Artificial Aging and Deterioration of Oil-Painted Fabriano Paper and Cardboard Paper Supports

Osama M. Elfeky,[1] Mohammad L. Hassan[2]

[1]*Department of Restoration and Conservation, Faculty of Archaeology, Cairo University, Cairo, Egypt*
[2]*Cellulose and Paper Department, National Research Center, Dokki, Cairo 12622, Egypt*

Received 21 May 2007; accepted 12 November 2007
DOI 10.1002/app.28226
Published online 23 April 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Fabriano paper and cardboard are commonly used for oil paintings as paper supports. There are different practices for oil painting. Sometimes, painters paint directly on paper supports. They may also impregnate paper supports with linseed oil before painting to prevent the absorption of the binder from the oil-based paint by the paper, or they may apply a background (e.g., animal glue and calcium carbonate) on the paper supports and then paint their drawings. The effects of aging by heat or ultraviolet light on the mechanical properties (tensile strength, tensile elongation, and tearing resistance), optical properties (changes in color indices), and pH of Fabriano paper and cardboard painted with the aforementioned practices were studied. In addition, the thermal stability of paper painted with these practices was studied with thermogravimetric analysis. J Appl Polym Sci 109: 1594–1603, 2008

Key words: aging; fabriano paper; cardboard; mechanical properties; optical properties; thermogravimetric analysis (TGA)

INTRODUCTION

Many artists have used paper and cardboard as supports for oil painting since the 16th century. Fabriano paper is a handmade, acid-free paper made from pure cellulose that was invented in Fabriano, Italy. The Italian Fabriano mills began making paper in 1283, and the paper has been praised and used by writers and artists such as Albrecht Durer, Michelangelo, Giambattista Bodoni, Francisco Goya, and Picasso.[1,2] Cardboard is a semiflexible material, thick, somewhat dense, and often gray in color, that is formed of layers of paper laminated together, well pressed, and glued.[3,4] It is made of recycled paper, and consequently, it has a lower price than Fabriano paper. Well-made cardboard is considered a very proper support for painting.[5] It does not crack, does not work under the effects of dampness or dryness, and consequently does not warp. It can also be primed and protected from moisture by a surface treatment, and the back can be protected by a treatment with hot paraffin wax and resin preparations. Many artists, such as Walter Sickert (1860–1942), the German-born painter George Grosz (1893–1959), and Lautrec (1864–1901),[6] have painted on cardboard using the natural tone of the board as part of the painting.

Painters can draw their painting on paper supports directly. However, sometimes the surface of the paper or cardboard supports is protected by a ground, which consists of a filler and an adhesive, to absorb excess oil from the paint layer, or is impregnated with an oil layer to prevent the binder of the paint from being absorbed by the paper fibers. Many oil paintings on paper and cardboard supports in the collections of art museums have become damaged and have deteriorated with time. Therefore, studying the main properties (mechanical and optical), pH, and chemical compositions of paper supports before and after artificial aging is very useful for determining the changes that occur, the steps of deterioration and its mechanism, and the best methods for protection and restoration.

Dupont et al.[7] studied cellulose and lignocellulose degradation in aged paper during accelerated aging using capillary zone electrophoresis; several compounds could be detected as a result of the degradation of cellulose, holocellulose, and lignin. Seves et al.[8] studied the effect of thermally accelerated aging on the mechanical and color properties of model canvas paintings with the aim of developing a laboratory technique to simulate the natural aging of canvas paintings, adopting artificial aging methods in air (thermal oxidation) and in the absence of light. An analysis of volatile organic compounds (VOCs) emitted from a groundwood pulp book that was naturally and artificially aged showed the emission of 36 VOCs, of which furfural, 5-methyl furfural, vanillin, and guaiacol can be considered to be

Correspondence to: M. L. Hassan (mlhassan2004@yahoo.com).

Journal of Applied Polymer Science, Vol. 109, 1594–1603 (2008)

relevant carbohydrates and lignin degradation compounds.[9,10] Proniewicz et al.[11] studied Fourier transform infrared and Fourier transform Raman spectra of hydrothermally treated samples of paper made from bleached sulfite softwood pulp under extremely humid conditions (100% humidity and 100°C). The results showed the oxidation of paper along with new carbonyl bands and the disappearance of C=C bands.

In addition to studies on paper aging, there are many studies on the aging of paints used in artwork because drawings represent a valuable cultural heritage. For example, ultraviolet (UV) artificial aging of 10 mixtures of some organic pigments, mixed with linseed oil and spread on cotton canvas strips, was studied with attenuated total reflection/Fourier transform infrared.[12] In another study,[13] a comparison of the physicochemical properties of paintings, particularly those of their material components, before and after aging procedures revealed significant differences that could be used as possible decay markers. Decay markers have been found for aged models containing linseed oil, copper resinate, white lead, and white zinc. Capillary electrophoresis was applied to analyze the long-chain fatty acid composition of vegetable oils and the degradation products that formed upon aging when drying oils were used as binding media in paints from paintings of the 19th century.[14] The degradation of lipidic paint binders induced by irradiation with UV light (365 nm), exposure to urban air pollutants such as NO_x and SO_2, and combinations of various treatments was studied.[15] The results showed that UV irradiation and exposure to NO_x and SO_2 increased the polymerization and crosslinking of paint, thus facilitating the cleavage of fatty acid chains as a result of progressive oxidation up to the formation of oxalic acid. In samples of paintings by Cimabue, Raffaello, and Boucher, oxalic acid and oxidized carboxylic acids have been found, confirming the results obtained from paint specimens. The oxidative degradation of naturally aged oil-based paint films by differential scanning calorimetry was studied.[16] The results revealed that it was possible to distinguish between linseed, walnut, and poppy seed oils used in paintings with differential scanning calorimetry.

The aim of this work was to investigate the aging and deterioration of cardboard and Fabriano paper supports painted directly with linseed-oil-based TiO_2 paint, painted after their impregnation with a linseed oil layer, or painted after a treatment with a background of animal glue and calcium carbonate. The results may help painters and restorers to choose the best practice for restoring damaged oil paintings and also for copying historical oil paintings on recent supports of paper or cardboard.

EXPERIMENTAL

Materials

Fabriano paper and gray cardboard used in oil painting were purchased from the market and used as received; the basis weights of the Fabriano paper and gray cardboard were about 140 and 950 g/cm^2, respectively.

Commercial-grade linseed oil for painting was used for impregnation. Commercial-grade animal glue for painting was mixed with calcium carbonate to form a workable paste and was used as a ground before painting. The paint was a fine grade of currently used and commercially available linseed-oil-based TiO_2 paint.

Painting of the paper supports

Three methods were used for painting the Fabriano (F0) and gray cardboard (C0) paper supports. In the first one, the paper supports were directly painted with linseed-oil-based TiO_2 paint (F1 and C1 series). In the second method, the paper supports were impregnated with linseed oil, left to air-dry for 2 weeks in the ambient atmosphere (~25°C and 60% relative humidity), and then painted with the linseed-oil-based TiO_2 paint (F2 and C2 series). In the third method, a ground consisting of animal glue and $CaCO_3$ was applied first and left for 24 h to dry; then, the linseed-oil-based TiO_2 paint was applied (F3 and C3 series). Figure 1 shows a schematic presentation of the methods.

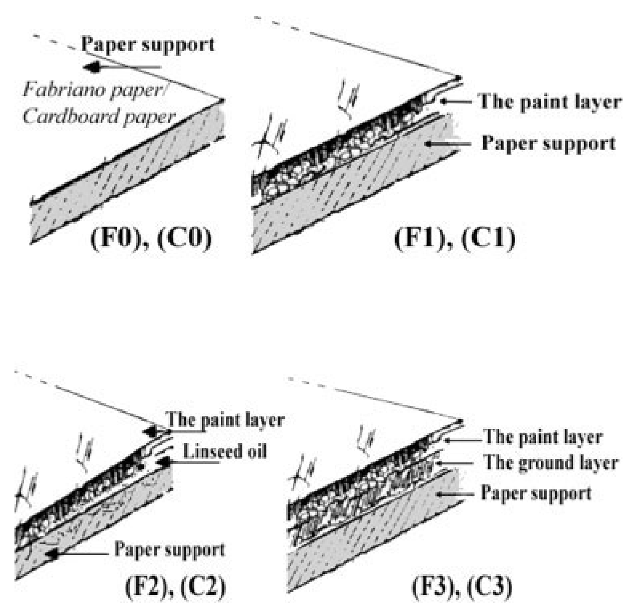

Figure 1 Schematic diagram of the methods of preparing the different Fabriano and gray cardboard samples.

Thermal and UV aging of the paper supports

For thermal aging, the different kinds of painted paper supports were aged at 100°C in an oven in which hot air was circulated by a fan for up to 150 h. For UV aging, a Fade-O-Meter instrument (Perkin-Elmer, Norwalk, CT) was used at room temperature for 50 h, and the temperature and humidity were set at 30°C and 50%, respectively. The wavelength range of emitted light was 350–430 nm. After the experiments, the paper supports were conditioned at 65% relative humidity and 25°C for 48 h before testing.

Testing of the paper supports

The tensile strength and tear resistance of the paper were measured with the known standard methods.[17] The changes in the color parameters L, a, and b were measured with a Hunterlab colorimeter; the L index of color represents black-to-white color, the a axis represent green-to-red color, and the b axis represents blue-to-yellow color. Five specimens were measured and the results were averaged. The pH of the paper was measured according to Tappi Standard T 252 om-85.

Thermogravimetric analysis (TGA)

The thermal stability of the different paper supports was examined with TGA. A PerkinElmer thermogravimetric analyzer was used. The heating rate was set at 10°C/min over a temperature range of 50–700°C. Measurements were carried out in a nitrogen atmosphere at a rate of flow of 50 cm^3/min.

RESULTS AND DISCUSSION

As mentioned previously, there are different practices for painting on paper supports: painting directly on paper, impregnating the paper with drying oil before painting, or applying a background to the paper and then painting on the background. The effect of artificial aging by heat or UV on the properties of blank paper supports and paper supports painted with the aforementioned practices was studied. The studied properties were the mechanical properties, optical properties, and acidity (pH) of the paper. Previous studies on the aging of paper sheets showed that 72 h of heating at 100°C is approximately equal to 25 years under ambient conditions.[18] The influence of one hour of the UV source in the Fade-O-Meter instrument was equivalent to the effect of 1 week of daytime light.

Effect of aging on the mechanical properties of the paper supports

Fabriano paper

Figures 2 and 3 show the effects of thermal and UV aging on the tensile strength, elongation at break, and tearing resistance of the Fabriano paper painted with the aforementioned practices. Because Fabriano paper is acid-free and made of pure cellulose, the thermal aging of blank samples (F0 series) had a slight effect on the tensile strength and tearing resistance. The tensile strength and tearing resistance decreased about 7 and 12%, respectively, after 150 h of heat treatment. There was a slight increase in the extension of the paper at break. Similar effects were found for UV aging but there was no significant effect on the elongation at break. The decreases in the tensile strength and tearing resistance of about 5 and 6%, respectively. The decrease in the mechanical properties of Fabriano paper due to aging could be attributed to the degradation of cellulose. A previous study using capillary zone electrophoresis showed that glucose and cellulose oligomers formed through the cleavage of the cellulose chain as a result of aging.[7]

When the paint was applied directly onto Fabriano paper (F1 series), the tensile strength of the paper was increased because of the drying and crosslink-

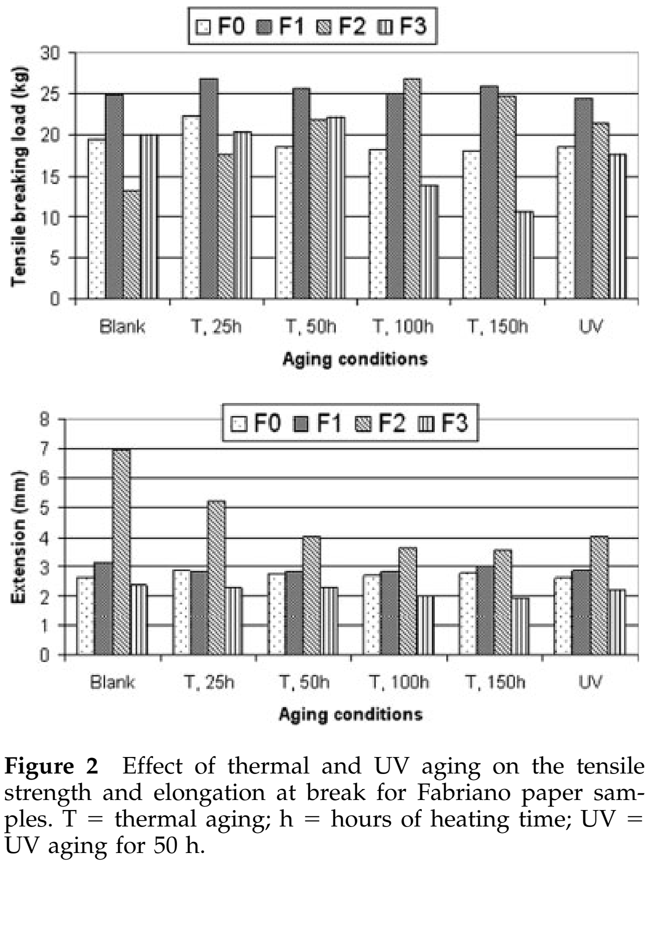

Figure 2 Effect of thermal and UV aging on the tensile strength and elongation at break for Fabriano paper samples. T = thermal aging; h = hours of heating time; UV = UV aging for 50 h.

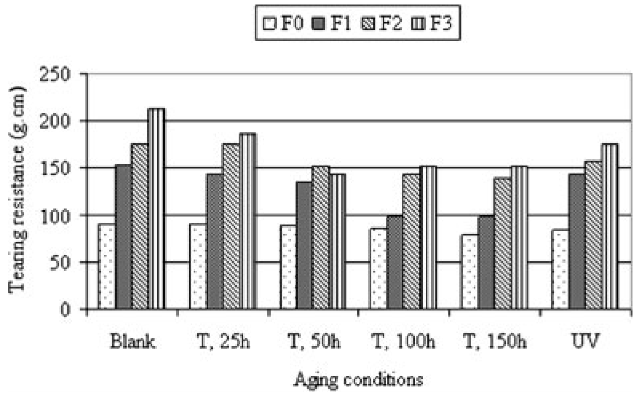

Figure 3 Effect of thermal and UV aging on the tearing resistance for Fabriano paper samples. T = thermal aging; h = hours of heating time; UV = UV aging for 50 h.

ing of linseed oil in the linseed-oil-based TiO_2 paint layer. TiO_2 is one of the most popular white pigments used in painting. When present in a polymer matrix, TiO_2 can act as a stabilizer that can terminate a free-radical reaction caused by UV rays.[19] Thermal aging of painted Fabriano paper resulted in a slight increase in the tensile strength after 25 h of heating followed by a decrease at longer aging periods, but the tensile strength was still higher than before aging. The slight increase in the tensile strength at the beginning of aging may be due to further crosslinking of the drying oil by the action of heat, whereas the decrease in the mechanical properties at longer heating times may have been due to aging of the paper support as mentioned previously for the aging of blank Fabriano paper (F0 series). A slight decrease in the elongation at break was observed, and the tearing resistance decreased by about 36% as a result of aging for 150 h. On the other hand, UV aging did not cause a significant change in the tensile strength or elongation at break, but the tearing resistance was reduced by about 6%. The lower negative effect of UV aging in comparison with thermal aging may be due to the presence of TiO_2 in the paint.

Linseed oil has been used in the creation and restoration of paintings.[20] It is a drying oil containing fatty acid fragments that are linear carbon chains with 18 carbon atoms. The drying of linseed oil to a solid occurs by oxidative crosslinking by the double bonds present along the carbon chain and finally leads to the formation of a solid film.[20] The drying reaction can be accelerated by heating of the oil in the presence of oxygen. Fabriano paper was impregnated with linseed oil and then oil-painted (F2 series). Thermal aging of the F2 series up to 100 h resulted in a remarkable increase in the tensile strength (∼103%) followed by a decrease on aging for a longer time and a remarkable decrease in the elongation at break (∼49%). The increase in the tensile strength and the decrease in the elongation could be attributed to the extensive crosslinking of linseed oil, whereas the decrease in the tensile strength after a longer period of thermal aging could be attributed to degradation of the paper support. Thermal aging for 150 h also resulted in a decrease in the tearing resistance of about 20%. On the other hand, UV aging resulted in an increase in the tensile strength, a decrease in the elongation at break, and a decrease in the tearing resistance of about 62, 42, and 11%, respectively.

In the case of the F3 series, an animal glue/calcium carbonate background was applied to the Fabriano paper before it was painted with TiO_2–linseed paint. Animal glue is made up of protein (polyamides), principally collagen, and many other components.[21] It was one of the strongest adhesives available before the development of synthetic polymers, and it still is commonly used for the conservation of furniture[22] and is used for the production of Japanese art materials.[23] A calcium carbonate filler is usually added to glue, or generally to polymers, for many reasons. The filler reduces the amount and cost of the polymer used in the formulation. It can also reduce the weight of the adhesive layer, reduce the polymer volume and thus restrict the possible shrinkage, increase the viscosity and resistance to flow of the polymer, and increase the strength and hardness of the set polymer.[24,25] In addition, calcium carbonate can act as a buffer and scavenger for the acidic compounds that are present in the environment or that form because of aging.[26] On the aging of the F3 series, there was an initial increase in the tensile strength up to 50 h of aging followed by a significant decrease with a longer period of thermal aging. The initial increase in the tensile strength could be attributed to the crosslinking of the linseed oil of the paint. The paper lost about 47% of its tensile strength after thermal aging for 150 h, whereas it lost only about 13% of its tensile strength upon UV aging. The paper had remarkably high tearing resistance before aging because of the tough and thick layer of the background (glue and calcium carbonate) and the paint (TiO_2–linseed oil) on the paper surface. Upon thermal and UV aging, the tearing resistance decreased by about 29 and 18%, respectively. This reflects the instability of the background layer applied with respect to heat and UV and its negative effect on the strength properties of paper upon aging. It is known that animal glue is partly hydrolyzed on heating in water and produces a soluble product.[21]

Gray cardboard

Figures 4 and 5 show the effects of heat and UV aging on the tensile strength, elongation at break,

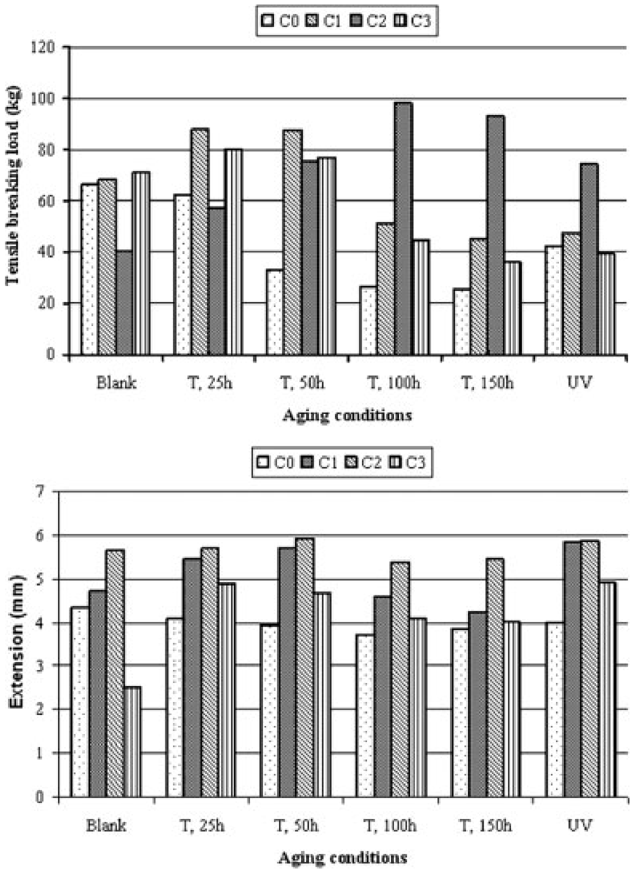

Figure 4 Effect of thermal and UV aging on the tensile strength and elongation at break for gray cardboard samples. T = thermal aging; h = hours of heating time; UV = UV aging for 50 h.

and tearing resistance of gray cardboard painted with the same methods mentioned previously for the Fabriano paper. As shown in the figures, the blank gray cardboard (C0 series) was much more sensitive to thermal and UV aging than the Fabriano paper. Blank gray cardboard lost about 61 and 25% of its tensile strength and tearing resistance, respectively, after 150 h of heating and 36 and 13% of its tensile strength and tearing resistance, respectively, after UV aging for 50 h. Decreases in the elongation at break were observed because of thermal and UV aging, and they were about 12 and 9%, respectively. The higher heat and UV liability of gray cardboard in comparison with the Fabriano paper could be attributed to the fact that the former is made of different waste papers including newsprint and magazine paper, which are made of mechanical pulp. The mechanical pulp contains lignin residues that can induce both thermal and UV degradation. In addition, hemicelluloses present in paper (made of either chemical or mechanical pulp) are more sensitive to heat aging. A previous study of the aging of lignocellulosic paper (paper made of mechanical pulp) showed that acetosyringone, 4-hydroxyacetophenone, 4-hydroxybenzaldehyde, vanillin, vanillic acid, furoic acid, and 4-hydroxybenzoic acid were formed as a result of the aging of the lignin fraction. Glucose and cellulose oligomers formed through cleavage of the cellulose chain, whereas hemicelluloses yielded mainly pentoses, among which arabinose and xylose were the most abundant.[7]

In the case of the C1 series, aging by heat resulted in initial increases in the tensile strength and elongation at break up to 50 h of heating, and then they remarkably decreased when the heating time further increased. There was a gradual decrease in the tearing resistance with the aging time increasing. The painted gray cardboard lost about 34 and 18% of its tensile strength and tearing resistance, respectively, after 150 h of heating. The loss in the strength properties was much more than what occurred in the case of Fabriano paper (series F1). UV aging caused decreases in the tensile strength, elongation at break, and tearing resistance of about 31, 7, and 14%, respectively.

In the case of the C2 series, thermal aging resulted in significant increases in the tensile strength, elongation at break, and tearing resistance of about 136, 5, and 11%, respectively. This increase was due to crosslinking of the impregnated linseed oil as well as that of the paint. However, the tensile strength and elongation at break tended to decrease with more than 100 and 50 h of aging, respectively. The decrease in the strength properties could be attributed to the decrease in the strength of the cardboard support as a result of thermal aging, as mentioned previously for the C0 series. UV aging for 50 h resulted in an increase in the tensile strength, elongation at break, and tearing resistance of about 83, 3.7, and 3%, respectively.

In the case of the C3 series, thermal aging caused a slight increase in the tensile strength at the start of aging followed by a rapid decrease; the loss was

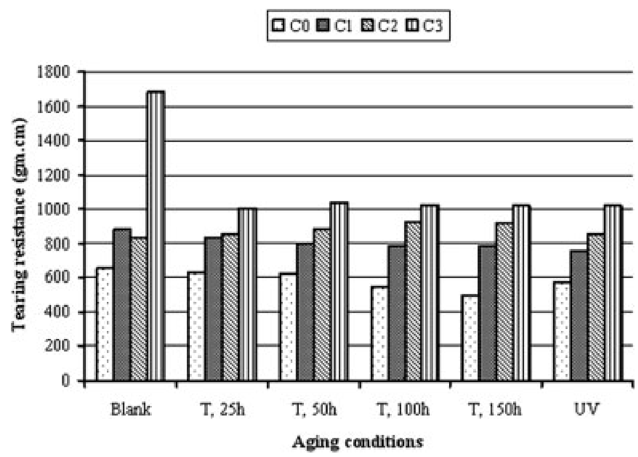

Figure 5 Effect of thermal and UV aging on the tearing resistance for gray cardboard samples. T = thermal aging; h = hours of heating time; UV = UV aging for 50 h.

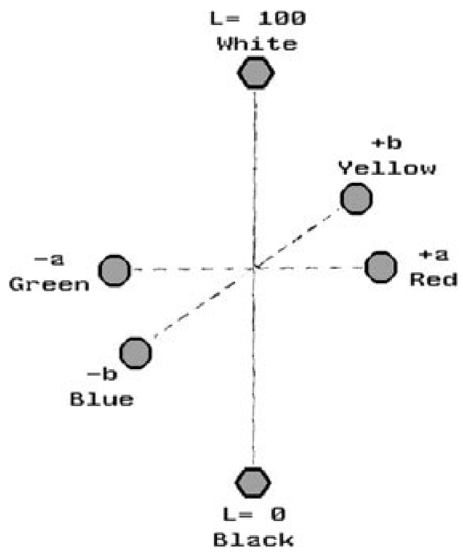

Figure 6 CIE color indices

aging resulted in darkening of color (decrease in the *L* index), a change toward the red hue (increase in the *a* index), and a very big change toward the yellow hue (increase in the *b* index). UV aging generally had an effect similar to that of thermal aging but to a much lesser extent.

In the case of thermal and UV aging of the F2 series, a slight decrease in the *L* index, that is, a color change toward darkness, occurred. The color index *a* moved toward the green hue, and the *b* index remarkably moved toward the yellow hue; that is, increases in the amounts of green- and yellow-absorbing chromophores occurred.

In the case of the F3 series, there were decreases in the *L* index, increases in the *a* index, and remarkable increases in the *b* index due to thermal aging, that is, changes to yellow and red hues. The same trend was found in the case of UV aging, except for the decrease in the *b* index.

about 50% after 150 h of heating. There was a drastic drop in the tearing resistance upon heating for 25 h, and then there was no remarkable change. UV aging had generally similar effects on the tensile strength and tearing resistance, that is, a decrease in the strength properties. The decrease in the strength properties could be attributed to the reasons discussed previously for the F3 series of Fabriano paper.

Effect of aging on the color parameters of the paper

The stability of the colors of artwork paintings is as important as the stability of their mechanical properties. Changes in the color of materials are related to changes in the chemical composition of the materials. In this work, the changes in the color indices due to thermal and UV aging for different Fabriano paper and gray cardboard series were studied; the Commission Internationale de l'Eclairage (CIE) color index system (*L*, *a*, and *b*) was used (Fig. 6).

Fabriano paper

Figure 7 shows the changes in the color indices of the different kinds of Fabriano paper supports due to aging. The color indices of the blank Fabriano paper (series F0) underwent negligible changes in the *L* index due to thermal and UV aging. However, there were noticeable changes in the *a* index and big changes in the *b* index toward red and blue hues, respectively, as a result of thermal and UV aging. These changes indicated that major increases in the amounts of red- and blue-absorbing chromophores occurred.

In the case of paper that was directly painted with the linseed-oil-based TiO_2 paint (F1 series), thermal

Gray cardboard

Figure 8 shows the changes in the color indices of the different kinds of gray cardboard supports due to aging. In the case of blank gray cardboard (the C0

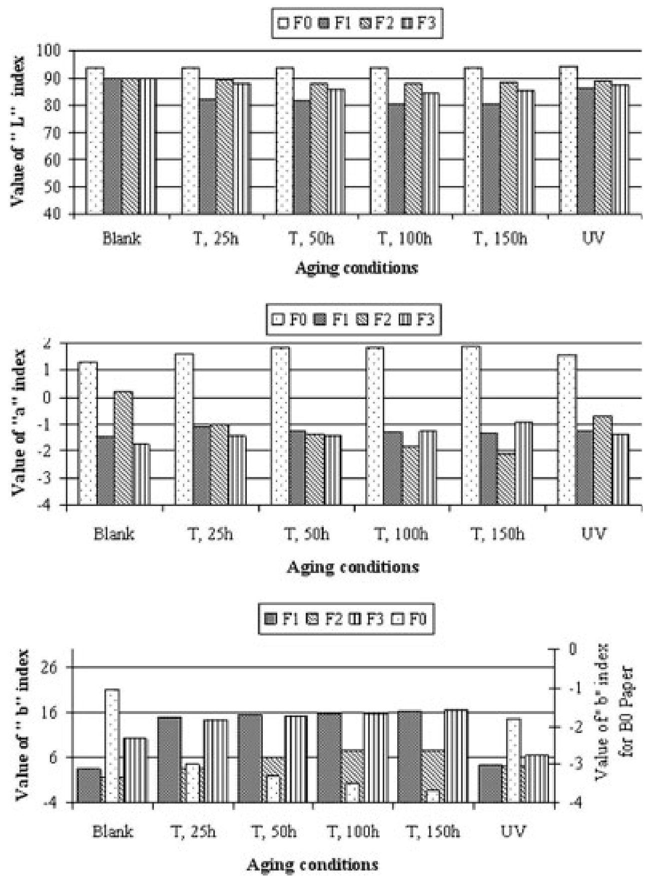

Figure 7 Effect of thermal and UV aging on color indices of Fabriano paper samples. T = thermal aging; h = hours of heating time; UV = UV aging for 50 h.

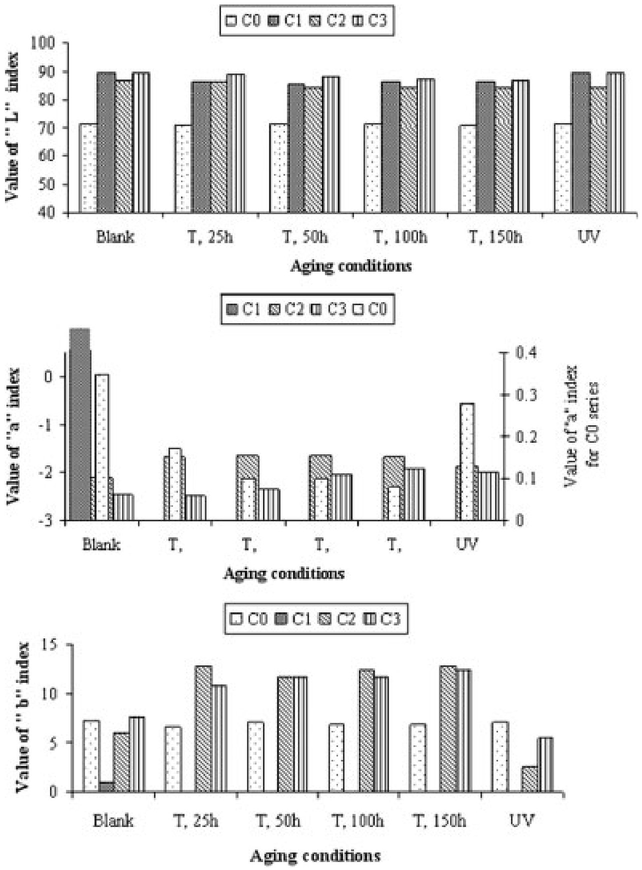

Figure 8 Effect of thermal and UV aging on color indices of gray cardboard samples. T = thermal aging; h = hours of heating time; UV = UV aging for 50 h.

series), there were negligible changes in the *L* and *b* indices, whereas there was a significant decrease in the *a* index toward the green hue as a result of the thermal and UV aging.

In the case of the C1 series, thermal aging resulted in a slight darkening of the color (decrease in the *L* index) and a significant shift toward the red and yellow hues (increase in the *a* and *b* indices). UV aging resulted in a change in the *b* index but, in contrast to the thermal aging, toward the blue hue. The effect of UV aging on the *L* and *a* indices was similar to that of thermal aging.

In the case of the C2 series, the changes in the *L*, *a*, and *b* indices indicated that thermal aging resulted in a slight darkening of color, a slight shift toward the red hue, and a significant shift to the yellow hue. UV aging resulted in a trend similar to the effect of thermal aging on the color indices, except for the shift of the *b* index to the blue hue.

In the case of the C3 series, the changes in the color indices indicated that heat aging resulted in a slight darkening and a slight shift toward the red and yellow hues. Also, UV aging resulted in a similar trend, except for the opposite effect on the *b* index because there was a shift to the blue hue and not to the yellow hue.

Usually, the overall change in color indices due to aging is expressed as ΔE according to the following formula:[27]

$$\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2} \tag{1}$$

where ΔL, Δa, and Δb are the differences between the values of the color indices before and after aging. Table I shows ΔE values for Fabriano and gray cardboard paper supports after 150 h of heating and 50 h of UV aging.

From the table, it is clear that blank Fabriano paper and blank gray cardboard are less liable to change with respect to color indices than painted ones because of thermal or UV aging. This means that the change in color is mainly due to the paint components, especially the linseed oil, and aging of the paper support itself does not have a significant effect on the overall color change. In addition, the application of a glue/$CaCO_3$ background or impregnation with linseed oil before painting could effectively reduce the change in color due to aging in comparison with direct painting.

Effect of aging on the acidity of the paper supports

An acidic condition is one of the reasons for paper deterioration. The effects of thermal and UV aging on the acidity of the Fabriano paper and gray cardboard supports were followed by the measurement of the pH of their extracts with the aim of understanding the mechanism of deterioration of these papers when used in oil painting.

Figures 9 and 10 show the changes in the pH due to heat and UV aging of the Fabriano paper and gray cardboard. Blank Fabriano paper (series F0) had a slightly alkaline pH that slightly decreased because of UV and thermal aging but was still above a neutral pH (Fig. 9). UV aging had a negligible effect on the pH of paper. Painting directly on the paper (F1 series), impregnating the paper with linseed oil before painting (series F1), or applying an animal glue/$CaCO_3$ background before painting (series F3) imparted an acidic pH to the paper. Thermal

TABLE I
ΔE Values of the Fabriano Paper and Gray Cardboard as a Result of Thermal and UV Aging

	Gray cardboard				Fabriano paper			
	C0	C1	C2	C3	F0	F1	F2	F3
ΔE for thermal aging	0.99	7.64	7.68	5.32	2.74	16.04	6.35	7.96
ΔE for UV aging	0.53	6.92	7.37	4.70	2.60	13.52	5.83	6.78

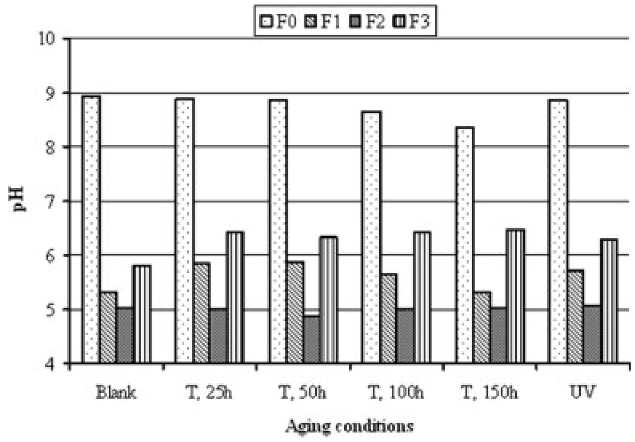

Figure 9 Effect of thermal and UV aging on pH of Fabriano paper samples. T = thermal aging; h = hours of heating time; UV = UV aging for 50 h.

aging of the F1 series resulted in a slight increase in the pH at the beginning followed by a decrease at extended heating times. UV aging resulted in a slight increase in the pH. In the case of the F2 series, thermal aging resulted in a decrease in the pH up to 50 h of heating, and then the pH tended to increase. In the case of the F3 series, there was an increase in the pH at the beginning of aging followed by a decrease at a longer heating time. These results indicate that the crosslinking of linseed oil by heating decreases the acidity of painted paper but at long aging times results in an increase in acidity, that is, a decrease in pH.

Figure 10 shows the effect of aging on gray cardboard samples. The blank gray cardboard had a slightly alkaline pH; aging by heat or UV caused a slight decrease in the pH, but it was still slightly above a neutral pH. In the case of the C1 series, the non-aged (blank) sample had a slightly acidic starting pH. Thermal and UV aging caused an increase in the pH. The effect of thermal aging was much more than that of UV aging. In the case of the C2 and C3 series, thermal and UV aging resulted in an increase in the pH. From these results, it is clear that the change in the pH of paper due to aging depends on the kind of paper used. Also, because only a slight change in the pH took place as a result of aging, deterioration of the strength properties probably did not occur mainly as a result of the pH change.

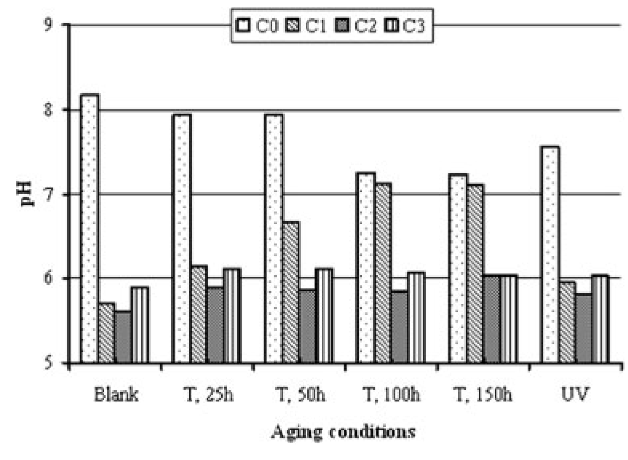

Figure 10 Effect of thermal and UV aging on pH of cardboard paper samples. T = thermal aging; h = hours of heating time; UV = UV aging for 50 h.

Thermal stability of the painted Fabriano and cardboard paper supports

The thermal stability of the Fabriano and cardboard paper supports painted with the aforementioned techniques was investigated with TGA. Figures 11 and 12 show TGA curves and differential thermogravimetry (DTG) curves of the different paper supports, and the data of these curves are summarized in Table II. As shown in the figures, the degradation of the different paper support samples involved two main degradation stages.

In the case of the Fabriano paper samples, the onset degradation temperatures of the blank and

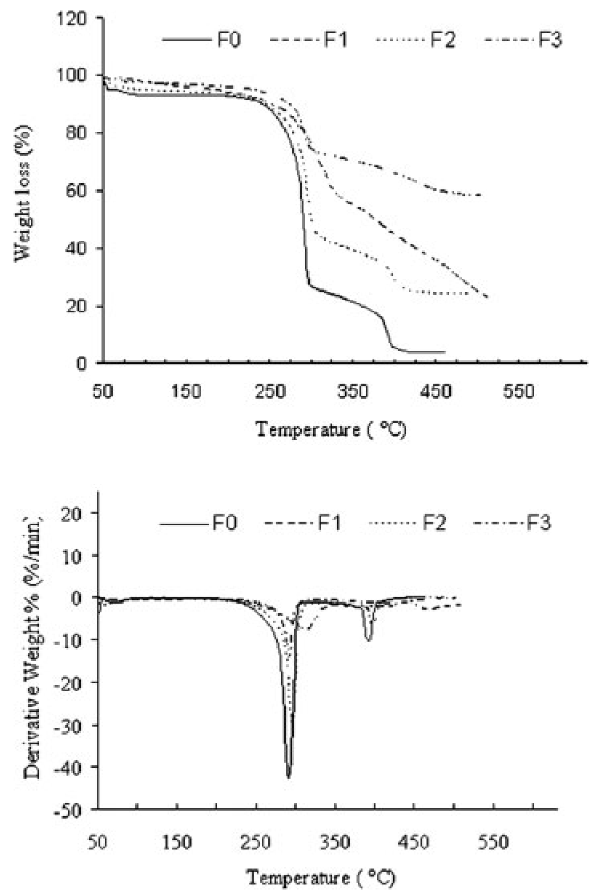

Figure 11 TGA and DTG curves of Fabriano paper samples.

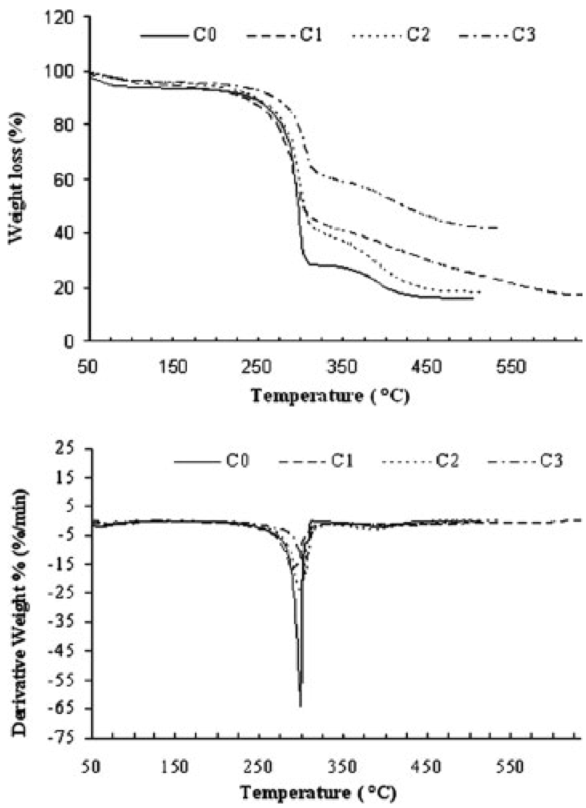

Figure 12 TGA and DTG curves of gray cardboard samples.

painted samples were close to each other, except for the F1 sample, which showed a lower onset degradation temperature than the F2 and F3 samples. This means that impregnating the paper with linseed oil or applying a background increases the thermal stability in comparison with painting directly on paper. A slower rate of thermal degradation was observed for the F1 sample as it was clear from the higher ash formation temperature. The order of the thermal stability of the painted Fabriano samples was F2 > F3 > F1.

In the case of cardboard paper supports, the blank sample (C0) showed higher thermal stability than the sample painted directly (C1) and the sample impregnated with linseed oil and then painted (C2) because the first had a higher onset weight-loss temperature. The cardboard sample to which an animal glue/$CaCO_3$ background was applied before painting (C3) had a higher onset weight-loss temperature than the blank cardboard. The order of the thermal stability of the painted cardboard samples was C3 > C2 > C1. Although the C1 sample had the lowest onset weight-loss temperature, it also had the lowest rate of degradation, as shown by the ash formation temperature. The second stage of degradation occurred at a constant rate, as could be concluded from the absence of a maximum weight-loss temperature for this stage in the DTG curve.

CONCLUSIONS

The impregnation of Fabriano paper and gray cardboard with linseed oil before oil painting is the best practice for protecting the painted paper against a loss of strength properties upon aging, whereas using an animal glue/$CaCO_3$ background before painting the paper is the practice least resistant to aging.

Thermal aging has a more detrimental effect that UV aging. This could be due to the use of TiO_2 in the paint formulation.

The change in color of the painted paper support is mainly due to the paint components, and aging of the paper support itself does not have a significant effect on the overall color change.

Because only a slight change in the pH takes place as a result of aging and the aging of painted paper supports results in an increase in the pH, the deterioration of the strength properties does not occur mainly as a result of a pH change toward an acidic condition.

The impregnation of paper supports with linseed oil or the application of an animal glue/$CaCO_3$ background increases the onset degradation temperature during the thermogravimetric analysis tests in comparison with painting directly on paper.

TABLE II
TGA Data for the Different Paper Supports

	Onset weight-loss temperature (°C) of the first stage	Maximum weight-loss temperature of the first stage[a]	Onset weight-loss temperature (°C) of the second stage	Maximum weight-loss temperature of the second stage[a]	Ash formation temperature (°C)
C0	213	299	312	393	490
C1	195	288	310	—	609
C2	211	299	307	390	488
C3	228	304	311	416	510
F0	228	290	300	393	425
F1	216	313	330	382	550
F2	230	296	303	395	439
F3	227	292	298	417	486

[a] Obtained from the DTG curves.

References

1. Smith, R. The Artist's Handbook; Dorling Kindersley: London, 1993.
2. Lunning, E.; Perkinson, R. The Print Council of America's Paper Sample Book: A Practical Guide to the Description of Paper; Print Council of America: Cambridge, MA, 1996.
3. Byrne, A. Conservation Paintings: Basic Technical Information for Contemporary Artists; Craftsman House G+B Arts International: Sydney, 1995.
4. Doerner, M. In The Materials of the Artist and Their Use in Painting with Notes on the Techniques of Old Masters; George, G., Ed.; Harrap: London, 1949.
5. Hiler, H. Notes on the Technique of Painting; Faber & Faber: London, 1934.
6. Smith, S.; Holt, F. T. The Artist's Manual: Equipment, Materials, Techniques; QUD: London, 1987.
7. Dupont, A.-L.; Egasse, C.; Morin, A.; Vasseur, F. Carbohydr Polym 2007, 68, 1.
8. Seves, A. M.; Sora, S.; Scicolone, G.; Testa, G.; Bonfatti, A. M.; Rossi, E.; Seves, A. J Cult Heritage 2000, 3, 315.
9. Lattuati-Derieux, A.; Bonnassies-Termes, S.; Lavédrine, B. J Cult Heritage 2006, 7, 123.
10. Lattuati-Derieux, A.; Bonnassies-Termes, S.; Lavédrine, B. J Chromatogr A 2004, 1026, 9.
11. Proniewicz, L. M.; Paluszkiewicz, C.; Ska, A. W.-B.; Ski, A. B.; Dutka, D. J Mol Struct 2002, 614, 345.
12. Marengo, E.; Liparota, M. C.; Robotti, E.; Bobba, M. Vibr Spectrosc 2006, 40, 225.
13. Arbizzani, R.; Casellato, U.; Fiorin, E.; Nodari, L.; Russo, U.; Vigato, P. A. J Cult Heritage 2004, 5, 167.
14. Surowiec, I.; Kaml, I.; Kenndler, E. J Chromatogr A 2004, 1024, 245.
15. Colombini, M. P.; Modugno, F.; Fuoco, R.; Tognazzi, A. Microchem J 2002, 73, 175.
16. Odlyha, M. Thermochim Acta 1988, 134, 85.
17. Casey, J. Pulp and Paper: Chemistry and Chemical Technology; Wiley-Interscience: New York, 1980; Vol. 3.
18. Williams, J. C. Restaurator 1979, 3, 81.
19. Mills, J. S.; White, R. The Organic Chemistry of Museum Objects; Butterworths: London, 1987.
20. Horie, C. V. Materials for Conservation; Butterworths: London, 1990.
21. Ward, A. G.; Courts, A. The Science and Technology of Gelatin, 2nd ed.; Academic: London, 1977.
22. Reventlow, V. In Restoration and Assembly of the Central Shrine of a Late Fifteenth Century Berman Altar from Cologne; Brommelle, N. S.; Moncrieff, A.; Smith, P. Eds.; Conservation of wood in painting and the decorative arts: Preprints of the contribution to the Oxford Congress, 17–23 September, 1978; p 99–102.
23. Winter, J. Natural Adhesives in East Asian Paintings. In preprints: Adhesives and Consolidants; Brommelle, N. S.; Moncrieff, A.; Smith, P. Eds.; Contributions to the IIC Paris Congress. London: International Institute for Conservation; 1984; p 117.
24. Katz, H. S.; Milewski, J. V. Handbook of Fillers and Reinforcements for Plastics; Katz, H. S.; Milewski, J. V., Eds.; Van Nostrand Reinhold: New York, 1978.
25. Amorsos, G. G.; Fassina, V. Stone Decay and Conservation; Elsevier: London, 1983.
26. Andrady, A. L.; Parthasarathy, V. R.; Song, Y. Tappi J 1991, 185.
27. George, W. Handbook of Material Weathering, 2nd ed.; Chem Tec: Ontario, Canada, 1995; Vol. 74.