INVESTIGATING OIL BINDER ABSORPTION INTO PAPER SUPPORTS WITH ULTRAVIOLET-INDUCED VISIBLE FLUORESCENCE AND ULTRAVIOLET REFLECTANCE PHOTOGRAPHY

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Abstract

Certain types of damage and the deterioration of the paper supports have been associated with the absorption of the oil binders from the oil colours or traditional printing inks. Ultraviolet induced visible fluorescence colour photography and ultraviolet reflectance photography have for the first time been applied to artificially aged mock-ups to record the behaviour of the oiled support upon ageing under UV radiation. Application of these non-destructive examination techniques succeeded in mapping the areas of oil absorption and the variations of oil concentration on paper, but they also provided indications of the condition of the oiled areas of the paper support as changes in the appearance of the fluorescence upon ageing signifying the progress of deterioration. The oil impregnated mock-ups present intense yellowish fluorescence at the initial stages of ageing, that gradually turns darker as it quenches upon the progress of ageing. The impact of the fibre content, the painting technique and the presence of pigments, fillers and additives on the results is also discussed. It is then demonstrated that the results can be used for the assessment of the condition of works of art on paper executed in oil media.

1 Introduction

Oil binders have been widely used in works on paper supports, such as oil sketches, oil studies, drawings and paintings, as well as, black and white and coloured prints, images and texts in books printed with traditional oil based inks. These types of works present evidence of damage associated with the presence of the oil medium in the paints or the printing inks and in particular with the absorption and diffusion of the oil medium into the paper support. The most indicative phenomenon is the discoloration, which is occasionally accompanied with loss of mechanical strength, fragility and embrittlement of the support1-8.

Although the effect of the oil medium on paper is evident on many works, a limited number of investigations which assess the effects of drying oils on paper deterioration have, until recently, been published5, 9-11. Recently, experimental work on the investigation of the effect of the oil medium on the paper support, including: pH measurement, mechanical strength measurements and, significantly, the analysis of the VOCs emitted by artificially aged oil impregnated paper mock-ups and original works of art has indicated that drying oils on paper greatly accelerate the deterioration of the support upon ageing12.

Drying oils, such as linseed, walnut, poppy seed, sunflower and safflower oil were the most popular binders or vehicles used for the preparation or the production of the traditional oil colours in the past centuries. Drying oils, mainly linseed and nut oil, have also been used as binder or vehicle in inks used for traditional printing techniques13. The degree of absorption of the oil binder by paper depends on several interrelated parameters, which include:

- the fibre and filler composition of the paper,
- the painting techniques employed,
- the viscosity of the oil, which may depend on the degree of heat treatment,
- the oil absorption properties of the pigments used\textsuperscript{3,4},
- and the proportion of the oil binder to pigment in the ink or the paint.

Recent experimental work on artificially aged mock-ups showed that diverse quantities of oil on paper result in discoloration that varies in intensity upon ageing. However, experimental results indicated that the intensity of the color changes on the oiled support also depends on the conditions of ageing, so discoloration does not provide an indication of a certain stage of ageing in every case\textsuperscript{14}.

Non-destructive examination techniques have been used as a tool to provide information about the composition of the materials, techniques and condition of artworks on paper, including characterisation of the state of deterioration of the paper support\textsuperscript{15-26}. In this context, non-destructive examination methods, including ultraviolet induced visible fluorescence photography, ultraviolet reflectance photography, hyperspectral imaging and false colour infrared photography were used in an attempt to record the areas of oil absorption in original works of art from the collections of the National Gallery and Alexander Soutzos Museum in Athens (Greece) and the General State Archives of Greece\textsuperscript{1,27}. However, the application of these analytical techniques to artificially aged mock-ups in different states of ageing was regarded as necessary for providing reference data for comparison with the recorded outcomes from the original works of art.

The subject of this paper is the application of ultraviolet-induced visible fluorescence photography and ultraviolet reflectance photography in artificially aged mock-ups in an attempt to record for the first time the behaviour of oil impregnated paper in the ultraviolet region of the spectrum upon ageing, aiming at recording the stages of deterioration of the oiled support. Papers with different fibre types and filler content, chosen to be representative of the papers found in the art collection, were used to study the resulting phenomena. In addition, the application of the same methodology is used to record the oiled areas, to map the variations of concentration of the oil binder locally and the related damage found, in association with various oil colour techniques. Our aim is to demonstrate that the results of this study can be used as a tool for the condition assessment of historic art-works on paper created with oil media.

2 Experimental

Three types of paper were selected for the preparation of mock-ups and mock-up-paintings: a pure cotton paper and two types of chemical wood pulp papers. In particular, a) white “Cotton paper” made of 100% pure cotton linters, unbuffered, with no fillers, additives or sizing (Munktel CxD pHoton paper, Conservation by Design Limited, UK), b) white “Montval paper”, a wood pulp based artist’s watercolour paper, made of softwood fibres, acid-free\textsuperscript{1}, with limited lignin content\textsuperscript{2} with presence of fillers and additives\textsuperscript{3} (Montval®, Canson®, Art & Hobby, Greece), and c) light brown coloured “Kraft paper”, an un-bleached, chemical pulp, containing softwood and hardwood fibres, with high lignin content\textsuperscript{2}, with fillers and additives\textsuperscript{3}, containing limited metal contamination as indicated by elemental analysis\textsuperscript{4}. This selection represents basic types of paper supports commonly used by artists, but also involve the fibre contents and characteristics similar to the supports of the works of art from the National Gallery being investigated as part of our overall project\textsuperscript{12}.

Linseed oil was selected to impregnate the mock-ups, since it is the most common oil binder used in oil painting and traditional printing techniques, and it was identified as the binding media in most of the works of the National Gallery\textsuperscript{12}. Cold-pressed linseed oil (Windsor and Newton, UK) was selected for the preparation of the mock-ups. Paper strips, 1 x 7 cm, were impregnated with equal volumes of linseed oil, 0,06ml, which was enough to saturate evenly a paper mock-up overall, without leaving any excess. The oil was applied with a syringe following the same pattern on all mock-ups, in parallel lines from the top to the bottom. Then, the oiled mock-ups were left to air dry in dark conditions for 40 days. The plain and oil impregnated paper mock-ups were then submitted to artificial ageing in a closed environment, a methodology also used for other analytical methods used for the investigation of the effect of the oil on paper supports reported elsewhere\textsuperscript{12}. The strips were suspended on cotton threads in headspace vials (SU860101 Supelco, Magnetic Screw Cap for Headspace Vials, stainless steel screw cap (magnetic, open-top), thread 18, PTFE/silicone septum, thickness 1,3 mm, Sigma-Aldrich Ltd., Dorset, UK) above 5mL of 15% sodium chloride (for analysis, MERCK, KGaA, Germany) solution to maintain conditions of 78% RH and aged at 90 °C for 1, 4, 7, 14, 21 and 28 days\textsuperscript{12}.

The three mock-up paintings were prepared by the artist, Thrassos Avariotsiotis, in order to study oil absorption by the paper support in association with his technique of paint application. The artist made an effort to reproduce a central theme, a mature pomegranate, in all three paper supports, working with the same technique. The artist prepared each colour on his pallet and then applied it to the three works at the same time, to achieve consistency in the creation of the three mock-up paintings. The works were executed with oil colours from commercially available tubes (Rembrandt-Talens), which were diluted with white spirit when necessary. Along the left hand side of each work, the artist created four sets of colours, using blue ultramarine (Ultramarurence No 506, Rembrandt-Talens), red vermilion (Vermilion No 311, Rembrandt-Talens) and yellow (Jaunechromoperm No 254, Rembrandt-Talens), that were applied with four different painting techniques: directly from the tube, diluted with cold-pressed linseed oil, diluted with white spirit and impasto, which are typical ways of application in oil painting.

To record UV-induced visible fluorescence, the mock-ups were photographed with a digital camera NIKON D70s with AF micro NIKKOR 60mm lens, employing a Kodak Wratten no 2E filter, which filters out wave-
lengths below 420nm, combined with a B+W 487 filter to cut out most of the infrared leakage of the lamps. To record UV reflectance, the mock-ups were photographed with an analogue photographic SLR camera CANON T70 with a CANON macro lens 50mm, using an ILFORD delta 100, professional black & white film, employing a Kodak filter no 18A, 75x75, which filters out the visible light frequencies, so as to record the mock-ups in the ultraviolet region exclusively. The mock-ups were photographed in a copy stand, illuminated with two PHILIPS MLW160 black light lamps, 160 W, 220V, that give UV wavelengths of 365 and 366nm but also some blue light at 436, 487 and 484nm.

3 Results

3.1 Mock-ups

3.1.1 Observations in visible light (VIS)

Plain paper mock-ups of all three types present minor colour changes upon ageing with optical observation in visible light (Figure 1). It was only the Montval paper mock-ups that had discernible changes after the 14th day of ageing. Linseed oil caused colour change of the mock-ups, light yellow for the Cotton paper, cream for the Montval paper and darkening of the Kraft paper after 40 days of air drying (Figure 2). At the first stages of ageing, both oil impregnated Cotton and Montval mock-ups obtained a light orange color and gradually turned to an intense dark tone at the final stages of ageing (Figure 1). Starting at an already brown color, the oil impregnated Kraft mock-ups turned into almost black at the final stages of ageing (Figure 1).

3.1.2 Ultraviolet-induced visible fluorescence colour photography (UVIVF)

Cotton paper, before ageing, showed hardly any or no fluorescence, only displaying the reflection of the dark violet-blue colour from the visible light component of the UV illumination (Figure 2). Plain Cotton paper mock-ups showed insignificant, minor changes upon ageing, turning slightly brighter blue-white at the final stages, where fluorescence begins to occur (Figure 3).

Oil impregnated Cotton paper, after 40 days of air drying, showed a bright light yellow coloured fluorescence (Figure 2). The overall fluorescence of the oil impregnated Cotton mock-ups became slightly darker in colour at the initial states of ageing, gradually turning to deep yellow, dark orange and orange brown upon the progress of ageing, as the fluorescence is gradually quenched (Figure 3). The colour of the fluorescence does not appear uniform due to the uneven absorption of the linseed oil locally.

Montval paper before ageing showed an overall bluish fluorescence, brighter than the appearance of the plain Cotton paper (Figure 2), possibly due to the presence of additives or perhaps due to the different fibre source. The overall appearance of fluorescence of the plain Montval mock-ups became first brighter due to increased fluorescence on initial ageing and gradually turned to darker and greyer upon further ageing, as the fluorescence is quenched (Figure 3).

Oiled impregnated Montval paper, after 40 days of air drying, showed an overall whitish yellow fluorescence, much more intense than that of the plain Montval paper (Figure 2). The overall appearance of fluorescence of the oil impregnated Montval mock-ups became more intense yellow at the initial stages of ageing, changing further to a reddish brown colour.
upon the progress of ageing, due to quenching of the fluorescence (Figure 3).

Plain Kraft mock-ups showed a slight white bluish fluorescence before ageing. The overall fluorescence of the mock-ups presents limited changes upon ageing, showing increased fluorescence up to the 14th day, which then gets darker in tone, again as quenching occurs (Figure 2). UVIVF images recorded the irregularity of the mixed fibre content, as the various fibres present different behaviour, some of them fluoresce strongly while others absorb intensively. It could be only assumed that metal contamination may contribute to UV absorption, since absorption is moderate. However, no discrete changes in their behaviour were recorded upon ageing.

Oil impregnated Kraft mock-ups, after 40 days of air-drying, present an overall blue-white fluorescence, with a yellow hue (Figure 2). The mixed fibre content can still be recorded after the application of the oil medium as many of these fibres retain their characteristic behaviour throughout aging. Again the appearance of the overall fluorescence becomes darker upon ageing (Figure 3).

3.1.3 UV reflectance photography (UVR)

Plain Cotton mock-ups showed intense UV reflectance (no absorption), appearing white in the UVR images before ageing and at all ageing periods. In contrast, the oil impregnated Cotton mock-ups, before ageing and at the initial stages of ageing, present limited UV reflectance, as they appear in tones of grey, while at the final stages they get darker, indicating more UV absorption (Figure 4).

Plain Montval mock-ups present intense UV reflectance (with only minor absorption), appearing greyish white before ageing. They gradually darken upon ageing. In contrast, the oil impregnated Montval mock-ups before ageing present moderate to limited UV reflectance, and therefore intense absorption, as they appear in tones of grey, darker than that of the oil impregnated Cotton mock-ups. At the initial stages they present moderate UV absorption appearing grey, while at the final stages they get darker indicating more intense UV absorption (Figure 4).

Plain Kraft paper mock-ups present moderate UV reflectance (moderate absorption), appearing grey before ageing and at all ageing periods. They do not present significant or distinct changes, until the 21st day and then the 28th day which appear slightly darker. The oiled Kraft paper mock-ups present moderate to limited UV reflectance, thus intense absorption, and they appear in darker tones of grey than that of the plain Kraft ones (Figure 4).

The oil-impregnated mock-ups for all three types of paper, at the initial stages of ageing, present uneven UV absorption, appearing as grey colour variations in the UVR photographs of the mock-ups, indicating uneven oil absorption locally. This is less obvious in Kraft mock-ups that present limited UV reflectance and appear darker. However, the mock-ups at the final stages are very dark grey to black, so macroscopically, the local variations are not clearly discerned (Figure 4).

3.2 Mock-up paintings

3.2.1 Observations in visible light (VIS)

On the recto side of all three mock-up paintings, limited oil diffusion beyond the edges of the central theme can be hardly observed locally (Figures 5a, 5b, 5c). On the verso side of all three mock-up paintings, on the area of the support behind the central theme, there is overall absorption of the oil medium, but intensities differ among the three works. Oil absorption is smallest on the Montval paper (Figure 5b). It appears to be more intense on Cotton paper, a fact which can be attributed to the lesser thickness of the Cotton paper, as well as to the lack of sizing, fillers and additives (Figure 5a). Oil absorption is most intense on Kraft paper (Figure 5c). Uneven saturation of the oil binder coincides with the different painted areas of the paintings.

On the yellow, blue and red colour sets, oil binder diffusion is difficult to see in visible light on the recto side of Cotton (Figure 6a) and Montval (Figure 6b) papers. On the Kraft paper, diffusion is more evident when applied impasto, diluted with linseed oil or applied directly from the tube (Figure 6c). On the verso side, oil absorption is more evident with the colours applied impasto, diluted with linseed oil and directly from the tube; highest intensities on Kraft paper (Figure 6c), lowest on Cotton paper (Figure 6a).

3.2.2 Ultraviolet induced visible fluorescence colour photography (UVIVF)

On the recto side of the mock-up paintings on Montval and Cotton paper, light yellowish fluorescence was recorded beyond the edges of the central theme and in the blank areas of the support within that, indicating diffusion of the oil binder that can be hardly noticed in visual light examination (Figures 5a, 5b). On the verso side of these paintings, the whole area of the central theme presents an intense yet uneven yellowish white fluorescence. On the area of the sets of colours, bright fluorescence was recorded beyond the edges of paint applications facilitating the observation of oil diffusion. The differences are more evident on the verso side. The fluorescence is always lowest when paint was applied diluted with white spirit (Figures 5a, 5b, 6a, 6b).

On the mock-up painting on Kraft paper, any yellow fluorescence on the areas of the support where oil has been absorbed/diffused can be hardly seen. These areas appear darker than the plain (non-oiled) support, but without showing UV absorption (Figure 5c).
Variations in the intensity were recorded locally on the verso side of the central theme (Figure 5c). On the area of the sets of colours, dark areas beyond the borders of colour indicate oil diffusion (Figure 5c). Observation of verso sides indicates the darkest effect with paint applied impasto, less with those diluted with linseed oil and applied directly from the tube, least when paint was diluted with white spirit (Figure 6c).

3.2.3 UV reflectance photography, UVR

On the recto side of all three mock-up paintings, the background of the central theme presents moderate, the pomegranate minor UV reflectance, appearing dark grey to almost black (Figures 5a, 5b, 5c). Oil diffusion beyond the edges of the central theme can be discerned only at the mock-up paintings on the Cotton paper, as it appears grey indicating moderate UV reflectance (Figure 5c). On the verso side, the areas of the supports that respond to the central theme present moderate UV reflectance. They appear grey with tone variations that respond to the different areas of the painted theme and possibly to inherent oil concentration (Figure 5a, 5b, 5c).

On the areas of the sets of colours, grey areas, indicating UV absorption, can be observed beyond the borders of colours and point out oil diffusion. Observation of the verso sides helped to indicate that oil diffusion and absorption was always lowest when paint was applied diluted with white spirit.

4 Discussion and application of results to assessment of original art-works

Before ageing, the three types of paper present different behaviour under UV radiation, due to their different composition (see above). However, the UV-induced visible fluorescence of the plain paper mock-ups of all three types presents minor further changes during ageing; these could be associated with the chemical reactions that take place upon ageing30,31.

The fluorescence of the oil impregnated mock-ups is brighter and more yellow than the plain mock-ups, and can be attributed to the linseed oil, as this has also been recorded for mock-ups of dried films of cold-pressed linseed oil on glass slides (Figure 7), and also in relevant studies32-34. However, at the early stages of ageing the changes of hue of the fluorescence appear to be slightly different for each of the three paper types, thus depending on both oil and paper. Possibly, changes of transparency caused by the oil application on paper contribute to that.

Experimental work has indicated that colour change of the oiled paper support at all ageing stages is mainly due to the linseed oil, but also influenced by the oxidation of cellulose which is promoted by the presence...
of the oil binder. Infra-red absorption analysis has previously revealed that changes in UV absorption by cellulose after oxidation are associated with increased numbers of aldehyde and carboxylic acid groups.

The oil impregnated mock-ups present discrete changes of fluorescence upon the progress of ageing. Their appearance changes to warmer and then to darker tones, following the colour changes in the visible light. The overall intensity of the fluorescence seems to fall as it is quenched upon ageing (Figure 4). In contrast artificially aged dried oil films on glass slides (i.e. not on paper) retain their fluorescence at all ageing stages and the appearance of the fluorescence is not greatly influenced by the colour changes in the oil film recorded in the visible light (Figure 7).

We suggest that on historical, naturally aged artworks, the fluorescence of the oiled areas of the paper support would present the same changes as those recorded in the oil impregnated mock-ups during ageing. In that way, the appearance of the fluorescence could provide indications for the degree of degradation of the support in oiled areas.

The distinct yellow fluorescence that has been recorded on oiled areas of the support presenting discoloration of variant intensity on an oil sketch by G. Fanelis, indicates that this work is at the initial stages of ageing (Figure 8). In contrast, the recording of an orange brown colour and faint fluorescence on discolored oiled areas of paper supports on an engraving of a map, would indicate that the oil-support system has
deteriorated further by more extensive oxidation (Figure 9).

UVR recordings showed that the application of the oil medium on the paper mock-ups of the three types resulted in the reduction of UV reflectance, which is getting lower upon the progress of ageing. However, UVR recordings have not provided discrete indications for certain ageing stages.

UVIVF and UVR images of mock-up strips and paintings help in providing indications of the variations of oil concentration on the paper support locally, before ageing and at initial ageing stages. UVIVF photography shows that the hue of the yellow fluorescence becomes more intense as the oil concentration increases, whereas this causes UVR photography to show reduced UV reflectance. Both UVIVF and UVR allowed the diffusion and absorption to be seen more easily than with the visible light images.

This leaves us to assume that the variations in the behaviour of the oiled areas of the support, in both UVIVF and the UV reflectance, are due to the different degree of saturation of support by the oil binder locally. However, the distinction between the areas of different oil concentration is more discrete in UVR recordings. This can also be seen on original works of art, for example in the G. Fanellis sketch where the different degrees of saturation of the support are evident in the UVR image (Figure 8c). In a sketch by N. Gyssis, where areas of high oil absorption, under the area of the pink skirt, appear dark grey in the UVR image, they also strongly fluoresce yellow in the UVIVF image (Figure 10).

The outcome of the UVIVF and UVR recordings may also indicate the degree of oil absorption associated with different oil painting techniques. With the mock-up paintings oil diffusion and absorption appear to be moderate on the areas of colours applied directly from the tube and intense of those applied impasto and diluted with linseed, due to the excess of the oil binder locally. On the areas where colours have been diluted with white spirit, there seemed to be limited oil absorption of the oil binder by the paper support, probably because the oil is diluted and at a lower proportion.

5 Conclusions

UV-induced visible fluorescence and ultraviolet reflectance photography on artificially aged mock-ups have provided information regarding the behaviour of the oiled paper upon artificial ageing. The changes in the appearance of the oiled paper under UV radiation are influenced by: the fibre composition and the presence of additives. Further research is recommended for the quantification of the results.

However, the use of ultraviolet induced visible fluorescence photography and ultraviolet reflectance photography can be a useful, non-destructive tool for paper conservators examining original works of art on paper executed with oil colours and/or traditional oil based inks. Yellow fluorescence of discoloured areas can indicate oil binder absorption (if associated with media or appearing as local stains), while the colour of fluorescence of the oiled paper can provide indications on the state of deterioration of the support. The combination of UV-induced visible fluorescence and UVR photography can record the areas of oil absorption and diffusion, and map the areas of paper with diverse oil concentration. Thus, UV-induced visible fluorescence and UVR photography can provide indications for the degree of saturation and the state of deterioration of the oiled support, factors significant for condition assessment.

6 Acknowledgements

Research was carried out for 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”, which aimed at the investigation and physicochemical documentation of the problems occurring in oil paintings on paper supports” within the framework of the operational program “Archimedes III: Funding of Research Groups in TEI of Athens”, 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. We therefore thank the Archimedes Project for funding.
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