

AN FTIR-BASED EXPLORATION OF THE EFFECTS OF WET CLEANING TREATMENTS ON ARTISTS' ACRYLIC EMULSION PAINT FILMS

TECHNICAL PAPER

Bronwyn Ormsby¹, Elina Kampasakali¹, Costanza Miliani²,
Tom Learner³

This paper is based on a presentation at the 8th international conference of the Infrared and Raman Users' Group (IRUG) in Vienna, Austria, 26-29 March 2008.

Guest editor:
Prof. Dr. Manfred Schreiner

1. Conservation Department, Tate,
London, U.K.

2. Istituto CNR Scienze e Tecnologie
Molecolari (CNR-ISTM), University of
Perugia, Perugia, Italy

3. Getty Conservation Institute, Los
Angeles, USA

corresponding author:
bronwyn.ormsby@tate.org.uk

Understanding changes to acrylic emulsion paint films during wet surface cleaning treatments is a priority for conservators of modern painted surfaces. To explore the presence, extraction and removal of soluble components from acrylic paint films, contemporary paint samples and works of art were examined using several FTIR-based techniques including: transmission microscopy, attenuated total reflectance (ATR) and *in-situ* non-invasive mid-IR reflectance spectroscopy. The major constituents identified on paint surfaces and extracted from bulk films were non-ionic polyethoxylate (PEO) type surfactants used as dispersing agents and emulsion stabilisers. The identification of other extracted constituents was hampered by low concentrations and the proprietary nature of many additives. Surface surfactant was removed within five to twenty seconds by aqueous swabbing treatment, by accelerated light ageing, and was relatively unaffected by aliphatic solvents. Monitoring of contemporary paint films after aqueous cleaning treatment confirms that surfactant continues to migrate to the surface. The analysis of contemporary paint films suggests surface surfactant abundance is primarily influenced by brand. Combined results from the *in-situ* analysis of five paintings dating between 1962 and 1973 confirmed the presence of surfactant on some paint layers and not others.

1 Introduction

Research into acrylic emulsion artists' paints has confirmed that non-ionic polyethoxylate-type (PEO) surfactants exude to the surface of acrylic emulsion paint films as small rounded crystals and/or coherent thin films.¹⁻³ These surfactants, such as the Triton series, were invented in the 1930s and have been used as wetting agents and stabilisers in emulsion formulations since the early 1960s.⁴ These materials remain the most IR-detectable compounds both on the surface and within aqueous extracts of acrylic emulsion paints. The presence of Triton X-405 (a non-ionic octylphenol ethoxylate surfactant) has

received: 30.06.2008
accepted: 10.05.2009

key words:
Painting, surfactant, FTIR, *in-situ*, spectroscopy, conservation

been confirmed in conjunction with other aqueous extractable materials such as preservatives via liquid chromatography-mass spectrometry⁵ and other mass spectrometry techniques.⁶⁻⁸ Triton X-405 and X-305 have also been identified via electrospray ionisation mass spectrometry in extracts from cotton swabs wetted with deionised water and rolled over the surface of several acrylic emulsion paintings.⁹

The presence of surfactants on the surface of acrylic emulsion paint films is of interest to conservators for several reasons: surfactant is original material to these paints; surface accumulation causes changes in gloss and surface unevenness; surfactant layers contribute to the retention of surface dirt through mechanical and hygroscopic interactions; PEO-type surfactants have proven to be readily water-soluble; and research into the short- and long-term consequences of surfactant removal on underlying paint layers is ongoing. Despite the growing body of evidence demonstrating that changes to the physical and optical properties of acrylic emulsion paints induced by aqueous conservation treatments are minimal or perhaps even beneficial,^{1,3,10-12} the presence of surface surfactant may also be associated with other cleaning process issues such as paint swelling, pigment removal and water-sensitivity.¹³

The migration of surfactant(s) to the surface of acrylic emulsion paint films is acknowledged by artists' paint manufacturers. For example Golden Artist Colours have explored the presence as well as the effect of surfactant migration and removal on several of their paint films.^{12,14} The migration of surfactants in unpigmented acrylic polymer dispersion films has also been well documented in the latex polymer field.^{15,16} One response to prevent surfactant migration is to incorporate the use of chemically bonded or cross-linked surfactants that are therefore (at least theoretically) unable to migrate to the surface; however, these materials have thus far not been adopted by the artists' paint industry due to their prohibitive cost.¹²

The occurrence and behaviour of surface surfactant on acrylic emulsion paint films has been explored as part of ongoing collaborative research at Tate, London. A series of contemporary acrylic emulsion artists' paint films were prepared in 2003 and have been subsequently monitored using infrared-based techniques after natural ageing; exposure to accelerated ageing, and simulated cleaning and solvent extraction treatments. While the investigation of contemporary paint films is essential to explore the conservation and preservation issues surrounding these paints, the surfaces of works of art also need to be examined -

and particularly as paint formulations have been (and continue to be) subject to frequent change. For this, a group of five paintings in Tate's collection dating from 1962-1973 were monitored for the presence and subsequent removal of surface surfactant during wet-cleaning treatments, including surface analysis via *in-situ* non-invasive reflectance spectroscopy made available through transnational access MOLAB.

2 Experimental

2.1 Samples

2.1.1 Contemporary Paints

Paint films were cast from professional grade artists' acrylic emulsion paints - encompassing the two main copolymers used in acrylic emulsion paints: butyl acrylate/methyl methacrylate *p*(BA/MMA) and ethyl acrylate/methyl methacrylate *p*(EA/MMA). Four paint brands: Winsor and Newton, Talens, Liquitex and Golden; and four pigments were used: titanium white (PW6); as well as azo yellow (PY3) and phthalocyanine green (PG7) as examples of synthetic organic pigments; and burnt umber (PBr7) which may contain more surfactant to aid pigment suspension. Films were cast onto Teflon-coated stainless steel plates and 10 ounce acrylic pre-primed cotton duck canvas pieces using a Sheen instruments adjustable film caster to a dry film thickness of $110 \pm 20 \mu\text{m}$. The dried films were stored in dark ambient conditions and had between 4 and 52 months drying time prior to analysis. Identification of the copolymer type, extenders and pigments present in each of the paints was carried out using Pyrolysis Gas Chromatography - Mass Spectrometry (Py-GC/MS), μ -FTIR spectroscopy, Energy Dispersive X-ray analysis (EDX) and Direct Exposure-Mass Spectrometry (DE-MS) the details of which have been published elsewhere¹ or contained in Table.

2.1.2 Accelerated Ageing

A sub-set of samples were thermally aged in a Fisons 185 HWC environmental oven (60 °C; 55% RH) for 16 weeks. Others were light aged at 15,000 lux for 16 weeks under Philips TLD 58W/840 daylight tubes with the UV component filtered by Perspex. Assuming reciprocity, this is equivalent to ~50 years exposure under normal museum conditions, hence approximating the age of the case study paintings examined.

2.1.3 Paintings

Five acrylic emulsion paintings on canvas were examined as case studies for the Tate AXA Art Modern Paints Project (TAAMPP) including: Jeremy Moon's *Untitled 2/72* (1972) and *Hoop-la* (1965), Andy Warhol's *Portrait of Brooke Hayward* (1973), Alexander Liberman's *Andromeda* (1962); one of the earliest acrylic paintings in Tate's collection and John Hoyland's *24.5.69* (1969). With the exception of the Warhol painting - where the priming and silkscreen ink areas were identified as oil modified alkyd media - all paints were identified as p(EA/MMA) copolymers, as listed in Table 1. Between them, the following pigments were identified: titanium white; cadmium red and yellow; cobalt blue; Mars red and black; umber; chromium oxide and the extenders calcium carbonate, calcium sulphate and barium sulphate. In addition, several synthetic organic pigments were identified via FTIR microscopy and/or Direct Exposure-Mass

Spectrometry (DEMS) as: PV19, PV23, PB16, PR3, PR122, PR181, PR207, PY3, and PV23.

2.2 Sample Preparation

2.2.1 Solid paint extracts

Samples of the same size and shape were removed from the contemporary paint films and subjected to 24 h, 20 µL deionised water extractions in glass vials. The extracts were then pipetted onto clean cavity slides to dry in dark, dust free conditions. Representative scrapings from each sample were analysed via transmission µ-FTIR spectroscopy.

2.2.2 Paint surface extracts

Aqueous surface extracts of contemporary paint films and paintings were prepared by pipetting 40-

Artist and Title	Paint sample description (colour)		Pigments identified	Extenders identified	Paint medium
Moon <i>Hoopla</i>	Red		Cadmium red	BaSO ₄	EA/MMA
	Blue		PB16	BaSO ₄	
Moon <i>Untitled 2/72</i>	Orange		Cadmium orange	BaSO ₄	EA/MMA
	Pink		PV19, Ti white		
Warhol <i>Portrait of Brooke Hayward</i>	Blue canvas	Blue	Cobalt blue, Ti white	CaSO ₄	EA/MMA
		Pink	PR122?, Ti white	CaSO ₄	EA/MMA
	Pink canvas	Dark pink	PR207, Ti white	CaSO ₄	EA/MMA
		Light pink	Organic red, Ti white	-	EA/MMA
		Silk screen	Carbon black, silica	-	Alkyd
	Green canvas	Aqua green	Unidentified green, Ti white	-	EA/MMA
		Yellow green	Cadmium yellow, chrome oxide, Ti white	CaSO ₄	EA/MMA
		Pink	PR207, Ti white	-	EA/MMA
		Priming	Ti white	CaSO ₄	Alkyd
	Yellow canvas	Yellow	Cadmium yellow, Ti white	BaSO ₄	EA/MMA
		Pink	PR122, Ti white	-	EA/MMA
		Orange	Cadmium yellow, PR122, Ti white, Mars red	BaSO ₄ , Chalk	EA/MMA
		Silk screen	Carbon black, silica	-	Alkyd
		Priming	Ti white	CaSO ₄	Alkyd
Liberman <i>Andromeda</i>	Dark green		Chrome green and Mars black	-	EA/MMA
	Dark purple		PV23 + PR181	CaSO ₄	
	Violet		PV23 + PR181 Ti white	-	
	Black		Mars black	-	
Hoyland <i>24.5.69</i>	Umber		Burnt umber	BaSO ₄ , Chalk	EA/MMA
	Fe oxide red		Iron oxide	BaSO ₄	
	Mid red		Cadmium red	BaSO ₄	
	Mid green		PY3, unidentified blue pigment	BaSO ₄	
	Scarlet red		PR3 and Cadmium red	BaSO ₄	
	Cadmium red		Cadmium red	BaSO ₄	

Table 1: Pigment and medium content of five case study acrylic emulsion paintings in Tate's collection; via FTIR microscopy, EDX, PyGCMS and DEMS analysis.

60 µL deionised water directly onto paint surfaces and leaving the water to extract for one to 2 min. The extract was then transferred, dried and analysed as described above.

2.2.3 Cleaning simulation

Contemporary paint samples were subjected to up to 1 min swab rolling treatments with one or more of the following wet systems: deionised water; 0.5% v/v. Triton X-100/XL-80N®; 1% w/v. triammonium citrate (TAC); 2% v/v. ethanol solution; Stoddard solvent (18% aromatic content) or 60-80/80-100 BP mineral spirits. Those samples requiring clearance were also swab rolled with deionised water for 10 s.

2.2.4 In-situ analysis

The paintings *Portrait of Brooke Hayward*, *Andromeda* and *25.4.69* were examined using the *in-situ* mid-IR reflectance system (described later). Analysis areas were chosen to include a single paint and a Mylar template was used to guide the reflectance probe to the same location after cleaning. Cleaning sites were photographed and x-y locations noted. Each test area was exposed to a 15s cotton swab roll with deionised water and/or 80-100 BP mineral spirits. Cleaned surfaces were left to air dry and after treatment data collected. It was noted that in most cases the cleaned area was visible in raking light due to the removal of soiling and surface surfactant.

2.3 Instrumentation

2.3.1 µ-FTIR Spectroscopy

For transmission mode collection a Nicolet Avatar 360 spectrometer was used with a single diamond cell and a Thermo-Nicolet Spectra Tech IR plan microscope; spectra were collected over 128 scans at 4 cm⁻¹ resolution, between 4000 and 600 cm⁻¹.

2.3.2 Attenuated Total Reflectance (FTIR-ATR)

For ATR analysis, a Germanium ATR crystal attachment was used with the Nicolet Avatar 360 spectrometer and the number of scans increased to 200. All ATR results presented are semi-quantitative due to the repeatable pressure achievable with the ATR unit used. At ~2000 cm⁻¹ the ATR system has a penetration depth of around 0.66 µm. All data was processed using Omnic 6.2 software.

2.3.4 Reflectance Mid-IR Spectroscopy

Reflectance mid-IR spectra were recorded *in situ* using a portable JASCO VIR 9500 spectrophotometer equipped with a Remspec mid-infrared fibre optic sampling probe. The probe was a bifurcated cable containing 19 chalcogenide glass fibres, 7 of which carried the IR radiation from the source to the sample, while the other 12 collected the radiation reflected from the surface. Interferograms were collected from 4000 to 900 cm⁻¹ at a resolution of 4 cm⁻¹ using a metal mirror plate reference. Three spectra were collected from each area. The probe was kept perpendicular to the sample surface (0°/0° geometry); the distance between probe and surface was fixed at about 5 mm. The investigated sample area width, determined by the probe diameter, was about 20 mm².

Spectral data are presented as pseudo absorbance A' [$A' = \log(1/\text{Reflectance})$] and were processed using JASCO software. The spectra in reflectance mode (at 0°/0° geometry) are strongly affected by specular and diffuse reflection, where distortion cannot be corrected by Kramers Kronig or Kubelka Munk corrections. In particular, the specular reflection is governed by Fresnel's law and depends upon both the absorption index (k) and refractive index (n) and wavenumber. Reflectance spectra of minerals and some organic compounds can be distorted by the inversion of bands showing the $k \gg n$ (*reststrahlen* effect), thus in reflection mode, those bands appear as negative signals. It has been demonstrated in another study that the intensity of the *reststrahlen* bands is proportional to the concentration of the analyte.¹⁷

3 Results

3.1 Characterisation of Surface Surfactant - Contemporary Paint Films

As stated earlier, the most abundant IR-detectable materials both on the surface and in aqueous extracts of acrylic emulsion films are PEO-type surfactants such as Triton X-405. In practice it is difficult to determine the exact structure of these surfactants with IR techniques as they are chemically similar and impurely synthesised. In addition, spectra taken from paints and paint surfaces can be affected by bulk film constituents, IR detection limits, surfactant migration patterns, other extracted/deposited materials, as well as residual water.

Figure 1a includes ATR and transmission spectra from a Talens titanium white (TiO₂) free film p(EA/MMA) and reference transmission spectra for Triton X-405, PEG-1500 (polyethylene glycol) and

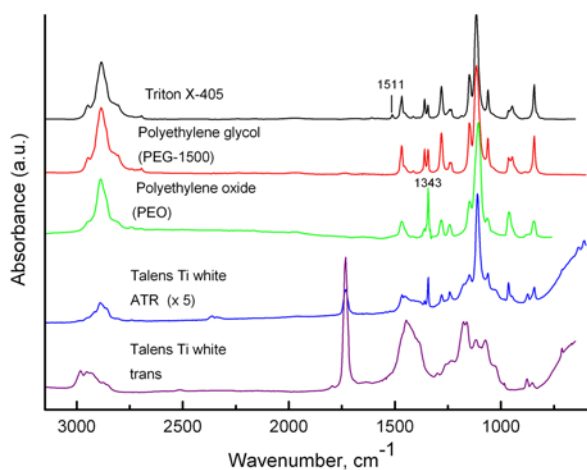


Figure 1a: Transmission IR spectra for Triton X-405, PEG and PEO (IRUG library) compared to ATR and transmission spectra from a contemporary Talens TiO₂ free film.

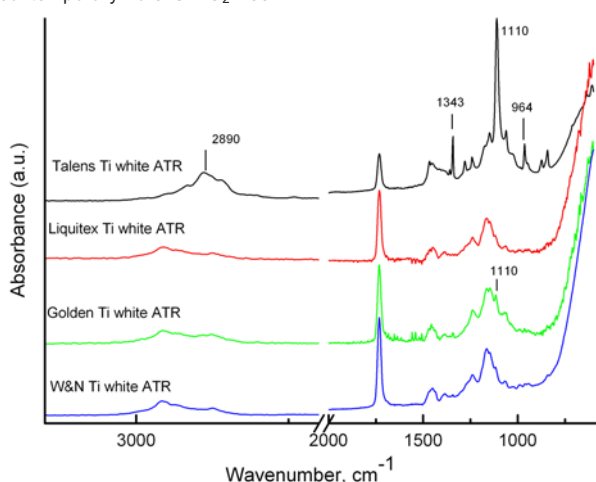


Figure 1b: FTIR-ATR spectra from the air interface of four contemporary TiO₂ free films.

PEO dry residues. The spectra for the standard materials illustrates how chemically similar they are, with commercial distinctions based primarily on molecular weight and occasional differences seen in the IR spectra such as the small band at 1511 cm⁻¹ and the single band at 1343 cm⁻¹. The characterisation of surface surfactant was duly affected by the extenders and pigments present in the paint films, potentially masking the 1511 cm⁻¹ band present in the Triton X-405 spectrum. The single band at 1343 cm⁻¹ on the Talens ATR spectrum (Figure 1a) does however suggest the presence of a polyethylene glycol-based material.

Figure 1b compares the ATR spectra taken from the air interface of four contemporary TiO₂ paint films. Due to the semi-quantitative nature of this analysis, the spectrum for the Talens paint indicates that there is a high abundance of a PEO-based material on the surface by the main group of bands at ~1110 cm⁻¹ and the C-H stretching region at ~2890 cm⁻¹. Similarly, the spectra for the three

remaining *p*n(BA/MMA) based paints demonstrates that these films have relatively little surfactant on the surface, where the spectra are dominated by bulk-film constituents. For the remainder of this paper, surfactant will be referred to as PEO-based unless otherwise identified.

3.2 Monitoring Surfactant Migration - Contemporary Paint Films

Figure 2 summarises the surfactant migration trends for two TiO₂ paints after natural, light and thermal ageing, as monitored with semi-quantitative ATR analysis. The relative abundances of surface surfactant are expressed as a ratio dividing the absorbance of the largest surfactant band at ~1110 cm⁻¹ with that of the corresponding carbonyl band at ~1730 cm⁻¹, contributed by the acrylic resin only. Higher surfactant abundance was consistently detected on the Talens paints *p*(EA/MMA) than the three *p*n(BA/MMA) based paints (as shown in Figure 1b) suggesting that abundance is primarily related to paint brand (or base-emulsion); although minor differences have been noted between different pigmented paints of the same brand.^{1, 3} The trend lines also illustrate that the amount of surface surfactant increases over time when paint films are stored in dark conditions. However due to the scaling used, it is difficult to observe the slight increase in surfactant detected on the naturally aged Liquitex sample over the 4 year period.

Surfactant could not be detected on either paint type immediately after accelerated light ageing, presumably due to the enhanced photo-degradation of the surface surfactant. To date, only trace levels have been detected on light-aged samples after 4 years natural ageing in dark conditions.³ Observations from case-study painting surfaces

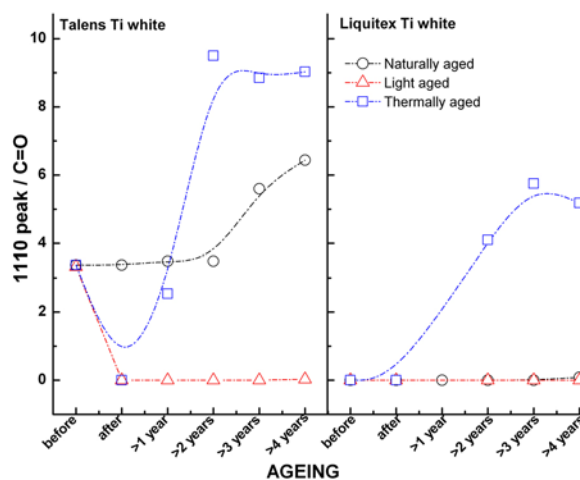


Figure 2: ATR monitoring of surfactant migration onto two TiO₂ free films - Talens (left) and Liquitex (right) after natural and accelerated ageing.

have confirmed that substantial amounts of surfactant can be present on paintings after 45 years or more natural ageing (see Figure 7), however many of the case study paintings had not been subjected to light exposure though display for prolonged periods.¹⁵ For both paint types, thermal ageing initially caused surface surfactant (melting point of $\sim 45^\circ\text{C}$) to melt and migrate back into the bulk film, however as illustrated, the migration rate post-ageing appears to have accelerated significantly due to increased polymer coalescence induced by the ageing regime and/or increased mobility resulting from thermal degradation of the surfactant within the bulk film.

3.3 Characterisation of Aqueous Extracted Material - Solid Sample Extracts of Contemporary Paint Films

Contemporary acrylic emulsion paint free-films were subjected to 24-h deionised water extractions as described in Section 2 *Experimental*, to identify components potentially vulnerable to extraction through aqueous cleaning. A PEO-type compound was detected in the extracts of many of the paints tested (i.e. four brands and four pigments) and also in paints with no detectable surface surfactant; confirming that prolonged exposures to aqueous systems can result in extraction of surfactant from the bulk paint film. The PEO-based surfactant extracted from the Liquitex white paint shown in Figure 3 was tentatively identified as Triton X-405 by the presence of the small band at 1511 cm^{-1} and the doublet at 1360 and 1342 cm^{-1} . The band at $\sim 1730\text{ cm}^{-1}$ probably originates from the paint medium (possibly residual acrylic acid) and the small, broad band at $\sim 1570\text{ cm}^{-1}$ may arise from residual water or from one of the many other

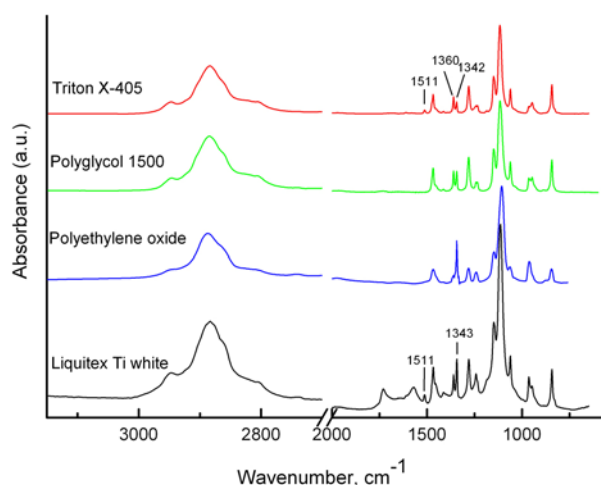


Figure 3: Transmission spectrum of a dried 24 h aqueous extract from a naturally aged Liquitex TiO_2 acrylic emulsion free film compared with library standards for Triton X-405, PEG and PEO.

paint additives used in these paints, such as the polycarboxylic acid-based pigment dispersant Tamol®.^{4,5}

3.4 Characterisation of Aqueous Extracted Material - Surface Extractions of Contemporary Paint Films and Paintings

To assess the presence of surfactant on the surface of paintings, short aqueous surface extractions were performed as described in Section 2 *Experimental*. Although clearly not suitable for all paint surfaces, this technique successfully facilitated the identification of surface surfactant and did not appear to extract material from the underlying paint films. Table 2 lists the results of surface extractions from several contemporary paint films on canvas and the case-study paintings. In all cases the major component present in the surface extracts was a PEO-based surfactant and in some cases a Tamol type product was tentatively identified. Extraction results correlate well with the corresponding ATR and portable IR spectroscopy data taken from the same paint films, for example, the Warhol painting was confirmed as having no surface surfactant present with all three IR techniques.

The data in Table 2 also suggests a possible link between the presence of surface surfactant and organic and iron-based pigmented films, which requires further exploration. This may be due to the relative difficulty of dispersing hydrophobic organic and iron-based pigments in acrylic dispersion media, necessitating the use of greater quantities of surfactant. As noted earlier, the presence of surface surfactant on the contemporary paint samples appears to be primarily brand dependent; hence it is also possible that the variations in surface surfactant abundance noted on the case-study paintings may result from the artists' use of different paint brands.

3.5 Monitoring the Effects of Cleaning Treatments on Surface Surfactant - Contemporary Paint Films

An earlier ATR study by the authors documented the removal of surfactant by several aqueous-based cleaning systems and the non-removal of surfactant using non-polar aliphatic solvents.¹ Figure 4 summarises the results of experiments designed to explore the time taken to remove surface surfactant from contemporary paint films via swab rolling with deionised water. As shown, all of the detectable surfactant was removed within 20 s,

Paint Painting	Paint type Sample description	Major pigments present	FTIR-ATR PEO surfactant on surface?	FTIR-PEO surfactant in 2 min aq. extract?	Additional components possibly identified
Liquitex	Gesso	PW6	No	Yes	Tamol?
	Ti white	PW6	No	No	Tamol?
	Azo yellow	PY3	No	No / Trace	-
	Phthalocyanine green	PG7	Minor	Yes	-
	Burnt umber	PBr7	Moderate	Yes	Tamol?
Talens	Gesso	PW6, CaCO ₃	Major	Yes	-
	Ti white	PW6, CaCO ₃	Major	Yes	Tamol?
	Azo yellow	PY3	Major	Yes	-
	Phthalocyanine green	PG7	Major	Yes	-
	Burnt Umber	PBr7	Major	Yes	Tamol?
Untitled 2/72 (Moon)	Orange	Cadmium orange, BaSO ₄	n/a	No	Silica
	Pink	PV19, BaSO ₄ , Ti white	n/a	Yes	-
Portrait of Brooke Hayward (Warhol)	All coloured paints	Organic reds PR122, 207, Cadmium yellow, Cobalt blue, Ti white, CaSO ₄	None detected on painted area on reverse	No	-
	Dark purple	PV23, PR181, CaSO ₄	-	Yes	Gypsum
Andromeda (Lieberman)	Dark green	Cr green and Mars black	-	Trace	Gypsum
	Black	Mars black	-	Yes	-
	Umber	Burnt umber, BaSO ₄ , chalk	-	Yes	-
25.4.69 (Hoyland)	Fe oxide red	Iron oxide, BaSO ₄	-	Yes	Tamol?
	Mid red	Cadmium red, BaSO ₄	-	No	-
	Scarlet red	PR3 and Cadmium red	-	No	Tamol?
	Cadmium red	Cadmium red, BaSO ₄	-	No	-

Table 2: ATR and transmission IR data from 2 min aqueous surface extractions of Liquitex and Talens contemporary paint films on canvas and four acrylic emulsion paintings on canvas dating from 1962 to 1973.

and in some cases within 5-10 s depending on initial surfactant abundance. The small rise in the curve for the Talens titanium white sample between 0 and 5 s is most likely accounted for by a slight pooling or swelling of the surfactant during cleaning, as previously observed using Atomic Force Microscopy.¹

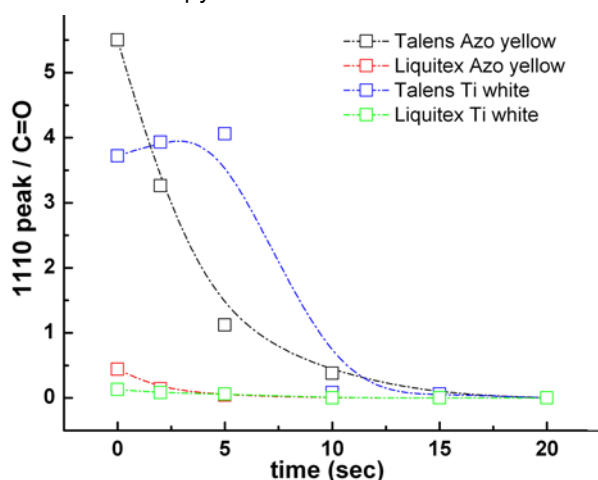


Figure 4: Monitoring the aqueous removal of PEO surfactants from the surface of four contemporary acrylic emulsion films on canvas - Liquitex and Talens titanium white (PW6) and azo yellow (PY3) - all tests repeated 3 times and data averaged.

3.6 Monitoring Surfactant Migration Post-cleaning - Contemporary Paint Films

The surfactant content of any paint film is finite (unless perhaps the film is replenished by cleaning with a surfactant-based solution); therefore, migration is expected to decrease over time. Some of the important questions surrounding the wet-cleaning of acrylic emulsion paint films are: whether one aqueous surface cleaning treatment is enough to clear paint films of surface surfactant permanently, whether surfactant continues to exude post-treatment, and/or whether the use of wet-cleaning methods affects the rate of subsequent migration.

To investigate this, TiO₂ and gesso samples were monitored for 4 years after one aqueous cleaning treatment where all detectable surfactant had been removed. The y-axes of the graphs in Figure 5 reflect the differences in amounts of surface surfactant initially present on each of the brands monitored. The control sample curves for all samples (i.e. no treatment) indicate that surface surfactant abundance has increased over time (also demon-

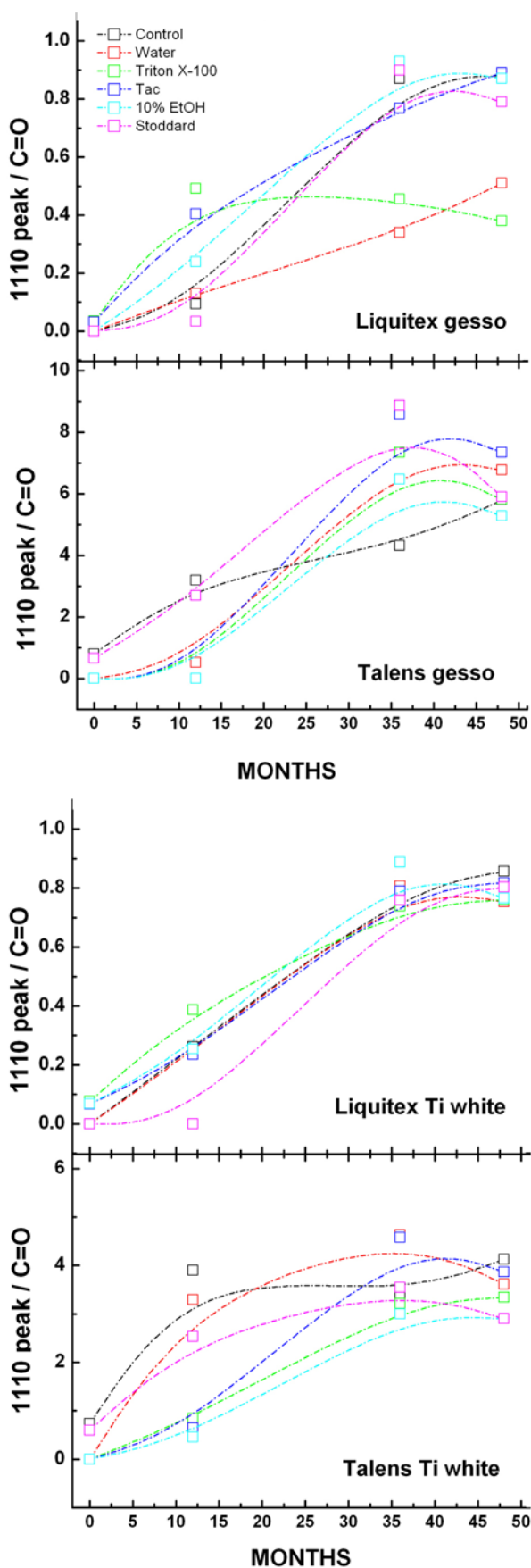


Figure 5: Post-cleaning ATR monitoring of four acrylic emulsion free films (Liquitex and Talens gesso and TiO_2) over a period of 4 years dark ambient storage - all tests repeated 3 times and data averaged.

strated by Figure 2) although the increases noted for the Liquitex samples are relatively small.

Taking each brand in turn, the surfactant migration rates for the cleaned Liquitex TiO_2 samples do not appear to have been significantly affected by any of the cleaning systems when compared to the control. The cleaned Liquitex Gesso samples are also similar to the control except for the deionised water and Triton X-100® treatments, which appear to have slightly reduced the post-cleaning migration rate. The post-cleaning rates for the cleaned Talens samples initially varied from the control, however over the four-year period these differences appear reduced. Although this data is preliminary and subject to error from data averaging and the presence of uneven surfactant films, it nonetheless confirms that the surfactant migration process is ongoing after one aqueous cleaning treatment, and therefore contributes to ongoing cleaning debates by suggesting that one aqueous cleaning treatment will not necessarily ensure a surfactant free paint(ing) surface in the future.¹⁹

3.7 In-situ Analysis - Contemporary Paint Films and Paintings

To assess the potential for portable mid-IR spectroscopy to detect the presence of PEO surfactants on the surfaces of paintings, the Talens titanium white control canvas film (high surfactant abundance) was analysed as a test case. Figure 6 shows a portion of the spectra containing the largest surfactant bands at around 1110 cm^{-1} , confirming that surfactant was detected on the surface. Due to the reflectance effect, the surfactant bands have an inverted form (reststrahlen effect) appearing as minima rather than maxima and each

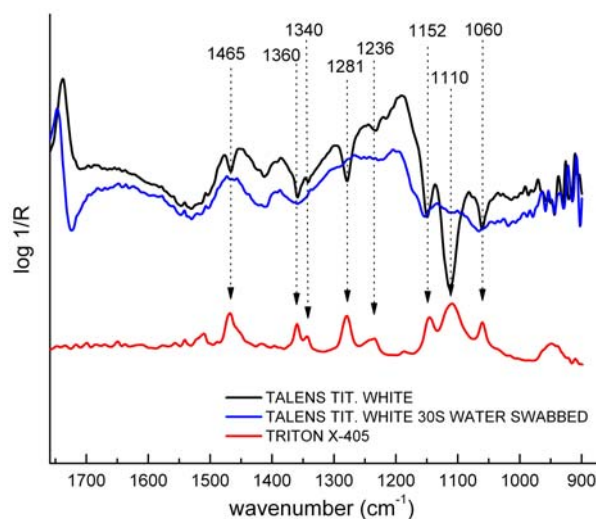


Figure 6: Reflectance mid-IR spectra from a Talens contemporary TiO_2 paint sample (black), a sample cleaned via 30 s swab rolling with deionised water (blue) and the reference spectrum of Triton X-405 (red).

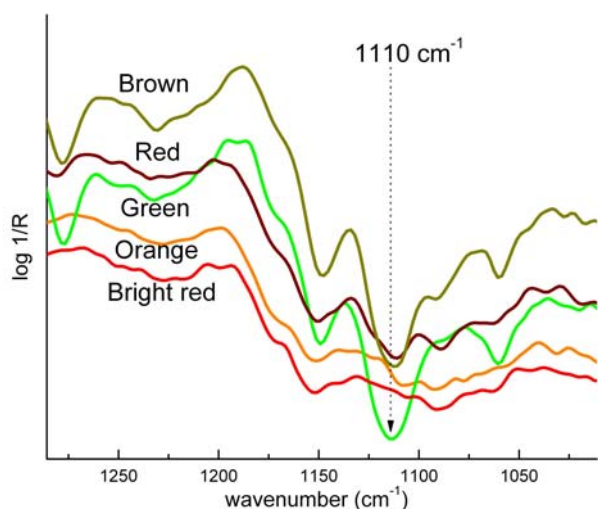


Figure 7: Reflectance mid-IR spectra from the surface of several paint passages on John Hoyland's 25.4.69 (1969), showing the presence of PEO surfactant (largest band at ca. 1110 cm^{-1}) on the brown, red and green paints.

minima are in good agreement with the maxima of the absorption bands of the surfactant spectrum acquired in transmission mode (red). The third spectrum (blue) clearly illustrates the removal of surfactant from the surface via a 30 s deionised water swabbing treatment through the disappearance of all inverted bands.

Three of the five case studies were also analysed with this system. Figure 7 shows a section of spectra from the painting 25.4.69 by John Hoyland, where the green (containing PY3) and brown (umber) paints have the highest surface surfactant abundance as indicated by the intensity of the band at *circa* 1110 cm^{-1} (inverted mode).

Interestingly, these colours also exhibited the greatest water sensitivity during aqueous cleaning tests, which requires further exploration. The iron-based red paint has some surface surfactant, although less abundant than the brown and green paints. The cadmium-based bright red and orange paints had minimal or no surface surfactant, which was also noted for the cadmium-based passages on both Moon paintings. Documentation of the removal of surface surfactant from these paintings with aqueous and non-aqueous systems was also achieved using this system, and is published elsewhere.⁹ On the whole, the results from this system concur with the ATR and surface extract data listed in Table 2.

4 Conclusions

The use of several IR-based techniques has contributed significantly to a growing body of information on the effects of wet cleaning treatments on acrylic emulsion paint films, aiding conservators

facing complex treatment decisions. For each of the techniques used (ATR, transmission μ -FTIR and portable reflectance mid-IR spectroscopy); the major materials identified on the surface and in aqueous extracts of acrylic emulsion paint films were PEO-type surfactants. However limitations caused by detection limits, interference from bulk paint film materials, residual water, similarities in the structures of PEO-based surfactants and the presence of other paint additives prevented their exact identification.

Nonetheless, these techniques proved particularly useful for documenting relative differences in surface surfactant abundance with respect to: paint brand; pigment type; response to accelerated ageing; changes induced by surface by cleaning treatments, differentiating between the effects of aqueous and aliphatic solvent systems; and tracking the migration of surfactant post-ageing and post-cleaning. The speed at which surfactant can be removed from these paint films was also tracked; proving in some cases that surfactant could no longer be detected after 5 s of aqueous swabbing. The portable reflectance IR system provided important information on the presence of PEO-type surfactants on painting surfaces, where it was noted that surfactant abundance may also be related to the presence of organic and iron-based pigments.

5 Appendix A

DEMS analysis conditions: analysis was carried out on a Varian 1200L MS detector with a Scientific Instrument Services Direct Exposure Probe. Sample was placed onto a rhenium (Re) filament and heated at 0.5 A/min for 3 min and 10 s with maximum amp value of 1.5. MS conditions: Source temp: 250 °C in EI mode (70 eV); scan range 50-1400 amu; scanned every 1 s for 3.5 min.

6 Acknowledgements

The authors would like to thank the Leverhulme Trust and AXA Art Insurance for funding research at Tate; Dr. Mark Underhill, Dr. Joyce Townsend and Patricia Smithen of Tate for DEMS, EDX analysis and treatment case studies respectively. The *in situ* analytical work was carried out through the Eu-ARTECH, MOLAB Transnational Access service supported by the EC within the 6th Framework Programme (Contract Eu-ARTECH, RII3-CT-2004-506171). Kenza Kahrim, Antonino Cosentino and Alessia Daveri of MOLAB are also acknowledged for their *in-situ* experimental work.

7 References

1. B. Ormsby, T. Learner, G. Foster, J. Druzik, M. Schilling, *Wet-cleaning acrylic emulsion paint films: An evaluation of physical, chemical and optical changes*, in: T. Learner et al. (eds.), *Modern Paints Uncovered*, Getty Conservation Institute, Los Angeles, 2007, 187-198.
2. S. Digney-Peer, A. Burnstock, T. Learner, H. Khanjian, F. Hoogland, J.J. Boon, *The migration of surfactants in acrylic emulsion paint films*, in: A. Roy, P. Smith (eds.), *Modern Art, New Museums: Contributions to the Bilbao Congress*, 13-17 September 2004, IIC London, 2004, 202-207.
3. B. Ormsby, E. Hagan, P. Smithen, T. Learner, *Comparing contemporary titanium-white based acrylic emulsion grounds and paints: characterisation, properties and conservation*, in: J.H. Townsend, T. Doherty, G. Heydenreich, J. Ridge (eds.), *Preparation for Painting: The Artists' Choice and Its Consequences*, Archetype, London, 2008, 163-171.
4. S. Croll, *Overview of developments in the paint industry since 1930*, in: T. Learner et al. (eds.), *Modern Paints Uncovered*, Los Angeles: Getty Conservation Institute, 2007, 17-29.
5. G.D. Smith, *A "single-shot" separation and identification technique for water extractable additives in acrylic emulsion paints*, in: I. Verger (ed.), *Preprints of the 14th Triennial Meeting, ICOM Committee for Conservation*, The Hague, James & James, London, 2005, 824-832.
6. J.J. Boon, F.G. Hoogland, J. van der Horst, *Mass Spectrometry of Modern Paints*, in: T. Learner et al. (eds.), *Modern Paints Uncovered*, Getty Conservation Institute, Los Angeles, 2007, 85-95.
7. F.G. Hoogland, J.J. Boon, *Development of MALDI-MS and nano-ESI-MS methodology for the full identification of poly(ethylene glycol) additives in artists' acrylic paints*, *International Journal of Mass Spectrometry*, 2009, **284**, 66-71.
8. F.G. Hoogland, J.J. Boon, *Analytical mass spectrometry of poly(ethylene glycol) additives in artists' acrylic emulsion media, artists' paints, and microsamples from acrylic paintings using MALDI-MS and nanospray-ESI-MS*, *International Journal of Mass Spectrometry*, 2009, **284**, 72-80.
9. B. Ormsby, P. Smithen, F. Hoogland, T. Learner, C. Miliani, *A scientific investigation into the surface cleaning of acrylic emulsion paintings*, *Preprints 15th ICOM Committee for Conservation 2008, Triennial Conference, India, September 2008*. *Scientific Research*, 2008, Vol. II, 857-865.
10. B. Ormsby, T. Learner, M. Schilling, J. Druzik, H. Khanjian, D. Carson, G. Foster, M. Sloan, *The effects of surface cleaning on acrylic emulsion paintings - a preliminary investigation*, in: C. Weyer (ed.), *Oberflächenreinigung. Materialien und Methoden*, VDR Schriftenreihe 2, Theiss Verlag, Stuttgart, 2006, 135-49.
11. E. Hagan, A. Murray, *Effects of water exposure on the mechanical properties of early artists' acrylic paints*, in: P.B. Vandiver, J. L. Mass, A. Murray, P.A. Warrendale (eds.), *Materials Issues in Art and Archaeology VII: Materials Research Society*. 2005, 41-48.
12. J. Hayes, M. Golden, G.D. Smith, *From formulation to finished product: causes and potential cures for conservation concerns in acrylic emulsion paints*, in: T. Learner et al. (eds.), *Modern Paints Uncovered*, Getty Conservation Institute, Los Angeles, 2007, 58-65.
13. B. Ormsby, P. Smithen, T. Learner, *Translating research into practice - evaluating the surface cleaning treatment of an acrylic emulsion painting by Jeremy Moon*, in: A. Pagliarino, G. Osmond (eds.), *Contemporary Collections, AICCM National Conference*, Brisbane, Australia, 17-19 October 2007, Canberra, The Australian Institute for the Conservation of Cultural Material (AICCM), Inc., 2007, 97-109.
14. Golden Artist Colours. *Conservation of Acrylic Paintings*. *Just Paint*, Issue 9, November 2001, <http://www.goldenpaints.com/justpaint/jp9article1.php> (accessed 15/10/2009).
15. K.W. Evanson, T.A. Thorstenson, M.W. Urban, *Surface and Interfacial FTIR Spectroscopic Studies of Latexes. II. Surfactant-Copolymer Compatibility and Mobility of Surfactants*, *Journal of Applied Polymer Science*, 1991, **42**, 2297-2307.
16. F. Belaroui, M.P. Hirn, Y. Grohens, P. Marie, Y. Holl, *Distribution of water-soluble and surface-active low-molecular-weight species in acrylic latex films*, *Journal of Colloid and Interface Science*, 2003, **261**, 336-348.
17. C. Ricci, C. Miliani, B. Brunetti, A. Sgamellotti, *Non-invasive identification of surface materials on marble artefacts with fiber-optic mid-FTIR reflectance spectroscopy*, *Talanta* 2006, **69**, 1221-1226.
18. Tate conservation records: Hoyland T01129, Moon T02052.
19. T. Learner, B. Ormsby, *Cleaning Acrylic Emulsion Paints: Putting Research into Context*, *SF-IIC Meeting Preprints*, 24-26 July 2009, Paris, France, 193-199.