UV Exposure and Temperature Effects on Curing Mechanisms in Thin Linseed Oil Films: Spectroscopic and Chromatographic Studies

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ABSTRACT: The influence of thermal and photochemical treatment in the curing mechanisms of thin linseed oil films is studied. The role of copper acetate pigments is also investigated under the above conditions. UV and FTIR absorption spectroscopy and chromatographic product analysis are used as the main analytical techniques, which allowed the identification of significant changes in the curing mechanism in each case. Yellowing, crosslinking, and fragmentation inside the film material proceed to a different extent according to the conditions. Peroxide destruction is induced by UV exposure at early curing stages and affects the course of the yellowing process. Yellow product formation is also favored by curing at elevated temperatures, which is accompanied in this case by decreased crosslinking in the cured film. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 936–949, 2002; DOI 10.1002/app.10117

Key words: linseed oil; UV curing; thermal curing; thin films; coatings

INTRODUCTION

Drying oils derived from natural products such as linseed oil have been used in a wide variety of applications in the coatings field. Curing of these oils comes as a result of oxygen-mediated processes, and their basic chemistry has been extensively studied.[1–4] However, the complexity of these processes and their dependence on parameters that are difficult to control pose severe constraints on their use; thus, synthetic polymers have replaced drying oils to a great extent during the last few decades. Nevertheless, the interest in curing mechanisms of these oils remains a significant topic for two reasons: first, because many organic coatings of the past, among them paintings of high artistic value, have been made using drying oils and especially linseed oil; and second, because the use of natural products and materials that mimic natural products can lead to technology directions that are environmentally friendly while satisfying the necessary performance demands, for instance, in applications where reduction of volatile organic compounds is desired, while keeping the advantages that oil-based organic media offer.[5–10]

In earlier reports of our team, we used using spin coating as an application technique to form thin linseed oil films containing copper pigments on glass, quartz, or silicon substrates, which en-

abled *in situ* UV and FTIR monitoring of the curing process.[11,12] In this way the study of the film composition influence on oxidative processes, including crosslinking, yellowing, and degradation through chain scission and formation of small volatile products, was possible. On the other hand, increased temperature and UV light are expected to largely influence the course of the curing process, accelerating either thermal or photochemical reactions, respectively. These effects are also encountered when laser techniques based on ablation are used in cleaning of art objects, where thermal or photochemical events necessary for ablation could probably influence the remaining film. The elucidation of the mechanisms of linseed oil curing under various conditions is therefore essential in the analysis and diagnosis of the oxidation effects during the application of techniques like laser cleaning in the conservation of art objects.[13,14] The importance of a detailed study on the influence of UV radiation on the curing process is also profound in cases where light is considered as an acceleration means.

This article presents the results on the effect of processing and ambient conditions on the overall oxidation course of linseed oil based films, with an emphasis on the role of increased temperature and exposure to light in the early stages of the process. The thermally and photochemically accelerated curing of films is compared to the curing of the films at room temperature in the dark (*natural curing*).

EXPERIMENTAL

Materials and Methods

The linseed oil (bleached, Schebeningen) was tested titrimetrically by means of electrospray mass spectrometry and gas chromatography–mass spectrometry (GC–MS). The acidity was found to be 1.1 ($\pm$0.08) mg KOH/mL. The electrospray mass spectrometry of fresh linseed oil resulted in a basic peak of m/z 874, the experimental details of which are presented elsewhere.[11] The GC–MS analysis of fresh linseed oil showed all expected fatty acid peaks as their methyl esters: methyl palmitate ($C_{16:0}$): m/z 43 (77), 55 (42), 74 (100), 87 (70), 143 (14), 270 (11); methyl stearate ($C_{18:0}$): m/z 42 (67), 44 (88), 69 (16), 74 (100), 87 (76), 143 (15), 298 (11); methyl oleate ($C_{18:1}$): m/z 43 (79), 55 (100), 69 (48), 74 (40), 87 (32), 96 (37), 180 (9), 264 (16), 296 (4); methyl linoleate ($C_{18:2}$): m/z 42 (22), 55 (83), 67 (100), 81 (90), 95 (67), 109 (29), 263 (4), 294 (12); methyl linolenate ($C_{18:3}$): m/z 41 (97), 55 (65), 67 (70), 79 (100), 95 (58), 108 (45), 135 (12), 149 (9), 292 (5).

The peak ratios of the esterified acid components were also determined: $C_{16:0}$ (palmitate)/$C_{18:0}$ (stearate) = 1.70, $C_{18:1}$ (oleate)/$C_{18:0}$ (stearate) = 34.30, $C_{18:2}$ (linoleate)/$C_{18:0}$ (stearate) = 3.23, $C_{18:3}$ (linolenate)/$C_{18:0}$ (stearate) = 53.19. No oxidated or low molecular weight acidic components were detected in fresh oil. The ratios of the saturated acids [$C_{16:0}$ (palmitate)/$C_{18:0}$ (stearate)] that typically remain constant in the course of the oxidation process were found to be 1.65 ($\pm$0.5) in all cured samples. The detection limit in GC–MS for methyl stearate was 10 pg in SIR mode under the conditions mentioned below.

Copper acetate and copper abietate were prepared and characterized as reported before.[11] Basic copper carbonate was purchased from Fluka.

Analytical Techniques

Thin linseed oil based films of controlled thickness (1.0–1.4 μm) and acceptable uniformity with respect to pigment dispersion were prepared through spin coating of the oil–pigment mixture on a Headway Research spinner at 3000–4000 rpm. Oil films containing 10 and 5% (w/v) copper acetate were prepared. Because neat linseed oil does not form a film on silicon, glass, or quartz, a supporting inert inorganic salt (10% w/v calcium chloride) was added to enable formation of pigment-free films (control samples).

The film thicknesses were measured with a Dektak profilometer. Films on quartz were ideal for UV absorption. The silicon wafers (0.5-mm thickness) that were selected as substrates for IR spectroscopy were sufficiently transparent below 2000 cm^{-1}. Prepared canvases were used in cases where thick films (>50 μm) were studied. Canvas coatings of higher thickness were prepared through brush application of the pigment–oil mixture.

A Perkin–Elmer Lambda-19 spectrophotometer was used for UV absorption spectroscopy. A Nicolet Magna 550 FTIR spectrometer was used for FTIR spectra, which were recorded as transmission spectra. Quantitative FTIR analysis was based on the absorbance spectra. In the photooxidation experiments the irradiation was carried using an Oriel Hg-Xe lamp (no filter, maximum output at 200–250 nm).

UV spectroscopy was used to monitor the chemical changes in the kinetic experiments performed during the early stages of the curing process. The temperature inside the instrument chamber was monitored. The behavior of all tested linseed oil films dispersed with copper salts were compared to control samples (i.e., linseed oil films containing the inert salt $CaCl_2$).

Product Analysis

The workup of samples prior to GC analyses included extraction and transesterification of the low molecular weight fraction of all films with methanol/HCl followed by extraction with a 1:1 mixture of water and ether. The analysis of linseed oil degradation products was achieved with GC–MS. The esterification procedure of the films is described elsewhere.[11]

The GC–MS used for the identification of oxidation products was performed on a Micromass Platform II mass spectrometer combined with a Fisons 8060 gas chromatograph equipped with a 30-m DB-5 MS column. The temperature program was 90–200°C (2°C/min), an isotherm was reached (40 min), and the gradient was 2°C/min up to 250°C. Quantitation of products was done on a Perkin–Elmer gas chromatograph (flame ionization detector) equipped with a 30-m SPB-1 column. The temperature program is the same as previously.

RESULTS AND DISCUSSION

In a previous article[11] the influence of various copper(II) salts on the natural curing process of thin linseed oil films was studied; it was found that copper acetate and copper abietate had a significant accelerating effect on oxidation. In the present work the influence of accelerated curing techniques on the oxidative process was studied. Artificial thermal and photo-induced curing was utilized to detect the influence of representative conditions on various paths of oxidative processes.

Linseed oil films containing copper acetate and containing no pigment (control samples) were both studied with respect to natural and artificial curing. In this study natural curing is storage of films in the dark at room temperature and artificial curing is either exposure of films to UV light (photochemical curing) or thermal treatment at a specified temperature and time (thermal curing).

The thicknesses of the tested films obtained with spin coating were 1.0–1.5 μm. The absorption peaks in the UV and IR regions that were attributed to the linseed oil peaks were monitored during the process under study, and GC was used for the analysis of the oxidation products.

Influence of UV Light on Curing Process

The influence of incident light during the early stages of oil film curing was first investigated and compared to room temperature in the dark. As previously reported,[11,15,16] linseed oil curing under natural (room temperature, darkness) conditions efficiently produces peroxides that strongly absorb at 238 nm. In the present work peroxide formation was monitored by UV absorption spectroscopy and is shown in curves a–c of Figure 1. In the oil film containing copper acetate, the 238-nm peak rapidly increases (curve b) and reaches a maximum within 200 min from the application of film. The simultaneous formation of a double shoulder at 273–285 nm within the same time scale (curve c) confirmed our previous observations and is attributed to oxidative dehydrogenation in the presence of copper carboxylates and formation of conjugated polyene chains (Scheme 1, route B).[11]{Scheme1} When the natural curing process was interrupted and the films were UV irradiated, a significant decrease in the intensity of the 238-nm peak was observed and its maximum shifted to 233 nm (Fig. 1, curve d). The double shoulder at 273–285 nm disappeared. The 238-nm peak tended to restore itself within a 40-min period after the UV lamp was shut off (curve e). Nevertheless, no clear restoration of the double shoulder was observed. Instead, a wide, rather uniform band at 270–300 nm was evident, tailing over 300 nm (minor yellowing), indicating the formation of a different material in these exposed samples. The basic features of the spectra at 233 and 270–290 nm were still dominant after 7 days of storage (room temperature in the dark, not shown).

The early stages of natural curing (22.0 ± 0.5°C) of an identical thin linseed oil film in the presence of copper acetate was spectroscopically monitored at 235 nm. In this case, a maximum in the peroxide buildup was observed within 4 h (Fig. 2, curve a). The initial rise rates were found to be approximately 14 times faster (Table I) than the rates observed during curing of a control linseed oil sample (Fig. 2, curve b) at the same temperature. A similar kinetic run of an identical oil
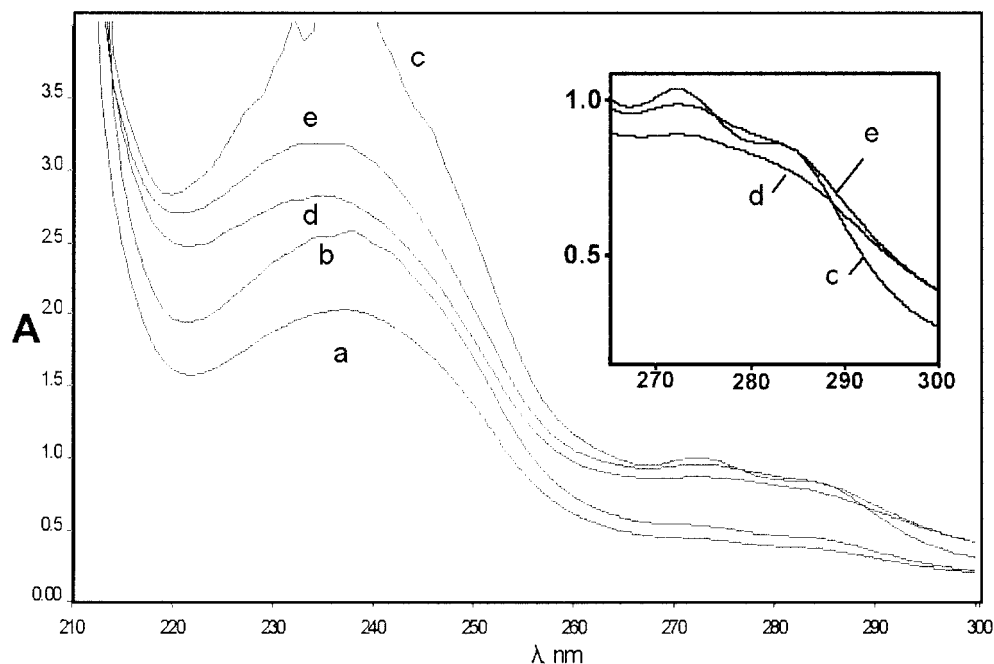
Figure 1   Absorption spectra of linseed oil films in the presence of copper acetate showing the influence of UV light during the early stages of room temperature curing in the dark at 18 (curve a), 33 (curve b), and 103 min (curve c, offscale) after film formation; after UV irradiation (curve d); and after UV irradiation and 40 min in the dark (curve e). The detail of curves c–e at the 265–300 nm region is shown in the inset.

film at $32.0 \pm 0.5°$C was interrupted at 100 min and irradiated with a UV lamp for 2 min, resulting in a sharp decrease in the absorption intensity, which also tended to restore itself after the lamp was subsequently shut off (Fig. 3).

Formation of peroxides in the early stages of linseed oil films has been recognized as a key step in the copper(II)-catalyzed oxidative degradation process.[3,11] The pentadiene structure of the unsaturated acids $C_{18:2}$ and $C_{18:3}$ has been shown to be very susceptible to this reaction. Monitoring of the process through the UV absorption spectroscopy reported here shows that copper acetate accelerates the formation of peroxides by at least an order of magnitude compared to a film containing no pigment. During this key step, oxygen is incorporated in the material with rates that greatly influence all subsequent steps of the process. The general mechanistic scheme for natural curing of linseed oil films as proposed in our earlier article[11] is shown in Scheme 1. In the course of discussing the results of the present article we indicate the modifications of the mechanism under the specified artificial aging conditions supported by the experimental data.

UV irradiation of the film results in a drastic reduction of peroxides, as evidenced by the UV spectrum, implying fast light-induced disruption of the peroxy bond. This occurs because of reactive alkoxy radicals formed in the film material (Scheme 1), which participate in the reactions forming conjugated carbonyl and hydroxyl containing products. On the other hand, photochemical cleavage of the peroxide bond also results in high concentrations of OH radicals in close proximity to the reactive sites, which can again lead to a material containing conjugated hydroxyl and carbonyl groups.

These kinetic experiments, beyond the illustration of the UV exposure influence, confirm our earlier qualitative results, which suggested a catalytic effect of selected copper containing pigments in the early oxidation stages of linseed oil. Similar runs (not shown) of samples containing copper abietate showed a peroxide rise rate comparable to that of copper acetate. On the other hand, peroxide rise rates in the presence of basic copper carbonate were comparable to those of the pigment-free sample.

Curing at Increased Temperature

A series of experiments were carried out involving UV and IR spectroscopic monitoring of thermal
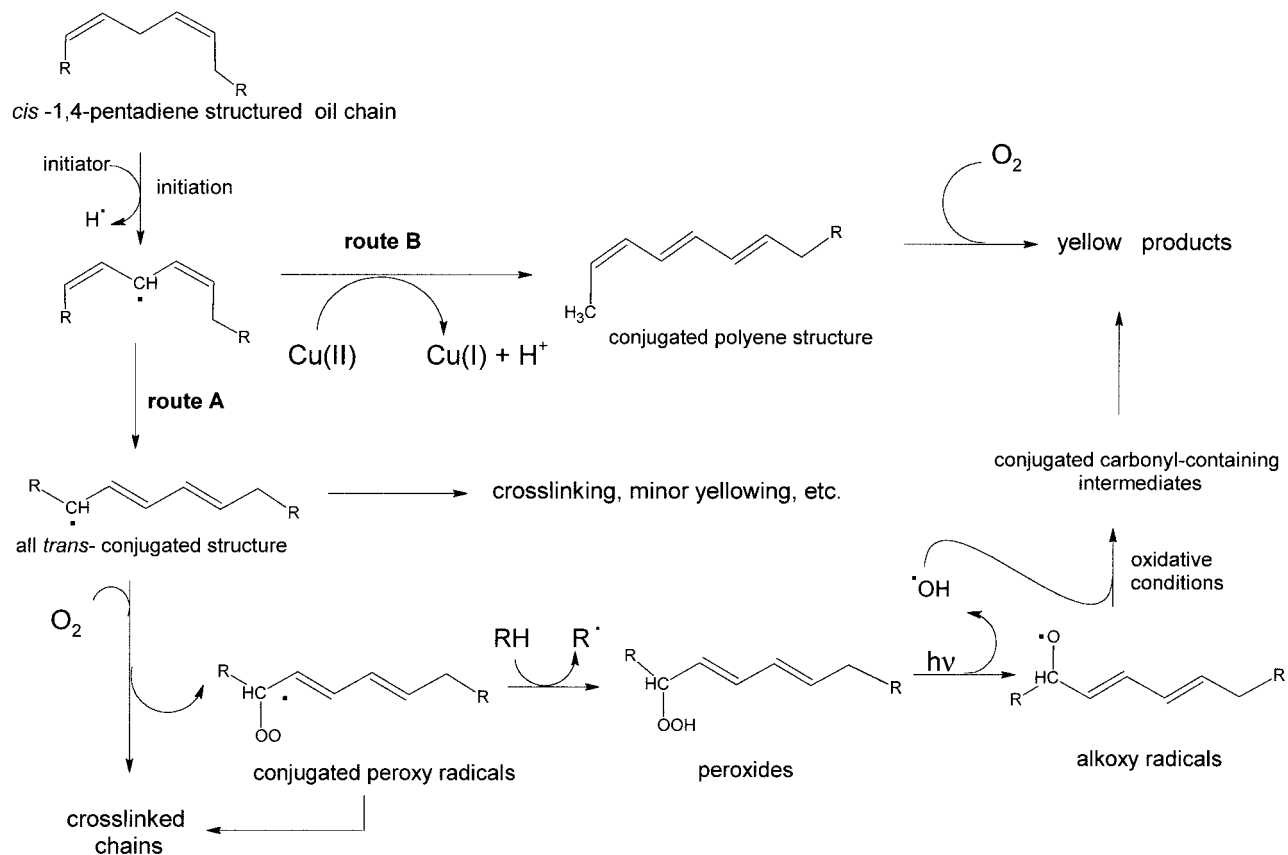
Scheme 1 The general mechanistic scheme for natural curing of linseed oil films.

curing of oil films containing copper acetate at 60 and 100°C. Intense yellowing was observed in both cases. UV absorption spectroscopy of films containing 10% (w/v) copper acetate thermally cured at 100°C for 2 h resulted in two wide shoulders at 225–235 and 270–290 nm tailing up to
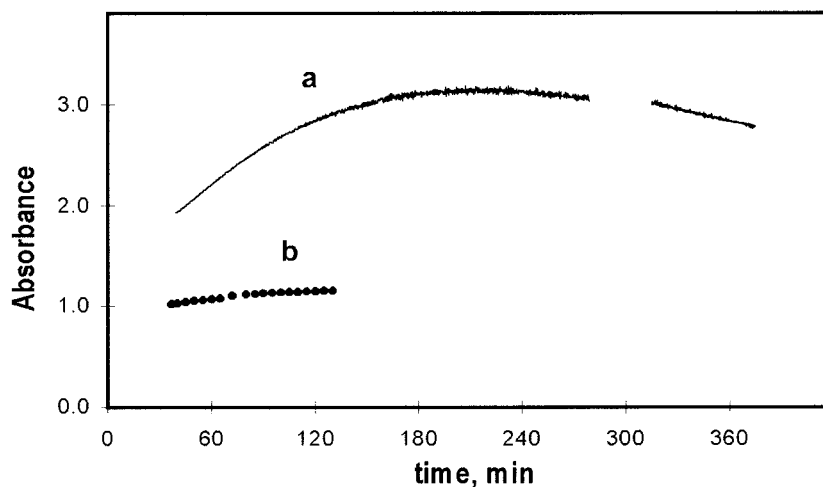

Figure 2 Spectroscopic monitoring through UV–vis spectroscopy of oil films at 230 nm. Curves correspond to films containing copper acetate (curve a) and the control sample (curve b).

Table I   Initial Rates of Peroxide Formation Monitored with UV Absorbances at 235 nm

Pigment	Temp. (°C)	Initial Rates (min^{-1})
No pigment	22	0.0019
Copper(II) acetate	22	0.0266
Copper(II) acetate	32	0.0509

450 nm (Fig. 4). On the other hand, films containing no copper pigment (control samples) exhibited no significant yellowing after thermal treatment at 100°C for 2 h. Thus, a remarkable copper acetate catalytic effect leading to enhanced yellow product formation is revealed. This effect is supported by additional experimental results presented and discussed in the following.

Figure 5 presents the results showing the artificial thermal curing effect dependence on the copper content and curing temperature. Films cured at 100°C and containing 10% (w/v) of the salt were 1.35 times higher in absorption at wavelengths above 250 nm than those containing 5% (w/v) of the salt. Similarly, curing at 100°C also resulted in much more intensely yellowed films

compared to 60°C; absorbances at 400 nm were 2.5 times higher in this case.

Intensely yellowed linseed oil films containing copper acetate and treated as above were bleached when subjected to UV exposure under a Hg-Xe lamp (Fig. 6). Following this process, the second shoulder decreased (curve c) and finally disappeared upon storage in the dark for 24 h (curve d). A featureless UV absorption band was thus obtained. The tailing of the film over 350 nm, which is responsible for the yellowing, slowly increased in more time in the dark at room temperature (curves not shown).

A detailed picture of the oxidative process is gained through FTIR absorption spectroscopy. Typical features in the FTIR spectra of the oil films under study include changes in the *cis*-CH, CH_2, OH, and C=O stretching band absorptions at 3012, 2990, 1750, and 3400 cm^{-1}, respectively.[17] The features at 1400–1600 cm^{-1} observed in spectra b and d in Figure 7 were noted in a previous report.[11] The sharp absorbance decrease of the 3012 cm^{-1} band was well established in naturally cured linseed oil films due to cis–trans isomerization of the C=C bonds. In our control experiments the 3012 cm^{-1} band completely disappeared within 4 h of natural curing in all tested
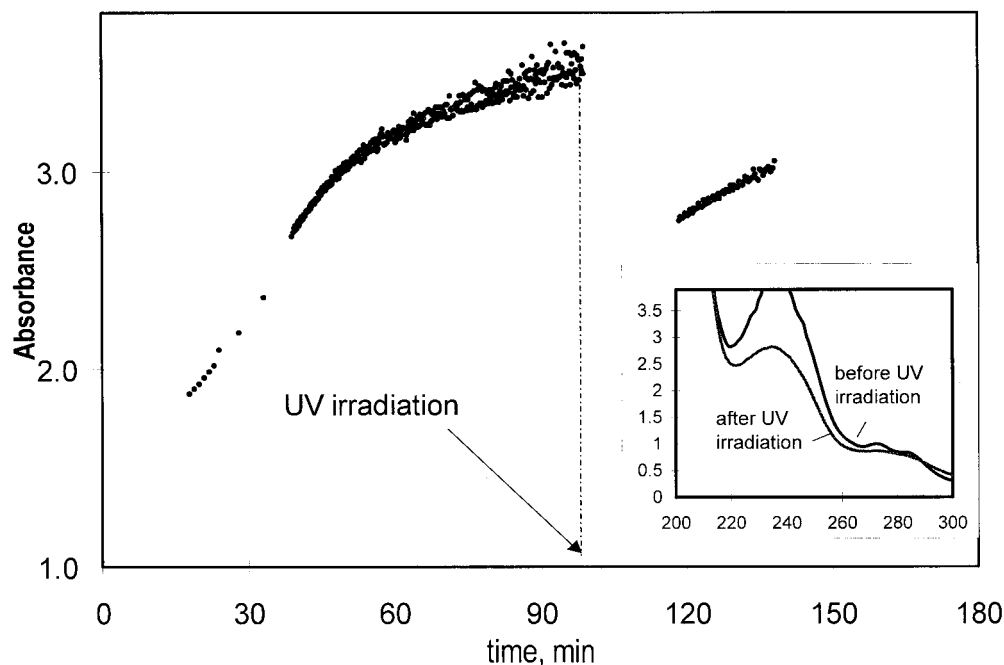

Figure 3   The effect of UV irradiation on the peroxide buildup (230 nm) in a linseed oil film containing copper acetate monitored through UV–vis spectroscopy. The spectra of the film before and after UV irradiation are shown in the inset.
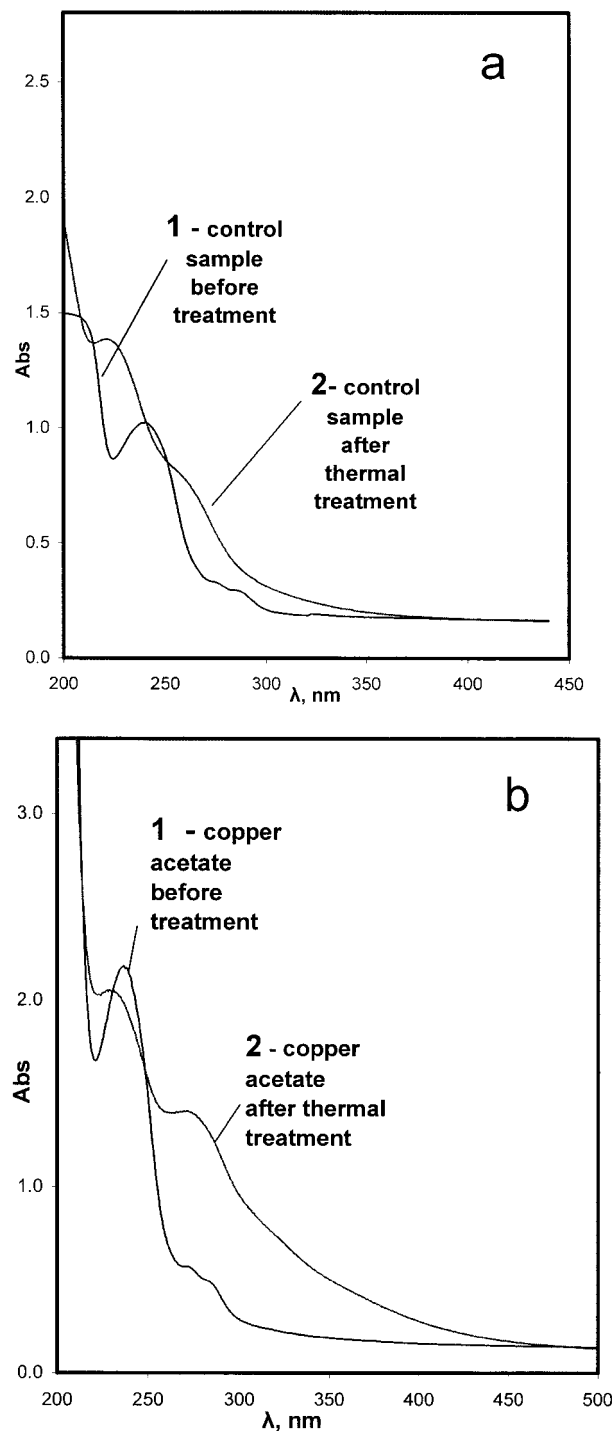
Figure 4 UV absorption spectra of linseed oil films (a) containing no pigment (control sample) before and after thermal treatment and (b) containing copper acetate before and after thermal treatment.

films. On the other hand, different behavior is revealed at elevated temperatures. Thermal treatment of the pigment-free film at 100°C also

showed that the 3012 cm^{-1} band completely disappeared, while films containing 10% (w/v) copper acetate retained almost 70% of their initial intensity after thermal treatment at 100°C. A minor reduction of the CH$_2$ band absorbance, indicative of a decrease in the hydrogen content of the material, was observed in films containing copper acetate as compared to a 20% decrease of the same band in the control sample. Differences in the decrease of CH$_2$ stretching absorbances also reflect differences in loss of weight and therefore, changes in the amount of crosslinking.[11,15,16] Transmittance FTIR spectra of thermally cured linseed oil films were recorded and are presented in Figure 7.

Incorporation of oxygen in the medium is reflected in the increase of the carbonyl peak and the formation of hydroxyl groups. The carbonyl FTIR band (due to fatty esters initially present in the material) was broadened (29% increase of absorbance based on peak areas, see inset in Fig. 7) within 2 h of artificial thermal curing of films containing copper acetate. This broadening continued with storage in the dark, and the rates were similar to those of naturally cured films. The carbonyl band remained practically unchanged in the control sample when further stored in the dark. Finally, formation of a broad band at about 3400 cm^{-1} due to newly formed hydroxyl groups, which are also known to occur in naturally cured linseed oil films,[11] was observed in all cases. The presence of copper acetate was however responsi-
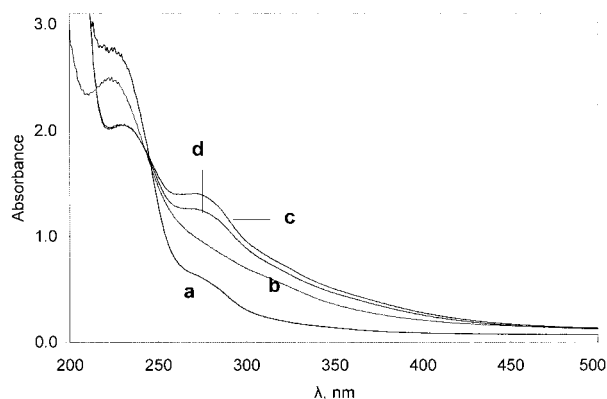

Figure 5 UV absorption spectra of yellowed linseed oil films containing copper acetate through thermal treatment under various conditions: 5% (w/v) copper acetate at 60°C (spectrum a), 5% (w/v) copper acetate at 100°C (spectrum b), 10% (w/v) copper acetate at 100°C (spectrum c), and 10% (w/v) copper acetate (thermally cured at 100°C) after UV irradiation (spectrum d).
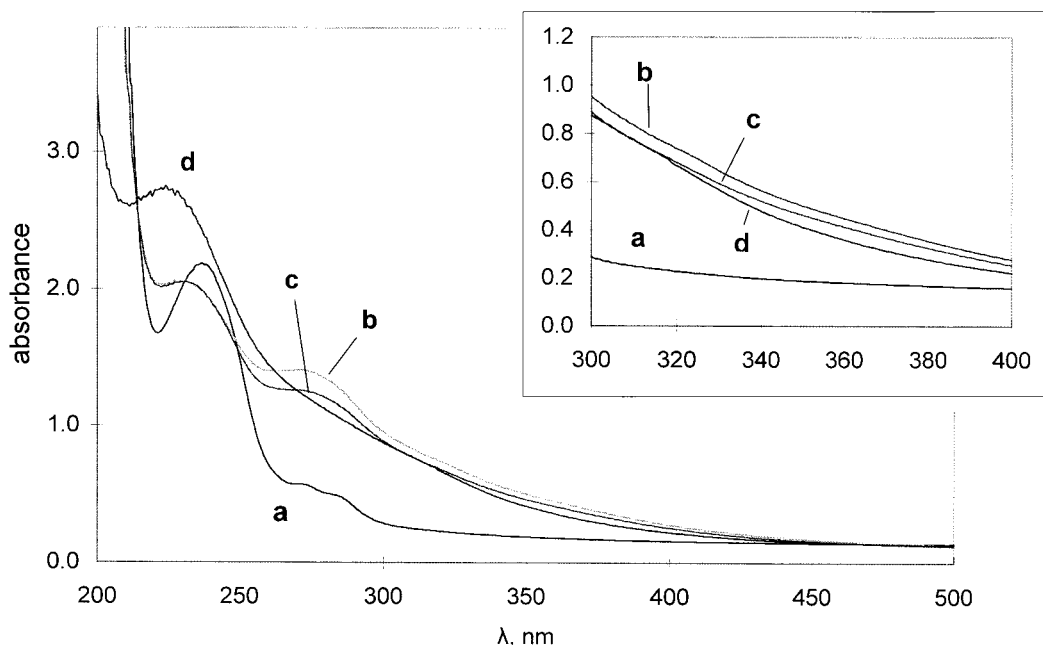
Figure 6 Absorption spectra of linseed oil in the presence of copper acetate directly after formation of film (spectrum a), after heating at 100°C for 2 h (spectrum b), after heating at 100°C for 2 h plus UV exposure (spectrum c), and after heating at 100°C for 2 h and 1 day in the dark (spectrum d).

ble for the more pronounced increase of this absorbance as seen in Table II.

The above results of linseed oil oxidation under thermal treatment of film indicate the existence of route B in Scheme 1, leading to a material containing increased quantities of carbonyl and hydroxyl groups and decreased quantities of CH_2 and CH_3 groups. This indicates that, at elevated temperatures, copper acetate catalyzes this route that competes with cis–trans conversion and results in hydroxyl and carbonyl containing conjugated products with a low degree of crosslinking. These products are responsible for the observed enhanced yellowing of the film.

Absorbances of the *cis*-CH bonds in the medium decreased with either natural curing or thermal treatment, reflecting conversion of cis unsaturation to trans. However, the absorbances of thermally cured films containing copper acetate decreased at a slower rate compared to those containing no pigment. Subsequent storage in the dark resulted in complete disappearance of cis unsaturation in all cases within 24 h. Plots of *cis* ═CH and C═O IR absorbances versus the curing time are shown in Figure 8.

Thermal treatment of pigment-free samples at 100°C for 2 h and subsequent storage in the dark

for the same period caused no significant change in C═O absorbance. However, in the case of copper acetate similar thermal treatment resulted in an abrupt increase of the carbonyl absorbance, which continued to increase at a moderate rate upon storage in the dark. This increase continued at a moderate rate during subsequent natural curing (storage in the dark at room temperature). After 87 days the absorbances were similar to those of an identical sample left to cure naturally for the same period.

Accelerated thermal oxidation of oil films containing copper acetate significantly enhanced the incorporation of oxygen in the material as evidenced by formation of hydroxyl and the increase of carbonyl FTIR bands at 3400 and 1750 cm^{-1}, respectively. In these samples the UV absorption bands of the cured material extend from 250 to 400 nm (intense yellowing). This yellowing, although in the presence of copper acetate, is accompanied by restricted crosslinking reactions, because the decrease of hydrogen (monitored through the decrease of CH_2 stretching absorptions in the FTIR spectroscopy) is not as significant as in the control sample. The overall oxidation route is different than that in the absence of the oxidizing salt. The decrease of cis unsatura-
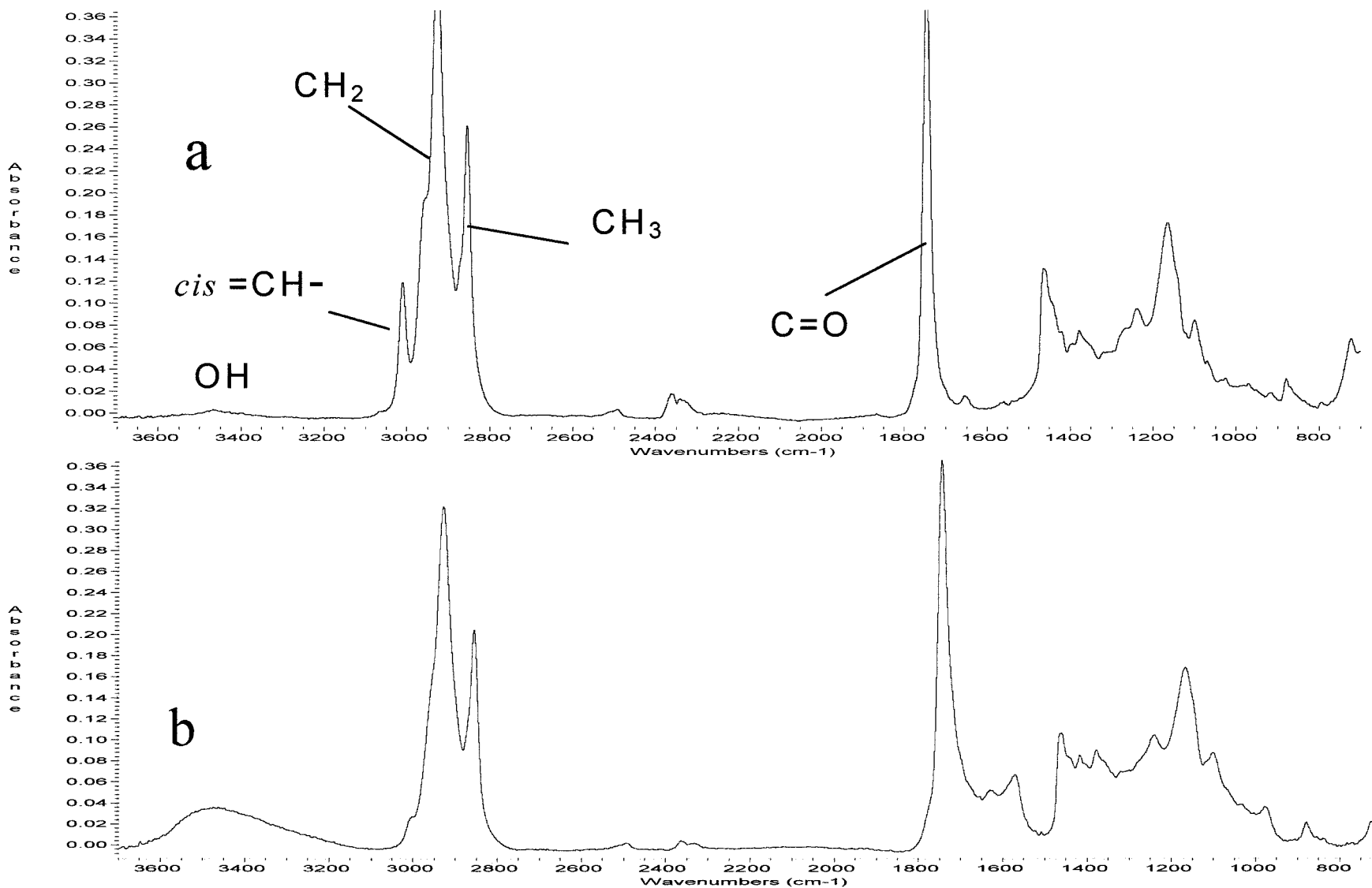
Figure 7 FTIR spectra of linseed oil films under the following conditions: initial for all samples (spectrum a), containing no pigment (control sample) and heated at 100°C for 2 h (spectrum b), containing copper acetate and heated at 100°C for 2 h (spectrum c), and containing copper acetate and heated at 100°C for 2 h after 48-h storage in the dark (spectrum d).
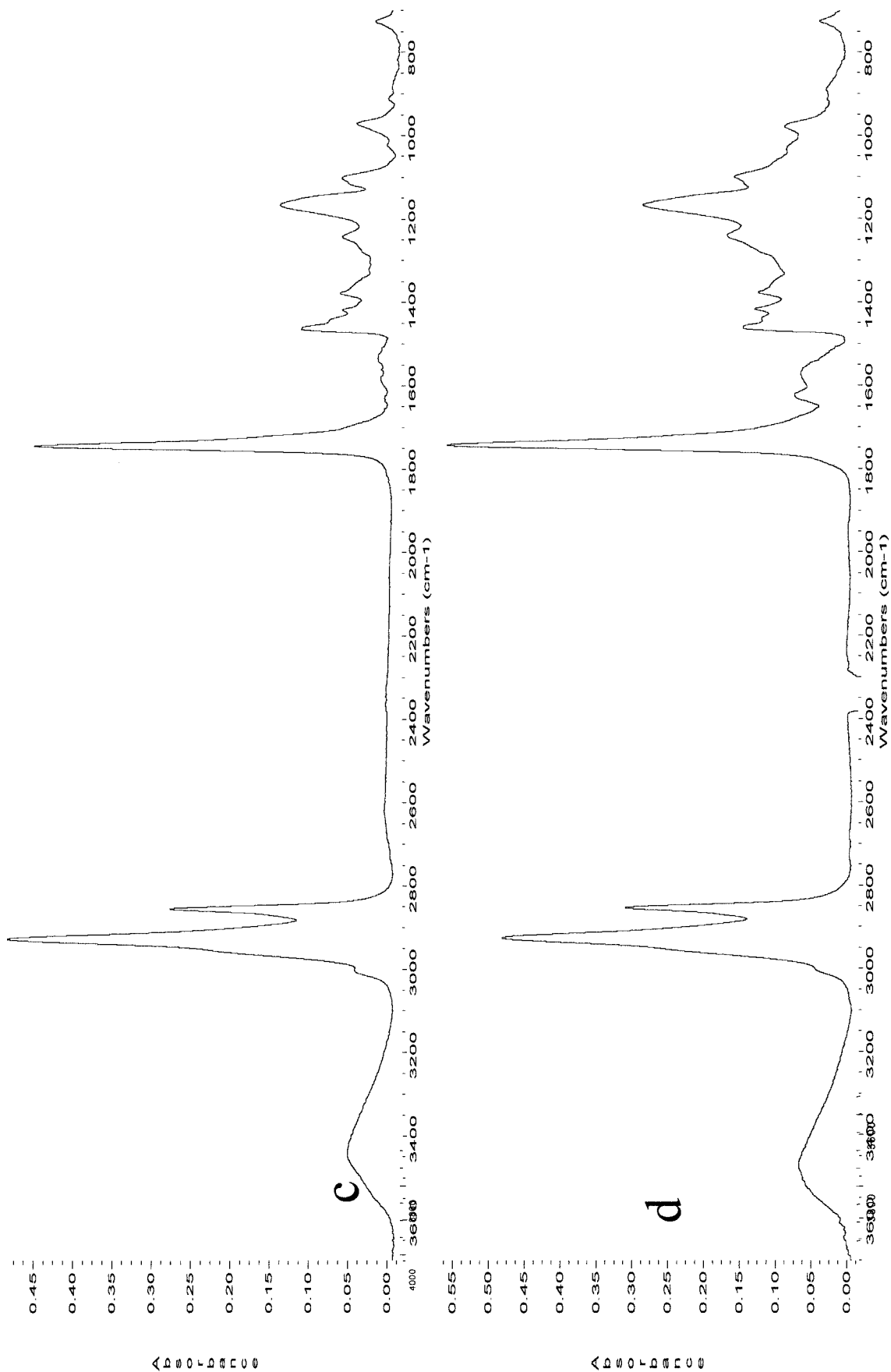
Figure 7 *(Continued from the previous page)*

Table II   Effect of Thermal (100°C, 2 h) and Subsequent Room Temperature Curing on FTIR Stretching Vibrations of Linseed Oil Films

Sample	cis-CH[a] 3012 cm^{-1}	CH$_2$[a] 2990 cm^{-1} (%)	C=O[a] 1750 cm^{-1} (%)	OH[b] 3400 cm^{-1} (%)
No pigment curing at 100°C	Disappears	−22	0	22
No pigment, artificial curing + 87 days natural curing	Disappears	−43	−12	100
Copper acetate	−27	−3	28	27
Copper acetate, curing at 100°C + 87 days natural curing	Disappears	−39	49	100

[a]Referring to the initial values of IR absorbances as the percentage of change in absorbance.

[b]Expressed as a fraction of IR absorbances as the percentage of the amount after 87 days of curing. The absorbances of films containing copper acetate were 1.3 times higher than those of the control sample.

tion occurring at the early steps of linseed oil curing (measured with FTIR spectroscopy) was inhibited in the presence of the copper salt.

Further confirmation of the above suggestions was obtained with oxidation product analysis performed with GC. It is established as a reliable technique for the investigation of the oxidation extent in oil films through the detection of low molecular weight compounds such as the remaining quantities of fatty acids at the end of the process.[18,19] Furthermore, low molecular weight compounds such as azelaic acid (C_9) that result from fragmentation reactions can be detected as end products.

Thermally cured (100°C for 2 h) linseed oil films containing copper acetate were analyzed with gas GC (typical chromatograms, Fig. 9) and were compared to similar films containing no pigment. All analyses were performed after transesterification of samples with hydrochloric methanol (see Experimental section). The quantities of esterified fatty acid residues such as methyl palmitate ($C_{16:0}$), stearate ($C_{18:0}$), oleate ($C_{18:1}$), linoleate ($C_{18:2}$), and linolenate ($C_{18:3}$), as well as monomethyl and dimethyl azelate (C_9), were measured under the areas of the corresponding chromatogram peaks. This measurement resulted in calculation of the $C_9/C_{16:0}$ (high values indicate high fragmentation extent in the medium), $C_{18:1}/C_{18:0}$ (low values indicate high extent of the overall oxidation process), and $C_{18:2}/C_{18:0}$ and $C_{18:3}/C_{18:0}$ (expected to approach zero for oxidized samples, because linoleic and linolenic acid are subjected to the various oxidative processes at a relatively higher rate than the monounsaturated oleic acid) ratios widely used as markers for oxidative degradation.

Products detected during curing at 100°C differ from those detected in naturally cured films. The results listed in Table III suggest a lower degree of chain fragmentation (evidenced by a lower $C_9/C_{16:0}$ ratio) and a lower degree of consumption (evidenced by higher $C_{18:1}/C_{18:0}$ and $C_{18:2}/C_{18:0}$ ratios) in thermally cured film containing copper acetate as compared to identical naturally cured films. The temperature of artificial curing also plays a significant role in the detected product ratios. Samples cured at 100°C were found to be higher in oleate and lower in azelate than those at 60°C. Furthermore, remaining quantities of linoleate and traces of linolenate were also found at the higher curing temperature. The results provide evidence that copper acetate is responsible for the lower amount of fragmentation products and the slower disappearance of the unsaturated fatty acids $C_{18:1}$ and $C_{18:2}$ in the film. Higher temperatures affect the catalytic rates and result in a positive effect on yellow product formation and a negative effect on oxidation of unsaturated acids.

The above has certain implications concerning the studied system, as shown in reaction Scheme 1. Participation of oxidizing copper(II) salts such as copper acetate in linseed oil films is responsible for yellow products, which are a result of induced unsaturation (polyene chains), and finally, incorporation of oxygen (Scheme 1, route B). Furthermore, copper acetate was responsible for the lower hydrogen loss of the material and decreased extent of crosslinking of the medium as confirmed through FTIR and GC product analysis. The cis–trans conversion of unsaturated acids shown in route A in Scheme 1 and the formation of an all-trans structure takes place in parallel to route
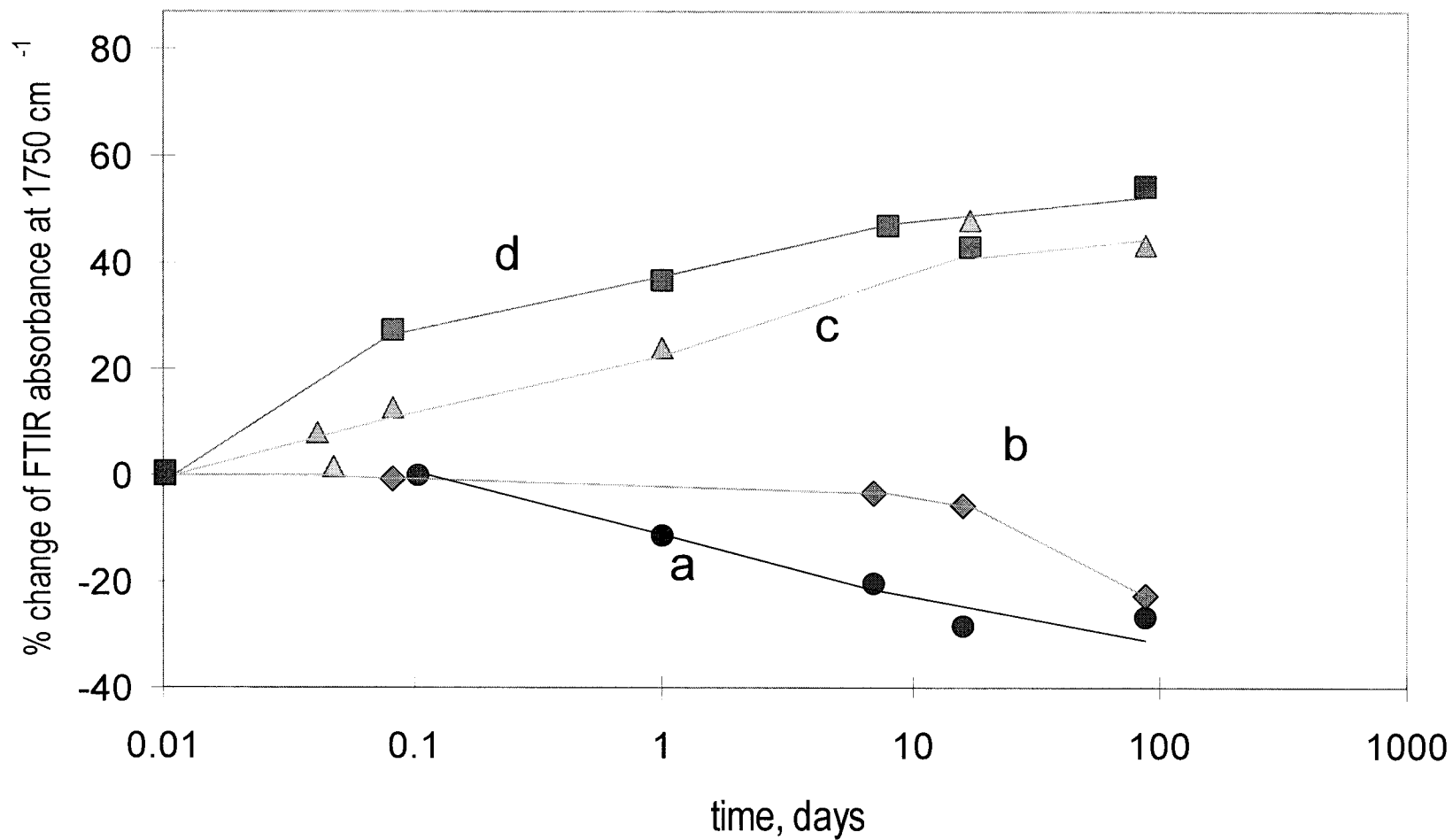
Figure 8 The trends of the C=O FTIR stretching absorption in oil films containing no pigment (control sample) after natural curing (curve a), containing no pigment after artificial curing (100°C, 2 h) followed by storage in the dark (curve b), containing copper acetate after natural curing (curve c), and containing copper acetate after artificial curing (100°C, 2 h) followed by storage in the dark (curve d).
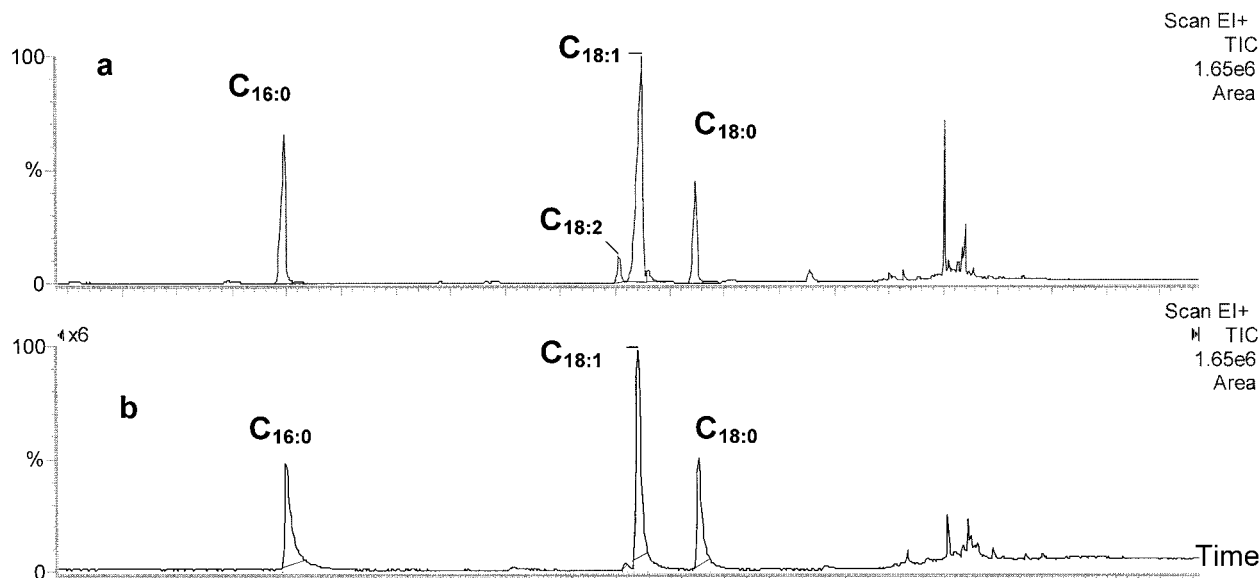
Figure 9 A typical gas chromatogram of GC–MS runs of samples from thermally cured (100°C for 2 h) linseed oil films (a) in the presence of copper acetate and (b) containing no pigment.

B. Hydrogen loss occurs in both routes. However, it is more pronounced in route A and leads basically to crosslinking while in route B it results in the formation of unsaturated regions of the oil chains. As a consequence, route A, which leads to intense weight loss and results in crosslinked and moderately yellowed material, occurs competitively to route B, which is catalyzed by copper acetate and results in yellow products.

CONCLUSION

The results of the present work on the curing of oil binding media at elevated temperatures or under photochemical action elucidate critical steps of the oxidation mechanism under various conditions. UV light exposure at the early stages accelerates curing through destruction of peroxides. On the other hand, curing of oil films containing oxidizing Cu pigments at elevated temperatures results in materials with decreased crosslink density. The thin film approach adopted in this work made the connection of these processes possible within the various types of samples, rendering implications for techniques generally applied in coatings based on unsaturated oils. Thus, careful consideration of these factors should be taken into account in the course of investigating the prehistory of a surface, as well as in applying a potentially damaging technique such as laser cleaning. It should also be empha-

Table III   Comparison of Ratios after Calculation of Areas of Corresponding Acids after Natural and Artificial Curing of Linseed Oil Films in Presence of Copper Acetate

Sample	Curing Conditions	$C_9/C_{16:0}$[a]	$C_{18:1}/C_{18:0}$[a]	$C_{18:2}/C_{18:0}$[a]
Copper acetate	Natural,[b] 2 days	0.86	2.75	Below limit of detection[c]
Copper acetate	Natural,[b] 64 days	1.60	2.26	Below limit of detection[c]
Copper acetate	60°C, 2 h	0.43	3.04	0.07
Copper acetate	100°C, 2 h	0.29	3.45	0.61

[a] C_9, azelaic acid; $C_{16:0}$, palmitic acid; $C_{18:0}$, stearic acid; $C_{18:1}$, oleic acid; $C_{18:2}$, linoleic acid. Fatty acids were detected as their methyl esters.
[b] In the dark at room temperature.
[c] See Experimental section.

sized that in thick films the underlying layers of binding media are basically in a noncured state and the process is similar to the early stages of curing in oil media.

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