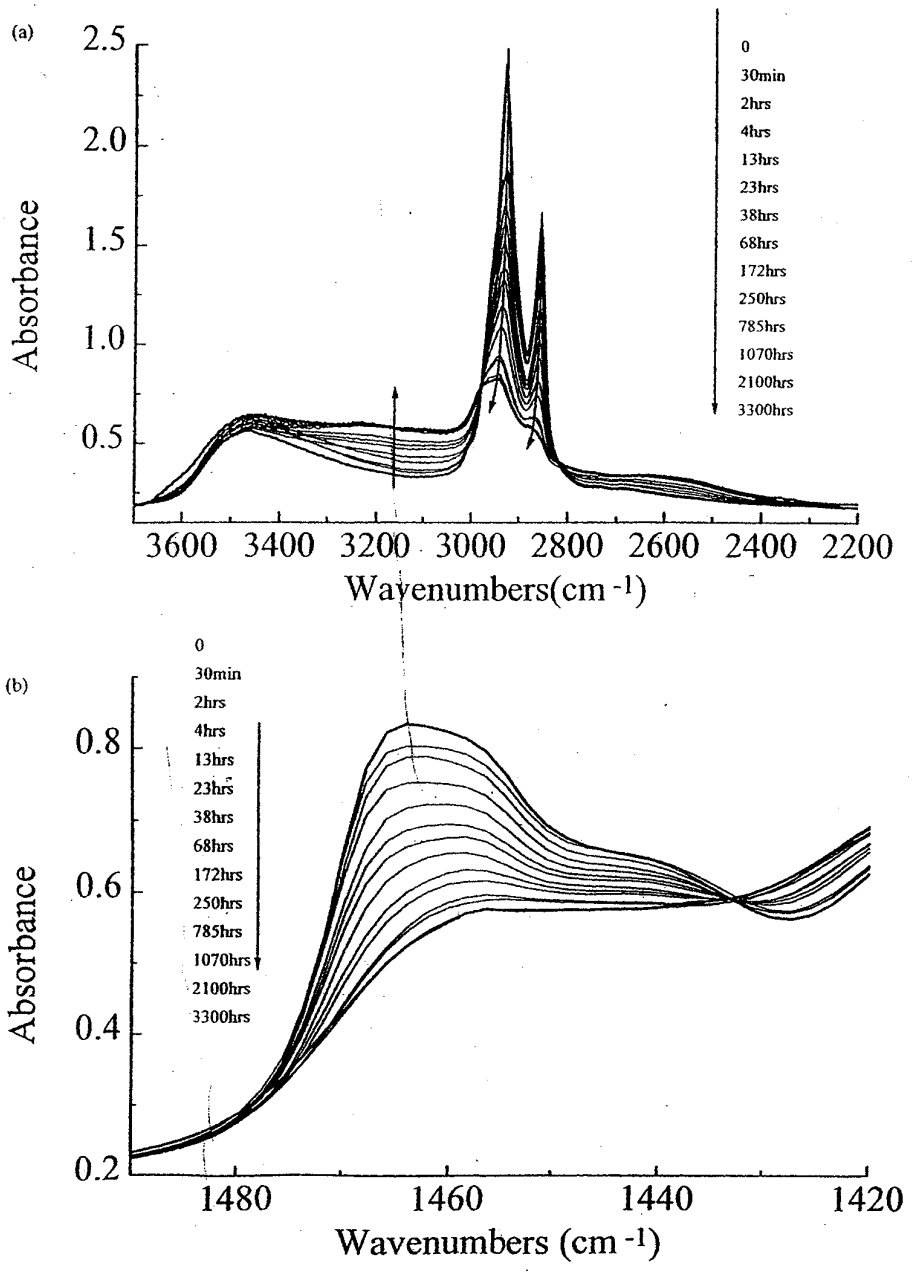

Fig. 1. Modifications of the spectra in the range 3600–2200 and 1500–1420 cm^{-1} as a function of irradiation time.

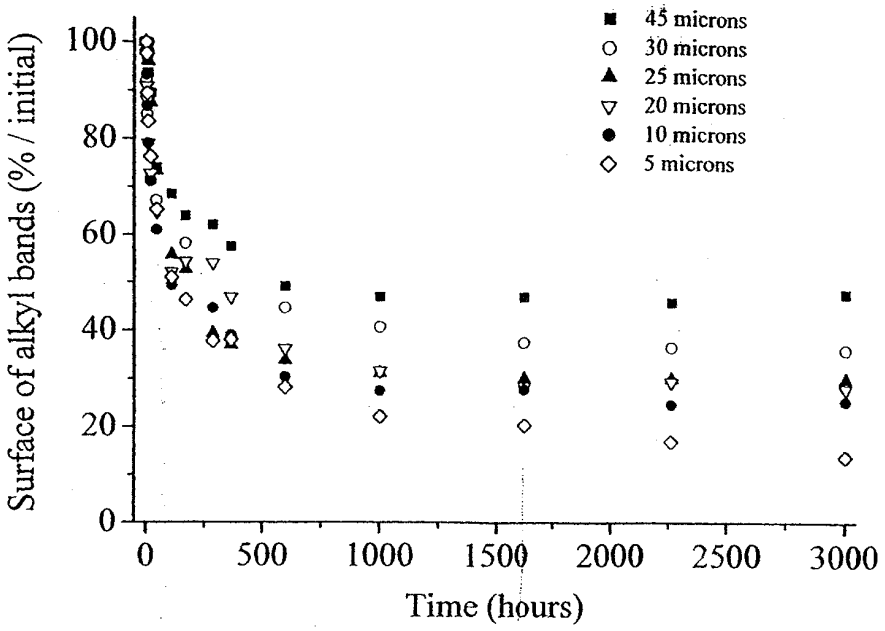

Fig. 2. Percentage of decrease of the alkyl bands absorbance as a function of irradiation times, for films with thicknesses ranging from 5 to 45 μm.

length $\mu = (\alpha/\pi f)^{1/2}$ (with α being the thermal diffusivity of the substrate, and f the modulation frequency) varies with the mirror velocity V and the wavenumber $\bar{\nu}$ ($f = 2V\nu$). The coefficient α is not known in the case of the substrate reported here. We have thus used a coefficient given in the literature for polyester resins [17] that have a structure not so far from the dried oils ($\alpha = 11.3 \times 10^{-8}$ m^2/s). Using this value, one can calculate the thicknesses of the analysed layers at 1462 and 2950 cm^{-1} for the six mirror velocities (Table 1).

The modifications of the spectrum of a photooxidized sample analysed with a minor velocity of 0.0475 cm/s indicate a decrease of the absorbance of alkyl bands at 1462 cm^{-1} (it is recalled that only the top 16.1 μm at the surface of the sample are taken into account).

Fig. 3 shows the PAS spectra obtained after 264 h of irradiation for a sample analysed with different minor velocities. The various spectra were calibrated following a reference absorption band.

Table 1
Thickness of the analysed layers at 1462 and 2950 cm^{-1} (calculated with $\alpha = 11.3 \times 10^{-8}$ m^2/s)

V(cm/s)	μ at 1462 cm^{-1} (μm)	μ at 2950 cm^{-1} (μm)
0.0158	27.8	19.6
0.0317	19.7	13.8
0.0475	16.1	11.3
0.1581	8.8	6.2
0.3165	6.2	4.4
0.6329	4.4	3.1

A dramatic decrease of the alkyl bands is observed in this figure, with an increase of the hydroxyl absorption corresponding to the formation of some of the oxidation products, as reported previously [6]. One can observe that the decrease of the alkyl absorbance is more accentuated when the mirror velocity increases, which corresponds to more superficial analysis. This behaviour confirms that the loss of alkyl groups is more important at the surface of the sample.

These profiles have been completed by micro-FTIR spectroscopic analysis to determine the behaviour of the layers located after the first 20 μm near the surface. Fig. 4 shows the results obtained by cross-sectional analysis of a photooxidized sample following the usual procedure [12].

Completing the results of PAS analysis by those of microspectrometry permits plotting the oxidation profiles for various irradiation times. This is illustrated by Fig. 5, which displays the variations of the loss of alkyl absorption with the distance from the exposed surface in the case of samples irradiated for durations up to 2200 h.

This figure shows that the oxidation of the surface layers increases continuously with irradiation times until 2200 h. After only 264 h exposure, the loss of alkyl groups is already strongly reduced. This suggests that the loss of alkyl groups resulting from photooxidation occurs readily and that all the potentially oxidisable sites are rapidly consumed. The curves displayed in Fig. 5 also show that the loss of alkyl groups is quite superficial. The shape of the various curves obtained for different irradiation times can be explained by crosslinking

of the polymer. This decreases the permeability to oxygen in the surface layers, which prevents oxygen from reaching the bulk of the sample. An explanation could be that crosslinking makes the migration of the low molecular weight products formed by chain scission difficult. These products are trapped in the matrix and no decrease of the alkyl bands is observed. Another way to study the effect of photooxidation is based on the determination of the concentration of residual unsaturation, measured by the absorbance at 973 cm^{-1} (Fig. 6).

The spectra displayed in Fig. 6 show that the oxidation of the polymeric matrix can extend up to 300 μm even if a heterogeneous distribution of the oxidation occurs (the spectrum at 350 μm was similar to the spectra of the sample before irradiation). This means that the results from Fig. 5 could be explained in terms of oxygen

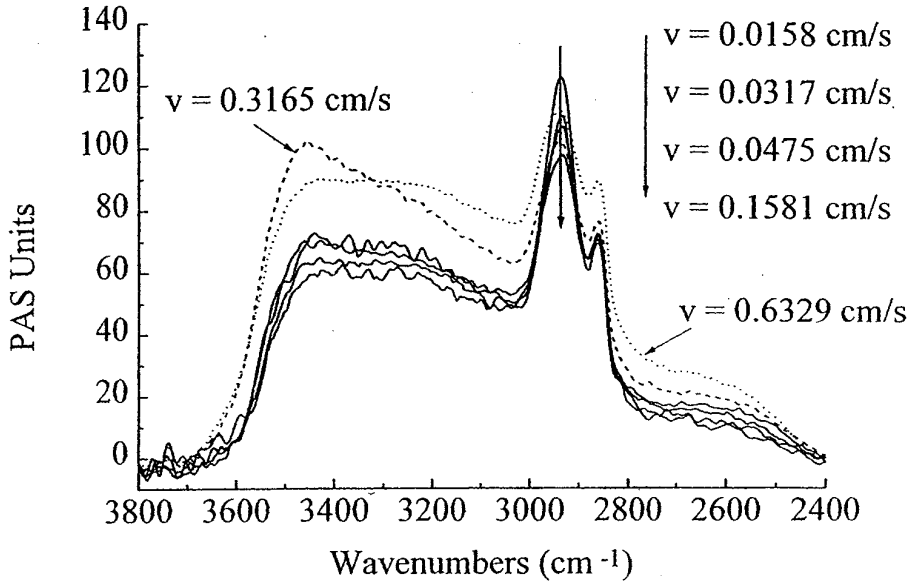

Fig. 3. PAS spectra of a sample photooxidized for 264 h and analysed at different mirror velocities.

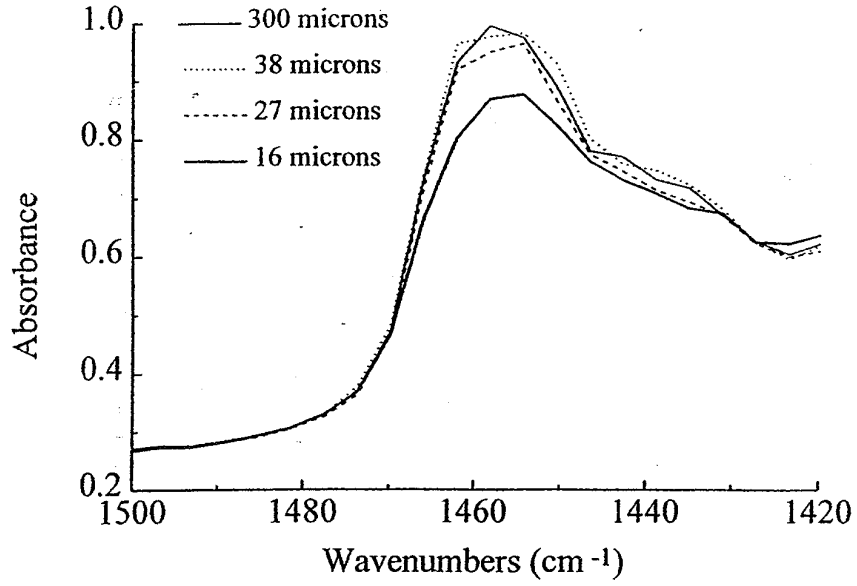

Fig. 4. Spectra of a dried linseed oil sample irradiated for 864 h obtained by cross-sectional analysis of microtomed samples (range 1500–1420 cm^{-1}).

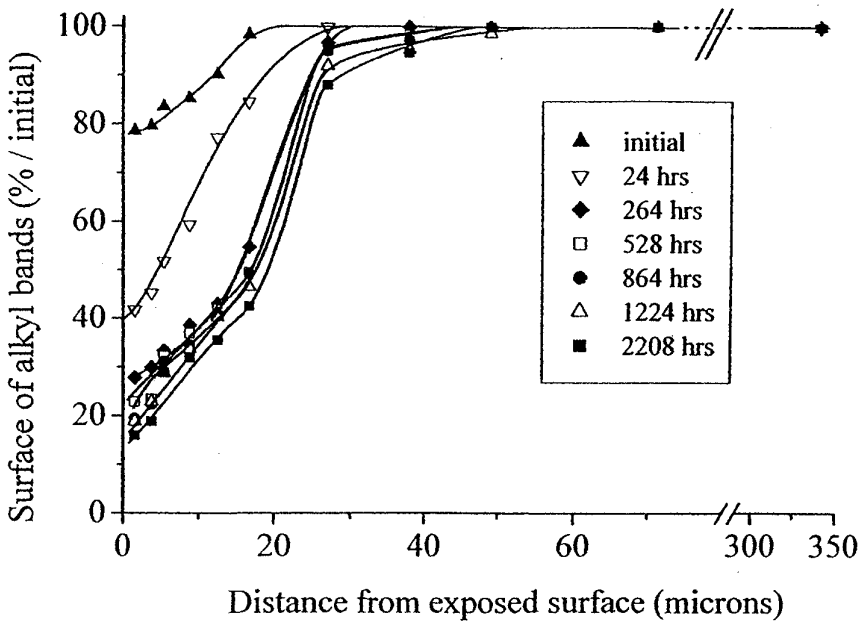

Fig. 5. Oxidation profiles determined by PAS spectrometry (0–30 μm) and micro-FTIR spectrometry (up to 350 μm).

diffusion and trapping of low molecular weight alkyl chains. However it will be shown below that oxidation can extend to the deeper levels, but the phenomenon cannot be revealed by the measurements of alkyl groups.

The photooxidized samples were also studied by fluorescence microspectroscopy. Fig. 7 shows the emission spectra of a photooxidized linseed oil recorded by shifting the area from the edge to the bulk.

The spectra presented in Fig. 7 show that the fluorescence intensity increases with the analysed thickness. This behaviour indicates the disappearance of the emitting species in the layers that are more accessible to oxygen by diffusion from the surrounding atmosphere. A decomposition of these species by photooxidation could then occur. Fig. 8 gives the evolutions of the fluorescence profiles for various irradiation times as a function of the thickness.

The shape of the profiles is different from those presented in Fig. 6, and one can observe that the oxidation of the emitting products occurs even in layers extending up to 300 μm, whereas the loss of alkyl absorption is limited to the first 50 μm. This result suggests that the limitation of the loss of alkyl groups to the first 50 μm near the exposed surface has mainly to be attributed to the fact that these groups are trapped in the matrix as a result of the crosslinking reactions due to photooxidation. It could be also considered that oxidation at

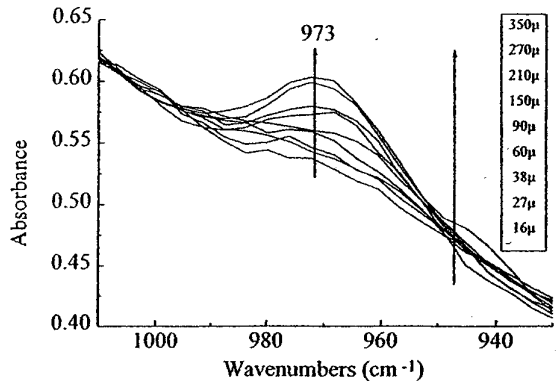

Fig. 6. Spectra of dried linseed oil sample irradiated for 484 h by cross-sectional analysis of microtomed samples (range 1020–920 cm^{-1}).

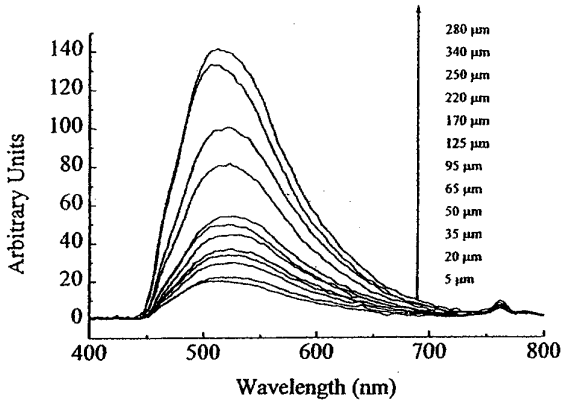

Fig. 7. Microfluorescence spectra of a dried linseed oil sample photooxidized for 1224 h.

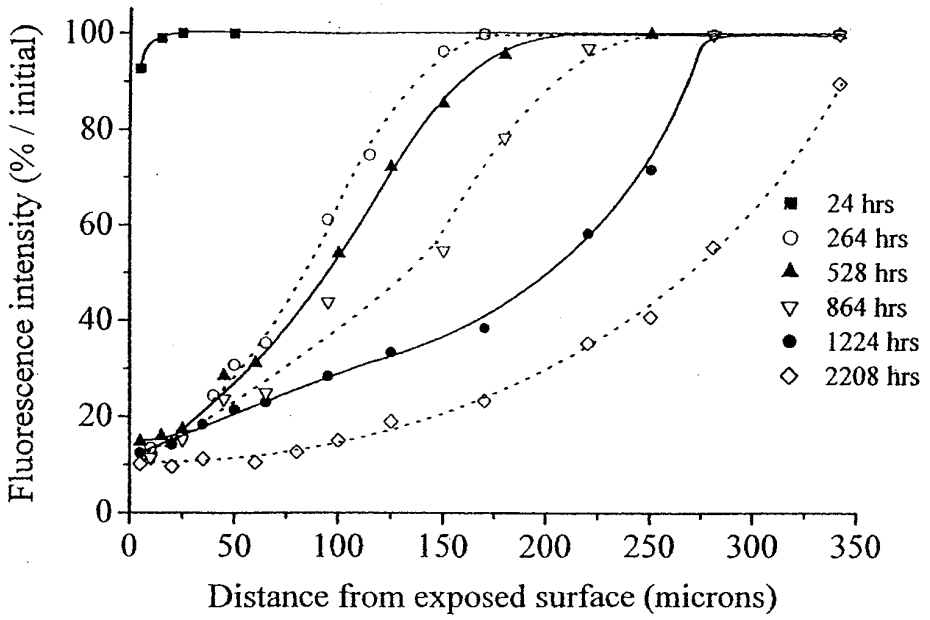

Fig. 8. Fluorescence profiles as a function of irradiation times.

deeper levels occurs with predominance of crosslinking and without elimination of alkyl groups.

4. Conclusion

Photooxidation of dried linseed oils is strongly dependent on the thickness of the samples. Variations of the fluorescence intensity with the distance from the exposed surface show marked oxidation profiles, which is confirmed by IR analysis of the double bond disappearance. Our results suggest that crosslinking resulting from photooxidation prevents low molecular weight photoproducts from migrating, which explains the shape of the curves indicating the loss of alkyl groups.

References

[1] Russel GA. J Chem Educ 1959;36:111–8.
[2] Frankel EN. Prog Lipid Res 1980;19:1–22.
[3] Chan HWS. The mechanism of autooxidation. In: Chan HWS, editor. Autoxidation of unsaturated lipids. London: Academic Press, 1987. p. 1–6.
[4] Frankel EN. J Am Oil Chem Soc 1984;61:1908–17.
[5] Mallégol J, Gardette JL, Lemaire J. J Am Oil Chem Soc 1999;76/8:967.
[6] Mallégol J, Gardette JL, Lemaire J. J Am Oil Chem Soc 2000;77:257.
[7] Mallégol J, Lemaire J, Gardette JL. Prog Org Coat 2000;39:107.
[8] Lemaire J, Arnaud R, Gardette JL. Le vieillissement des polymères. II-Principe d'étude du photovieillissement. Rev Gen Caoutch Plast 1981;613:87–92.
[9] Tang L, Sallet D, Lemaire J. Photochemistry of polyundecanamides. 1. Mechanisms of photooxidation at short and long wavelengths. Macromolecules 1982;15:1432–7.
[10] Jouan X, Gardette JL. Polym Commun 1987;28:239.
[11] Dittmar RM, Palmer RA, Barr NE, Morosoff N. Appl Spectrosc 1997;51:1238.
[12] Delprat P, Gardette JL. Polymer 1993;34:933.
[13] Gonon L, Vasseur OJ, Gardette JL. Appl Spectrosc 1999;53:157.
[14] McClelland J, Jones RW, Bajic SJ, Power JF. Mikochim Acta 1997;14(Suppl.):613.
[15] Jiang Y, Palmer RA, Barr NE, Morosoff N. Appl Spectrosc 1997;51:1238.
[16] Rosencwaig A, Gersho A. J Appl Phys 1976;47:64.
[17] Van Krevelen DW. Properties of polymers. 3rd ed. Netherlands: Elsevier Science, 1990.