



Scientific investigation into the water sensitivity of twentieth century oil paints



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ABSTRACT

In order to develop a better understanding at the molecular level of water sensitivity in twentieth century oil paintings, water sensitive Winsor & Newton oil paint swatches and twentieth century oil paintings were characterised using gas chromatography–mass spectrometry (GC–MS) and direct injection electrospray ionisation mass spectrometry (ESI–MS), and the data were analysed using principal component analysis. Liquid chromatography coupled with tandem mass spectrometry based on quadrupole and time of flight mass detectors and electrospray interface (HPLC–ESI–Q–ToF) was also used to obtain a better insight into the molecular composition of a selection of samples. The study highlights a strong relationship between the molecular composition of the binding medium and the type of pigment present in the paint, which relates to water sensitivity. Consistently non-water sensitive lead white, titanium white, and zinc white paints [all containing zinc oxide] contained a relatively low proportion of extractable diacids, and a relatively high proportion of extractable short chain monoacids. These paints also contained a relatively low level of unsaturated and hydroxylated glycerides. Water sensitive iron oxide and ultramarine paints are associated with both a relatively high degree of oxidation and a high proportion of extractable diacids, as well as a relatively high content of unsaturated and hydroxylated glycerides. Water sensitive cadmium red, yellow and orange paints were generally not highly oxidised, but they also contained a relatively high content of unsaturated and hydroxylated glycerides. It is hypothesised that water sensitivity relates to a low degree of saponification and crosslinking and possibly, on the relative content of dicarboxylic acids.

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1. Introduction

The phenomena of the water sensitivity of twentieth century oil paintings is of concern to conservators since it can complicate or prevent surface cleaning treatment and consolidation [1]. There are many examples of water sensitive unvarnished twentieth century oil paintings reported in the literature including works by Karel Appel, Jasper Johns, Robyn Denny, Wassily Kandinsky, Kazimir Malevich, Piet Mondrian, Clyfford Still, Paula Rego, Patrick Heron, Francis Bacon and Per Kerkeby [1–5]. There is currently a need to develop an understanding at the molecular level of the characteristics and causes of water sensitivity in twentieth century oil paintings in order to inform the development of suitable materials and methodologies for surface cleaning [6]

as well as potentially limiting the development of water sensitivity in paints. This is critical in order to ensure that water sensitive modern oil paintings will be in a condition fit for display in the medium to long term.

There are many causal factors that are believed to be implicated in the development of water sensitivity in twentieth and twenty first century oil paintings [7]:

- modern oil paint formulation including the choice of pigment, binder, extender and additives such as metal soaps and driers
- environmental conditions such as relative humidity, UV light and atmospheric pollutants
- artists' use and modification of commercially prepared materials

The conversion of magnesium carbonate [an extender used by Winsor & Newton (W&N)] to form water soluble magnesium sulphate heptahydrate upon exposure to environmental SO₂ is one known cause of water sensitivity in modern oil paintings [8]. In addition, a

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high dicarboxylic acid content has been observed in some water sensitive oil paint samples [9] suggesting that the composition of the binding medium may relate to water sensitivity.

Artists' oil paints are typically made using drying oils and semi-drying oils such as linseed, poppy and safflower oil [9]. Drying oils - which are initially comprised of triglycerides containing saturated and polyunsaturated fatty acids - cure via a complex process based on autoxidative radical chain reactions [10]. The first step of curing is the abstraction of a hydrogen free radical, followed by oxygen addition, leading to the formation of a peroxide. A peroxide can evolve through two main pathways, in competition with one another, one leading to polymerisation, and one leading to oxidative scission [7] which results in the formation of α,ω -dicarboxylic acids as final products [11]. Nonanedioic (azelaic) acid along with octanedioic (suberic) and decanedioic (sebacic) acids are the major diacids produced as a result of oxidative scission. The hydrolysis of ester bonds that occurs upon ageing results in the formation of diglycerides, monoglycerides, free fatty acids and diacids, as well as glycerol [12]. Certain cations contained in pigments and extenders, including lead, zinc, copper, cobalt, etc., are able to form metal soaps with carboxylic moieties produced by oxidation and hydrolysis [13,14].

In this study the relationship between the molecular composition of the binding medium and water sensitivity was further investigated. Samples taken from W&N artists' oil paint swatches (samples painted out by the manufacturer during production to monitor drying behaviour) dating from 1945 to 2003 and naturally aged since then and samples from a wide series of case study twentieth century oil paintings were analysed using a combination of Fourier transform infrared spectroscopy (FTIR), gas chromatography–mass spectrometry (GC–MS), direct injection electrospray ionisation mass spectrometry (ESI–MS), and liquid chromatography coupled with tandem mass spectrometry based on quadrupole and time of flight mass detectors and electrospray interface (HPLC ESI–Q–ToF). These techniques have been successfully used for the analysis of lipid binding media [15–19]. Sample preparation for GC–MS typically involves extraction of lipids, hydrolysis of glycerides and metal soaps, and derivatisation to increase the volatility of extracted compounds [20]. In this case (*m*-trifluoromethylphenyl) trimethylammonium hydroxide (TMTFTH) in methanol was used as a one-step derivatisation (transesterification/methylation) agent (Meth Prep II) [21,22] that does not require complex sample pre-treatments or extraction steps and therefore minimises loss of sample, and the risk of contamination [23]. When applied to oil paint samples, TMTFTH converts non-crosslinked fatty acids and diacids originally present as glycerides, as metal soaps or as free fatty acids into the corresponding methyl esters [21], giving information on the whole organic content, with the exception of the crosslinked polymeric network. Direct injection electrospray ionisation mass spectrometry (ESI–MS) was used to analyse the ethanol extracts of the paint samples. This, in combination with the fact that data used were acquired in the negative mode, allowed the gathering of information on the most polar and soluble constituents of the paints, including free fatty acids and dicarboxylic acids, as well as non-crosslinked glycerides containing at least a dicarboxylic acid. Liquid chromatography coupled with ESI–Q–ToF mass spectrometry (HPLC ESI–Q–ToF), was used to evaluate the glyceride profile from a qualitative and semi-quantitative point of view [19]. Finally, multivariate analysis was used to support data interpretation, allowing the identification of trends in the large data set as well as differences between water sensitive and non-water sensitive samples.

2. Materials and methods

2.1. Samples

Winsor and Newton (W&N) produced paint swatches to monitor the drying behaviour of each batch of manufactured paint. Samples of paint were applied to primed canvas or a paper support (using a palette knife or draw-down bar). A group of 27 water sensitive and non-water

sensitive naturally aged W&N Artists' Oil Colour swatches dating from 1945 to 2003 (see Table 1) were selected. Their water sensitivity was evaluated with an established swab rolling method [3] and the basic paint composition of the investigated W&N swatches is published in detail elsewhere [24]. In addition to the paint swatches, a total of 86 non-water sensitive and water sensitive samples were taken from selected case study paintings as listed in Table 2. The composition of the samples (i.e., pigment, binding media and extender) removed from case study paintings is shown in Supplementary data, Table A.1.

2.2. Fourier transform infrared spectroscopy (FTIR)

Transmission FTIR spectroscopic analysis was carried out on a Thermo scientific Nicolet iN10 MX microscope using a single diamond cell. 64 scans were collected at a resolution of 4 cm^{-1} across a wavenumber range of $4000\text{ to }600\text{ cm}^{-1}$. Data was processed using Omnic 8 software.

2.3. Electrospray ionisation mass spectrometry (ESI–MS)

Direct injection ESI–MS analyses were carried out on paint samples of 0.1–0.5 mg after solvent extraction using ethanol [25]. The extract was mixed 1:1 with 20 mM ammonium acetate (NH_4Ac) in ethanol. Samples were delivered to the MS system with a Micromass CapLC system: MS analysis was carried out with a Micromass Q–tof–2, equipped with a nano probe and ESI source. MS data were collected and interpreted using MassLynx 4.0 software (Waters). All spectra were collected in high mass resolution mode. Since the molecular formula of the ions is unambiguous for all ions in this study, only nominal masses are presented.

2.4. Gas chromatography–mass spectrometry (GC–MS)

Two surface scrapings (of $<1\text{ mg}$) and two bulk samples (of around 1 mg) were taken from each W&N swatch. Surface samples only were taken from case study paintings. Samples were derivatised using Meth Prep II (Grace™ Alltech™). Details on the analytical procedure are reported elsewhere [22]. GC was carried out on a Varian CP–3900 GC coupled with a 1200L MS detector. Oven program: $80\text{ }^\circ\text{C}$ ramped to $320\text{ }^\circ\text{C}$ at $10\text{ }^\circ\text{C}/\text{min}$ then held for 5 min at $320\text{ }^\circ\text{C}$. Total run time was 29 min. Split (20:1) injection volume was $1\text{ }\mu\text{L}$, and the helium flow was $1.0\text{ mL}/\text{min}$. MS conditions: source temperature: $220\text{ }^\circ\text{C}$; transfer line temperature: $270\text{ }^\circ\text{C}$, injection port set at $300\text{ }^\circ\text{C}$. Column: Phenomenex Zebron ZB–5 column (30 m length; 0.25 mm i.d. ; $0.25\text{ }\mu\text{m}$ film thickness). EI mode (70 eV); scan group 1: $45\text{--}300\text{ amu}$; Group 2: $45\text{--}700\text{ amu}$ at 16 mins, every 1 s. Chromatographic peak areas were used to calculate ratios between the abundances of significant analytes.

2.5. HPLC–ESI–Q–ToF

For the HPLC–ESI–Q–ToF analyses samples (2–3 were subjected to extraction assisted by microwaves in a microwave oven Ethos One (Milestone, U.S.A.) (power 600 W), with $300\text{ }\mu\text{L}$ of a chloroform–hexane (3:2) mixture at $80\text{ }^\circ\text{C}$ for 25 min. The extracts were dried under a nitrogen stream, diluted with $600\text{ }\mu\text{L}$ of elution mixture, and filtered on a $0.45\text{ }\mu\text{m}$ PTFE filter (Grace Davison Discovery Sciences, U.S.A.) just before injection.

HPLC–ESI–Q–ToF analyses were carried out using a 1200 Infinity HPLC, coupled with a Quadrupole–Time of Flight tandem mass spectrometer 6530 Infinity Q–ToF detector by a Jet Stream ESI interface (Agilent Technologies). The chromatographic separation was carried out using a Poroshell 120 EC–C18 column ($3.0\text{ mm} \times 5.0\text{ mm}$, $2.7\text{ }\mu\text{m}$ particle size) with a Zorbax eclipse plus C–18 guard column ($4.6\text{ mm} \times 12.5\text{ mm}$, $5\text{ }\mu\text{m}$ particle size) at a flow rate of $0.3\text{ mL}\cdot\text{min}^{-1}$ and at $45\text{ }^\circ\text{C}$. Aliquots of $10\text{ }\mu\text{L}$ were injected and the elution gradient was

Table 1
List of W&N swatches selected for study.

Swatch (Pigment)	Year	Swatch (shorthand)	Water sensitive	Extenders/additives ^a	Ratio of the FTIR peak areas of amorphous metal soaps vs. carbonyl absorption ^b		Crystalline zinc soaps detected	Epsomite detected ^c
					Average ratio	Standard deviation		
Burnt Umber (iron oxide)	1949	BU49	Y	None detected	1.8	0.5	N	N
	2003	BU03	Y	Magnesium carbonate	0.5	0.1	N	N
Cadmium Lemon (cadmium sulphide)	1963	CdL63	Y	Magnesium carbonate, barium sulphate, alumina	1.5	1.0	N	Y
	1993	CdL93	N	white (hydrated aluminium oxide)	1.7	0.6	N	N
Cobalt Blue Deep (cobalt zinc silicate)	2003	CdL03	Y		2.3	0.4	N	N
	1965	CoBD65	Y	Magnesium carbonate	1.6	1.6	N	N
Cobalt Green (cobalt zinc oxide)	2003	CoBD03	Y		0.5	0.5	N	N
	1962	CoG62	N	Magnesium carbonate, alumina white (hydrated	1.8	1.4	N	N
Cobalt Green (cobalt titanate green spinel)	1993	CoG93	N	aluminium oxide)	2.8	1.6	N	Y
	2003	CoG03	Y		0.8	0.3	N	N
Flake White (lead white + zinc oxide)	1957	FIW57	N	Cobalt + zirconium driers	9.4	3.9	Y	N
	2003	FIW03	N	None detected	2.5	0.8	Y	N
French Ultramarine (sodium aluminosilicate)	1949	FrU49	Y	None detected	2.0	0.5	N	N
	2003	FrU03	Y	Magnesium carbonate	0.6	0.2	N	N
Oxide of Chromium (chromium oxide)	1945	OxCr45	Y	Magnesium carbonate	1.9	0.3	N	N
	1948	OxCr48	N		1.2	0.2	N	N
Rose Doré (madder)	2003	OxCr03	Y		0.5	0.1	N	N
	1945	RD45	N	Alumina white (hydrated aluminium oxide),	1.9	0.4	N	N
Titanium White (titanium oxide and zinc oxide)	2003	RD03	N	aluminium stearate	1.0	0.1	N	N
	1966	TiW66	N	Barium sulphate	11.5	2.6	Y	N
Winsor Green (phtalocyanine green)	2003	TiW03	N	Magnesium carbonate, barium sulphate	1.6	0.3	Y	N
	1949	WG49	N	Barium sulphate	0.8	0.2	Y	N
Zinc White (zinc oxide)	1964	WG64	Y		0.3	0.2	Y	N
	1993	WG93	N	Barium sulphate, magnesium carbonate	0.4	0.1	Y	Y
	2003	WG03	Y		0.2	0.1	Y	N
	1973	ZnW73	N	None detected	9.5	1.1	Y	N
	2003	ZnW03	N		3.4	0.8	N	N

^a Samples were previously characterised using scanning electron microscopy–energy dispersive X-ray spectroscopy (SEM–EDX) and Fourier transform infrared spectroscopy (FTIR), and data are published and discussed elsewhere [24].

^b Amorphous metal soaps were detected in the W&N swatches using FTIR on the basis of a broad absorption band present in the region $\sim 1650\text{--}1550\text{ cm}^{-1}$, the carbonyl absorption band appears at $\sim 1740\text{ cm}^{-1}$. The corrected peak areas of these bands were determined using Omnic 8 software for x6 FTIR spectra that were acquired for two bulk samples taken from each W&N swatch. Ratios of the FTIR peak areas of amorphous metal soap:carbonyl absorption bands were calculated for each spectra, the results averaged, and standard deviation calculated, based on triplicate measurements.

^c Epsomite was identified on the basis of SEM imaging in conjunction of SEM–EDX elemental mapping of surface samples taken from swatches [24].

programmed using methanol/water 85:15 (eluent A) and *iso*-propanol (eluent B) as follows: 90% A for 5 min, followed by a linear gradient to 90% B in 30 min (held for 10 min). Re-equilibration time for each analysis run was 10 min.

ESI operating conditions: drying gas (N_2 , purity > 98%): $350\text{ }^\circ\text{C}$ and $10\text{ L}\cdot\text{min}^{-1}$; capillary voltage 4.5 kV; nebuliser gas 35 psig; sheath gas (N_2 , purity > 98%): $375\text{ }^\circ\text{C}$ and $11\text{ L}\cdot\text{min}^{-1}$. High resolution MS and MS/MS spectra were acquired in positive mode in the range $100\text{--}1700\text{ m/z}$. The fragmentor was kept at 200 V, nozzle voltage 1000 V, skimmer 65 V, octapole RF 750 V. The MS/MS spectra presented in the text were obtained at 50 V. The collision gas was nitrogen (purity 99.999%). The data were collected by auto MS/MS acquisition with an MS scan rate of $1.03\text{ spectra}\cdot\text{sec}^{-1}$ and an MS/MS scan rate of $1.05\text{ spectra}\cdot\text{sec}^{-1}$; only one precursor was acquired per cycle (relative threshold 0.010%). The mass axis was calibrated daily using the Agilent tuning mix HP0321 diluted in water and acetonitrile (Agilent Technologies). MassHunter® Workstation Software (B.04.00) was used to carry out mass spectrometer control, data acquisition, and data analysis. The structures of the triglycerides (TAGs) were identified by the evaluation of their exact mass, the interpretation of their tandem mass spectra and by comparison with previously published mass spectra data [19,26].

2.6. Multivariate analysis

Principal Component Analysis (PCA) on the covariance matrix of selected mass spectral data was carried out using XLSTAT 2015.3.01 (Addinsoft).

3. Results and discussion

3.1. Comparison of the data sets

The key differences between the analytical techniques used as described in this study are summarised in Table 3. None of the techniques used are a direct measure of the cross-linked fraction nor the degree of crosslinking. Similarly none of the techniques used are a direct measure of the metal soap content of the paint samples (including added metal soaps or those formed *in situ*). As a measure of the degree of oxidation, azelaic acid/palmitic acid (A/P) ratios derived from GC–MS data are considered more representative of the overall degree of oxidation of the paint film than equivalent ratios derived from the ESI–MS data set (which only relates to the polar extractable organic components of the paint).

3.2. W&N swatches

Negative mode ESI–MS mass spectra (e.g. Fig. 1) yielded the most interesting information about the extractable polar glycerides and fatty acids. The attribution of the most significant fragment ions observed in the ESI–MS mass spectra are listed in Table 4. This set of 28 ions was the most abundant in the mass spectra for all samples, and were therefore selected for PCA analysis as the most significant. The 28 ions were identified on the basis of their nominal mass and information available in the literature [15,25] and were analysed using an

Table 2

List of case study paintings selected for study. The colour of non-water sensitive and water sensitive passages are noted. For further details of paint composition including pigment type see Supplementary data (Table A.1).

Painting	Colour of water sensitive passage(s)	Colour of non-water sensitive passage(s)
1 Frank Auerbach <i>Oxford Street Building Site I</i> 1959–60 (Tate, T00418)	Brown, ochre, yellow, mars red	n/a
2 Derek Boshier <i>Shy Cowboy</i> 1980 (Tate, T07475)	Bright orange, bright red, dark green, brown, dark brown	Pink, grey, white
3 The Hon. Dorothy Brett <i>Massacre in the Canyon of Death: Vision of the sun God</i> 1958 (Tate, T00285)	Brown, ochre, orange, yellow	Light green, white
4 Avinash Chandra <i>Hills of Gold</i> 1965 (Tate, T00724)	Red, orange, yellow, dark green, black	Light blue, white
5 Prunella Clough <i>Bypass 1</i> 1960 (The Courtauld Institute of Art, P.1984.AH.66)	n/a	White, brown, blue, green, orange, yellow
6 Prunella Clough <i>Wire Tangle II</i> 1978 (The Courtauld Institute of Art, P.1984.AH.67)	n/a	White, yellow, grey
7 Alan Davie, <i>Image of the Fish God</i> , 1956 (Tate, T01748)	Dark blue, yellow, maroon, white priming	White
8 Adrian Heath <i>Painting in Brown and Black</i> 1960 (Tate, T00396)	Orange, light brown	Black, white
9 Ferdinand Kulmer <i>Brown Picture</i> 1960 (Tate, T00429)	Brown, dark blue, maroon	n/a
10 Joan Mitchell <i>Chord II</i> 1986 (Tate, T12429)	Blue, bright green, dark green	Bright red, white
11 Emile Nolde <i>Sea B</i> 1930 (Tate, T00865)	Dark blue, orange	Yellow, white, purple, light blue
12 Ray Parker <i>Untitled</i> 1959 (Tate, T00441)	Bright red, dark red	Bright red, white, pink
13 Pablo Picasso <i>Nude Woman in a Red Armchair</i> 1959 (Tate, N06205)	Bright red, dark green	White, lilac, light yellow, light green, brown, black, grey
14 Pablo Picasso <i>The Three Dancers</i> 1925 (Tate, T00729)	Dark green	Dark brown
15 Jean-Paul Riopelle <i>Perspectives</i> 1956 (Tate, T00123)	Dark blue, light blue, bright red, green, ochre, yellow	Black, white
16 Wilhelm Sasnal <i>Gaddafi I</i> 2011 (Tate, T14241)	n/a	Black, yellow, blue, bright red, bright green, brown, white
17 William Scott <i>Reclining Nude (Red Nude)</i> 1956 (Tate, T00811)	Dark orange, light orange	Red
18 Richard Smith <i>Painting</i> 1958 (Tate, T01588)	Yellow, red	White
19 Sir Matthew Smith <i>The Young Actress</i> 1943 (Tate, N05440)	Blue, red	Pink, red, brown, blue
20 Ethel Walker <i>The Zone of Love: Decoration</i> 1930-2 (Tate, N05668)	Dark blue, bright yellow (localised areas only)	White, maroon, red, blues, brown

unsupervised multivariate pattern analysis method: Principal Component Analysis (PCA).

Having normalised the intensity of the 28 m/z to their sum, the intensities of related species were summed according to the following groups: short chain monocarboxylic acids (C6–C10); dicarboxylic acids (diC7–diC10); monoglycerides of dicarboxylic acids (MAG(diC8);MAG(diC9)); hydroxy derivatives of C18 fatty acids, diglycerides containing only suberic and/or azelaic acids; diglycerides containing palmitic acid and diacids; diglycerides containing stearic acid and diacids; triglycerides containing three azelaic acid moieties. Free palmitic, stearic, and oleic acid were also included in the data matrix of 11×27 variables [shown in Supplementary data, Table A.2] analysed via PCA of the covariance matrix.

The scatter plot of the first two principal components (PCs) (Fig. 2) shows that the composition of the extracts relates primarily to the pigment type [particularly the presence or absence of zinc oxide] rather than to the age of the samples, even where the age difference is up to 58 years. Non-water sensitive white (Flake White, Zinc White and Titanium White) and green paints (Cobalt Green), all of which contain zinc

oxide, cluster at positive values of PC1, which relates to the monocarboxylic acid content (see loading plot in Fig. 2). The extracts of coloured paints that do not contain zinc oxide (Burnt Umber, Cobalt Blue Deep, Cadmium Lemon, French Ultramarine, Oxide of Chromium, Rose Doré, Winsor Green) appear more closely related, and cluster toward more negative values of PC1, which is associated with a higher relative abundance of diacids. The ESI-MS mass spectra shown in Fig. 1 exemplify these trends; the extract of the non-water sensitive Zinc White (1973) paint has a relatively higher proportion of free short chain monoacids and a relatively lower proportion of diacids when compared with the Burnt Umber (1949) paint, which shows a relatively lower proportion of free short chain monoacids and a relatively high proportion of diacids.

The relationship with extenders is less clear, as seen in Table 1 magnesium carbonate, alumina white (hydrated aluminium oxide) and barium sulphate are commonly used by W&N, however, all of these extenders are found in paints that are associated with positive and negative values of PC1. For example, Titanium White paints contain barium sulphate and magnesium carbonate extenders, yet the chemical composition of their extracts and the values of the PCA scores are very similar

Table 3

Species detected by the different adopted analytical techniques.

Technique used	Species detected					
	Free fatty acids			Bound fatty acids		
	Free fatty acids including those originating from hydrolysed glycerides and hydrolysed metal soaps (excluding dicarboxylic acids)	Dicarboxylic acids	Fatty acids present in sample bound as metal soaps	Crosslinked fraction	Glycerides containing dicarboxylic acids	Full glyceride profile
GC-MS (Meth Prep II)	✓	✓	✓	✓/– ^a	✓/– ^b	✓/– ^b
ESI-MS (negative mode, direct injection, ethanol extracts)	✓	✓	–	–	✓	–
HPLC ESI-Q-ToF (positive mode, chloroform/hexane extracts)	✓	–	–	–	✓	✓

^a Unpolymerised carboxylic acids and dicarboxylic acids bound as glycerides, or present as a metal carboxylates are released after hydrolysis and are detected as free carboxylic acids and dicarboxylic acids in the GC chromatogram.

^b Intact glycerides are not detected, rather they are hydrolysed prior to analysis such that the carboxylic acids and diacids formerly bound as glycerides are present in the GC chromatogram.

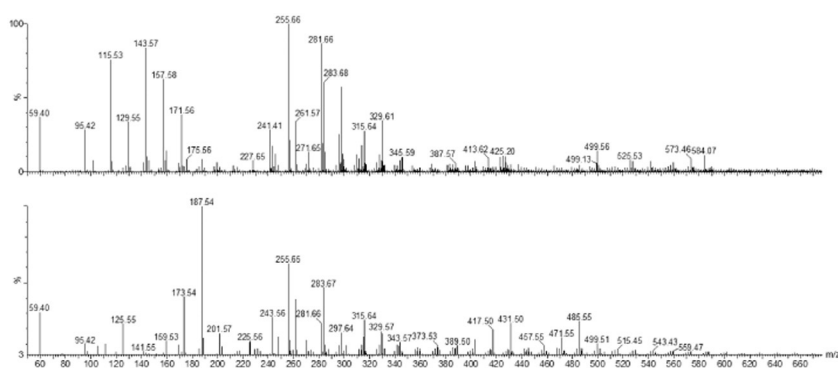


Fig. 1. ESI-MS mass spectra of the extracts of non-water sensitive Zinc White 1973 (top) and water sensitive Burnt Umber 1949 (bottom) W&N swatches. See Table 4 for attributions of the main ions.

to those of Flake White and Zinc White paints that do not contain any extenders. The Cobalt Green samples of all years were made with the same combination of extenders, yet only the samples containing zinc oxide, cluster toward positive values of PC1. Furthermore if Winsor Green is considered up until 1964 the paints only contained barium sulphate, afterwards magnesium carbonate is also used. Yet the Winsor Green paints are not clustering according to the extender type, indeed it is the two oldest samples which cluster closest together (1949, 1964). This suggests that these extenders do not exert a significant influence on the degree of hydrolysis and oxidation of the paints.

Examination of the loadings plot in Fig. 2 shows all of the water sensitive samples scoring at more negative values of PC1, which relates to a relatively higher content of diacid containing species. White paints, which are consistently non-water sensitive, and the non-water sensitive Cobalt Green paints, are associated with more positive values of PC1, which relates to relatively lower contents of diacid containing species. In fact all of these samples contained zinc oxide pigment as one of the main pigments in the paint formulation. As a general trend it is clear

that the pigment type is related to both the chemical profile of the paint and the incidence of water sensitivity (see Fig. 3).

Dicarboxylic acids and short chain monocarboxylic acids are both products of oxidation. Unsaturated fatty acids oxidise to form hydroperoxides, which may break down as a result of homolytic fission to form a peroxy radical. Beta scission of the peroxy radical, results in the formation a vinyl radical and an aldehyde species [27]. Subsequent oxidation of the vinyl radical or aldehyde species can yield either a diacid, a short chain monoacid, or a variety of other oxygenated compounds [27]. PCA analysis of the relative abundances of fragmentation ions ascribable to diacids containing species (m/z 159, 171, 173, 187, 201, 247, 261, 403, 417, 431, 471, 485, 499) and short chain monoacids (m/z 115, 129, 143, 157 and 159) highlights that the two groups are negatively correlated, showing that the two types of oxidation products are in competition (see loadings plot, Fig. 2). Short chain monocarboxylic acids have been detected in previous studies of aged lead soaps of unsaturated fatty acids [28]. Although their formation can be the result of beta scission reactions following from the oxidation of unsaturated acids, their anticorrelation in the PCA loading plot with dicarboxylic acids suggests

Table 4
The significant [M–H][−] ions present in ESI-MS negative mode mass spectra were identified. C_nx = monocarboxylic acid, with n carbon atoms, and x double bonds; diC_n = dicarboxylic acid with n carbon atoms; TAG, DAG, MAG = triglyceride, diglyceride, and monoglyceride respectively nDB = n number of double bonds in the alkyl chain, nO = n number of oxygen atoms in alkyl chain.

m/z	Attribution	Originating species	Species abbreviation
1	[C ₆ H ₁₂ O ₂ –H] [−]	Hexanoic acid	C6
2	[C ₇ H ₁₄ O ₂ –H] [−]	Heptanoic acid	C7
3	[C ₈ H ₁₆ O ₂ –H] [−]	Octanoic acid	C8
4	[C ₉ H ₁₈ O ₂ –H] [−]	Nonanoic acid	C9
5	[C ₇ H ₁₂ O ₄ –H] [−]	Heptanedioic acid (pimelic acid)	diC7
6	[C ₁₀ H ₂₀ O ₂ –H] [−]	Decanoic acid	C10
7	[C ₈ H ₁₄ O ₄ –H] [−]	Octanedioic acid (suberic acid)	diC8
8	[C ₉ H ₁₆ O ₄ –H] [−]	Nonanedioic acid (azelaic acid)	diC9
9	[C ₁₀ H ₁₈ O ₄ –H] [−]	Decanedioic acid (sebacic acid)	diC10
10	[C ₁₁ H ₂₀ O ₆ –H] [−]	Diacid-MAG	MAG(diC8)
11	[C ₁₆ H ₃₂ O ₂ –H] [−]	Hexadecanoic acid (palmitic acid)	C16
12	[C ₁₂ H ₂₂ O ₆ –H] [−]	MAG of azelaic acid	MAG(diC9)
13	[C ₁₈ H ₃₄ O ₂ –H] [−]	Octadecenoic acid (oleic acid)	C18:1
14	[C ₁₈ H ₃₆ O ₂ –H] [−]	Octadecanoic acid (stearic acid)	C18:0
15	[C ₁₈ H ₃₂ O ₃ –H] [−]	Epoxy octadecenoic acid and/or hydroxy octadecenoic acid	Epoxy-C18:1 and/or hydroxy C18:2
16	[C ₁₈ H ₃₄ O ₃ –H] [−]	Epoxy octadecanoic acid and/or hydroxy octadecanoic acid	Epoxy C18 or hydroxy-C18:1
17	[C ₁₈ H ₃₈ O ₄ –H] [−]	Dihydroxy octadecanoic acid	Dihydroxy-C18
18	[C ₁₈ H ₃₈ O ₅ –H] [−]	Trihydroxy octadecanoic acid and/or dihydroxy epoxy octadecanoic acid	Trihydroxy-C18:1
19	[C ₁₈ H ₃₂ O ₉ –H] [−]	DAG of x2 octanedioic acid	DAG (2diC8)
20	[C ₂₀ H ₃₄ O ₈ –H] [−]	DAG of octanedioic acid and nonanedioic acid	DAG (diC8 + diC9)
21	[C ₂₁ H ₃₆ O ₉ –H] [−]	DAG of x2 nonanedioic acid	DAG (2diC9)
22	[C ₂₆ H ₄₈ O ₇ –H] [−]	DAG of hexadecanoic acid and heptanedioic acid	DAG (C16 + diC7)
23	[C ₂₈ H ₅₂ O ₈ –H] [−]	DAG of hexadecanoic acid and octanedioic acid	DAG (C16 + diC8)
24	[C ₂₉ H ₅₄ O ₈ –H] [−]	DAG of hexadecanoic acid and nonanedioic acid	DAG (C16 + diC9)
25	[C ₃₁ H ₅₈ O ₈ –H] [−]	DAG of octadecanoic acid and nonanedioic acid	DAG (C18 + diC9)
26	[C ₃₁ H ₅₈ O ₁₀ –H] [−]	DAG of oxidised octadecanoic acid and nonanedioic acid	DAG (C18 + diC9 + 2O)
27	[C ₃₁ H ₅₆ O ₁₁ –H] [−]	DAG of oxidised octadecanoic acid and nonanedioic acid	DAG (C18 + diC9 + 1 DB + 3O)
28	[C ₃₀ H ₅₀ O ₁₃ –H] [−]	TAG of x3 nonanedioic acid	TAG(3diC9)

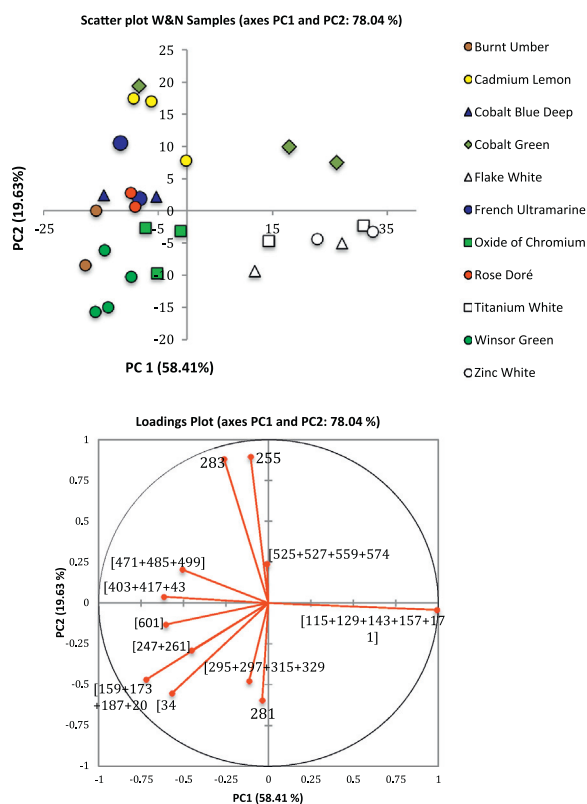


Fig. 2. Scatter plot W&N Samples (PC1 and PC2: 78.04% of total variance) and corresponding loadings plot (labelled with the ions of m/z assigned in Table 4) based on ESI-MS data is shown below (see Supplementary data, Table A.2 for the related ESI-MS data matrix used for the PCA analysis).

that their origin and mechanisms of formation warrants further investigation.

All the white W&N swatches (non-water sensitive) and non-water sensitive Cobalt Green paints contained either lead carbonate and/or zinc oxide (see Table 1) which are pigments that readily form metal soaps in oil [29]. These paints are characterised by a relatively low proportion of extractable diacids. Furthermore as the white paints contain a comparatively high proportion of extractable short chain monoacids (which, like diacids, are products of oxidative scission) this could

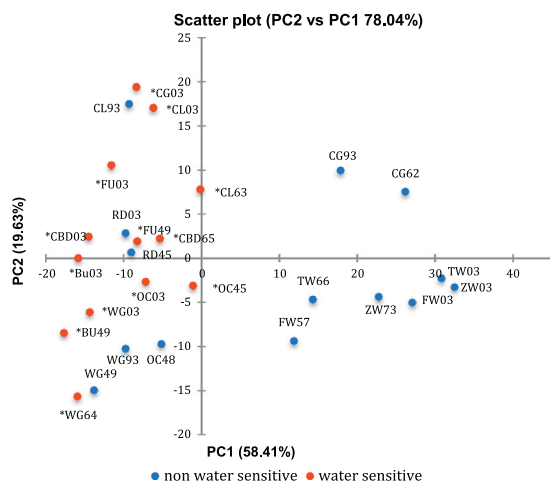


Fig. 3. Scatter plot W&N Samples (PC1 and PC2: 78.04% of total variance) based on ESI-MS data is shown below (see Supplementary data, Table A.2 for the related ESI-MS data matrix used for the PCA analysis). The scatter plot is the same as that shown in Fig. 2, but recoloured to show water sensitive and non-water sensitive samples, labels indicate the colour and year of each sample. FW57 = Flake White, 1957.

suggest preferential saponification of diacids over monoacids. Since diacids contain two carboxylic acid groups they are more likely to undergo saponification on at least one metal carboxylate group than an equivalent monoacid. Given that metal soaps are not soluble in ethanol, diacids are less likely to have been extracted than corresponding monoacids. Thus in the paints that are prone to the formation of metal soaps (i.e. lead carbonate and zinc oxide containing paints), the ethanol extract result would be likely to contain a higher proportion of monoacid species relative to diacid species. In paints that do not contain these reactive pigments it is therefore less likely that diacids species become under-represented in the ESI-MS mass spectra.

The metal soaps present in the non-water sensitive white paints are detected using FTIR as broad absorptions in the region $\sim 1650\text{--}1550\text{ cm}^{-1}$ [spectra not shown] which is characteristic of amorphous metal soaps present as an ionomeric network [30]. Although amorphous metal soaps were identified in all of the W&N samples using FTIR analysis (see Table 1) their relative abundance is significantly more intense in the non-water sensitive white paints [Flake White (1957), Titanium White (1966, 2003) and Zinc White (1973, 2003)]. The FTIR peak area ratio of the amorphous metal soap absorption band vs. carbonyl absorption band was calculated as a measure of the relative content of amorphous metal soaps (see Table 1) and was compared to the clustering observed in the PCA analysis (see Fig. 4). The non-water sensitive white paints containing lead and/or zinc white that are associated with more positive values of PC1 tended to contain the most intense amorphous metal soap absorption band indicating that these paints are likely to contain the most developed ionomeric network, which would presumably incorporate diacids and could account for their low extractability in these paints. This suggests that for lead and zinc white containing paints, the presence of ionomeric lead and zinc soaps (that are not soluble in water) may be contributing toward the stability and non-water sensitivity of these paints. However it was also apparent that for many water sensitive [Burnt Umber (1949), Cadmium Lemon (1963, 2003), Cobalt Blue Deep (1965), French Ultramarine (1949), Oxide of Chromium (1945)] and non-water sensitive samples [i.e. Cadmium Lemon (1993) Cobalt Green (1962, 1993), Oxide of Chromium (1948), Rose Doré (1945, 2003), Flake White (2003)] there was little apparent difference in the relative intensity of the amorphous metal soap absorption band (see Fig. 4). Further research is needed to explore possible quantitative relationships between the metal soap content of non-water sensitive and water sensitive paint samples, but these preliminary results tend to suggest that an extensive ionomeric network contributes toward the stability of the paint, but other factors, such as the degree of crosslinking, may influence the water sensitivity of a paint film.

However it is also possible that paints containing metal ions that promote cross-linking, contain polymerised dicarboxylic acids, which would also reduce the relative amount of dicarboxylic acids detected. As lead and zinc promote crosslinking [31], the enrichment of short chain monoacids in the white paints may also be due to these paints having a more highly crosslinked network which prevents or slows down evaporation of the short chain monoacids. Given that monoacids are more capable of migrating through a paint film than diacids owing to their comparatively lower molecular weight, they are also more likely to evaporate from the paint surface than diacids. Therefore in paints with a comparatively low degree of crosslinking, monoacids are more likely to have exited the paint film through a process of evaporation. Highly crosslinked paints may prevent this process by physically trapping short chain monoacids and preventing their evaporation. This could result in the more crosslinked paints appearing to contain a higher proportion of short chain monoacids and vice-versa.

It has to be stressed, though, that the ESI-MS spectra of non-water sensitive samples present lower signal-to-noise ratios (Fig. 1), indicating that water sensitive paints produce more highly concentrated ethanol extracts of the species listed in Table 4. This indicates that the major part of the non-cross-linked fractions of the non-water sensitive paints

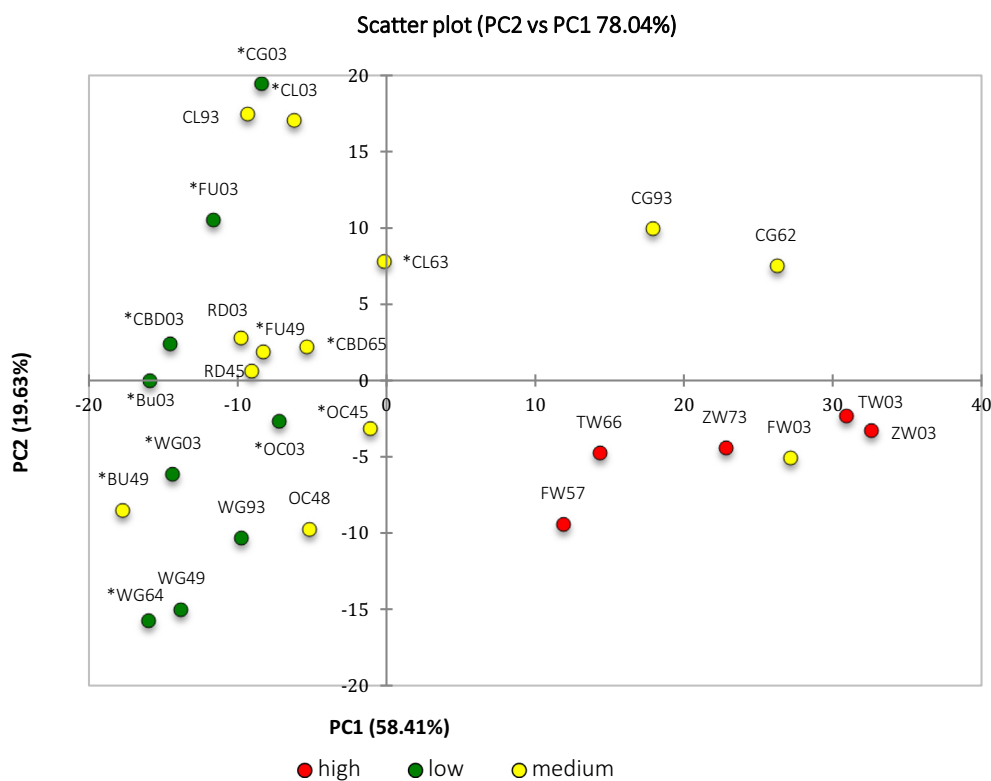


Fig. 4. Scatter plot of W&N Samples (PC2 and PC1: 78.04% of total variance) based on ESI-MS data. * indicates a water sensitive sample. The scatter plot is the same as that shown in Fig. 2, but is here re-coloured on the basis of the FTIR peak area ratio of amorphous metal soap absorption bands vs. carbonyl absorption bands [shown in Table 1]: red, high ratio (>3); yellow, medium ratio (1–3); green, low ratio (<1).

is saponified, and thus not extractable, which might account for the non-water sensitivity of these paints.

Water sensitive samples are generally associated with the diacid content and anti-correlated to the monoacid content (see loadings plot, Fig. 2) i.e. water sensitive samples contain relatively more extractable diacids¹ than non-water sensitive samples. Monocarboxylic and dicarboxylic acids all show similar pK_a values, but have different aqueous solubilities (Table 5). Diacids are more soluble in water than equivalent monoacids, given the presence of two polar carboxylic acid groups, rather than one polar carboxylic acid group, which confers additional polarity and solubility. For this reason paints that contain a high relative content of free diacids (i.e. generally the water sensitive samples) may be expected to be more vulnerable to water-induced swelling and solubilisation leading to the observed water sensitivity.

However it is important to note that the scatter plot shown in Fig. 3 also shows that some non-water sensitive samples do not follow this trend [Rose Doré (1949,2003), Winsor Green (1949, 1993), Oxide of Chromium (1948), Cadmium lemon (1993), all of which do not contain zinc white or lead white] are also associated with more negative values of PC1 i.e. a relatively higher content of diacids. This suggests that other factors such as degree of crosslinking, could be conferring extra stability to these paints. This merits further investigation.

The ratio of azelaic acid to palmitic acid (A/P) as determined using GCMS is widely used as a measure of the degree of oxidation in an oil paint film [17]. This is because diacids derive from the oxidation of unsaturated fatty acids. The azelaic acid: stearic acid ratio (A/S) may also be used as an indication of the degree of oxidation, but this ratio is also influenced by other factors, e.g. the addition of metal stearates.

Factors such as UV light exposure and the pigment content are known to influence A/P and A/S ratios [17]. For each W&N swatch the A/P, and A/S ratio of two samples taken from the surface of the paint and two samples taken from the paint below the surface (bulk) was determined. The results are shown in Table 6. As seen in Table 6, surface samples generally have a higher A/P and A/S GCMS ratios than bulk samples. However water-sensitive and non-water sensitive samples often had similar A/P and A/S ratios. This indicates that water sensitive paints are not necessarily more oxidised than non-water sensitive samples.

The relationship between the diacid content and water sensitivity in W&N swatches was further investigated using GC-MS. The chromatographic peak areas of palmitic, stearic and oleic acid, as well as C6-C10 diacids were obtained for each surface and bulk sample relating to each swatch and normalised to their sum. The data matrix of 8×108 variables (shown in Supplementary data, Table A.3) was analysed by PCA of the correlation matrix. The results are shown in Fig. 5. PCA analysis of GCMS data confirms clearly the previous observation, that surface samples tend to have a higher diacid content than bulk samples. This might be due to greater availability of oxygen at the paint surface - that is common to all samples - and that favours oxidation reactions. Another possible explanation is that diacids are more mobile [33] and tend to move to the paint surface. The scatter plot also highlights that Burnt Umber and Cobalt Blue samples which were water sensitive (both surface and bulk samples, of all years available) have the highest A/P ratios of all the samples. This suggests that these paints are the most highly oxidised and it is possible that this relates to the catalytic properties of the pigments, containing Co and Mn, respectively.

It should however be noted that the GCMS analysis did not identify a general tendency for water sensitive samples to have the highest A/P (and A/S) ratios (see Supplementary data, Fig. A.1). These data indicate that the overall degree of oxidation [with the exception of Burnt Umber and Cobalt Blue paints] does not appear higher in water sensitive paints.

¹ Ions of m/z 159, 171, 173, 187, 201, 247, 261, 403, 417, 431, 471, 485, 499.

Table 5
pKa of the main acids and diacids detected in the samples studied, and their related aqueous solubility values.

Category	Species	pKa (at 25 °C)	Aqueous solubility at 20 °C (mg/L) [32]	Aqueous solubility at 20 °C (mols/L) [32]
Short chain monocarboxylic acids	Hexanoic acid	4.85	9607.0	0.08270000
	Heptanoic acid	4.89	243.0	0.01870000
	Octanoic acid	4.89	679.5	0.00471200
	Nonanoic acid	4.96	259.9	0.00164300
	Decanoic acid	4.90	150.0	0.00087060
Dicarboxylic acids	Heptanedioic acid	4.71 (pKa1), 5.58 (pKa 2)	50,000.0	0.31220000
	Octanedioic acid	4.52 (pKa 1), 5.50 (pKa 2)	1565.0	0.00898600
	Nonanedioic acid	4.53 (pKa 1), 5.33 (pKa 2)	2400.0	0.01272000
	Decanedioic acid	4.59 (pKa 1), 5.59 (pKa 2)	1000.0	0.00494400
Saturated long chain fatty acids	Palmitic acid	4.75	7.2	0.00002808
	Stearic Acid	4.95	3.0	0.00001055

Table 6
GC–MS azelaic acid/palmitic acid (A/P) and azelaic acid/stearic acid (A/S) ratios for surface and bulk samples taken from W&N Swatches.

W&N swatch	Date	Water sensitive	Surface		Bulk	
			A/P	A/S	A/P	A/S
Burnt Umber	1949	Y	5.5	10.1	1.0	1.2
			3.0	4.1	1.7	2.4
Cadmium Lemon	1963	Y	4.5	10.0	1.9	3.7
			7.2	16.6	2.3	4.2
			2.2	9.2	0.4	0.9
Cobalt Blue Deep	1965	Y	8.1	14.2	1.1	1.9
			1.9	4.5	1.0	2.3
			2.1	4.2	1.7	2.4
			1.1	2.0	1.0	3.7
Cobalt Green	1962	N	1.3	5.2	0.9	2.9
			1.6	7.7	1.0	1.9
Flake White	1957	N	2.0	3.3	1.2	1.7
			1.9	2.7	1.0	1.2
			2.1	4.2	0.9	1.2
French Ultramarine	1949	Y	1.3	2.7	1.4	1.7
			0.7	2.3	0.7	1.6
Oxide of Chromium	1945	Y	2.1	4.5	1.2	2.1
			1.9	4.0	1.1	2.1
			1.9	7.3	0.6	1.6
Titanium White	1966	N	2.1	6.8	2.6	5.9
			2.5	8.7	2.1	5.6
			2.1	6.8	2.6	5.9
			1.3	5.2	0.9	2.9
Winsor Green	1949	N	1.6	7.7	1.0	1.9
			2.0	3.3	1.2	1.7
Zinc White	1973	N	1.9	2.7	1.0	1.2
			2.1	4.2	0.9	1.2
			1.3	2.7	1.4	1.7
			1.1	2.0	1.0	3.7
Zinc White	2003	N	2.5	8.7	2.1	5.6
			2.1	6.8	2.6	5.9
Zinc White	2003	N	1.3	5.2	0.9	2.9
			1.6	7.7	1.0	1.9
Zinc White	2003	N	2.0	3.3	1.2	1.7
			1.9	2.7	1.0	1.2
Zinc White	2003	N	2.1	4.2	0.9	1.2
			1.3	2.7	1.4	1.7
Zinc White	2003	N	1.3	2.7	1.4	1.7
			0.7	2.3	0.7	1.6
Zinc White	2003	N	2.1	4.5	1.2	2.1
			1.9	4.0	1.1	2.1
Zinc White	2003	N	1.9	7.3	0.6	1.6
			2.1	6.8	1.3	2.7
Zinc White	2003	N	2.1	4.3	1.4	1.8
			1.9	4.6	0.8	1.1
Zinc White	2003	N	1.2	3.5	1.4	2.8
			1.4	3.5	1.4	3.3
Zinc White	2003	N	2.3	3.3	1.3	1.8
			4.1	5.2	1.3	1.5
Zinc White	2003	N	2.2	5.3	1.9	3.2
			2.3	5.6	0.0	0.0
Zinc White	2003	N	1.2	4.8	0.8	3.0
			0.9	3.5	1.0	2.9
Zinc White	2003	N	1.7	3.9	1.2	2.3
			1.9	5.0	0.0	0.0
Zinc White	2003	N	3.2	4.4	1.5	2.2
			3.6	5.5	1.1	1.4
Zinc White	2003	N	2.5	4.4	1.7	3.8
			2.3	4.5	1.6	2.5
Zinc White	2003	N	1.4	2.7	1.2	2.3
			1.5	2.5	1.4	2.5
Zinc White	2003	N	1.3	1.8	1.3	2.4
			1.4	3.1	1.0	1.3
Zinc White	2003	N	0.0	0.0	0.7	11.5
			2.1	5.7	1.6	2.7
Zinc White	2003	N	1.6	4.0	1.0	2.2

It has to be taken into consideration, though, that the curing of the paints is not completely finished, as it was demonstrated by HPLC-ESI-Q-ToF analyses of the glycerides still present in the paint, discussed in the following paragraph.

3.3. HPLC-ESI-Q-ToF

In order to obtain a comprehensive picture of the lipid profiles of the paint layers, HPLC-ESI-Q-ToF analysis were performed. The triglyceride profiles of all the samples were characterised by the presence of PPO (*m/z* 855.7, [M + Na]⁺), OOP (*m/z* 881.7, [M + Na]⁺), OLS (*m/z* 907.7, [M + Na]⁺), PPS (*m/z* 857.7, [M + Na]⁺), OSP (*m/z* 883.7, [M + Na]⁺), OOO (*m/z* 907.7, [M + Na]⁺), PSS (*m/z* 885.7, [M + Na]⁺), OOS (*m/z* 909.7, [M + Na]⁺), OSS (*m/z* 911.8, [M + Na]⁺), SSS (*m/z* 913.8,

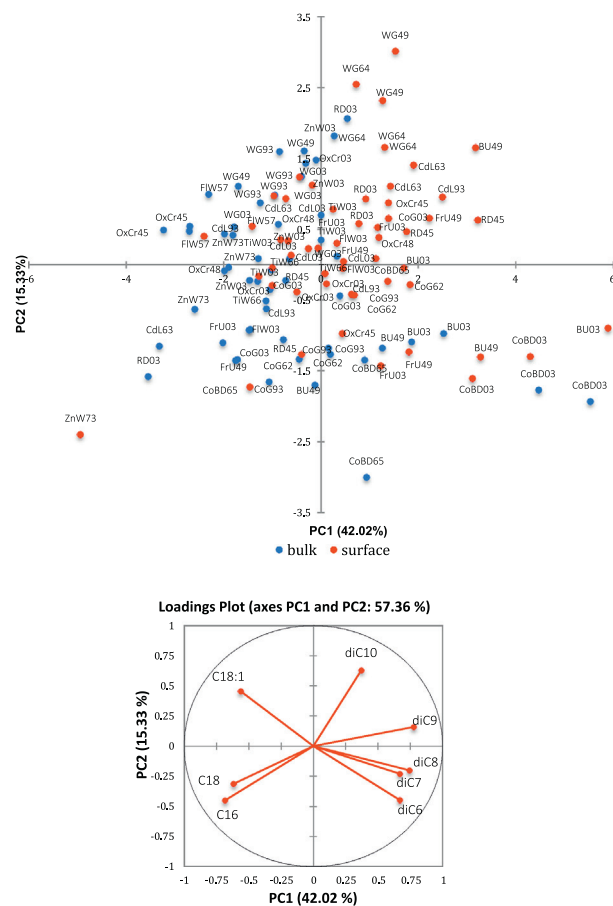


Fig. 5. Scatter plot (axes PC1 and PC2: 57.35% of total variance) and associated loadings plot of W&N surface and bulk samples based on GC–MS data (see Supplementary data, Table A.3 for the related data matrix used for the PCA analysis).

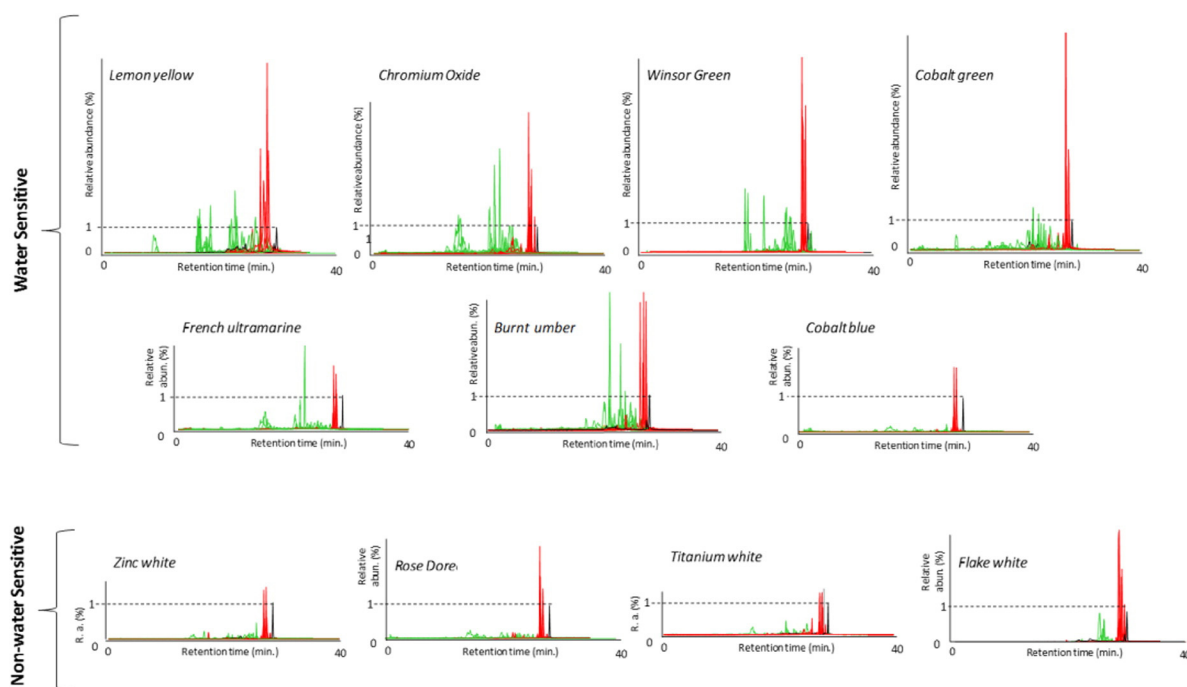


Fig. 6. Extract ion chromatograms obtained in the HPLC-ESI-Q-ToF analysis of W&N samples from 2003. Red line: TAGs; green line: oxidised DAGs and TAGs. Intensities have been rescaled to a fixed intensities of the peak of tristearin (black line).

$[M + Na]^+$, $ArSO$ (m/z 939.8, $[M + Na]^+$), and $ArOO$ (m/z 937.8, $[M + Na]^+$), as main surviving triglycerides.² As far as oxidised species are concerned, the lipid profiles were characterised by the presence of diglycerides and triglycerides containing hydroxylated fatty acids as acyl substituents (OxDAGs and OxDAGs).

In detail the main OxDAGs were $OC_{18:1(OH)}$, (m/z 659.5, $[M + Na]^+$), $SC_{18:1(OH)}$ (m/z 661.5, $[M + Na]^+$), $SC_{18(OH)}$ (m/z 663.5, $[M + Na]^+$), $SC_{18:1(2OH)}$ (m/z 677.5, $[M + Na]^+$), and $SC_{18(2OH)}$ (m/z 679.5, $[M + Na]^+$). The main OxDAGs were $POC_{18:2(OH)}$ (m/z 895.7, $[M + Na]^+$), $POC_{18:1(OH)}$ (m/z 897.7, $[M + Na]^+$), $PC_{18:2(OH)C_{18:2(OH)}}$ (m/z 909.7, $[M + Na]^+$), $PC_{18:1(OH)C_{18:2(OH)}}$ (m/z 911.7, $[M + Na]^+$), $PC_{18:1(OH)C_{18:1(OH)}}$ (m/z 913.7, $[M + Na]^+$), $PC_{18:1(OH)C_{18(OH)}}$ (m/z 915.8, $[M + Na]^+$), $PC_{18(OH)C_{18(OH)}}$ (m/z 917.7, $[M + Na]^+$), $OOC_{18:2(OH)}$ (m/z 921.8, $[M + Na]^+$), $OOC_{18:1(OH)}$ (m/z 923.8, $[M + Na]^+$), and $OOC_{18(OH)}$ (m/z 925.8, $[M + Na]^+$). Among these, the OxDAGs with m/z 895.7, 909.7, 911.8, and 913.8 together with OOP, POP and OSP can be related to the presence of linseed oil, while the oxidised species with m/z 915.8, 921.8, 923.8, 925.8, and the TAGs OOO, OOS, ArSO, AOO were characteristic of safflower oil. This indicates that all samples contained a mixture of linseed oil and safflower oil. This suggests that water sensitivity does not appear to be dependant to the nature of the paint binder.

The hydroxyl moieties in TAGs and DAGs are generated during autooxidative radical chain reactions taking place during curing, and in particular hydroxylated fatty acids are relatively stable intermediate reaction products, which may, with time, lead to both cross-linking (via formation of C—O—C bonds) or to further oxidation (via formation of an aldehyde moiety, which further oxidises to an acidic moiety).

As the molecular composition of a mature paint is dependent on several factors, among which time plays a fundamental role, we decided to perform a semiquantitative comparison of the chromatograms of all the paints that were prepared in 2003. Assuming that the rate of hydrolysis of hydroxyl triglycerides is the same as triglycerides containing saturated and unsaturated acyl substituents, all the chromatograms were

normalised to the peak of tristearin (SSS) in order to perform a semi-quantitative comparisons of the various chromatographic profiles.

Chromatograms (Fig. 6) clearly show that water sensitive paints exhibit a relatively high content of unsaturated and hydroxylated containing TAGs and DAGs.³ This seem to indicates that water sensitive paints are less cured than non-water sensitive paints, suggesting that water sensitivity might be related to the fact that the paint has not sufficiently cross-linked.

Samples Flake White 2003, Titanium White 2003, Zinc White 2003, and Winsor Green 2003 all contained castor wax, as could be inferred by the presence of 2,3-di(12-hydroxy-octadecanoyloxy)propyl 12-hydroxy octadecanoate in the chromatograms (data not shown) [34]. Clearly there is no relationship between the presence of such paint additive (castor wax is a rheology modifier), and water sensitivity, as all white samples were non-water sensitive, while Winsor Green 2003 was water sensitive, despite these all containing castor wax.

4. Case study paintings

ESI-MS negative mode data relating to the samples taken from the case study paintings was explored using PCA. The intensity of all m/z listed in Table 4 were normalised to their sum and the data matrix of 29×84 variables (shown in Supplementary dataTable A.4) was analysed by PCA of the correlation matrix. The resulting scatter and loadings plots are shown in Fig. 7.

Whilst there is not a complete separation between water sensitive and non-water sensitive samples based on the ESI-MS data only, there is a cluster of predominantly water sensitive samples associated with positive values of PC1 (Fig. 7). The wider distribution of the remaining samples largely relates to differences associated with PC2. The more positive values of PC1 correlate to the diacids/diacid containing species. In order to determine if the clustering observed related to pigment type and/or the painting that each sample was from, the scatter plot shown in Fig. 7 was coloured to show the painting that each sample was taken from (Fig. 8) and the main pigment in each sample (Fig. 9).

² Triglycerides are named according to the following fatty acid abbreviations: P: palmityl (C16:0); O: oleyl (C18:1); S: stearyl (C18:0); Ar: arachidyl (C20:0). Cn:m (aOH): fatty acid with n carbons, m saturations and a hydroxyl moieties.

³ The only exception is represented by cobalt blue paint.

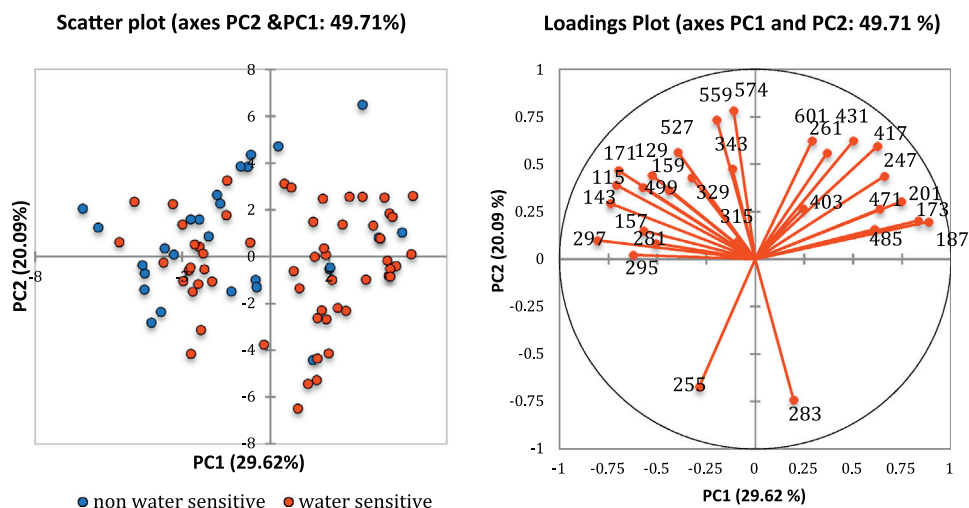


Fig. 7. PCA scatter and loadings plot of ESI-MS negative mode data of samples taken from paintings. Labels on the loadings plot are the *m/z* listed in Table 3.

With reference to Fig. 8 it can be seen that whilst there is some degree of clustering of the samples taken from the Auerbach painting (no. 1 in legend, see Table 2), samples taken from the other paintings seemed reasonably dispersed i.e. the samples do not cluster according to the painting they were taken from.

Of the case study paintings examined, the following paints were often water sensitive: iron oxide (Fe_2O_3), Prussian blue ($\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$), ultramarine ($\text{Na}_{8-10}\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_{2-4}$), cadmium yellow (CdS), chrome yellow (PbCrO_4) and cadmium orange ($\text{CdS} + \text{CdSe}$). The behaviour of cadmium red ($\text{CdS} + \text{CdSe}$) paints was more inconsistent, as in some cases it was water sensitive, in other cases it was non-water sensitive. This could not be explained through consideration of

other components of the cadmium red paints. Only two of the non-water sensitive cadmium red paints contained admixtures of lead white [Ethel Walker, sample 4], and titanium white with zinc oxide [Ray Parker, sample 4] that could have prevented water sensitivity. As was seen with the W&N swatches, lead white ($2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$), and zinc white (ZnO) containing paints of the case study paintings were always non-water sensitive. This trend confirmed that the main influence in determining the water sensitivity of the paint layer is exerted by the type of pigment, as was observed in the paint swatches. Of course the samples taken from case study paintings feature a wider range of variability given the greater variation in parameters such as sample age, painting technique, artists' choice of

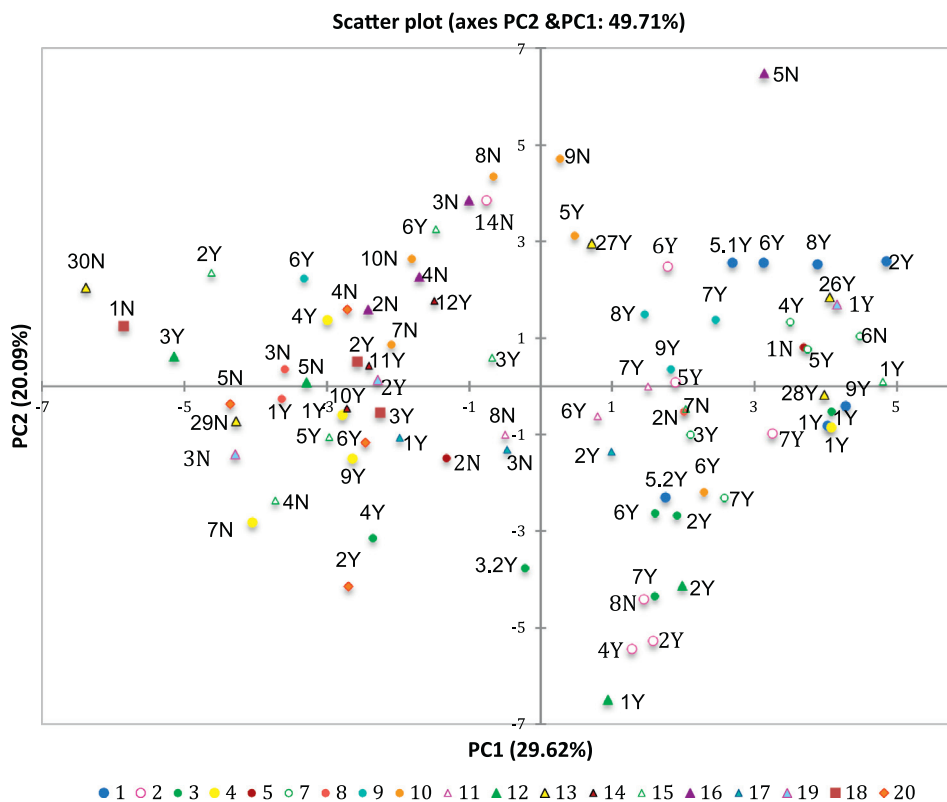


Fig. 8. PCA scatter plot of ESI-MS negative mode data of samples taken from paintings. The scatter plot is the same presented in Fig. 7 but coloured to allow identification of the painting that each sample was taken from; the numbered legend corresponds to the paintings numbered in Table 2. The labels adjacent to each data point are the given sample numbers (see Supplementary data for composition of each sample), with water sensitive (Y) and non-water sensitive samples identified (N).

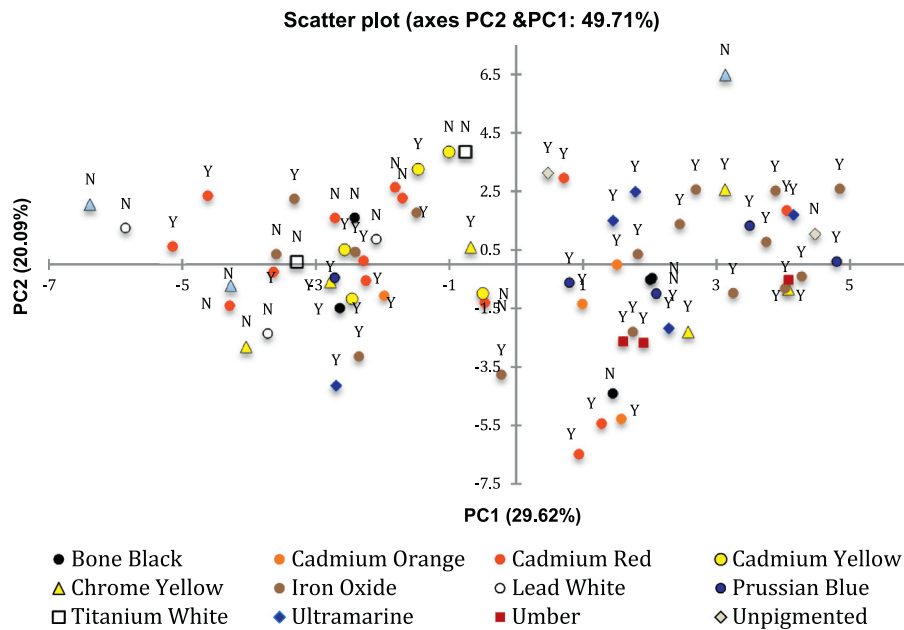


Fig. 9. This figure shows the same scatter plot as in Fig. 7 but coloured to show the main pigment present in each sample taken from the case study paintings. The labels indicate whether each sample was water sensitive (Y) or non-water sensitive (N).

materials and environmental conditions. Therefore it may be expected that the effect of pigment is relatively less evident than in the W&N swatches. Fig. 9 and the related loadings plot presented in Fig. 7 show that although there is no distinctive clustering according to pigment type, as was seen with the Winsor & Newton samples, there were some identifiable trends.

Iron oxide, burnt umber, and ultramarine paints tend to cluster toward more positive values of PC1, where mainly water sensitive samples are located (Fig. 7). This suggests these paints, contain a higher proportion of diacid/diacid containing species in the extractable fraction (refer to loadings plot, Fig. 7). Cadmium red and cadmium yellow pigments tend to cluster toward negative values of PC1, suggesting

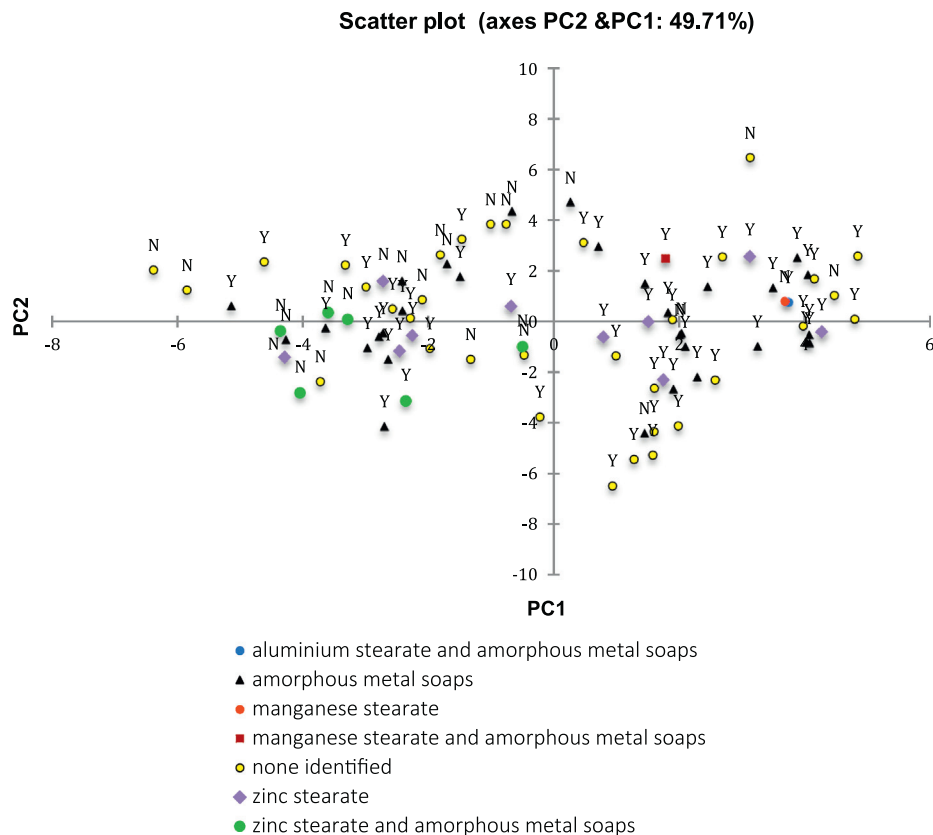


Fig. 10. This figure shows the same scatter plot as in Fig. 7 but coloured to show the metal soaps identified using FTIR in each sample taken from the case study paintings. The labels indicate whether each sample was water sensitive (Y) or non-water sensitive (N).

that for water sensitive paints made with these pigments the cause of water sensitivity isn't related to the content of extractable diacids. As with the W&N samples non-water sensitive lead white, titanium white and zinc white paints (all containing reactive lead white and/or zinc white pigments) also tend to cluster toward negative values of PC1, which is again anticorrelated with most diacid species.

As previously stated the non-water sensitivity, and low extractability of diacids in the case of zinc and lead containing white paints can be related at least in part, to metal soap formation. Amorphous metal soaps (where the metal cation was not specifically identified) indicating an ionomeric network [30] were frequently observed as a broad band between $\sim 1650\text{--}1550\text{ cm}^{-1}$ in the FTIR spectrum of samples taken from paintings. As was observed in the W&N swatches amorphous metal soaps were found in both non-water sensitive and water sensitive paints, including in those samples that did not contain lead or zinc ions according to SEM-EDX analysis (refer to Supplementary data, Table A1). Amorphous zinc soaps have been shown to exhibit a broad infrared absorption band with a maxima at 1590 cm^{-1} [35], but further research is

required to identify the presence of amorphous metal soaps likely based on other metal cations in samples from paintings that contain complex inorganic mixtures. Crystalline zinc soaps with a sharp absorption at 1540 cm^{-1} were frequently identified in non-water sensitive and water sensitive samples from paintings; these may be present as paint additives, or may have formed in situ. Aluminium stearate and manganese stearate (which are both insoluble in water) were each identified in one sample only. No other crystalline metal soaps were identified using FTIR although it is possible that these may be present below the detection limit: metal soap additives are typically used at levels $<5\%$ w/w by commercial artists' oil paint manufacturers [36]. As with the W&N swatches, water soluble metal soaps based on an alkali metal cations were not identified using FTIR in any of the samples taken from paintings. There appears to be no correlation between the type of metal soaps identified using FTIR and the incidence of water sensitivity, or the clustering observed in the paint samples (see Fig. 10). However as was seen in the W&N paint samples, it was clear that for non-water sensitive lead and zinc white paints, the amorphous metal soap band was

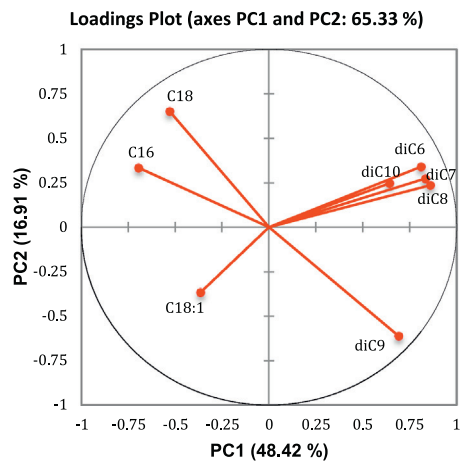
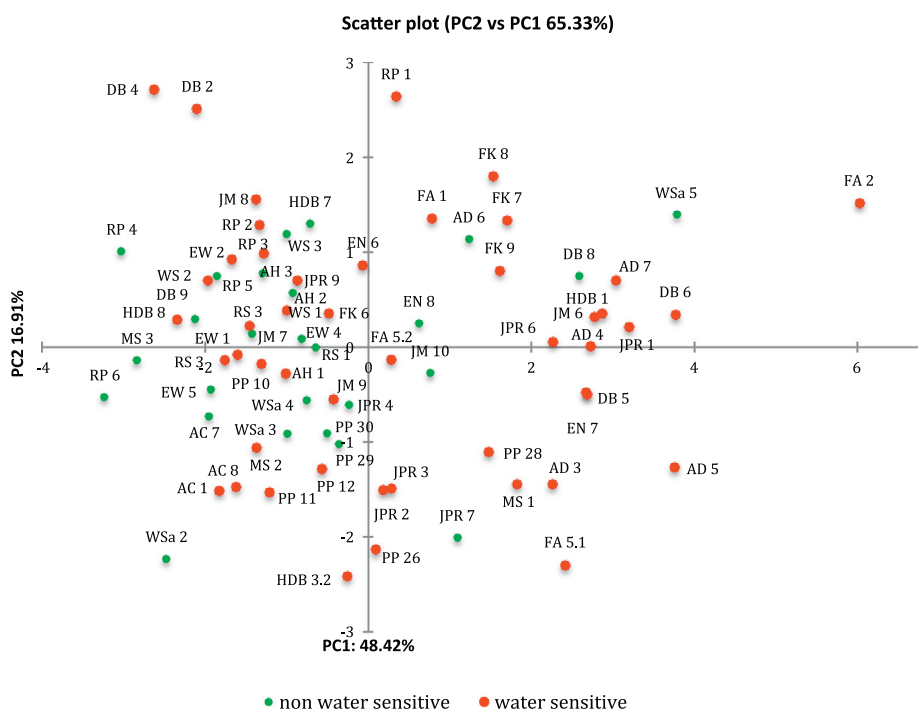


Fig. 11. PCA scatter plot of GC–MS data of samples from paintings (axes PC2 and PC1: 65.33%) with corresponding loadings plot. Samples have been labelled with artist name and sample number: FA = Frank Auerbach, DB = Derek Boshier, HDB = Dorothy Brett, AD = Alan Davie, AH = Adrian Heath, FK = Ferdinand Kulmer, JM = Joan Mitchell, EN = Emile Nolde, RP = Ray Parker, PP = Pablo Picasso, JPR = Jean-Paul Riopelle, WSa = Wilhelm Sasnal, WS = William Scott, MS = Matthew Smith, RS = Richard Smith, EW = Ethel Walker.

typically far more prominent than in amorphous metal soap band in other colours, confirming the hypothesis discussed above. This suggests that there could be a quantitative relationship between amorphous metal soap formation that is largely the result of pigment-medium interactions and water sensitivity i.e. paints that have a more developed ionomeric network would be expected to be less vulnerable toward solvents such as water.

GC–MS results which provide a measure of the total lipid content were investigated to determine how the ESI-MS observations may relate to the degree of oxidation. The peak areas of palmitic, stearic and oleic acid, as well as diacids (diC6–diC10) present in GC–MS chromatograms were used to investigate the samples from paintings using PCA. The peak areas were normalised to their sum and the data matrix of 8×75 variables (shown in Supplementary data, Table A.5) was analysed by PCA of the correlation matrix. The resulting scatter plot and loadings plot are shown in Fig. 11.

As with the W&N swatches GCMS A/P ratios for samples taken from paintings (GCMS ratios for case study paintings are shown in Supplementary data, Table A.6) were often similar for water sensitive and non-water sensitive paint samples and indeed Fig. 11 shows that for many water sensitive and non-water sensitive samples there is no separation according to the content of diacids. Although most non-water sensitive paints present negative values of PC1. Again, among those samples presenting a positive value of PC1, the large majority were water sensitive. Positive values of PC1 are associated with a relatively higher content of dicarboxylic acids. Interestingly of these 23 water sensitive samples with a positive value of PC1, 14 were paints that contained either iron oxide pigments or ultramarine paints, or blends of the two, indicating that these paints are more oxidised [contain more diacids] than other samples. This is entirely consistent with the behaviour of iron oxide and ultramarine samples taken from the W&N swatch samples, and suggests a consistent pattern of behaviour that is dictated largely by the pigments. This might be explained by suggesting that ultramarine and iron oxide pigments promote oxidative scission. Since both earth and ultramarine pigments have a long history of use in oil paintings, and only a recent association with water sensitivity, it might also be hypothesised that the significantly reduced particle size of modern pigments that are often nanosized [37], may result in enhanced catalytic properties of these pigments, thus enhancing their oxidative action. Given that oxidative scission is in competition with crosslinking [7], it is likely that ultramarine and iron oxide paints are poorly crosslinked. Indeed iron oxide paints are associated with poor mechanical strength and a vulnerability toward leaching of mobile components [31] which is consistent with a low degree of crosslinking. A high content diacids makes for a polar paint film that may be particularly susceptible to swelling and extraction in response to water, especially when associated with a poor degree of crosslinking.

5. Conclusions

Water sensitivity may be caused in some cases by epsomite formation [8], or by the presence of physically underbound paints [7]. Therefore it is possible that these factors, which were not taken into consideration, are contributing toward the water sensitivity in some of the paints. Despite this, the present study has demonstrated the presence of strong relationship between water sensitivity and pigment type: paints formulated with zinc oxide and/or lead white: Lead White, Titanium White, Zinc White, and Cobalt Green were consistently non-water sensitive. Zinc oxide and lead white are pigments that readily form metal soaps in oil [29] and catalyse polymerisation [31]. Indeed these paints were characterised by a strong amorphous metal soap absorption indicative of a well developed ionomeric network which suggests that metal soap formation and degree of polymerisation must play a fundamental role in determining the non-water sensitivity of paints containing these pigments.

Through the chemical characterisation of a wide number of paint samples it has been possible to demonstrate that there are likely to be two different causes of water sensitivity that relate to the composition of the binding medium: in some paints, as in the case of iron oxide and ultramarine paints, water sensitivity may relate to enhanced oxidation [oxidative scission], which is likely to be related to a low degree of crosslinking (as the two phenomena are competitive). In these cases, we can hypothesise that a low degree of crosslinking coupled with heightened polarity (owing to the heightened oxidation) and a possible lack of metal soap formation, results in a paint film that is physically vulnerable and prone to water-induced swelling. In other cases water sensitivity appears to relate to the proportion of extractable diacids (i.e. a lack of saponification and/or a high degree of hydrolysis and low degree of polymerisation) but not the general degree of oxidation of the paint. Water sensitivity could then be due to several factors. Short chain diacids are slightly water soluble. As a consequence, a sample rich in relatively high amounts of free [unbound and non-saponified] dicarboxylic acids (that are more water soluble than monocarboxylic acids), may be water sensitive via a swelling mechanism. In the same way, if the degree of hydrolysis is low, or dicarboxylic acids are saponified, and the paint is well polymerised, then the paint is less likely to be water sensitive.

The processes involved in paint curing (oxidation and polymerisation), including their dependence on the pigment and the possible particle size, as well as hydrolysis and saponification, all appear to play a fundamental role (alone, or in combination) in determining the water sensitivity of modern oil paints, and further research is necessary to shed more light on these aspects.

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Supplementary data

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