Investigating the effect of oil mediums on the supports of the worksof art on paper

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Abstract

Oil paintings, oil sketches and studies on paper supports, as well as black and white and coloured prints, printed books, etc. present evidence of damage that has been associated with the presence of the oil medium in the paint or the ink used. The most common problems are absorption and diffusion of the oil medium by the paper support, related with discoloration, loss of mechanical strength, fragility and embrittlement of the support. However, research of the system oil-paper proved to be a complex matter.

Aim of research is the investigation of the effect of the oil medium on the paper support, as well as of the parameters that trigger and/or aggravate the occurence of the phenomena of damage. Research on original artworks and artificially aged mock ups, involving colorimetry using CIELab* colour space, measurements of light levels transmittance, tear resistance testing and analytical techniques using Head Space Solid Phase Micro Extraction combined with GC-MS, provide indications on the optical, mechanical and chemical changes caused by the absorption of the oil binder by the paper supports upon ageing.

Research was carried out through a project entitled "Oil paintings on paper support: Documentation of the state of preservation using multispectral imaging and chemical analysis. Determination of evaluation criteria - conservation treatment proposals", organised and conducted by the Laboratory of Physical Chemical Methods for Diagnosis – Documentation of the Department of Conservation of Antiquities and Works of Art in the Technological Educational Institution of Athens, with scientific responsible Dr. Athena Alexopoulou.

Fig. 1 Atlas of damage

Experimental

Three types of paper were investigated: a) cotton pHoton™ high purity paper by the Munktel paper Mill, 80gsm , b) Canson® Montval® watercolour paper, 185gsm and c) Kraft paper, 135 gsm. These papers were chosen because they had fibre content and characteristics similar to some of the works of art from the National Gallery in Athens being investigated in this project. Half the mock ups were impregnated with cold pressed linseed oil (Windsor & Newton, London). Strips were suspended on cotton threads in headspace vials above 5ml of 15% sodium chloride for analysis solution and aged at 90oC at 78% RH for 1, 4, 7, 14, 21 and 28 days.

The effect of oil application on the transparency of the paper was studied with the measurement of the intensity of the light transmitted by the plain and oiled mock ups at every stage of ageing with a digital lightmeter. The change of colour was measured using the CIE Lab* colour space, following the TAPPI standard T524om-94. The L*a*b* measurements were performed with a Lovibond Reflectance tintometer.

The degradation of cellulose caused by the presence of linseed oil on paper was investigated with the analysis of the volatile organic compounds (VOC) emitted from paper samples, with and without oil application, in the various stages of a close environment artificial ageing program, as well as areas of damage on original works of art. The VOCs were trapped with a SPME needle and analysed with GC-MS. The VOCs emitted from areas of damage on original artworks were absorbed with a SPME needle and analysed with GC-MS.

The changes in the mechanical properties of the oiled paper supports were examined with tear resistance measurments using an Elmendorf-type apparatus (ISO 1974, 1990).

Chemical Cahnges

Fig. 2 **Cotton mock ups.** Left: Non oiled and oiled mock ups before ageing. Right: From the tope to the bottom, the mock ups at 1, 4, 7, 14, 21 and 28 days of ageing.

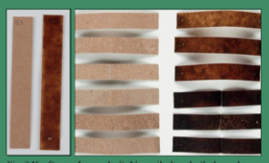
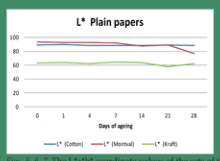


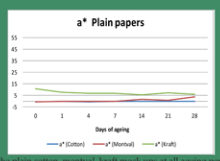
Fig. 3 **Kraft mock ups.** Left: Non oiled and oiled mock ups before ageing. Right: From the tope to the bottom, the mock ups at 1, 4, 7, 14, 21 and 28 days of ageing.

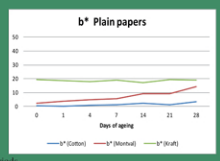
Fig. 4 **Montval mock ups.** Left: Non oiled and oiled mock ups before ageing. Right: From the tope to the bottom, the mock ups at 1, 4, 7, 14, 21 and 28 days of ageing.

It is likely that linseed oil application is principally responsible for the colour changes during ageing, though oxidation of the cellulose in the paper may also contribute to the colour change, especially if the oil is enhancing the rate of oxidation of the paper, as indicated in the VOC emission studies. This is more evident in the white mock ups of cotton and watercolour paper that present a similar pattern of variations of the L*a*b* coordinates values upon ageing. However, results indicate that fibre and paper pulp content, the colour and the weight of the paper influence these values.

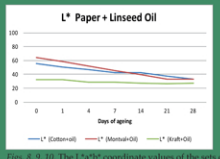
In all three paper types, oil application results in the significant reduction of brightness, and analogous decrease of yellow colour upon ageing. For the white colour papers the increase of the red colour, and the fluctuation pattern within that, could be indicative of the chemical changes. Also differences in colour through each mock up are strongly associated with the oil concentration on the paper locally.

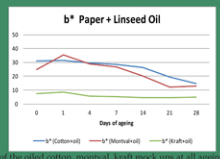


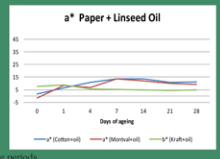




Figs. 5, 6, 7. The L*a*b* coordinate values of the sets of the plain cotton, montval, kraft mock ups at all ageing periods.







Figs. 8, 9, 10. The L*a*b* coordinate values of the sets of the oiled cotton, montval, kraft mock ups at all ageing periods.

Transparency

The plain paper mock ups of the three paper types present completely different behaviour, regarding the changes of the intensity of light passing through the mock ups upon ageing. This can be due to the different fibre and pulp content and distribution, but also to the changes that take place on the paper upon the progress of ageing. The pure cotton paper mock ups showed a stable behaviour with a minor fall, while the watercolour paper "Montval" ones showed an intense reduction after the 14th day of ageing (when the phenomena of the discoloration occured) and the kraft ones a limited reduction in an uneven pattern. The changes in the transparency can be assosiated with the morphological changes recorded to the SEM Images of the plain mock ups upon ageing. The fibre net of the mock ups becomes more compressed and more dense upon ageing, especially that of the montval paper. This fact influences the trasnmitance of the light through the mock ups and consequently their opacity.

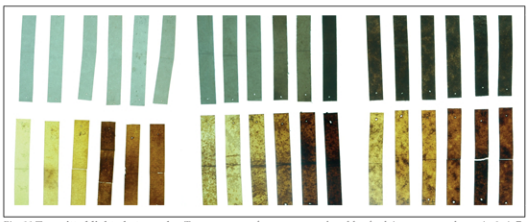


Fig. 11 **Trasmitted light photography.** Top row: sets of cotton, motval and kraft plain paper mock ups in 1, 4, 7, 14, 21and 28 days of ageing. Lower row: sets of oiled cotton, motval and kraft paper mock ups at all ageing periods.

On the other hand, the oiled mock ups of the three types of paper present similar behaviour. The results indicate that the application of oil increases the transparency to all paper types. Upon the prograss of ageing, the amount of light passing through the mock ups is reduced, turning gradually the mock ups more opaque. The measurement values of all three paper types are getting quite close, especially at the 14, 21 and 28 days of ageing. This could indicate that linseed oil inputs a common behaviour in the three types of paper as far as the intensity of light passing through the mock ups upon ageing is concerned.

The refractive index value of a solid film of linseed oil rises slightly with age, causing slightly more scattering perhaps which subsequently means that the paper would allow less light to pass through. In addition, the morphological changes upon ageing cause much greater changes to the system, increasing the light scattering , so the mock ups appear to be less transparent with age as the oil film shrinks within the system.

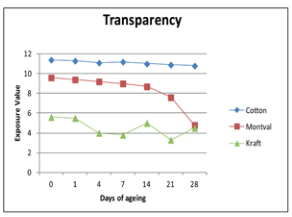


Fig. 12 Measurments of the light intensity passing through the plain cotton, montval and kraft paper at all ageing periods.

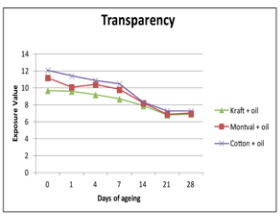


Fig. 13 Measurments of the light intensity passing through the oiled cotton, montval and kraft paper at all ageing periods.

Mechanical properties

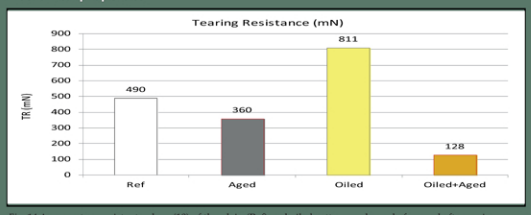


Fig. 14 Average tear resistant values (10) of the plain (Ref) and oiled cotton mock ups before and after ageing.

Tear resistance measurements in plain and oiled cotton paper mock ups before ageing procedure indicated that paper mock ups become stronger after the application and drying of the oil for 40 days. This is in accordance with the observation of the visual examination that the oiled mock ups appear stiffer and more resilient. It could be suggested that as the fibres bonded within the dried elastic polymer, a kind of elasticity and extra strength is provided to the support.

Tear resistant measurements in plain and oiled cotton paper mock ups after 28 days of ageing indicated that mechanical strength of the oiled mock ups reduces dramatically, while for the plain paper that is limited. Loss of mechanical strength was apparent during visual examination, since even careful handling of the mock ups could cause damage to the mock up.

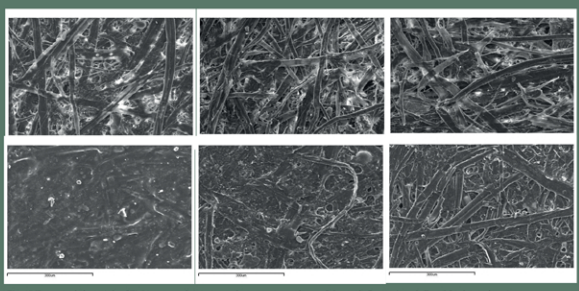


Fig. 15 Top row, left to right: SEM images, plain watercolour paper mock ups (Montval, Canson) at 0, 7 and 21 days of ageing. Lowere row, left to right, oiled watercolour paper mock ups at 0, 7 and 21 days of ageing.

Shrinkage and loss of elasticity of the oil film upon ageing in combination with the degradation of cellulose caused by the presence of the oil could justify the phenomena recorded for the oiled mock ups. It has been recorded that cracking or breaking of the support in the original works of art on paper occurs in the areas where oil absorption appears to be more intense. Thus, further investigation is required to investigate the parameter of the oil quantity absorbed by the paper in the changes of the mechanical changes properties of the support. In addition, VOC analysis indicated that oil accelerates more the degradation wood based papers, so the parameter of the fibre content should be investigated as well.

Chemical changes - VOC analysis

Fig. 16 Sewing Studio by Nikolaos Gyzis (recto), oil sketch on paper, 19th c., National Gallery - Alexander Soutzos Museum, Π3434.

Fig. 17 Sewing Studio, Π3434 (verso), the position of the SPME needle is noted with the white arrow, while the glass lid with a red circle

Figs. 18, 19. The red circle on the top detail marks the position of the glass lid on the *verso*

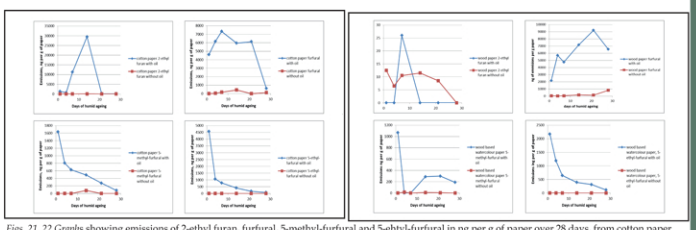
Six original works were selected for this experimental procedure, providing different case studies regarding phenomena assosiated with the absorption of the oil binder. It involved encasing both the artwork and the SPME needle in a glass set up to track the VOCs emitted. The absorbing tip of the SPME needle was placed over an area of damage on the verso of the work and then exposed for 24 hours. GC-MS analysis of the VOCs a large range of aromatic and straight chained aliphatic hydrocarbons, straight chained aldehydes, some volatile carboxylic acids and esters and the range of furan and furfural and furanone derivatives singled out for monitoring for the study of the mock-ups (compounds given only by paper and not by oil films).

VOC analysis of mock ups

The presence of oil in the cotton paper has greatly accelerated the emission of furfural, 2-ethyl furan, 5-methyl, 5- ethyl furfural and 5-pentylfuranone during ageing, while in the wood based papers has greatly accelerated the emission of furfural, 5-methy furfural, 5-ethyl furfural and 5-pentylfuranone.

It could be concluded that for both cotton paper and wood based papers at least dried linseed oil in the paper greatly accelerates and increases the emission of volatile cellulose degradation products. Therefore it is reasonable to assume, that since the chemistry of drying oils are similar to that of linseed oil, probably other drying oils increase the rate at which cellulose in paper degrades.

It can be speculated that furfural is a favoured product of cellullose degradation in the presence of oil. However, furfural emissions are greater from oiled wood based paper impregnated with linseed compated to those of the cotton paper impregnated with linseed oil. The increased levels of furfural are an indication that the lignin and/or hemicelluloses present in the wood based papers are accelerating the degradation even further in the presence of oil. However it seems that in the wood based paper the amount of furfural produced is increased whereas the levels of the other four compounds studied seems to decrease. Perhaps at least part of the decreased levels can be explained by the lower percentage of cellulose present in wood based papers and that the increased levels of furfural are an indication that the lignin and/or hemicelluloses present in the wood based papers are accelerating the degradation even further in the presence of oil.



Figs. 21, 22 Graphs showing emissions of 2-ethyl furan, furfural, 5-methyl-furfural and 5-ehtyl-furfural in ng per g of paper over 28 days, from cotton paper mock ups (left table) and wood based (Montval) paper mock ups (right table) with and without linseed oil application.

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