Investigating the conservation problems of oil paintings on paper supports

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ABSTRACT

The initial results of a research project on the investigation of problems presented by a collection of oil paintings on paper supports are presented. The project focuses on the effect of the oil medium on the deterioration of cellulose, on the materials and techniques used by the artists and on comprehension of the resulting problems.

Non destructive methodology was used to record the behaviour of the materials when examined in several regions of the electromagnetic spectrum which gives an indication of areas of damage. . Various analytical techniques were applied to investigate the painting materials and supports in original works of art. The increase in rate of the oxidation of cellulose in paper, when the paper is coated in oil, is investigated by analyzing volatile organic compounds emitted during ageing tests.

The assessment of the results obtained will act as a pilot for a more extensive program of research, the ultimate aim of which is the formulation of a recommended methodology as a tool for the evaluation of the condition of these types of works, as well as the determination of conservation and care parameters.

INTRODUCTION

Although the application of oil colour on paper appears to be an incompatible match, it has served several artists' intentions, from brief sketches to complete full scale compositions. Paper makes an accessible and convenient support, while oil paint provides versatile technical possibilities, rendering effects that range from a wash to an impasto.

Sketches in oil on paper barely appear in the early 17th century and they were originally created as preparatory studies or *modelli.* Oil studies were made when the artist was initially conceiving the idea for a composition and were used as a medium, through which he explored, tried out, worked through and perfected his ideas for a composition, before working the composition on the canvas. Oil studies tend to be quite small and rough, characterised by rapid execution, the spontaneity and free, swift brushwork. *Modelli* tend to be more 'finished', more polished, less 'sketchy' or rough they were often made to gain the approval of the patron (or potential patron) for the design of a larger commissioned painting [1]. They were also used as designs to be followed by for specialists in other media, such as printmaking or tapestry.

From the early 18th century onwards, it became very common for artists to use both paper and paper board[1] for oil sketching outdoors. A variety of types of papers and boards, with or without preparatory size, ground or priming (aqueous or non-aqueous e.g. animal glue or oil, often combined with pigments) have been used by artists for oil painting, sketching, etc.; these include hand made laid paper, wove, fair quality wrapping papers, laminated papers, millboards, paste boards and pasteless boards. Not all of these supports were designed for oil painting though paper supports for oil painting were commercially available by the 19th century. Paper was easily accessed, light weight and convenient painting support, while boards provided smooth surface, absorbency, thickness, strength and rigidity [2,3]. In the 19th and the 20th century, oil paintings on paper supports were used to execute full scale compositions, producing independent works. However, oils on paper were generally being treated as drawings [4].

A survey of the National Gallery - A. Soutzos Museum's collections showed that over than 400 works executed either exclusively in oil paint or mixed with other media on paper supports are included both in the

[1] According to Bower ,"sheets below 150gsm^{-2} in weight are paper, sheets over 250 gsm^{-2} are boards and sheets between 150 and 250gsm^{-2} may be either"[1] .

Main collection and the Koutlidis collection[2]. A significant number of 131 important Greek artists, including N. Gysis, N. Kantounis, K. Volanakis, N. Lytras, G. Iakovidis, A. Prosalentis, K.Roilos, I. Altamouras, T. Vryzakis, S.Papaloukas, T. Rallis, K. Parthenis, K. Maleas, G. Bouzianis and N. Xidias among them, as well as, 23 foreign artists representing the French, German, Belgian, Russian and Czech Schools of Art, have used the combination of oil colour on paper or paper board to create these works of art. The works date from the 17th - 20th c., and vary from sketches to complete works, presenting a range in technique, style and subject, from classic-academic to contemporary art. Works of this type can be also found in several other collections of public and private museums and institutions in Athens[3].

Common problems

Oil paintings on paper supports present particular problems which have been attributed to the oil medium in the paint. In cases where the composition does not extend over the whole surface of the paper support, the most common phenomenon is the appearance of brown discolouration around the brush strokes, caused by the diffusion and oxidation of the oil medium.

Plate 1. Oil painting on paper (20th c.), recto.

Plate 2. Verso side

In cases where the paint layer covers the whole surface of the paper support on the recto, discolouration is evident on the verso (see *Plates 1,2*). The intensity of discoloration varies, usually corresponding to areas of particular colour, possibly depending on the pigment used. The discoloured paper support, gradually looses its mechanical strength, becomes weak and brittle and breaks locally or in parts (see *Plates 5,6*). This condition is aggravated by the presence of wood in the fibre content of the support. According to Corrigan et al. [5], the condition is even worse if the work is varnished.

Plate 3. Detail

A typical problem of works executed on paper boards is the tendency of the support to delaminate (see *Plate 4*). Loss of cohesion between the paper layers has an effect on the stability and rigidity of the support resulting in planar distortions, intense creases and tears on the board that cause cracking, flaking or even loss of the paint layer (see *Plate3*).

Plate 4. Detail

Occasionally, the paper support was adhered to canvas to be stretched on

[2] Only 49 works have been executed on paper by 27 Greek artists.

[3] Such as the Bank of Greece, The National bank of Greece cultural foundation, B & M Theoharakis foundation for the fine arts and music, Museum of the city of Athens (Vourou-Eutaxia), etc.

wooden frame, stretcher or wooden panel or directly onto wooden and probably copper panels [4]. In those cases the resulting problems have been attributed to the stretching application as well as the materials involved. Finally, problems of discolouration and loss of mechanical strength of the paper support have been recorded in books and archival material with printed text, as well as on prints, which are attributed to the oil binders in the printing inks [6].

Despite the conservation and preservation issues raised by this phenomenon, there are only sporadic references to the problem in the literature and limited publication of research into this matter. The majority of the publications refer to the painting materials, the types of support and the preparation and application required for the various techniques used, the terminology and their distinction respectively [1,2,3,7]. There are a limited number of articles referring to the condition of and the problems presented in this type of works, or on the conservation treatments and the risks involved. They are mostly focused on oil stain removal, colour change reversion, repair and lining techniques, and on methodology to support the fragile paper in rigid secondary supports for display and storage [4,7].

Previous related studies

Non destructing methodology, including technical examination using various wavelengths of the electromagnetic spectrum and multispectral imaging systems have been used to record and evaluate the condition of the paper in cases of tide lines in the wet/dry interface, discoloration, foxing, copy or iron gall inks corrosion [8,9,10,11,12].

Plate 5. Oil painting on paper (20th c.), recto.

Plate 6. Verso side.

Many methods are available for the investigation of paper degradation. Several scientists have used fluorescence techniques [13]. The oxidation reactions of cellulose involve the primary and secondary hydroxyl groups of pyranose ring and result in carbonyl and carboxyl groups. These groups are able to absorb visible radiation; carbonyls are chromophores and as such are responsible for the discolouration of the paper. The oxidation reaction can be, but is not necessarily, accompanied by the opening the pyranose ring. In both cases the glycosidic bond becomes weaker; the formation of carboxyl increases acidity, providing conditions for hydrolysis reactions, so induces depolymerisation [14]. These changes can be monitored by various methods. Some scientists have used Fourier transform infrared spectroscopy (FTIR) and gas chromatography coupled to mass spectrometry (GC/MS) to identify/record products which result from cellulose degradation [15,16,17]. GC-MS permits the separation of compounds of quite high molecular weight, such as saccharides. It has been used, for example, to analyse extracts of artificially aged paper which result from different sets of aging conditions [18].[4]

Although the effect of the oxidation of the oil medium or binder on paper applies to a variety of objects, very little work has up to now been achieved in assessing the effects on paper. Kosek and Green have employed the Russell effect to investigate the oxidation of paper in a collection of oil sketches on paper [19]. Some preliminary work has been also carried out investigating the condition of two oil sketches on paper and using

[4] Several analytical techniques have used for the investigation of cellulose degradation, the characterisation of the oxidation products of paper and the measurement of the degree of polymerisation. Since they do not apply to the aims of this particular research, there will be no further reference.

size exclusion chromatography to measure molecular mass change in mock ups of paper with or without drying oils coatings [20].

Current research project

The work reported here is in the form of a pilot program of application of selected methodologies for the assessment of the condition of 'oil on paper' collections. Research includes non destructive methodology in combination with micro-analytical techniques to assess materials and the effects of degradation on the artefacts and also includes a short study of the effect of oil on the rate of volatile organic emissions from cotton based paper

The aim of research was the formulation of a recommended methodology to be used as an evaluation tool for the condition of works in oil on paper, and thus, to determine the conservation and preservation parameters.

Four works from the collections of the National Galley were selected to be examined for this pilot project; *Escape to Egypt* (Π 3174) by P. Doxaras (18th c.), *Art & handcraft, study* (Π 581/3) and, *The spirit*, study (Π 588) by N. Gysis (19th c.) and Π 8445, *Houses* by N. Tiniakos (20th c.).These works represented diverse case studies and appeared to correspond to the varying parameters of date and art school/movement, type of work and technique, paper support and condition, set to serve the aims of the project. Tiniakos' work is a full scale work of art, a modern oil painting on paper, Gysis' works could be described as oil studies or oil sketches and while Doxara's belong to a series of *modelli*. The oil medium of the paint in the four works was confirmed to be typical of their era respectively[5]. The fact that the works also differ in the extent of coverage of the support with oil paint, was substantial for their choice.

The selected works are all executed on paper supports, since the thickness and the multilayer nature of the paper boards was considered to be limitative and obstructive for certain applications of research. The works have been executed on four different types of European paper[6]. The paper support in Gysis work *Π581/3,* it's a light grey-brown, medium weight, wove paper. Fibre analysis indicated the presence of linen, cotton and possibly coniferous wood. The paper support appears like a low grade quality paper and refers to the type of wrapping papers. The paper support in Π588 refers to a tracing or transparent or translucent paper. Fibre analysis indicated the presence of linen and cotton fibres. For Doxaras work, fibre analysis indicated the presence of linen fibres that infers a traditional rag paper, which is presumable from the date of the work. For Tiniakos works, fibre analysis indicated the presence of chemical soft wood, possibly with china clay as a filler, typical of 20th century machine made, wove paper, possibly manufactured for artistic purposes.

Some, but not all of the works presented severe condition or problems that could be directly attributed to the use of oil colour on paper support. However, the explorative character of the pilot research project supported the choice of all the works.

EXPERIMENTAL

Non destructive methodology

*Ultra violet reflectance and fluorescence photography (**UVR - UVFC**)*

Given that organic materials and especially oil media present fluorescence when excited by UV radiation, areas in both recto and verso sides of the works were examined using UV lamps in order to locate such phenomena. The behaviour of the paper support was also examined. The reflectance and the fluorescence of the surface layer of the sketches under UV radiation at 365nm were recorded photographically. [7]

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[5] Medium analysis showed that in both works of Gysis, the paint was bound either with walnut oil or more probably combination of linseed oil and poppy seed oil mixed with either Kauri or Manilla copal, probably for added gloss. For Doxaras work, medium analysis showed that the paint was bound with raw linseed oil. For Tiniakos' work, the presence of ink and paint was confirmed. The ink was found to be a typical stand oil based ink while the paint is a modern o-phthalate drying alkyd.

[6] During fibre analysis, samples were prepared by teasing the fibres apart in a drop of water on a microscope slide with dissection needles. They were mounted on microscope slides with Meltmount® 1.66 resin (McCrone, London, UK) and examined with a James Swift MP3500A polarising microscope.

[7] For the procedure the following were used: Canon T-70 camera with 52mm macro lenses and macro ring, Ilford FP4 Plus 125 b/w photographic film and Kodak 18A filter for Ultra violet reflectance photography (UVR), Fujifilm Provia and Kodak Wratten filter 2E for UVFC, and special ultraviolet black light bulb lamps Philips E-27 MLW 160W for illumination in both techniques.

*Hyperspectral infrared imaging (**IRRef**) – Coloured Infrared Reflectography (**FCIR**)*
Specifically, the hyperspectral imaging system MU.S.IS HS was used. Its spectrum sensitivity initiates at 400nm and reaches up to 1000nm. The software enables the acquisition of a spectral cube, which comprises images of a chosen area within the aforementioned space with a 20nm step (31 images per cube). It also has the ability of depicting false colour infrared images on demand. False colour infrared images and visible colour images were also acquired with the MU.S.IS HS system. [8]

Artificial ageing tests - Investigation of the effect of linseed oil on the oxidation of paper during.

Sample preparation
Samples of a pure cotton paper, (Whatmans number 1 Filter paper) were obtained. One batch of the paper samples was coated with linseed oil (Windsor and Newton , raw linseed oil) and allowed to dry for three months. Paper samples with and without oil coatings were prepared for artificial ageing in an identical way except for the method by which the quantity of paper was measured, see below.

Control samples of oil films were prepared by mixing a 5% manganese dioxide with linseed oil and painting out onto microscope slides. After three months in dust free conditions the oil films were lifted form the glass and the same areas as determined for the oil on paper samples were aged and analysed as below.

Ageing
Two different artificial ageing procedures were applied: dry heat ageing and humid heat ageing. Three replica tubes for each accelerated ageing time were prepared in order to ensure the eproducibility of the data.

Dry heat ageing
Seventy five mg of paper were cut into small pieces and placed in a 20 ml 'head space' sample vial (Pyrex glass). Each open tube was sealed with a Teflon-lined polypropylene cap.

Six sets of three identically sealed vials were placed into a controlled temperature dry heat oven at 90 ± 2 °C for 1, 3, 7, 14, 21 and 28 days. This temperature was selected in agreement with the conditions of accelerated ageing in accord with the standards ISO 5630-1, 2, 3 and 4 [21]. The temperature inside the vials should be 90 ± 2 °C. The relative humidity inside the vials was not be evaluated. After removal from the oven at the different times, each vial was opened after cooling, 1 ml of water was added and the VOCs immediately extracted, as described below.

Humid heat ageing
Seventy five mg of paper were cut into small pieces. The small paper sample pieces were threaded onto a cotton wire and were suspended a few centimetres above 1 ml of distilled water in 20 ml 'head space' sample vials. Each tube was then sealed with a Teflon-lined polypropylene cap. Six sets of three identically sealed vials were placed into a controlled temperature dry-heat oven at 90 °C. for 1, 3, 7, 14, 21 and 28 days, respectively. Temperature and relative humidity in the vials should be 90 ± 2 °C and 100% RH, respectively. The vials were removed from the oven at the different times, opened after cooling, and the small pieces of paper removed from the wire and dropped into the 1ml of water and extraction of the VOCs was then immediately carried out, as described below.

Papers coated with oil
The area of several 75g pieces of the above paper was measured and averaged. This same area of paper coated with oil was measured for each of the paper + oil samples, so as to age the same quantity of paper in each sample as in the studies without oil. Otherwise the samples were treated in exactly the same way as above for both dry and humid heat ageing, except that the dry aged oil samples were tested at 15 days instead of 14 days.

Extraction procedure and HS-SPME analyses.

The same headspace-microextraction procedure was applied to both oil coated and non-oil coated papers aged paper samples (dry and humid heat ageing). Regardless of the type of ageing, VOC s extracted from the

[8] Halogen display optic lamps of 3400 K, type Osram 650 W 64540 GX 6.35, were used for the illumination of the works.

paper samples were then characterised using GC-MS under the same conditions, as described below. The extraction of the compounds from both naturally and artificially aged paper was performed manually with an SPME holder (Supelco, Bellefonte, PA, USA). The 50/30μm divinylbenzene-carboxen/poly (dimethylsiloxane) fibre (DVB-CAR/PDMS) was inserted into the vial, a few centimetres above the sample. According to the supplier's instructions, the fibre was pre-conditioned in the GC injection port at 230°C. The vial and the fibre were placed into a heating block (Pierce and Warriner, UK) set to 60°C and 1 hour. After exposure, the fibre bearing the concentred analytes was retracted and removed from the sample vial. Analytes adsorbed were then manually injected immediately by insertion of the fibre into the injector port of the chromatograph. The desorption time and temperature were set at 10 min and 230°C. This time set to ensure total desorption and no memory effects (i.e. partial desorption) [21].This was confirmed by desorbing the same fibre a second time after the initial desorption. Indeed, fibre blanks were run between each sample injection to ensure removal of contaminants before exposure to paper samples, as recommended [21]. The VOCs thermally desorbed from the fibre were then transferred onto the gas chromatograph/mass spectrometer for their identification. In order to verify the HS-SPME/GC-MS signal reproducibility, three replica runs of each analysis were performed.

Instrumentation and chromatographic conditions

The volatile compounds were identified by gas chromatography-mass spectrometry (GC-MS) analysis with a Thermo focus GC (Thermo, Hemel Hempsted, UK) coupled with a DSQ mass spectrometer (Thermo, Hemel Hempsted,UK). The chromatographic peaks were identified either by comparison with a reference mass spectral library (US National Institute of Standards and Technology, NIST MS Search 2.0). The chromatograph was equipped with a Thermo TR-5 capillary column of 30m length (Thermo, Hemel Hempsted, UK). The chromatographic elution was temperature programmed as follows: isothermal at 35 °C for 10 min, then from 35–250 °C at a rate of 5 °C/min, and isothermal hold at 250 °C for 30 min. The carrier gas was helium with a constant flow of 1 ml/min. The split/splitless injector was used in splitless mode and its temperature was maintained at 230°C. The interface temperature was set at 270°C. Mass spectra were acquired under electron ionisation mode (EI) at 70 eV and recorded from m/z 35–650 at 0.9 cycles per second.

RESULTS AND DISCUSSION

Non destructive examination

The purpose of non destructive technical examination, supported by image processing techniques, was to investigate the condition of the works, and particularly the effect of oil medium on paper, locating and recording areas with relevant phenomena in different regions of the spectrum. Non destructive methodology included: ultra violet reflectance and fluorescence photography (UVR - UVFC), hyperspectral infrared imaging and coloured infrared reflectography (which provides black and white visible to infrared and false colour infrared images). The approach of the methodology had a trial character, since there was no similar research application to refer to.

In every object, areas that could relate to problems and the phenomena under investigation were selected to be photographed with the various non destructive techniques, so as to maximise the gathering of information and to enable comparison. Additionally, the same methodology was applied to a set of pure cotton paper (Whatman number 1) samples, with or without the addition of oil, aged for various times (see above).

Plate 7a. Gysis Π581/3, recto.

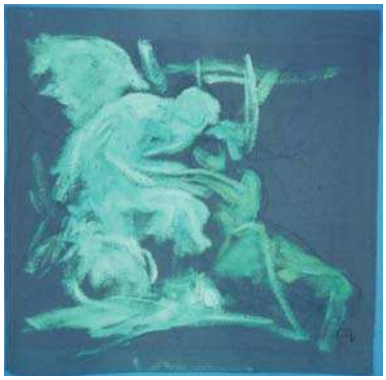

Plate 7b.Gysis Π581/3, recto, UVFC

Plate 7c.Gysis Π581/3, recto, UVR

Plate 8a. Π588, detail.

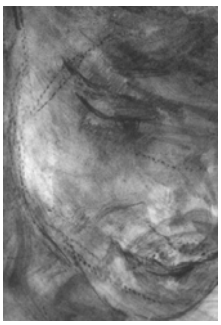

Plate 8b. IRRef

Plate 8c. FCIR

Plate 8d. UVFC

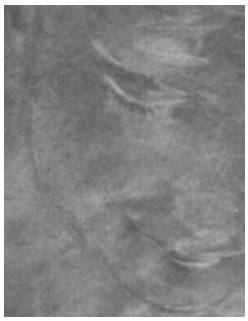

Plate 8e. UVR

The comparative study of the images obtained in the visible, ultraviolet and infrared regions of the spectrum led to the formulation of the following general observations:

Generally, the works have a uniform behaviour in UV reflectance. Even though, meticulous search for oxidation phenomena was carried out, foxing stains, spots or any other related indications could not be recorded. Photoxidation of the paper was able to be recorded on certain areas. The boarders of the paper support appear lighter in tone, since they were protected by the mount once attached: the mount burn was appearing very distinctively.

In some cases the painted areas of the works exhibited intense fluorescence under UV light, due to the oil medium. Due to the intense fluorescence, brushstrokes which were hard to see in the visible light could be easily discerned and recorded. Furthermore, variation of the colour of fluorescence can also be observed in some cases: white and cold fluorescence or in a more yellowish tone (see *Plates 7a, 7b, 7c*).

In some cases, the IR images could contribute to the estimation of the condition. It was decided to focus on the 980nm ones, as they provide better image quality, maximum penetration of the IR radiation, without the image being saturated. The FCIR results provided information about the pigments used for the execution of the works, due to the different false colour they exhibited). This enabled the monitoring of the areas of different pigments as well as their diffusion on the front and the back side of the paper.

All the works was carefully examined for the typical problems and phenomena related to the effect of oil medium on paper, such as oil absorption, diffusion, leaching, discoloration, etc., in visible light and the other regions of the spectrum, on both sides of the works. Research was concentrated in those that had no distinct signs in visible light, but there was barely any considerable recording in the other regions of the spectrum. If it existed, it should be at least visible due to the high fluorescence of the medium under UV light. Only in the case of the tracing paper, it could be assumed that the transparentizing agent prevent the absorption or the migration of the oil medium and the consequent problems.

The technique and materials involved at each work influence their behaviour in the various wavelengths. In particular:

In the case of Gysis bilateral sketch (Π588), the UVFC images exhibit the details of each side, without the reverse side interfering with the front side image at normal photography mode. On the painted side, the colours do not fluoresce, they appear dark. On the contrary, the paper substrate presents an intense fluorescence, due to the fact that it is impregnated in oil or other transparentising substance (see *Plates 8a,b,c,d,e*). In such cases, UVFC cannot provide information about oil medium as there are no reference areas to compare. Only white brush strokes present intense fluorescence. This can be either due to the pigment or to the oily medium, which as known from the literature to present warm fluorescence. In this

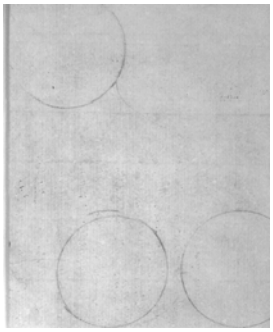

Plate 9a. Π3174, verso, detail, IRRef

Plate 9b. FCIR

Plate 9c. UVFC

Plate 9d. UVR

Plate 10a. Π8445, verso, detail.

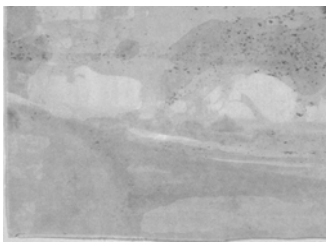

Plate 10b. IRRef.

Plate 10c. UVFC

Plate 10d. UVR

Plate 10e. FCIR.

case, the fluorescence is visible because it is not covered by a dark colour.

In both works of Doxaras, imaging was mainly focused in the recording of the verso side of the painting and mainly in the areas with stains and spots, which in visible light appeared like discolouration. Although, they could be attributed to oil absorption by the paper support, they did not present fluorescence, and the large stain seemed to be darker than the smaller spots. On the contrary, unexpectedly, the surface of hand made rag paper substrate presented intense fluorescence in its entirety. The extensive area of discoloration, as well as the spots was transparent in the IR indicating the presence of an organic material (see *Plates 9a,b,c,d*).

In Tiniakos work, interpretation of the experimental results was very difficult due to the mixed technique the artist used and the diffusion of one material to another, as well as into the paper support. Ultra violet fluorescence recordings mainly of the verso side depicted areas which presented strong fluorescence. However, it was not possible to attribute this fluorescence exclusively to the oil medium as mixing and diffusion phenomena of the materials were very intense. Several organic pigments have been used in this painting, so it was not easy to distinguish whether the fluorescence was due to the organic pigment or the oily medium.(see *Plates 10a,b,c,d,e*) Furthermore, some yellow areas, suspected of being oil, did not present the fluorescence of an oil material.

Investigation of the effect of linseed oil on the oxidation of paper during artificial ageing tests.

In order to investigate as to whether the presence of oil may increase the rate of cellulose oxidation in paper in such works of art, some initial tests were carried out on pure cotton paper. Samples with and without linseed oil applications were, after allowing the oil to dry for three months, submitted to dry and humid ageing for various lengths of time ranging from 1 day to 28 days. Each sample was then investigated by Head Space Solid phase Micro Extraction coupled to Gas Chromatography-Mass Spectrometry (HS-SPME-GC-MS analysis) according to a method based on that of Lattuati-Derieux et al. [21] but with some modifications, including the addition of water to increase volatile organic emission from the aged papers. As Lattuati-Derieux et al. [21] we also included the preparation of three files for each type and ageing period, so as to obtain a result that is a mean value of three experimental values. Oil films which had been prepared with added manganese dioxide drier (5%) and which had been allowed to dry for three months was also aged for 28 days and tested for emissions in the same way and non of the VOC's emitted by the oil, mainly an homologous series of straight chained aldehydes, were included in the study.

Lattuati-Derieux et al. [21] aged wood paper, without oil, and had discovered several emitted volatile organics from wood paper, including furfural and 5-methyl furfural emissions which peaked after 21 days. In contrast we found that furfural and, another different product, 5-ethyl furfural were only emitted from 21 days onwards from the cotton based paper with oil which had been heat aged in humid conditions (Figure 1) but, from cotton paper with oil which had been heat aged under dry conditions only traces of furfural were found at 21 days and 28 days no 5-ethyl furfural was found even within 28 days (Figure 2).

Other furan derivatives found in the oil coated papers included 2-pentyl furan and 2-ethyl furan which peaked at 7 days for the humid aged samples and declined after the first day for the dry aged samples. 5-ethyl furanone was also detected and peaked at 15 days for the dry aged sample and at 21 days for the humid aged sample. None of these furan derivatives appeared in the paper without oil, nor in the oil only samples (no paper) within 28 days. Furanic degradation products are reported as occurring in aged paper, for example Furfural is said to arise from levoglucosan, a thermal degradation product of cellulose or directly from cellulose via a series of elimination and hydrolysis steps [22].

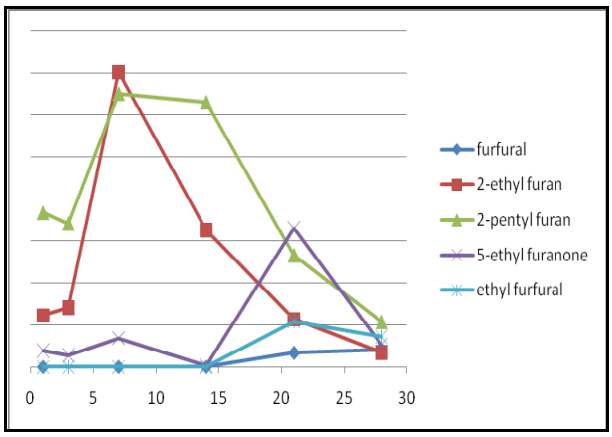

Figure 1 VOC emissions from samples of cotton paper impregnated with linseed oil aged for 1,3,7,14,21 and 28 day at 90 °C and 100% RH. Average of three measurements on three separate samples for each number of days. Plot shows absolute peak area against number of days aged.

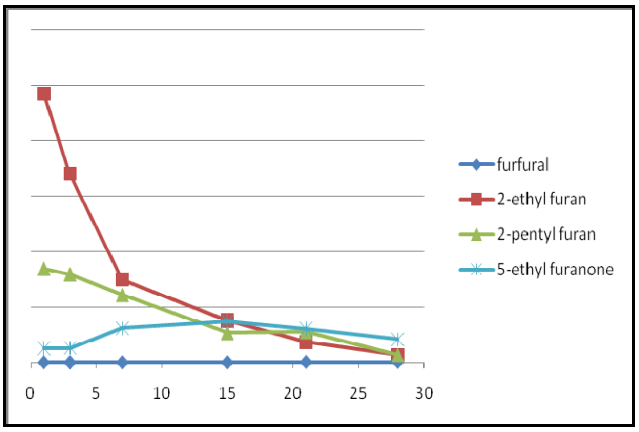

Figure 2 VOC emissions from samples of cotton paper impregnated with linseed oil aged for 1,3,7,14,21 and 28 days at 90 °C. Average of three measurements on three separate samples for each number of days. Plot shows absolute peak area against number of days aged.

The same authors report that hemicellulose may also be an important source of furfural and other furanic degradation products.

Hence we might conclude, by comparison with previous work [21] that cotton paper is much more stable than wood paper under these artificial ageing conditions but, importantly, we might also conclude that the presence of oil in cotton based paper hastens the emission of certain cellulose degradation products such as furfural, especially under humid ageing conditions.

CONCLUSIONS

Non destructive documentation of case studies of original art works gave interesting results about the paint medium, since the presence of oil resulted in intense fluorescence under UV light, while comparison of images from both IR and UV regions contributed to a better assessment of condition of the works. Study showed that the quality of paper (fibre content, composition, method of manufacture), the pigments and dyes used for the execution of the work, affect the behaviour of the oil medium and the associated problems-phenomena. The presence of oil medium was easily detected and recorded only in straightforward cases. In mixed techniques, a version of these methods oriented in spot analysis (e.g. Fibre Optics Diffuse Reflectance Spectroscopy) might be more effective.

The research led to a significant volume of experimental results, the exploitation of which, if combined with other techniques, for example IR transmitted reflectography, and the support of laboratory prepared samples can provide more precise and detailed information. Another area of interest could be the exploitation of false colour rendition towards the identification of the pigments used. Finally, we have shown that oil accelerates the rate of cellulose degradation, as indicated by emission of furfural and other furan based degradatioin products, at least for cotton based paper.

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REFERENCES

1. Gritsay, N., Larionov, A., Durante. S.S., Vegelin, E. & Woodall, J., *Peter Paul Rubens: Oil sketches and related works from the State Hermitage Museum and Courtlauld Institue Gallery*, Prestel Publishing Ltd, 2004.
2. Bower, P., 'A brush with nature: An historical and technical analysis of papers and boards used as supports for landscape oil sketching', in Daniels, V., Donnithorne, A. & Smith, P. (ed.) *Works of art on*

paper. Books, documents and photographs. Techniques and conservation, contributions to the IIC Baltimore Congress, 2-6 September 2002, IIC, pp.16-20.
3. Cove, S., 'Constable's oil sketches on paper and millboard', in S. Fairbrass (ed.) *IPC Conference Papers Manchester 1992,* Institute of Paper Conservation, Leigh, pp.123-128.
4. McAusland, 'Problems with works of art in oil on paper and their support: A paper conservator's viewpoint'*, General Meeting of the Association of British Picture Restorers*, on the 29th November of 1989, UK.
5. James, C., Corrigan, C., Enshaian, M.C., & Greca, M.R., *Old Master prints and drawings*, translated and edited by Marjorie B. Cohn, University Press, Amsterdam, 1997.
6. Stijnman, Ad., 'Oil-based printing ink on paper. Bleeding, browing blanching and peroxides', *Papier Restaurierung - Mitteilungen der IADA*, vol.1, 2000, pp.61-68.
7. 'Oil media and stains on paper', section in S. Fairbrass (ed.), *IPC Conference Papers Manchester 1992*, Institute of Paper Conservation, Leigh, UK, 1992.
8. Alexopoulou A., Banou P., Gerakari K, Kaminari A.& Stassinou A., *'*Copy books:Non destructive documentation on the H. Schliemann's copy letters archive*'*, *The 2nd Iron gall meeting – MIP final conference*, 24-27 of January 2006, Newcastle upon Tyne (UK).
9. Reissland, B. *Visible progress of paper degradation caused by iron gall inks*. I.G.I.M.((cf.ref.2).
10. Bicchieri, M., Pappalardo, G., Romano, F.P., Sementilli, F.M. & De Acutis, R., 'Characterization of foxing stains by chemical and spectrometric methods*'*, *Restaurator: International journal for the preservation of library and archival material*, Vol.22, No1, 2001, pages 1-65.
11. Dupont, Anne-Laurence, 'Degradation of cellulose at the wet/dry interface. I: the effect of some conservation treatments on brown lines*'*, *Restaurato: International journal for the preservation of library and archival material r* , Vol**.** 17, No. 1, 1996, pp. 1-21.
12. Havermans, J., Hadeel, A.A. & Scholten, Hans, S.*,* 'Non destructive detection of iron gall inks by means of multispectral imaging. Part 1: development of the detection system', *Restaurator: International journal for the preservation of library and archival material*, Vol. 24, No.1, 2003, pp.55-60.
13. Pedersoli Júnior, J.L., Ligterink, F.J., Di Pietro, G., 'Browning of paper Fluorescense changes accompanying the discolouration of artificially aged paper', *PapierRestaurierung - Mitteilungen der IADA*, Vol. 1, 2000, pp. 47-54.
14. Marguti S., Conio G., Calvini P. & Pedemonte E, 'Hydrolytic and oxidative degradation of paper', *Restaurator: International journal for the preservation of library and archival material,* Vol.22, No.2, 2001, pp.67-83.
15. Dupont, Anne Laurence, 'Degradation of cellulose at the wet/dry interface: II. An approach to the identification of the oxidation compounds' *Restaurator: International journal for the preservation of library and archival material* Vol.17, No.3, 1996, pp.145-164.
16. Lojewska, J., Lubanska, A., Lojewski, T., Miskowiec, P. & ;Proniewicz, L.M., 'Kinetic approach to degradation of paper: in situ FTIR transmission studies on hydrolysis and oxidation', *e-Preservation Science,* No.2, 2005, pp.1-12.
17. Erhardt, D. & Tumosa, C. S., 'Chemical Degradation of Cellulose in Paper over 500 Years', *Restaurator:Iinternational journal for the preservation of library and archival material,* Vol.26, 2005, pp.151-158.
18. Erhardt, D., Von Endt, D. & Hopwood, W., 'The comparison of accelerated aging conditions through the analysis of extracts of artificially aged paper' *Preprints of papers presented at the fifteenth annual meeting of the American Institute for Conservation of Historic and Artistic Works*. Vancouver, British Columbia, Canada, May 20-24, 1987, pp.43-55.
19. Kosek, Joanna; Green, Lorna R., 'A survey of oil paintings and sketches on paper in the collection in the British Museum: an assessment of stability' in S. Fairbrass (ed.), *The IPC: Conference papers Manchester 1992*, Institute of Paper Conservation: Worcester, 1992, pp.96-102.
20. Sian P., 'The Conservation of Two nineteenth century oil sketches on paper, attributed to Josephine Bowes with scientific investigation into the effects of the media on paper', *MA. Dissertation*, Northumbria University, 1995.
21. Agnès Lattuati-Derieux, Sylvette Bonnassies-Termes, Bertrand Lavédrine, 2006, 'Characterisation of compounds emitted during natural and artificial ageing of a book. Use of headspace-solid-phase microextraction/gas chromatography/mass spectrometry', *Journal of Cultural Heritage,* 7**,** pp.123–133.
22. John Scheirs, Giovanni Camino, Mauro Avidano, Wander Tumiatti, 1998, 'Origin of furanic compounds in thermal degradation of cellulosic insulating paper', *Journal of Applied Polymer Science*, 69, pp.2541–2547.