

Water sensitivity of modern oil paint films

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Abstract

Samples of 20th Century oil paintings made by Winsor & Newton and a painting by Ethel Walker dated c.1930 made using paints from the same manufacturer were analysed to investigate the cause of water sensitivity. Samples of water sensitive surfaces in both the painting and the W&N paints contained UV-fluorescent skins of medium and indicated the presence of Epsomite. Further indicators for water sensitivity in the W&N samples included high concentrations of polar chemical groups toward paint surfaces characterized using microscopy and Fourier Transform infrared spectroscopy.

Introduction

Recent research has focused on understanding the causes of water sensitivity during surface cleaning of unvarnished oil paintings (Van den Berg et al., 2014). The problem is worthy of investigation due to the demand for exhibition of modern works, in particular unvarnished paintings, that require removal of surface dirt before display. As water based systems have hitherto been the most effective method for surface cleaning oil paintings, that once cured would not be expected to be sensitive to water, this paper reports recent findings that is part of a wider study of the cause of sensitivity in modern oil paints, that aims to identify diagnostic indicators that can inform conservation documentation and practice. Studies that examine the composition of paints thus provide data that can inform alternative methods for treatment.

The methodology for examining water sensitivity has included chemical analysis of samples taken from paintings together with a more systematic study of paint samples. The samples forming the main focus of this paper were prepared as part of the process of testing batches of oil paint manufactured by Winsor & Newton (W&N) together with samples of paints prepared in the laboratory and artificially aged (Silvester et al., 2014). While the availability of artists' Colourmens' samples that are aged naturally are an invaluable resource for material analysis, the preparation of aged samples provides a significant surface area for testing water sensitivity using methods used by conservators for surface cleaning.

Previous phenomenological case studies of modern paintings have suggested a range of factors that can contribute to the sensitivity to surface cleaning of passages of paint in oil media using aqueous solvents (Cooper et al., 2014). These include aspects of the physical structure of the paint film, such as surface roughness, porosity, cracking or the formation of hygroscopic degradation products on the paint surface. In some cases there are no physical indicators of water sensitivity however the paint is rendered soluble on first contact with a single water-dampened swab (Burnstock et al., 2008). The complexity of the phenomena that has more than one cause is clear from studies of paintings. Other studies have focused on examination of the physical, surface and chemical composition of individual artists and student quality oil paints, aged naturally or artificially to more closely define the different parameters that influence water sensitivity of the dry films (Mills et al., 2008, Tempest et al, 2013).

The present study investigated the distribution of inorganic materials and organic functional groups in samples from swatches of artists' quality oil paints manufactured in the 20th Century by British artist's material suppliers, W&N. This study also included analysis of samples from an unvarnished painting by British artist Ethel Walker (1861-1951) who used W&N paints that showed water sensitivity of some areas during surface cleaning. The study of manufacturers' samples and those removed from paintings aims to provide guidelines for conservators in their assessment of the condition of these and works made using similar materials.

Experimental

Paint samples

A set of 27 samples of W&N manufactured artists' quality oil paints were selected for investigation, based date of manufacture and an evaluation of water sensitivity testing by three conservators using swab rolling methods (Mills et al., 2008). Previous studies identified presence of water soluble medium skins that exhibited UV fluorescence (Mills et al., 2008). Evidence of the separation of medium from pigment and the formation of a skin at the surface of paint films provided evidence for an hypothesis that there is a difference between the surface and bulk paints that is related to water sensitivity on swabbing. To test this hypothesis an infrared study of the W&N samples was carried out to examine evidence for chemical gradients. Separate analyses of the paint from the surface and bulk of the paint samples were studied.

Samples of paint from areas of water sensitive and non-sensitive paint were examined from an unvarnished painting by Ethel Walker, *Draped Woman standing by a Mantlepiece*¹. Samples from the painting were prepared as and cross sections for examination using LM and ESEM-EDX and also as unembedded samples for ESEM imaging, to examine the bulk paint and surface.

Table 1 summarizes the samples, and results of tests and analyses, carried out using Light Microscopy (LM) environmental scanning electron microscopy with energy dispersive X ray spectroscopy (ESEM-EDX), Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR), Fourier transform infrared spectroscopy (FTIR) and Evolved Gas Analysis Mass Spectrometry (EGA-MS). Films were chosen where paints of the same name exhibited different sensitivity to water swabbing. The paints included 11 named batches: Burnt Umber, Cobalt Blue Deep and French Ultramarine (all water sensitive); Cadmium Lemon, Winsor Green, Oxide of Chromium, Cobalt Green (some of which were sensitive), and Rose Dore,

Titanium White, Flake White, Zinc White none of which were water sensitive

LM, FTIR, ESEM-EDX and evolved Gas Analysis Mass Spectrometry (EGA-MS)

Samples from the W&N paint swatches were prepared as embedded cross sections to examine the distribution of materials in the bulk and surface of the paint films using light microscopy (Leica DM4000), a FEI™ environmental scanning electron microscope fitted with an Oxford instruments energy dispersive X-ray spectroscopy light element detector. A scalpel was used to separate material from the surface and bulk paint that were examined using a diamond cell. FTIR was carried out in transmission mode using a Thermo scientific Nicolet iN10 MX microscope and IR spectra were manually baseline corrected, and normalised in order to facilitate visual comparison of the IR spectra of surface and bulk samples. Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy was used for chemical imaging of embedded cross sections, using a Bruker Hyperion 3000 FTIR microscope equipped with a Germanium MCT (mercury cadmium telluride) detector.

Semi-quantitative information on medium content and composition of samples from the paintings was obtained using EGA-MS, carried out using a Frontier Laboratories Ltd. PY-2020D microfurnace pyrolyzer. The microfurnace was mounted onto the split inlet of an Agilent Technologies 5975C inert MSD/7890A gas chromatograph/mass spectrometer via a heated syringe needle interface. A deactivated transfer line (Frontier Ultra ALLOY DTM EGA tube, 2.5 M x 0.15 mm) connected the GC inlet to the MS detector via a Frontier Vent-Free adaptor. The injector was set to 320 °C. For analysis a 50 µl stainless steel Eco-cup loaded with c. 100 µg sample ground in the cup, was placed into the cool upper zone of the microfurnace where it was purged with helium for three minutes prior to heating. Sample vapor was generated by ramping the temperature of the microfurnace from 100 °C to 700 °C at 20 °C /minute, followed by a 5 minute isothermal period. The mass spectrometer was scanned from 10-600 amu. (See Van den Berg and Schilling, manuscript on the method in preparation).

Results and discussion

W&N paint swatches

Table 1 summarizes the results of tests and analyses of samples from the W&N paint swatches. Element mapping of the W&N samples showed the presence of magnesium (Mg) in all except titanium white, Rose Dore and Zinc White paints. Mg was also identified in all the samples from the painting by Walker. The presence of this element is indicative of magnesium carbonate used as an extender for oil paint (Silvester et al., 2014) and magnesium stearate used as a rheology modifier in oil paints produced by the manufacturer². Selected samples of water sensitive paints showed rod-shaped crystals characteristic of

| Batch Name | Year of production | Water sensitive Y/N | FTIR | XRF analysis (paint layer + support) | | SEM-EDX (paint layer only) | Likely Paint Composition |
|--------------------|--------------------|---------------------|--|---|---|--|--|
| | | | | Major elements present | Other elements Present | | |
| Burnt Umber | 1949 | Y | Oil, metal carboxylates including: Mn and Zn soaps, possible metal (Ca) oxalate. | Fe (Ka and Kb), Mn (Ka) | Al (Ka), S (Ka), Ca (Ka), Ti (Ka) or Ba(La), Zn (Ka), Pb (La, Lb) | Al Mg Fe Mn Si S (P Ti Cu) (Ca in bulk only) | Oil, Umber, Manganese and Zinc soaps, calcium carbonate/sulphate |
| | 2003 | Y | Oil, magnesium carbonate, metal carboxylates, aluminium hydroxide. | | | Al Mg Fe Mn (K Ca P) | Oil, Umber, Al and Mn Soaps, Calcium Phosphate, calcium carbonate/sulphate, Magnesium Carbonate, K Al silicate |
| Cadmium Lemon | 1963 | Y | Oil, magnesium carbonate, barium sulphate, silica. | Zn (Ka and Kb), Cd (La, Lb, Ka, Kb), Ba(La, Lb, Ka), Pb (Ma, La, Lb) | - | Al Mg Cd S (Ba Si Ca) | Oil, Cadmium Sulphide, Al soap, Ba sulphate, Magnesium carbonate, Ca sulphate or carbonate, Co driers |
| | 1993 | Y | Oil, magnesium carbonate, barium sulphate, silica, cobalt drier, metal carboxylates. | Zn (Ka and Kb), Cd (La, Lb, Ka, Kb), Ba(La, Lb, Ka) | - | Al Mg Cd S Zn (Ba) | Oil, Cadmium Zinc Sulphide, Barium Sulphate, Aluminium Soap, possible Co drier. |
| | 2003 | Y | Oil, magnesium carbonate, barium sulphate, metal carboxylate, possible cobalt drier, possible alumina hydrate. | | | Al Mg Cd S Zn (Ba) | |
| Cobalt Blue Deep | 1965 | Y | Oil, magnesium carbonate, cobalt blue, metal carboxylates, possible calcium oxalate. | Co (Ka, Kb), Pb (La, Lb) | Co (Ka, Kb), Zn (Kb) | Al Mg Co (Ca S Si Cu Na) | Oil, Cobalt Aluminate, magnesium carbonate, calcium carbonate/sulphate, barium sulphate, possible aluminium soaps. |
| | 2003 | Y | Oil, cobalt blue pigment, magnesium carbonate, possibly some calcium carbonate, possible azelaic acid derivatives. | Co (Ka, Kb), Zn (Ka, Kb) | Al (Ka), S (Ka, overlaps with Pb Ma), Ca (Ka, Kb), Ba (La, Lb, Ka, Kb), Fe (Ka) | Al Mg Co Ba S Zn (Si Ca) | Oil, Cobalt aluminate, magnesium carbonate, possible Al soaps, Calcium carbonate/sulphate, barium sulphate. |
| Cobalt Green | 1962 | N | Oil, magnesium carbonate, aluminium hydroxide, metal carboxylate). | Zn (Ka, Kb) Co (Ka, Kb) | Al (Ka), S (Ka), Ca (Ka, Kb), Ti (Ka, Kb), Cr (Ka, Kb?) Mn (Ka), Fe (Ka) | Zn Co Ba S Sn Al Si Mg | Oil, Cobalt stannate, Barium sulphate / zinc sulphide, Aluminium soap, magnesium carbonate. |
| | 1993 | N | Oil, magnesium carbonate, metal soaps. | Zn (Ka, Kb), Co (Ka, Kb), Cr (Ka, Kb), Ti (Ka, Kb) or Ba (La, Lb, Ka) | Al (Ka), S (Ka), Ca (Ka, Kb) Fe (Ka) Ni (Ka) | Al Mg S Cr O | Oil, Chromium oxide, magnesium carbonate, possible Barium Chromate), Aluminium soap, Calcium carbonate. |
| | 2003 | Y | | | | Al Mg S Ti Cr Co Zn Ca (Cu) | Oil, Zinc chromate, Cobalt Aluminate, Mg Carbonate, Al soaps, Calcium sulphate or carbonate. |
| French Ultramarine | 1949 | Y | Ultramarine, oil, carboxylic acids, metal carboxylates, cobalt drier. | Pb (Ma?, La, Lb), S? (Ka) | Al (Ka), Si (Ka), K (Ka), Ca (Ka), Ti (Ka, Kb), Fe (Ka, Kb), Ni (Ka), Zn (Ka) | Na Al Si S Mg (CaCl K Fe Cu) | Oil, French Ultramarine, Aluminium soap, calcium carbonate/sulphate, Magnesium carbonate or magnesium stearate. |

| | | | | | | |
|------|---|---|----------------------------------|---|---------------------------------|---|
| 2003 | Y | Ultramarine, oil, metal carboxylates, alumina hydrate, cobalt drier. | S (Ka) | Si (Ka), Al (Ka), K (Ka), Ca (Ka, Kb), Ti (Ka, Kb), Mn (Ka), Fe (Ka, Kb), Ni (Ka), Cu (Ka), Zn (Ka). | Na Al Si S Mg (K) | Oil, French Ultramarine, Aluminium soap, calcium carbonate/sulphate, barium sulphate, magnesium carbonate or magnesium stearate. |
| 1957 | N | Oil, metal carboxylates (including zinc soaps), lead carbonate, likely cobalt drier. | Pb (La, Lb), Zn (Ka, Kb) | Sr (La), Ca (Ka, Kb), Ti (Ka, Kb) or Ba (La, Lb), Fe (Ka), Co (Ka), Ni (Ka), Zr (Ka) | Pb Zn Ba S Co Zr (Mg Ca) Si Al | Oil, Lead Carbonate and Zinc Oxide, Calcium carbonate, barium sulphate, magnesium carbonate or magnesium stearate, Aluminium soaps, Pb/Zr/Sr/Co drier possibly present. |
| 2003 | N | Oil, metal soaps (including zinc soaps). | Pb (La, Lb), Zn (Ka, Kb) | Ca (Ka, Kb), Ti (Ka) or Ba (La, Lb), Fe (Ka), Co (Ka). | Pb/S Zn Al | Oil, Lead carbonate and Zinc Oxide, Calcium carbonate, Barium Sulphate, Cobalt drier. |
| 1945 | Y | Oil, carboxylic acids, metal soaps, magnesium carbonate. | Cr (Ka, Kb) | Al (Ka), Si (Ka), S (Ka), K (Ka), Ba (La, Lb) and/or Ti (Ka, Kb), Fe (Ka), Ni (Ka), Ca (Ka, Kb), Pb (La, Lb), Lg), Sr (Ka). | Cr Al Mg S | Oil, Chromium oxide green, Al-soap, silica, barium sulphate, lead drier, calcium carbonate, magnesium carbonate. |
| 1948 | N | Oil, magnesium carbonate, metal carboxylates, chromium oxide green, aluminium hydroxide. | | | | |
| 2003 | Y | Oil, chromium oxide green, carboxylic acids, metal carboxylates, magnesium carbonate, possible inorganic sulphates (magnesium sulphate?), possible aluminium hydroxide. | Cr (Ka, Kb) | Al (Ka), S (Ka), Ca (Ka), Ti (Ka, Kb) and/or Ba (La, Lb), Fe (Ka), Ni (Ka, Kb), Zn (Ka), Br (Ka). | Cr S Mg (Si Al) Al S Ni Cu P Si | Oil, Chromium oxide green, Al-soap, calcium sulphate, barium sulphate. |
| 1945 | N | Oil, metal carboxylates (inc. aluminium stearate), organic madder lake, alumina hydrate. | Pb (Ma, La, Lb), Zn (Ka, Kb) | Al (Ka), Si (Ka), K (Ka), Ca (Ka, Kb), Ba (La, Lb), Ka, and possibly Ti (Ka, Kb), Cr (Ka, Kb), Fe (Ka), Co (Ka), Ni (Ka), Cu (Ka), Zn (Ka, Kb). | Al S (Ca Cu Si) | Oil, Madder Alumina, possible Calcium sulphate/carbonate, aluminium soaps. |
| 2003 | N | Oil, carboxylic acids, organic madder lake, metal carboxylates inc. aluminium stearate. | S (Ka) or Pb (Ma) – peak overlap | Al (Ka), K (Ka), Ca (Ka, Kb), Ti (Ka, Kb) and possibly Ba (La, Lb), Fe (Ka), Co (Ka), Ni (Ka), Cu (Ka), Zn (Ka). | Al S (Mg Na Si Cu Ca) | Oil, Madder Alumina, Calcium carbonate/sulphate, barium sulphate, cobalt drier. |
| 1966 | N | Oil, titanium white pigment, barium sulphate, possible silica, metal carboxylates (inc. zinc carboxylates), likely inorganic carbonate (Ca or Mg), possible Co drier. | Ti (Ka, Kb), Zn (Ka, Kb) | Al (Ka), Si (Ka), S (Ka) and/or Pb (Ma), Ba (?) (La, Lb), Fe (Ka, Co (Ka), Ni (Ka), Pb (La, Lb), Sr (Ka, Kb), Ba (Lb, Ka), Ca (Ka, Kb). | Ti Zn Al S Ba (Co) | Oil, Titanium Oxide, Zinc Oxide, Al soaps, Calcium carbonate/sulphate, Barium Sulphate, Magnesium Carbonate, Cobalt drier. |

| | | | | | | | | | | |
|--------------|------|---|--|---|--|--|--|---------------------------|---|--|
| 2003 | | N | | | | | | | Surface: Ti Zn Mg S Al Ba (Co) | Oil, Titanium Oxide, Zinc Oxide, Al soaps, Calcium carbonate/sulphate, Barium Sulphate, Magnesium Carbonate, Cobalt drier. |
| Winsor Green | 1949 | N | | Ba (La, Lb) and/or Ti (Ka, Kb), Cu (Ka, Kb) | | | | Cl Mg Al Ba S(Si P Ca Cu) | Oil, Phthalocyanine Green, Barium sulphate, Al (as Al-soap or aluminium salt), magnesium carbonate or magnesium stearate, calcium carbonate/sulphate. | |
| | 1964 | Y | | Ba (La, Lb), and/or Ti (Ka, Kb), Cu (Ka, Kb), Pb (La, Lb) | | Al (Ka), Si (Ka), S (Ka) or Pb (Ma), Ca (Ka, Kb), Fe (Ka), Ni (Ka), Cu (Ka, Kb), Sr (Ka, Kb) | | Cl Ba S Al Mg (Co Cu Ca) | Oil, Phthalocyanine Green, Barium sulphate, Calcium carbonate/sulphate, magnesium carbonate or magnesium stearate, Al soap, Cobalt Drier. | |
| | 1993 | N | | Ba (La, Lb, Ka), and possibly Ti (Ka, Kb), Cu (Ka, Kb), Br (Ka, Kb) | | Al (Ka), S (Ka) or Pb (Ma), Ca (Ka, Kb), Ni (Ka), Sr (Ka, Kb), | | Cl Mg Al S (Ba Ca Cu) | Oil, Phthalocyanine Green, Barium sulphate, Calcium carbonate/sulphate, magnesium carbonate or magnesium stearate, Al soap, Cobalt drier. | |
| | 2003 | Y | | | | | | Cl Mg Al (Ba S Cu) | Oil, Phthalocyanine Green, Barium sulphate, magnesium carbonate or magnesium stearate, Al soap, Cobalt drier. | |
| Zinc White | 1973 | N | | Zn (Ka, Kb) | | S (Ka), Ca (Ka), Ti (Ka) or Ba (La), Fe (Ka), Co (Ka), Ni (Ka) | | Zn (Ti Al Cl) S | Oil, Zinc White (ZnO), Al (as aluminium soap, or aluminium salt), calcium carbonate/sulphate, cobalt and lead drier. | |
| | 2003 | N | | | | | | Zn (Ni S Al) | Oil, Zinc White (ZnO), Calcium carbonate, barium sulphate, cobalt drier. | |

magnesium hepta-hydrate (Epsomite) on the paint surface. These included Cobalt Green 1993, Cadmium Lemon 1963 (fig. 1). Previous studies suggest that many $MgCO_3$ containing paints may form Epsomite on the surface to some extent (Silvester et al. 2014, Cooper et al. 2014).

Aluminium (Al) was found in all the paints, indicative of Aluminium stearate soaps that in general were evenly distributed in the bulk paint films. According to the W&N archive³, Alumina White (aluminium hydroxide) is an additive listed in recipes for various paint formulations dating from 1940⁴. No clear evidence, however for the stearates could be found using EGA-MS.

EGA-MS indicated that all paints were made with oil, probably primarily linseed, or mixtures with linseed and other oils. The only exception was the Flake White paint from 1957 which contained at least high proportion of poppyseed oil indicated by a high P/S ratio of c.3.0. (fig. 2). W&N shifted from the use of poppy oils for some paints to safflower oil in the late 1960s (Ian Garrett personal communication 2014), using refined linseed and safflower primarily from then on (Pearce 1992). For paints after that date it is difficult to accurately detect the use of either safflower or linseed oils, especially in mixtures, since their P/S ratios are so similar.

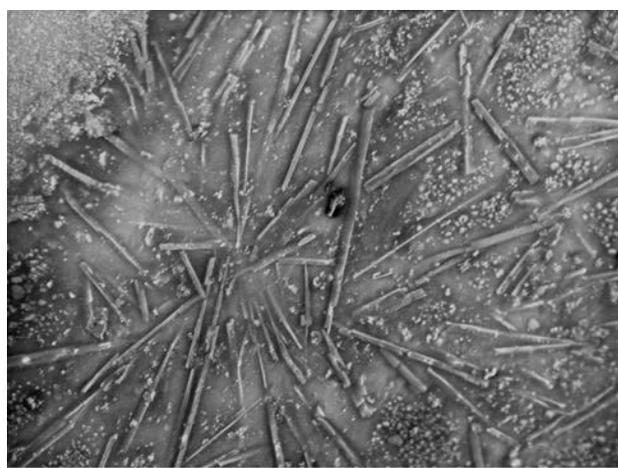


Fig. 1 (above). ESEM Backscattered electron image (BE) of the surface of Cadmium Lemon 1963 showing needles of Epsomite.

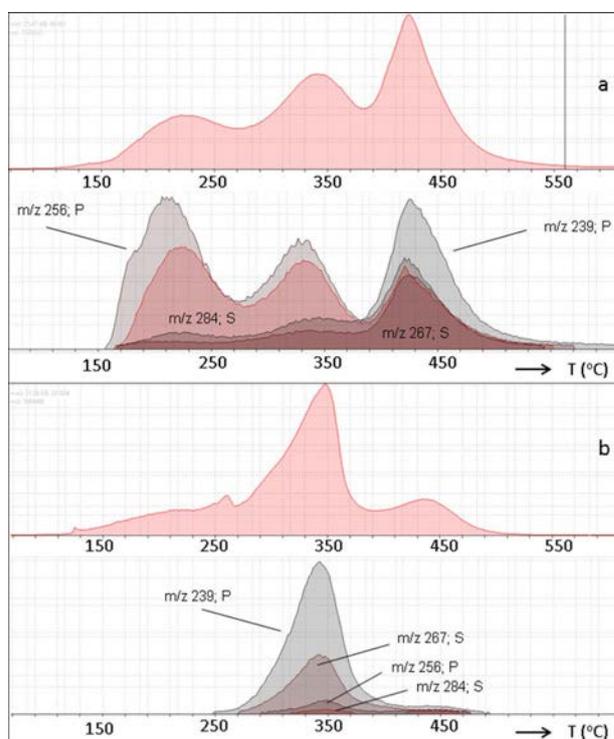


Fig. 2 (right). EGA Total Ion Chromatogram (above) and Single Ion Chromatograms of individual ions linked to palmitic (m/z 256, 239) and stearic fatty acids (m/z 284, 267) (below) of a) water sensitive Winsor Green from 1964, and b) not water sensitive Flake White from 1957. P/S ratios indicate the presence of linseed and poppyseed oil respectively with no added metal stearate. Note the high proportion of free fatty acids in Winsor Green, as most fatty acids in Flake White are present as metal soaps.

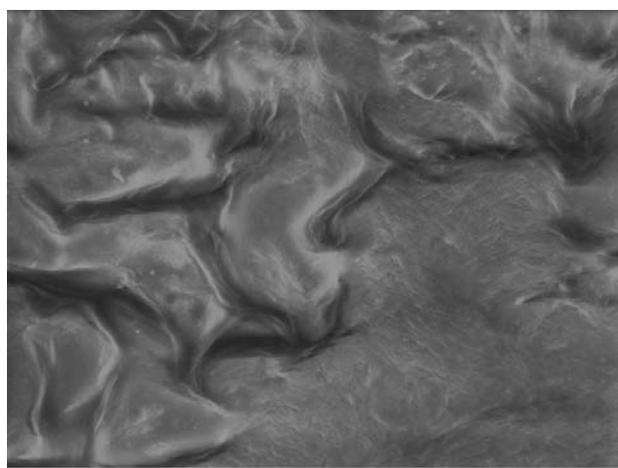


Fig. 3. W&N French Ultramarine ESEM-Secondary electron (SE) image of surface showing medium skin.

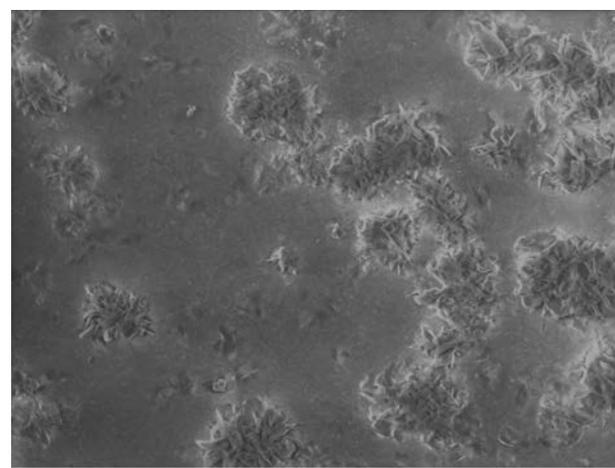


Fig. 4 ESEM SE image of the surface of a sample of W&N Burnt Umber 1949 showing fatty acid efflorescence.

ESEM examination showed that most of the paints exhibited a skin of medium at the paint surface, while ESEM and LM study suggested that the skin in the water sensitive paints was thicker than in the non-sensitive paints, typically 3 microns or more. Some samples, exemplified by a sample of W&N French Ultramarine 1949 (**fig. 3**) showed a significant layer of organic material at the surface. Similarly, surface imaging of a film of Burnt Umber 1949 showed medium skin and fatty acid efflorescence (**fig. 4**). Other paint samples that showed medium skins included Cobalt Blue, Cobalt Green and Cobalt Blue Deep. Another group of samples including Cadmium Lemon 1963 and 2003 showed a medium skin and water sensitivity while the swatch made from a batch of the same name prepared in 1993 had a homogenous composition and was not water sensitive. The samples of Winsor Green made in 1949 and 1964 had skins and sensitivity to water swabbing while the 1993 sample has no skin and was not water sensitive.

Most of the W&N paint swatches (including white paints) featured a distinct surface fluorescence when examined under UV light and particularly in regions where the paint is thickest. Water sensitivity testing of W&N swatches dated between 1945–1965 showed no correlation between surface fluorescence and water sensitivity. It was therefore concluded that UV fluorescence cannot be used as a simple diagnostic tool for water sensitivity in W&N artists' oil paints. Furthermore, cross sections from samples of both water sensitive and non-water sensitive swatches consistently featured using L Light Microscopy M bands of fluorescence toward the upper and lower surfaces, situated within an otherwise homogenous paint layer, this is exemplified in **fig. 5** by Flake White (1957).

In an earlier study of student grade W&N paints, visible bands of fluorescence toward upper surfaces were observed in cross sections taken from water sensitive including French Ultramarine, Chrome Green and Raw Sienna (Silvester, 2011). Similar results were found for all the samples examined with the exception of Burnt Umber (1949, 2003) French Ultramarine (1949), Oxide of Chromium (2003), and Winsor Green (1949, 1964, 1993) all of which were water sensitive. FTIR absorptions which appeared more intense or broader for surface samples were noted, as were any absorptions that were unique to the surface. As IR band intensity is proportional to concentration (Smith, 1999) differences in the intensity of selected bands for surface and bulk samples could be used to evidence the concentration gradient of chemical species in the films. However, band intensity is also influenced by other factors such as the change in dipole moment of chemical bonds, and the quantity of material in the beam path (Smith, 1999; van der Weerd, 2002). Further evidence from ATR-FTIR chemical imaging of paint cross sections showed chemical gradients and offered higher spatial resolution than the initial surface-bulk FTIR measurements. Both water sensitive and non water sensitive paints featured broad hydroxy absorption bands with a higher intensity and sharper maximum at the paint surface. A higher concentration of hydroxy absorptions were measured at the surface relative to the bulk paint in 18 of the 27 samples (the exceptions were Cobalt Green (1962, 1995), Flake White (1957, 2003), Rose Dore (1945, 2003), Titanium White (1966), Burnt Umber (2003), and Cadmium Lemon (1993). This indicates a general trend in the enrichment of polar hydroxy containing functional groups at the paint surfaces. Previous results obtained from Gas Chromatography-Mass Spectrometry and direct Electrospray Ionisation Mass Spectrometry (Van den Berg, Van den Doelen et al. manuscript in preparation, this Journal// these proceedings; Burnstock and Van den Berg 2014) indicated that this enrichment is largely due to the presence of relatively high quantities of diacids such as azeleic acid, either in the free form or as glycerides. Application of other methods of instrumental analysis would be necessary to investigate the cause of formation of other hydroxyl groups such as hydroperoxides, monocarboxylic acids, or alcohols (Chan, 1987).

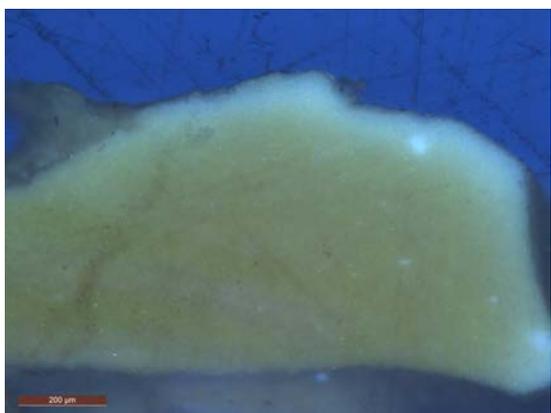


Fig. 5. Cross section from W&N Flake White 1957 taken in LM-UV showing bands of fluorescence toward the upper surface.

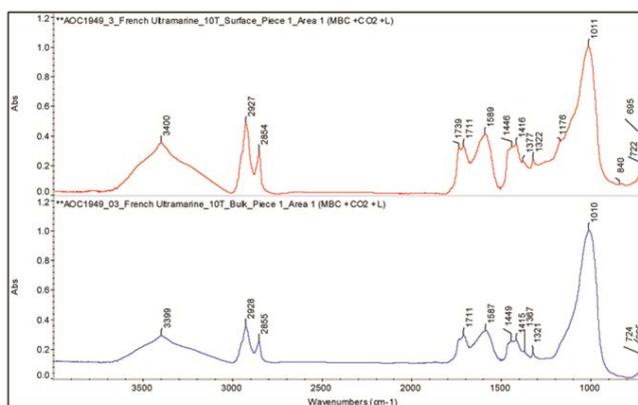


Fig. 6. FTIR spectra of surface (red) and bulk (blue) sample from W&N French Ultramarine 1949. The ester carbonyl absorption is a split doublet at 1739 and 1711 cm^{-1} .

All the W&N samples examined featured an asymmetric and/or symmetric absorption band of metal carboxylates which appeared more intense and/or more broad at the surface. ATR-FTIR imaging revealed the same general trend, that both water sensitive and non-water sensitive paints featured an increased intensity of carboxylate absorptions toward the paint surface. These results may point to an increased concentration of organic acids at the paint surface which are stabilised by metal ions where present in the paint formulation, to form metal carboxylates. An enrichment of organic acids could indicate hydrolysis of triglycerides, oxidation occurring preferentially at the paint surface, or polarity driven phase separation.

Several water sensitive paints presented an IR absorption band at $\sim 1710\text{cm}^{-1}$ which appeared more intense at the surface. These samples included Burnt Umber (1949), Cobalt Blue Deep (2003) Cobalt Green (2003) and French Ultramarine (2003). Other water sensitive samples including Cobalt Blue Deep (1965), Winsor Green (1964) and French Ultramarine (1949) (**fig. 6**) featured a split carbonyl absorption band appearing as a doublet at $\sim 1740/1710\text{cm}^{-1}$ for both surface and bulk samples. Oxide of Chromium (1945, 2003) featured a split carbonyl absorption only in the surface sample. None of the non-water sensitive paints analysed showed the split carbonyl absorption band.

Oxidation reactions are known to result in the formation of a range of carbonyl containing compounds which overlap with the carbonyl absorption due to carboxylic acids and contribute toward the broadening of the ester carbonyl absorption at $\sim 1740\text{cm}^{-1}$ (Lazzari & Chiantore, 1999). Without suitable derivitisation techniques (Zumbühl, Scherrer, & Eggenberger, 2014) carboxylic acids cannot be identified with complete certainty using IR spectroscopy alone. Nevertheless previous researchers have tentatively assigned absorptions at $\sim 1710\text{cm}^{-1}$ to carboxylic acids where this absorption was accompanied by bands at $3200\text{--}2600$, 1415 and 915cm^{-1} (van der Weerd, 2002). The consistent presence of absorption bands at $\sim 1320\text{cm}^{-1}$ corresponds to the C-O stretch of carboxylic acids (known to occur in the range $1320\text{--}1210\text{cm}^{-1}$ (Smith, 1999) provided additional evidence for the assignment of the band at 1710cm^{-1} to the carbonyl absorption of carboxylic acids. Therefore enhanced absorptions at $\sim 1710\text{cm}^{-1}$ particularly where the absorption is of greater or equal intensity than the ester carbonyl absorption at $\sim 1740\text{cm}^{-1}$ may suggest of hydrolysis of ester bonds (van der Weerd, 2002; van der Weerd, van Loon & Boon, 2005). The presence of the split car-

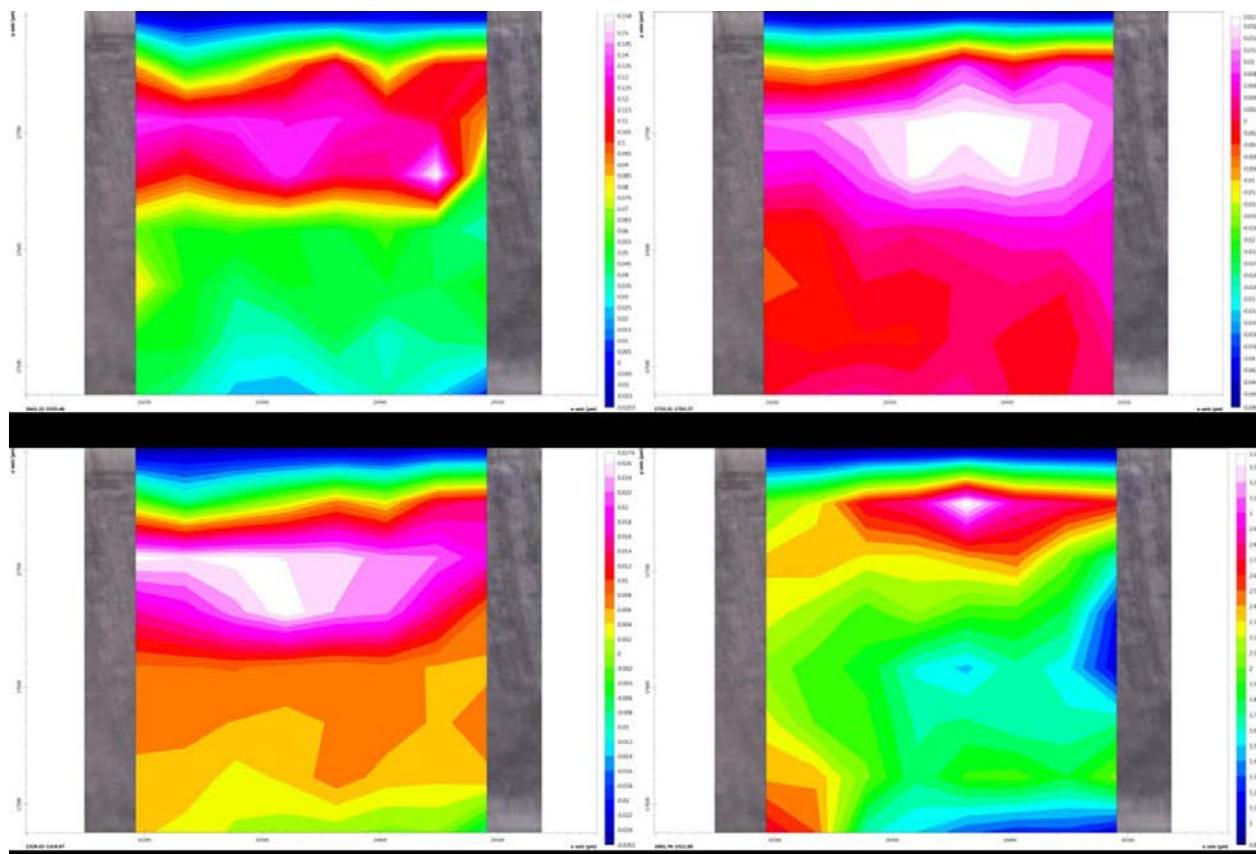


Fig. 7. ATR-FTIR imaging maps W&N French Ultramarine 1949. Hydroxy absorption $3441\text{--}3355\text{cm}^{-1}$. Carbonyl absorption of Carboxylic acid $1715\text{--}1703\text{cm}^{-1}$ C-O absorption of Carboxylic acid $1329\text{--}1316\text{cm}^{-1}$. Asymmetric stretch of metal carboxylate $1661\text{--}1511\text{cm}^{-1}$.

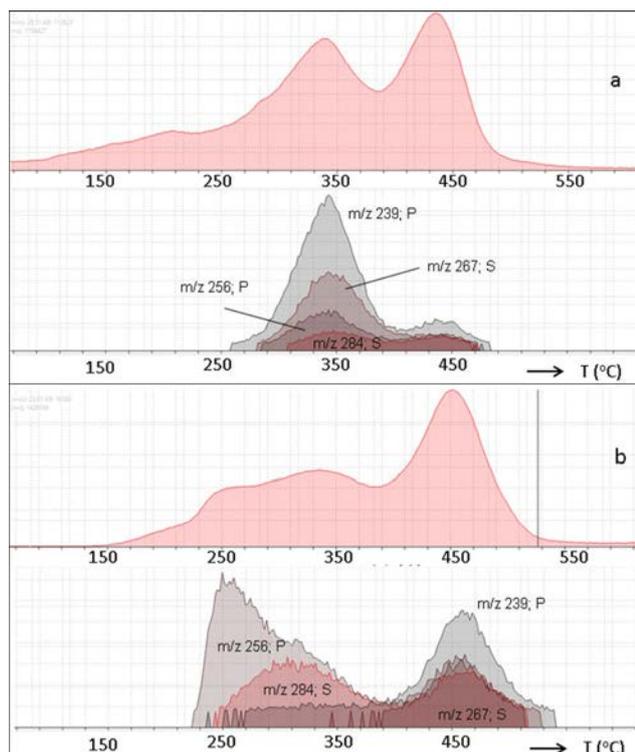
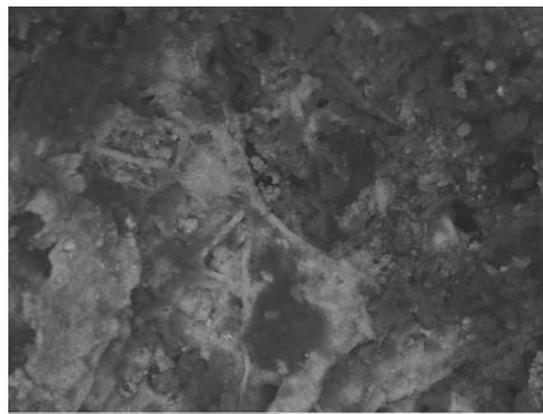


Fig. 8. EGA Total Ion Chromatogram (above) and Single Ion Chromatograms (below; See Fig. 2) of a) a moderately water sensitive dark green paint b) acutely sensitive light blue paint. Both analyses indicate the presence of linseed oil. The green paint analysis shows abundant free fatty acids, while the light blue paint contains primarily metal soaps, similar to the flake white W&N paint (see also Fig. 2b).

Fig. 9. ESEM-BE image of a sample from a water sensitive area of cadmium orange containing paint from *Draped Woman standing by a Mantlepiece* by Ethel Walker showing fungal hyphae suggestive of the effects of high RH.



bonyl may also signal oxidative degradation processes resulting in the production of acids. According to reference FTIR spectra, a split carbonyl band at $1740/1713\text{cm}^{-1}$ is a feature of the FTIR spectrum of esters of azelaic acid (C9 diacid). A split carbonyl at $\sim 1740/1710\text{cm}^{-1}$ has also been reported where oil paint films are exposed to SO_2 as an atmospheric pollutant (Marinescu, Emandi, Dului, & Stanculescu, 2014).

In agreement with surface-bulk IR spectra, the ATR-FTIR imaging showed a concentration of the absorption at $\sim 1710\text{cm}^{-1}$ toward the surface of water sensitive Burnt Umber (1949), Cadmium Lemon (1963), Cobalt Blue Deep (1965, 2003), French Ultramarine (1949, 2003), Oxide of Chromium (1945, 2003) and Winsor Green (1993). ATR-FTIR mapping of areas that showed prominent absorption at $\sim 1710\text{cm}^{-1}$ also showed strong absorption at $\sim 1320\text{cm}^{-1}$, a broad hydroxy absorption at $\sim 3500\text{--}3100\text{cm}^{-1}$ and metal carboxylate absorptions at $1650\text{--}1540\text{cm}^{-1}$ and $1450\text{--}1360\text{cm}^{-1}$ (Smith, 1999). This trend is illustrated in ATR-FTIR imaging maps of French Ultramarine in **fig. 7**. These results again point to the concentration of polar carboxylic acids toward the surface of water sensitive paints (Van den Berg et al. this Journal/these proceedings). The correlation between carboxylic absorption bands and the absorption bands characteristic of metal soaps exemplifies the conversion of free fatty acids to metal carboxylate in the presence of metal ions that occurs in paint films.

The results of ATR-FTIR imaging showed that non water sensitive paint films featured a higher concentration of ester carbonyl, and aliphatic C-H absorptions toward paint surfaces than most of the water sensitive paints. This suggests that the hydrolysis of ester bonds may provide a source of carboxylic acids at the surface of water sensitive paint films. For water sensitive Burnt Umber (1949) the ATR-FTIR imaging map (not shown) clearly shows a reduction in the concentration of ester carbonyl absorption at the paint surface.

Ethel Walker painting samples

Selected samples of water sensitive areas from the Ethel Walker painting taken from areas containing cobalt blue and cadmium containing paints showed rod-shaped crystals characteristic of magnesium sulphate hydrate (Epsomite) on the paint surface. In addition, the samples showed medium skins similar to those observed in the W&N paint samples. In this case the surface skin was embedded with surface dirt and grime. EGA-MS shows the presence of oil binders in all instances, although some showed different proportions of low MW and free fatty acids (**fig. 8**).

The samples from the Walker painting also show the presence of fungal hyphae that may have developed as the result of exposure to raised relative humidity (**fig. 9**). The formation of highly hygroscopic Epsomite by reaction of environmental sulphides with magnesium carbonate in oil paint films in both samples and paintings has been shown in a previous studies (Silvester et al., 2014).

Conclusion

ATR-FTIR together with LM/ fluorescence and ESEM imaging of W&N paint swatches suggested that water sensitive paints feature a higher concentration of polar compounds rich in carboxylic acids and hydroxy functional groups toward paint surfaces. The fluorescent, organic rich upper layers of many of the paints prepared as cross sections may correspond with an increase in concentration of metal carboxylates toward the surface.

Qualitative characterisation of concentration gradients of these polar functionalities evidenced by IR analysis of surface-bulk samples and ATR-FTIR imaging of embedded cross sections suggested potential causal factors for water sensitivity, due to the concentration of polar species at or close to the paint surface. However many of the samples including water sensitive paints did not feature discernable chemical gradients. This could be explained if the degradation processes have occurred evenly across the depth of the paint film or progressed to a point where concentration gradients are no longer detectable using infrared spectroscopy. The identification of specific oxidized polar compounds could be further examined using quantitative mass spectrometry, together with a quantitative evaluation of the ratio of metal carboxylates to polar organic acids.

Samples from the painting by Ethel Walker showed medium skins similar to those observed in W&N paint samples. In this case the surface skin was embedded with surface dirt and grime, characteristic of some unvarnished aged paintings. Medium skins have been observed in water sensitive passages of paint in a number of paintings (Burnstock et al., 2008). The findings for both the W&N paints and the painting examined were consistent in the difference between the surface and bulk paint and a relatively high concentration of organic material, or conversely a lower pigment concentration at the surface.

None of the white paints or the W&N Rose Dore paints showed water sensitivity. These samples were characterised by homogeneous composition of pigment and medium observed using ESEM. In common with Zinc and Titanium whites, these paints do not contain magnesium carbonate. This underpins previous findings (Silvester et al., 2014; Cooper et al 2014) that this extender plays a major role in water sensitivity.

The formation of epsomite crystals on the surface of some paint swatches and samples from the Walker painting is favored in the presence of moisture and acids; the presence of fungal hyphae on the surface of the painting is evidence of its physical history that included exposure to high humidity. The formation of lead soaps also observed in the painting may also be favored in the presence of moisture. Concomitantly, the preferred oxidation of binder constituents as well as potential hydrolysis of ester bonds observed in this study is likely to contribute to the chemical gradient in the sensitive paints. This points to the importance of environmental control in the prevention of water sensitivity in some paintings. It is proposed that both water sensitivity and soap formation may be facilitated by moisture transferred across and within paint films via fungal hyphae. This may be worthy of future investigation.

The complexity of the issue of water sensitivity is highlighted in the case study of the Walker painting, that included areas of water sensitivity where vulnerable paints may be mixed with paints that would otherwise not be sensitive, or alternatively be stabilised by admixtures of pigments. An understanding of the composition of paints is therefore useful for predicting the likelihood of water sensitivity in paintings.

Note

- ¹ Dame Ethel Walker CIA 2050 *Draped Woman standing by a Mantlepiece*, unvarnished, on the reverse of reverse of *Contrajour, Woman Seated at a Window*, 1938, Courtauld Gallery, 27.3 x 101.6cm, Mr and Mrs Marion Kratochwil gift 1973. Six samples were taken from the unvarnished reverse image, from water sensitive areas or blue, yellow, brown and red paint and non-sensitive white paint of the drapery, mantlepiece and background. Samples sites are documented in an archive report by Sara Wohler and Aviva Burnstock, 2015, Department of Conservation & Technology, Courtauld Institute of Art.
- ² W&N Archive, Hamilton Kerr Institute, Cambridge.
- ³ The W&N archive is currently held at the Hamilton Kerr Institute, Cambridge.
- ⁴ Personal communication Ian Garrett 2014.

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