Thin-Film Study on the Oxidation of Linseed Oil in the Presence of Selected Copper Pigments

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In the context of investigating the thermal degradation and yellowing of painting media by oxygen, the effect of the green copper compounds, malachite (basic copper carbonate), verdigris (basic copper acetate), and copper abietate, on the oxidation of linseed oil films was studied. To this end, an experimental methodology suitable for in situ spectroscopic investigation has been introduced. Spin-coating is used for the preparation of thin oil films of controlled thickness (1.0–1.4 μm) on quartz, glass, or silicon wafer substrates, enabling UV-absorption and IR spectroscopic studies to follow the course of thermal oxidation. The study is supported by chromatographic analysis of oxidative degradation products obtained at different processing conditions. A differentiation in oxidation of linseed oil is confirmed in the presence of the different copper pigments. On the other hand, light bleaching of yellow films is accompanied by degradation of the medium. On the basis of these results, the factors influencing the mechanism of oxygen-mediated polymerization, yellowing, and degradation of artist's oils in the presence of copper-based pigments are discussed.

Introduction

A major problem with organic materials encountered in art objects is their relatively short lifetime due to their susceptibility to various degrading processes. In the case of art paintings in particular, discoloration, cracking, and degradation are the results of chemical and physicochemical processes that usually originate from oxygen and exposure to UV light.[1] These processes can be further investigated if the specific chemical nature of the paint medium is considered.[2]

Linseed oil is traditionally one of the most commonly encountered paint media. Lately, as the search for reduction of volatile organic compounds released from coatings has come into focus, the interest in linseed oil for modern technological applications has been renewed.[3] The processes induced by oxygen diffused into this medium start with the desirable drying of the painting but in later stages result also in discoloration and damaging. The various chemical processes that occur during aging of the film can be categorized as cross-linking, yellowing, and chain degradation with formation of small volatile products. All these processes constitute an overall interdependent chemical behavior and occur almost simultaneously, although to varying extents depending on the composition of the film and the environmental conditions.

Detailed knowledge of the various degradation mechanisms is necessary in specific applications. For instance, in restoration of art objects, it has always been a matter of concern what technique best removes a surface layer of degraded material at a desired depth without damaging the rest of the film. Generally, this has been traditionally accomplished with the use of appropriate solvents, but more recently laser ablation techniques have been also proposed.[4] Since applicable methods aiming at restoring works of art must take into account their history and the potential damage these methods could impose, a more detailed insight into these phenomena is needed. This insight can lead to the elucidation of the domain at which the three major types of the previously mentioned chemical processes hold and intersect. Especially for laser-based cleaning techniques of art objects, where both photochemical and thermal phenomena are present depending on conditions, investigation of thermal and photochemical aging of the

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binding medium of paintings can be used in guiding the restoration process.

The presence of metal salts in many of the known pigments used in painting induces another potential factor of concern, because these compounds contribute to the oxidation of the medium and can possibly accelerate the thermal and photochemical discoloration and degradation processes. Copper(II), commonly present in older paintings, has long been known as an effective oxidizing agent of organic compounds.[5,6] The complex role of copper salts in influencing the oxidative processes in oil-based painting media has been recognized in thick-film studies by Rasti and Scott.[7]

The present work aims at demonstrating the usefulness of a thin-film-based methodology[8] that enables both spectroscopic (UV and IR) monitoring of the system and good control of the influencing factors (absorption of light, oxygen diffusion) affected by the film thickness. Gas chromatographic product analysis is also used in support of the spectroscopic data. The results obtained provide an overview of the whole oxidation process from the early to the late stages and allow comparison of different film compositions and processing conditions. Linseed oil oxidation in the presence of copper pigments is, in particular, the subject of the present study.

Experimental Section

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

Oil films containing 10% and 5% w/v pigment were tested. The pigments used were basic copper carbonate, $CuCO_3 \cdot Cu(OH)_2$ (malachite), copper acetate $(CH_3COO)_2Cu \cdot 2(H_2O)$, also known by the empirical name verdigris), and copper avietate $(C_{19}H_{29}COO)_2Cu$. Pigment-free linseed oil where calcium chloride (or sodium carbonate where noted) had been added to enable film formation was also used to prepare control samples.[9] Basic copper carbonate was purchased from Fluka, copper acetate was prepared according to a technique common in pigment manufacturing (copper leaves left upon vinegar for several months followed by scraping of the formed salt), and copper avietate was prepared upon reaction of avietic acid with copper(II) acetate (Fluka) at 120 °C. Structures were confirmed through IR and X-ray analysis.

Ultraviolet absorbance spectroscopy was performed with the use of a Perkin–Elmer Lambda-19 spectrophotometer. Infra-Red spectroscopy was carried out on a Nicolet Magna 550 FTIR spectrometer. In the photooxidation experiments, irradiation was carried out using an Oriel Hg–Xe lamp with a 254 ±30 nm broadband filter, where noted, for wavelength selection.

Linseed oil (bleached), purchased from Schebeningen, Holland, was tested titrimetrically and by means of UV and IR spectroscopy, gas chromatography, and mass spectrometry. Acidity was found to be 1.1 (±0.08) mg KOH/ml. Electrospray mass spectrometry of crude linseed oil dissolved in methanol fed through a Jasco LC pump was performed on a Platform II mass spectrometer (mobile phase methanol, electrospray capillary voltage 4.00 kV, HV lens 0.38 kV, counterelectrode voltage 70 V, ion energy 1.4 V, source temperature 60 °C) and resulted in a basic peak of m/z 874.

Gas chromatography was performed on a Perkin–Elmer gas chromatograph with a SPB-1, 30-m column. Temperature was programmed at 90°–200 °C (2 °C/min), isotherm (40 min), then gradient 2 °C/min up to 250 °C. Gas chromatography–mass spectrometry was performed on a Fisons MD-800 mass spectrometer combined with a Fisons 8000 gas chromatograph with a DB-1, 15-m-column, temperature programmed at 60 °C (isotherm 4 min), 3 °C/min gradient up to 250 °C and 10 °C/min up to 230 °C, isotherm (50 min).

Workup of samples prior to gas chromatographic analyses included extraction and transesterification of the low MW fraction of all films with methanol/HCl, followed by extraction with a 1:1 mixture of water–ether. Fresh linseed oil exhibited all expected fatty acid peaks as their methyl esters identified by mass spectrometry: methyl palmitate m/z 43 (20.9), 55 (11.3), 74 (26.6), 87 (18.51), 143 (3.74), 270 (2.8); methyl stearate m/z 42 (18.0), 44 (23.6), 69 (4.3), 74 (26.7), 87 (20.4), 143 (3.9), 298 (3.0); methyl oleate 43 (20.9), 55 (26.6), 69 (12.8), 74 (10.7), 87 (8.42), 96 (9.81), 180 (2.28), 264 (4.29), 296 (1.02); methyl linoleate 42 (5.1), 55 (19.5), 67 (23.4), 81 (21.0), 95 (15.6), 109 (6.68), 263 (1.0), 294 (2.8); and methyl linolenate 41 (20.1), 55 (13.54), 67 (14.54), 79 (20.8), 95 (12.1), 108 (9.3), 135 (2.4), 149 (1.8), 292 (1.0). Peak ratios in fresh oil, determined with gas chromatography (FID detector), were found as follows: $C_{18:1}$ (oleate)/ $C_{18:0}$ (stearate) = 4.0, detected $C_{18:2}$ (linoleate) and $C_{18:3}$ (linolenate) peaks unresolved. No azelate was detected in fresh oil. Ratios of saturated acids, $C_{16:0}$ (palmitate)/ $C_{18:0}$ (stearate), typically unchanged in the course of the oxidation process, were found 1.6 (±0.2) in both fresh and aged samples. No linoleate and linolenate were detected in aged samples due to fast oxidation. Oxidation products observed under our conditions have been identified through mass spectrometry (see Table 2).

Results

In situ Spectroscopic Monitoring of the Overall Aging Process. Aiming at the investigation of the influence of copper(II) salts in the complex processes of linseed oil curing and deterioration, we have first focused on the spectroscopic study of identifiable species or groups within this medium. Control of film thicknesses close to 1 ìm was essential for successful UV spectroscopic monitoring of the samples. IR spectroscopic monitoring of such films was also possible. Also, thin films of 1.0–1.4 μm, used in our experiments, are considered to permit a uniform oxygen in-depth diffusion according to previous theoretical calculations which predict oxygen starving in much higher depths, approximately 100–150 μm.[10]

The general course of the oxygen-mediated aging process was first followed by UV spectroscopy. Keeping pigment content below 10% ensures that all observable UV absorptions are due to linseed oil and its changes (Figure 1). Short- and long-term examinination of these

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(9) Neat linseed oil does not form a film on silicon, glass, or quartz. With the addition of a supporting inert medium (e.g., a salt), film formation is enabled.

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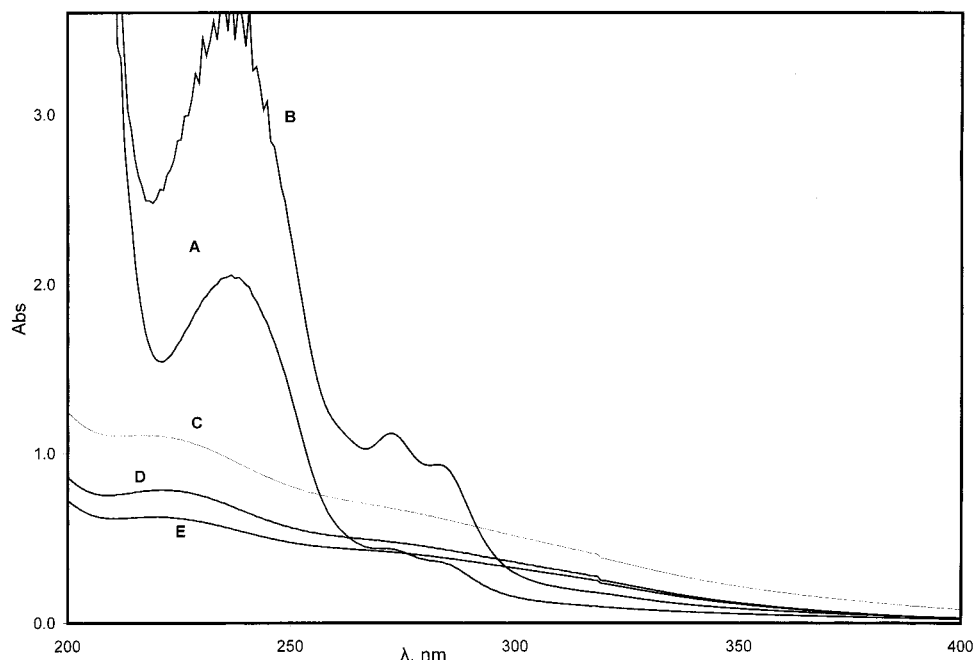
Figure 1. Characteristic UV spectra of an oil film containing copper acetate at different stages of aging: **A**, initial (within 5 min from spin coating); **B**, 2 h in the dark (fine structure at the 245 nm region is an artifact due to very high absorbance of formed peroxides); **C**, 68 days in the dark; **D**, 8 months in the dark; **E**, 8 months in the dark + hν (6 min).

Scheme 1. General Mechanistic Scheme
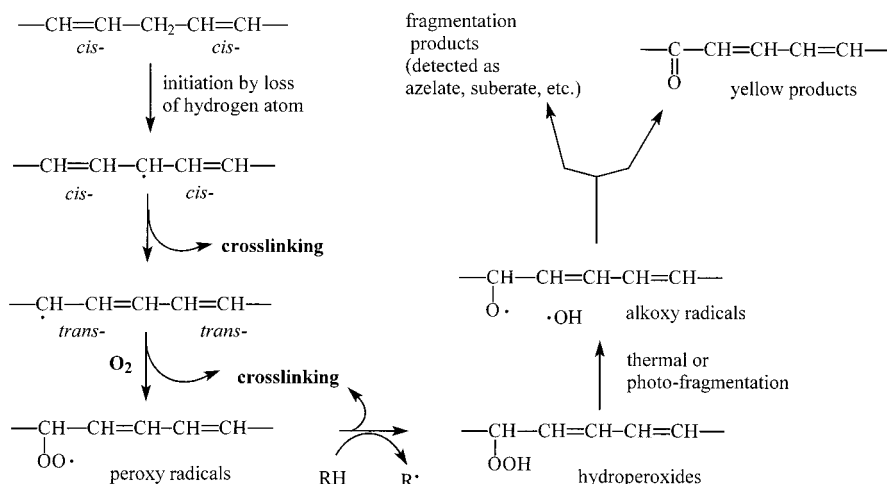
changes can be summarized as follows: formation of unsaturated peroxides absorbing at 235 nm as a result of oxygen attack and redistribution of C=C bonds of the unsaturated oil backbone[6a] is observed during the first stages; a characteristic weak double shoulder at 276 and 278 nm, presumably due to extended conjugated structures,[6c] forms and disappears almost simultaneously; formation of strong peaks at 220 and 280 nm, attributed to conjugated carbonyl compounds, follows; finally, a featureless, broad, uniform band extending up to approximately 400 nm emerges after prolonged aging, indicating yellowness of the material through extended conjugation.

The early stages of linseed oil degradation are best understood on the basis of the easily abstractable hydrogens attached to the pentadiene-containing linoleate chains (see illustration in Scheme 1 in Discussion section), resulting in fatty chain radicals, which, upon reaction with oxygen, produce peroxides or hydroperoxides.[9,14] Formation of peroxides appears to be the

main feature during the initial stages of the oxygen-mediated processes of oil films, with or without the presence of copper(II) salts. Samples that gave intense peroxide peaks also resulted in faster decomposition of the same feature. This is in accordance with a previous finding,[7b] suggesting copper salt acceleration of the decomposition of cumene hydroperoxide.

Infrared spectroscopy appears as an ideal tool for studying oil films, providing information about the groups involved in the curing process. Assignment and analysis of major IR peaks of aged linseed oil have been presented earlier by others.[11,12] Among the general features, transformation of all-cis polyunsaturated chains

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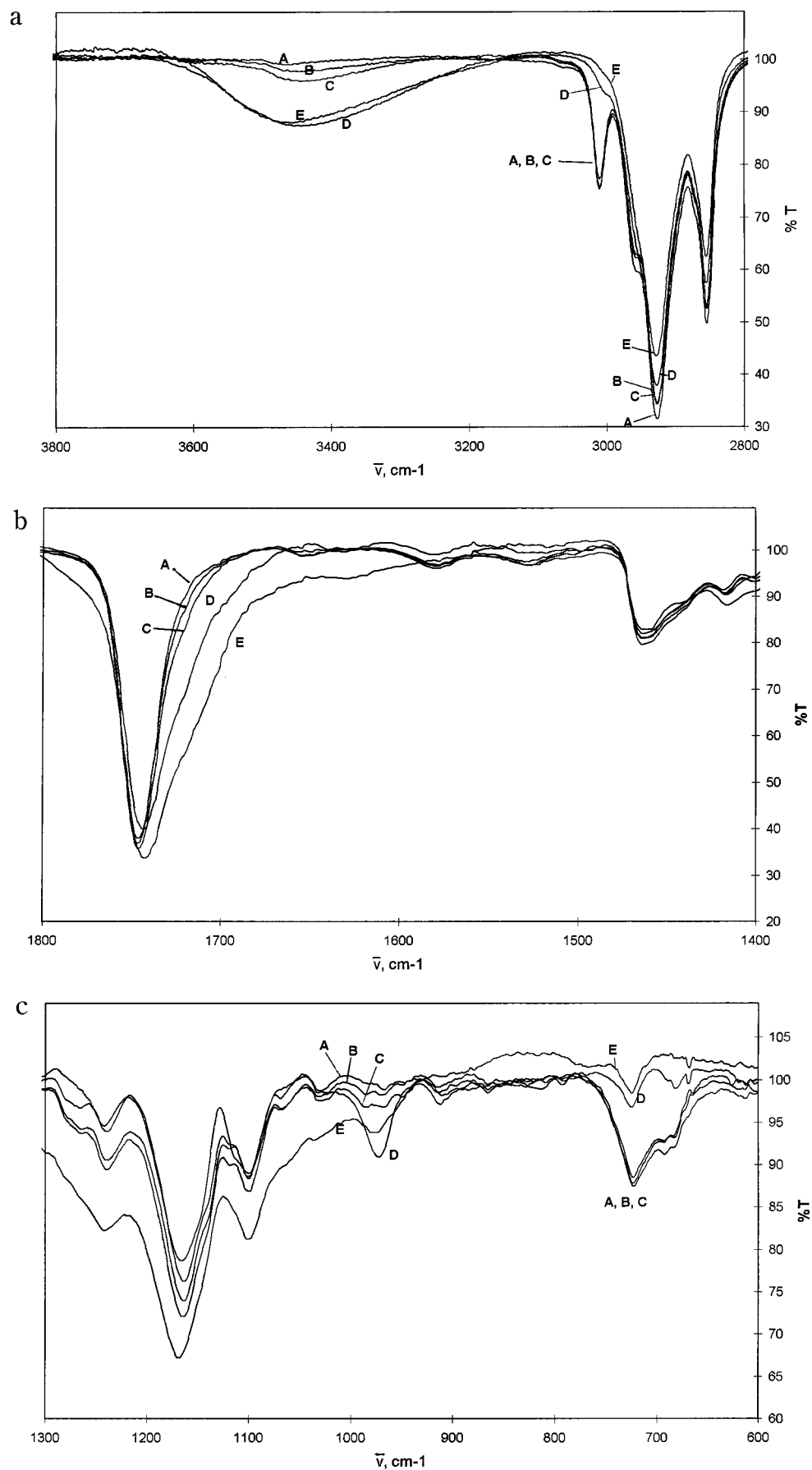
Figure 2. IR spectra of linseed oil thin films containing copper acetate depicting changes in (a) the OH and the C−H stretch; (b) the C=O stretch and the 1573 cm^{-1} band, and (c) C=C−H deformation frequencies at different times of thermal aging: **A**, initial (within 5 min from spin coating); **B**, 1:10 h; **C**, 2 h; **D**, 1 day; and **E**, 17 days.

Figure 3. IR spectra of linseed oil thin films containing no pigment, depicting changes in (a) the OH and the C−H stretch; (b) the C=O stretch and the 1573 cm⁻¹ band, and (c) C=C−H deformation frequencies at different times of thermal aging: **A**, initial (within 5 min from spin coating); **B**, 1:10 h; **C**, 2 h; **D**, 1 day; and **E**, 17 days.
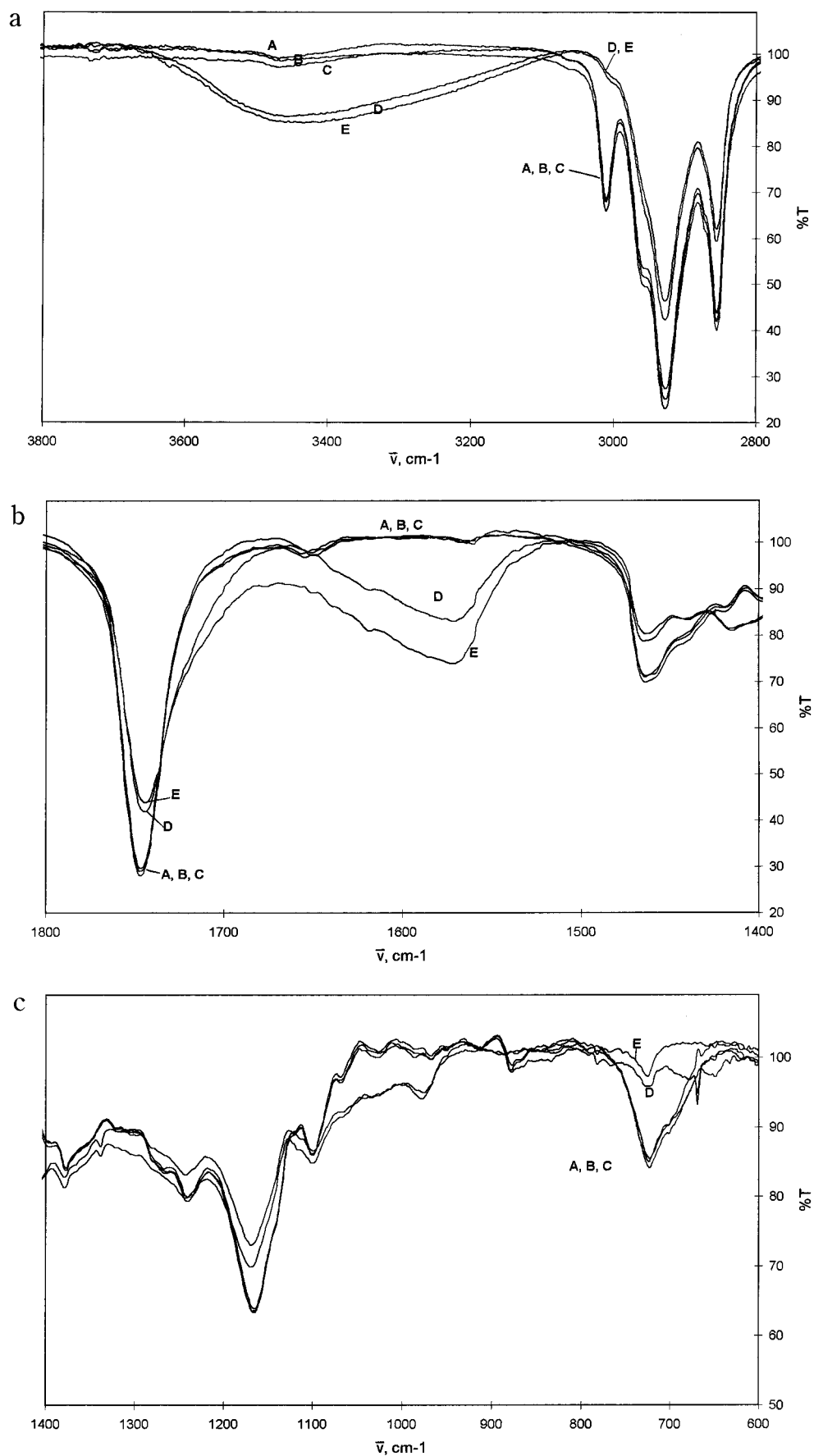
Table 1. Monitoring of Linseed Oil Major Uv Peaks in the Presence of Tested Pigments

sample	max of peak, 235 nm	max of double peak, 276 and 278 nm	max of peak, 220 nm
basic copper carbonate	3 d	3 d	10−12 d
copper acetate	$3^{1}/_{2}$ h	$3^{1}/_{2}$ h	3 d
copper abietate	$3^{1}/_{2}$−4 h	$3^{1}/_{2}$−4 h	3−4 d
no pigment	3−4 d	3 d	7 d

to cis,trans and finally, to all-trans, loss of hydrogens attached in the saturated chains and increase of carbonyls have been reported. In our experiments, both short- and long-term aging resulted in spectral differences, where a number of general features were confirmed. In Figures 2 and 3, IR spectra of copper acetate and pigment-free oil films are shown. Spectral features of the films containing the other two pigments are similar to the ones containing copper acetate. The most significant short-term effects are: a sharp decrease of the cis =C−H stretching band at 3040 cm^{-1} within 24 h of aging; formation of a weak and broad peroxidic OH peak at 3400 cm^{-1}; a gradual decrease of the CH$_2$ stretch (2958−2850 cm^{-1}); decrease of the cis =C−H deformation peak at 726 cm^{-1} followed by increase of the trans =C−H peak at 976 cm^{-1} after 1 day's aging and finally, disappearance of all =C−H deformations at aging longer than 2 days.

On the other hand, the following long-term effects were observed: a significant broadening and minor shift to lower frequency of the carbonyl stretching peak at 1740 cm^{-1}; formation of a broad hydroxylic peak (3461 cm^{-1}), typical in all tested films; disappearance of the weak cis C=C stretch band (1640 cm^{-1}) within several days; and formation of a weak peak at 1624 cm^{-1} in all samples, possibly due to conjugation of C=C bonds. Moreover, a shoulder at 1776 cm^{-1}, proposed by Mei-lunas et al. as diagnostic for aged linseed oil media,[12] was confirmed. Formation of a moderately broad peak at 1573 cm^{-1} and a weaker one at 1404 cm^{-1} was observed in pigment-free films and, according to previous suggestions,[12] it has been attributed to the asymmetrical and symmetrical stretching of coordinated carboxylate anions, respectively. However, an alternative explanation involving carbonyls participating in extended conjugation with C=C bonds cannot be excluded for the 1573 cm^{-1} peak.

Comparison of Aging Process in the Presence of Different Copper Pigments. *UV Spectroscopic Monitoring.* The time of appearance and the intensities of all UV bands observed during the aging process differed among the films containing the various salts tested. Short-term observation showed peroxides formed in all cases, but at different time domains. The 235 nm peak (peroxides) forms and disappears faster in the presence of copper acetate and abietate (Table 1). The time domain of presence of these bands can be used as a measure of the influence of copper pigments in the progress of degradation. From this point of view, faster modes of action can be considered in the cases of copper acetate and copper abietate. At long aging times (60 days or more), the featureless UV absorption band extending up to 400 nm (yellow products) was observed in all cases. All samples resulted in yellowed films after prolonged aging.

IR Spectroscopy. Comparison of the successive IR spectra results in evaluation of the critical differences in the extent of oxidative processes among all tested copper salts. Transformation of cis to trans C=C bonds (decrease in the 3012 cm^{-1} band) seems to have been similarly completed in all samples within the first 100 hours of aging (Figure 2). On the other hand, weight loss in the form of hydrogens, as measured by decrease in CH$_2$ bands (2990 cm^{-1}) observed over a period of 87 days, was moderate for all copper salts (slightly stronger for basic copper carbonate) and more pronounced for the pigment-free sample (Figure 4). This reflects considerably more intense weight loss and, therefore, cross-linking of the material under less oxidative conditions.

Formation of alcoholic OH and carbonyl band widening is a result of the oxidative degradation in a polymer film. Significant formation of the hydroxylic band was evident in all cases (OH absorbances at 3460 cm^{-1}). On the other hand, a significant widening in the carbonyl band (1741 cm^{-1}) has been observed especially for copper acetate, while the same band was practically unchanged in the pigment-free film (Figure 3). Furthermore, weak peaks at 947 and 984 cm^{-1} due to C=C conjugation also appear only in copper acetate with prolonged aging. In light of these data, increase in the carbonyl region (Figure 4) constitutes an important mode of oxygen incorporation, mainly in the form of aldehydes and acids (as GC product analysis, later in this section, suggests), while conjugated C=C bonds constitute a mode of film yellowing.

Analysis of Oxidation Products. *Thin Film Studies.* Oxidative cleavage and production of low MW volatile products as one of the end results in the process was investigated by gas chromatography analysis, which gave significant evidence for the degree of oxidation in oil films. All analyses were performed on trans-esterified samples with hydrochloric methanol. A typical GC trace is shown in Figure 5. Identification of the majority of the detected products was achieved with the use of GC-MS. Table 2 lists selected identified products in a typical aged sample of linseed oil in the presence of copper abietate. 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$_9$), have previously been used extensively as a measure of various oxidative routes.[13]

After prolonged aging, amounts of azelate were detected, resulting in a substantial C$_9$/C$_{16:0}$ ratio, commonly accepted as a measure for the formation of low MW products and therefore, fragmentation. No lower-molecular-weight products were detected in fresh linseed oil. Linoleate, exhibiting the basic 1,4 pentadiene structure, has previously been shown to undergo fast oxidative degradation.[14a] In the linseed oil films studied, linoleate and linolenate residues disappear within the first day during natural aging, causing C$_{18:2}$/C$_{18:0}$ and C$_{18:3}$/C$_{18:0}$ ratios to decrease sharply, approaching zero values. Oleate, and therefore the ratio C$_{18:1}$/C$_{18:0}$, remains the only characteristic measure for the unsaturation remaining in the system in its initial form. The ratios C$_{18:1}$/C$_{18:0}$, C$_{18:2}$/C$_{18:0}$, and C$_{18:3}$/C$_{18:0}$ had their highest values in fresh linseed oil. It can be seen that with the exception of copper acetate, short oxidation
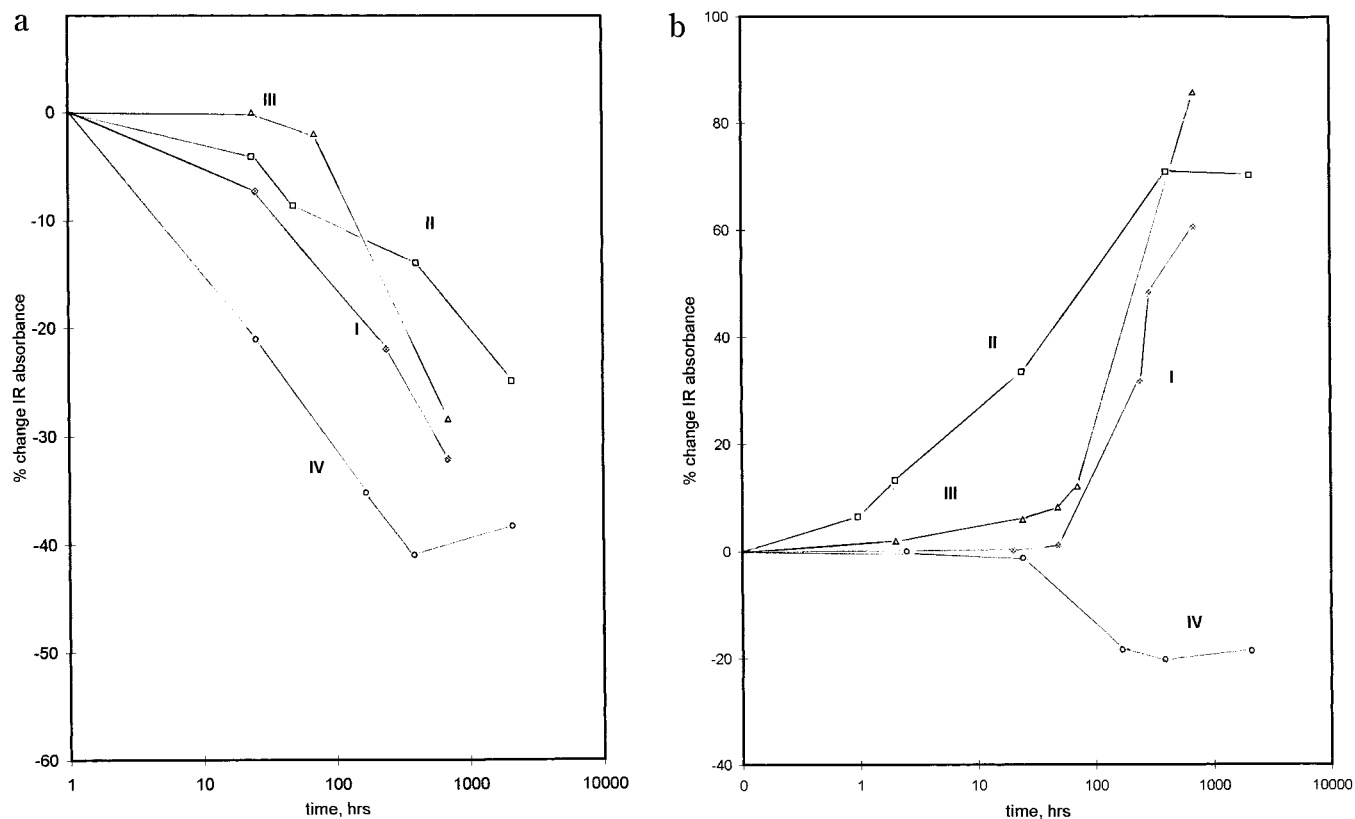
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Figure 4. The effect of copper pigments in the change of IR absorbances on the (a) CH_2 band at 2990 cm^{-1}, and (b) the carbonyl band at 1741 cm^{-1}.
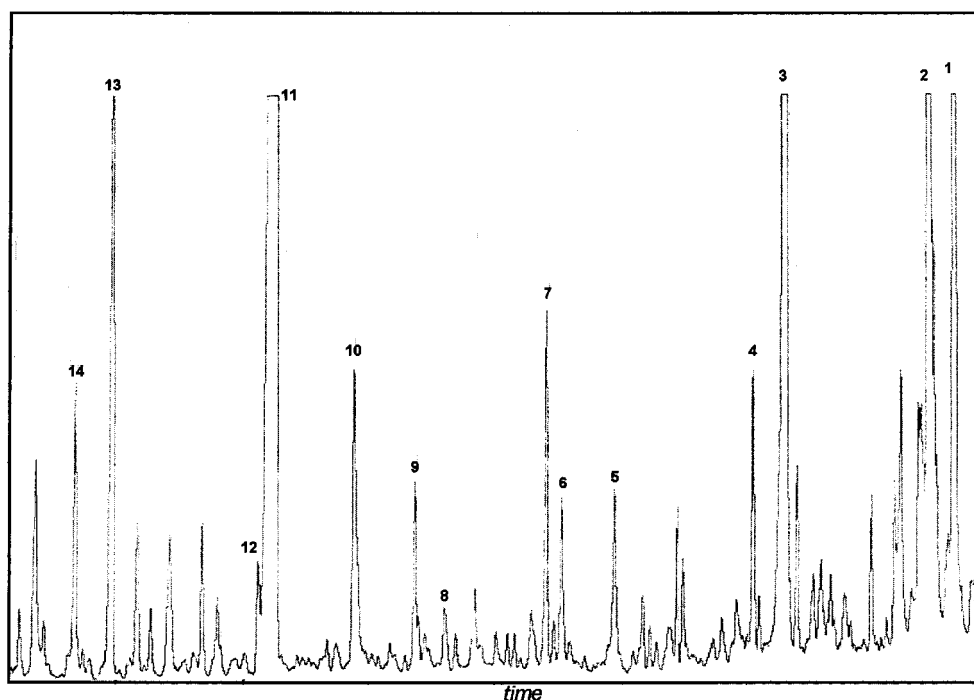

Figure 5. Typical GC−MS trace of thermally aged linseed oil containing copper acetate (film on glass substrate), showing remaining linseed oil components and main oxidation products: **1**, methyl stearate; **2**, methyl oleate; **3**, methyl hexadecanoate; **4**, methyl hexadecenoate; **5**, dimethyl dodecanedioate acetal; **6**, dimethyl undecanedioate acetal; **7**, methyl tetradecanoate; **8**, 4-oxo-nonanedioic acid monomethyl ester; **9**, dimethyl decanedioate; **10**, dimethyl acetal; **11**, dimethyl nonanedioate (azelate); **12**, methyl dodecanoate; **13**, dimethyl octanedioate; **14**, methyl azelate semialdehyde.

times did not result in significant amounts of fragmentation products, while oleate was still present in significant amounts. The above results are illustrated in Table 3.

Longer times (64 days) showed basic copper carbonate and pigment-free samples lower in fragmentation and relatively higher in oleate than the rest. On the other hand, samples containing copper acetate and copper

Table 2. Products Identified Through GC−MS in a Typical Aged Sample of Linseed Oil in the Presence of Copper Abietate[a]

carboxylates	methyl hexanoate, methyl heptanoate, methyl octanoate, methyl nonanoate, methyl decanoate, methyl 3-octenoate, methyl 3-decenoate, methyl nonadecanoate, methyl eicosanoate, dimethyl butane dioate, dimethyl pentane dioate, dimethyl hexane dioate, dimethyl heptanedioate, dimethyl octane dioate, dimethyl nonane dioate, dimethyl decane dioate, dimethyl undecane dioate, dimethyl 2-butene dioate, dimethyl 2,5-heptadiene dioate
aldehydes−ketals	octanal, nonanal, 1,1-dimethoxy *n*-octane, 1,1-dimethoxy *n*-nonane, 1,1-dimethoxy *n*-decane, 1,1-dimethoxy n-dodecane, methyl suberate semialdehyde, methyl azelate semialdehyde, methyl 4-oxo-nonanoate
fatty acid derivatives	epoxy methyl oleate, 9,10-dihydroxy methyl oleate, 9,10-dimethoxy methyl oleate

[a] Compounds existing in non-aged material are not mentioned).

Table 3. Comparison of Ratios $C_9/C_{16:0}$ and $C_{18:1}/C_{18:0}$[a] During Thermal Oxidation of Thin Films on Glass or Quartz Substrates

	2 days		64 days	
sample	$C_9/C_{16:0}$	$C_{18:1}/C_{18:0}$	$C_9/C_{16:0}$	$C_{18:1}/C_{18:0}$
basic copper carbonate	0.3	3.1	1.0	2.3
copper acetate	0.9	2.8	1.6	2.3
copper abietate	0.3	4.6	1.4	1.2
no pigment	traces	4.5	0.9	2.2

[a] C_9, dimethyl azelate; $C_{16:0}$, methyl palmitate, $C_{18:1}$, methyl oleate; $C_{18:0}$, methyl stearate.

abietate exhibited higher degrees of fragmentation. The former was also found significantly low in oleate. These findings confirm the picture we already have outlined on the basis of spectroscopic monitoring, characterizing copper acetate and copper abietate as strongly catalyzing the oxidation processes in a linseed oil thin film.

Thick-Film Studies. Investigation of thin oil films prepared as mentioned comprises a model situation convenient for spectroscopic observation and minimizing experimental uncertainties. Thin films resemble reasonably well the upper layer of real paintings, but they lack the entire complexity encountered in these media. A first comparison of the results obtained in thin films with results based on GC analysis in thicker than 10 μm films is reported in the following. High thicknesses severely induce certain obstacles within the given scopes of this study. Light is severely prevented from penetrating deeper than 0.5−1 μm in these films. As a consequence, UV absorption monitoring of thick films was not possible because of very high absorbances. Natural aging of such films (longer than 260 days) generally resulted in less perfectly dried layers of linseed oil and, in the case of copper abietate and acetate, led to the formation of a dark surface layer. The results of product analysis with gas chromatography, listed in Table 4, confirm the basic trends also observed in thin films.

Photochemical Aging of Linseed Oil Films. UV irradiation of previously thermally aged films (64 days at room temperature in the dark) resulted in significantly less yellowing as evidenced by UV absorption spectroscopy (Figure 6). The absorption spectrum continued to change after the irradiated films were stored in the dark at room temperature, appearing more uniform, while the part of the band between 250 and 350 nm decreased further. On the other hand, no significant changes in the IR absorbances of assigned peaks after UV irradiation of thermally aged films could

Table 4. Comparison of Ratios $C_9/C_{16:0}$ and $C_{18:1}/C_{18:0}$[a] During Thermal and Photo oxidation of Thick Films on Canvas

	42 days in the dark		42 days in the dark + UV light	
sample	$C_9/C_{16:0}$	$C_{18:1}/C_{18:0}$	$C_9/C_{16:0}$	$C_{18:1}/C_{18:0}$
basic copper carbonate	0.2	4.8	0.9	2.2
copper acetate	1.1	1.9	1.3	1.7
copper abietate	1.0	3.0	1.1	2.9
no pigment	traces	5.0	0.6	2.3

[a] C_9, dimethyl azelate; $C_{16:0}$, methyl palmitate; $C_{18:1}$, methyl oleate; $C_{18:0}$, methyl stearate.

be detected.

Gas chromatographic analysis of UV-irradiated samples showed an increase of azelate and a simultaneous decrease of oleate as compared to the nonirradiated ones. This finding reveals that UV bleaching is accompanied by further degradation (increase in chain scission and decrease of conjugation products). Palmitate ($C_{16:0}$) and stearate ($C_{18:0}$) peaks were used as internal reference testing the accuracy of the method, because the corresponding fatty acid chains are not significantly oxidized within the time frame of our experiments. Finally, no significant changes of assigned IR peaks in all tested films after UV irradiation could be detected.

Photooxidation of coatings of higher thickness on prepared canvases was not expected to be uniform because of the mentioned restrictions that result from the nature of the medium. Gas chromatographic analysis of photochemically bleached samples showed a slight increase of ratio $C_9/C_{16:0}$ and a decrease of $C_{18:1}/C_{18:0}$, indicating only minor further degradation of the medium.

Discussion

The methodology presented in this work was used to monitor the overall oxidation process of oil films in the presence of copper(II) salts and to investigate the influence of the film composition and of the various process parameters. The thin oil film technique allowed simultaneous in situ monitoring of the chemical changes within the linseed oil film by the use of UV and IR spectroscopy, whereas GC analysis of the products supported the spectroscopic data. A general mechanistic scheme (Scheme 1) is presented to illustrate the main points and facilitate further discussion.

The process of degradation of a linseed oil medium under oxidative conditions involves simultaneous polymerization and chain scission reactions. Transformation of cis bonds to trans in initially formed radicals (steps 1 and 2 in mechanistic scheme) is followed by immediate formation of peroxides (step 3).[13,15] It is generally accepted that unsaturated fatty acid carbon chains undergo rapid autoxidation. As direct reaction of oxygen with hydrocarbon chains is a spin-forbidden process and therefore unlikely to happen, the concept of an initiator producing a radical out of the pentadiene chain has been introduced.[15] Furthermore, the particular ease with which linseed oil chains participate in

(15) (a) Kochi, J. K. *J. Am. Chem. Soc.* **1962**, *84*, 3271−3276. (b) Richardson, W. H. *J. Am Chem. Soc.* **1966**, *88*, 975−979.
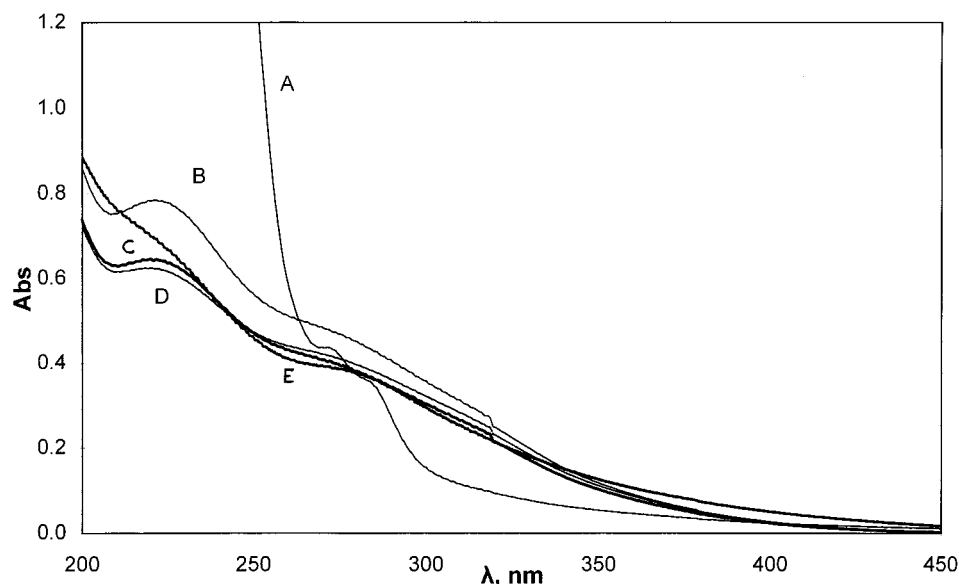
Figure 6. Effect of UV irradiation on linseed oil films containing basic copper carbonate as studied by UV absorption spectroscopy: **A**, 20 min in the dark; **B**, 8 months in the dark; **C**, 8 months in the dark + *hν* (2 min); **D**, 8 months in the dark + *hν* (6 min), and **E**, 2 days additional thermal aging.

oxidative processes has been attributed to the pentadiene-containing chain of linoleate which, in the presence of an initiator, forms the stabilized pentadienyl radical. Linolenate also behaves in a similar way. This radical, after rearrangement of the C=C bonds, with the action of oxygen produces the peroxy radical, and finally results in a conjugated carbonyl-containing chain. The redistribution of C=C double bonds in the fatty acid chain results in conjugation involving the newly formed carbonyls, yellowing being an end result.

In this study, the used spectroscopic techniques monitor critical steps of the mechanism. IR absorbance changes reflect the transformation in the cis C=C bonds to trans (stage II) and give the picture of a reaction starting with formation of the pentadiene radical **2** (stage I) and propagating through the trans conjugated diene peroxide (stage IV). Changes of UV absorbance reflect the formation and consequently, the thermal and/or photochemical removal of peroxides as shown in stages III, IV, and V. Gas chromatography results, on the other hand, give experimental evidence for the formation of low-molecular-weight products (stage VI). Finally, with UV and IR absorption spectroscopy, long-term formation of yellow products and of conjugated chains, respectively, are followed (stage VII). The observed changes during linseed oil oxidation are indicated in the general mechanistic scheme.

Previous studies focusing on the influence of metals in similar systems show copper acetate (verdigris) to accelerate the decomposition of peroxides,[7,15b] while in other studies, it has been found to photostabilize linseed oil.[7] In standard studies on polymer degradation, on the other hand, copper(II) salts have been proposed to participate in a redox cycle involving Cu(I), which is then reoxidized by oxygen to the bivalent species.[6]

The extent of oxidative processes can be measured by oxygen incorporation, while that of cross-linking, by hydrogen loss (decrease in IR absorbances corresponding to CH₂). Both processes are preceded by loss of cis unsaturation and peroxide formation. In our case, a copper(II) catalytic effect in the oxidative changes in all linseed oil films was observed. Furthermore, differentiation in reactivity among tested salts was detected, as copper acetate and abietate significantly increase the amount of peroxides. The same salts caused a significant increase oxygen incorporation (measured with carbonyl IR absorbances): Basic copper carbonate caused a moderate one, while the pigment-free film was almost unchanged. Gas chromatography product analysis also showed the same copper salts to significantly catalyze the formation of azelate and the simultaneous disappearance of oleate in the long run. On the other hand, the effect of copper pigments in weight loss (decrease of CH₂ IR absorbances) seems to proceed in the opposite way. Copper salts, therefore, especially the ones with the highest oxidizing capacity, appear to retard the cross-linking processes.

Copper(II) salts have been reported to participate in catalytic cycles through the unstable copper(I) state, occasionally involving complexation with oxygen and unsaturated substrates.[15] In the long run, this path results in oxidation products of unsaturated oil chains. Similar reactions of unsaturated short chain compounds have been reported to occur faster with copper(II) carboxylate salts.[15a] It is therefore reasonable to attribute the observed increased reactivity of copper acetate and copper abietate in a linseed oil medium to the fact that both these salts bear a carboxylate anion.

Yellowing is the major effect in UV absorbance spectroscopy in the long term. Generally, all copper-containing samples showed increased yellowing as compared to the ones containing no pigment. Films containing copper abietate proved to be the most intensely yellowed samples. The conjugated C=C bonds observed through IR spectroscopy, in the case of copper acetate, indicate carbonyl conjugation as a possible mode for yellowing.

Gas chromatographic results, showing oleate ratios low and fragmentation products of the medium increased, confirm the UV and IR spectroscopy observations concerning the copper acetate and abietate.

The picture is finally completed with the effect of UV irradiation on previously thermally aged oil films. Loss of yellowing, chain scission, and formation of low MW products with further decrease of oleate were mainly observed. A possible mechanism (see Scheme 1) involves photochemical cleavage of the carbonyl-containing chains resulting in reduction of yellowing, as a consequence of chain scission, conjugation, and consequent formation of small MW products. To account for the small changes in GC products in the case of copper acetate and abietate in thick films, we propose that dark surface layers of oxidized medium, formed during the thermal aging process, prevented further oxidation of inner layers. These dark layers were readily observed in thick films of linseed oil containing copper acetate and abietate. The pigment-free and copper carbonate-containing samples, on the other hand, not forming a similar dark surface layer during thermal aging, were more significantly changed with respect to the fatty acid ratios, showing values corresponding to the expected further degradation.

Conclusions

In situ spectroscopic investigation of the oxidation of linseed oil was possible by the use of thin films formed on suitable substrates. In the methodology used, UV data, reflecting the yellowing processes in the medium, are complementary with respect to chemical information, to the more specific IR spectroscopy, and to GC product analysis.

A rate increase in the oxidative degradation of films was confirmed in the case of copper acetate and copper abietate. The same salts showed decreased activity with respect to weight loss of the film. The colored products that mainly affect the appearance of linseed oil-based paintings bleach to a certain degree during photooxidation, a process accompanied by further degradation of the films, especially in the case of copper acetate.

The techniques used can lead to the elucidation of critical steps of the mechanism in order to define the deterioration routes under realistic conditions and diagnose the degradation degree of oil paintings with cleaning techniques. Real time, in situ monitoring during cleaning could be possibly developed in the future, based on the described methodology.

CM9806578