Tate AXA Art Modern Paints Project (TAAMPP): 2006-2009

Research summary

Overview

The TAAMPP, funded from 2006 to 2009 through an AXA Art Research Grant, has provided important information about the properties of acrylic paints to a wide range of stakeholders including conservators, collectors, artists and heritage scientists. The main aim of the project was to help ensure that the preservation and conservation of acrylic emulsion-based works of art is appropriate to this paint type. Up to date preventive conservation advice, summarised in the *Caring for Acrylics: Modern and Contemporary Paintings* Tate and AXA Art produced booklet, available at: http://www.tate.org.uk/ research/ tateresearch/majorprojects/conservation_modernpaints.htm, will help minimise the risks associated with soiling accumulation, in addition to providing guidance on best practice for the display, storage and transportation of acrylic emulsion-based works of art.

An enhanced understanding of the surface character of acrylic emulsion paints - including how time, soiling and conservation treatment may alter paint surfaces - has contributed useful original information that is now beginning to influence conservation practice (see *general properties*). An evaluation of the surface cleaning treatment of five acrylic emulsion paintings in Tate's collection (see *case studies*) has provided vital information on the surface and properties of naturally aged and soiled paint films. Exploring the effects of cleaning treatments on works of art has also resulted in the development of an assessment methodology involving a range of practical and scientific tools, including the first applications of portable non-destructive analytical instrumentation to acrylic paintings including mid IR reflectance spectroscopy and Atomic Force Microscopy (AFM); accessed through MOLAB (Perugia).

The TAAMPP team with 3 of the 5 case study paintings in background.

From left to right: Dr. Elina Kampasakali, AXA Art Research Fellow (full-time post funded by AXA Art); Patricia Smithen, Head of Paintings Conservation (funded 1 day;/week by AXA Art); Dr. Bronwyn Ormsby, Senior Conservation Scientist; and Dr. Mark Underhill, Analyst (funded part-time by AXA Art for one year).

The pioneering TAAMPP varnish study (see *varnishing acrylic paints*) has revealed that none of the group of varnishes tested proved to be ideal for acrylic emulsion paintings; as adhesion, solubility and pigment removal issues were encountered. However interestingly, the surface cleaning treatment of the Cohen painting appeared to benefit from an artist-applied wax coating (see *case studies*). Significant contributions towards the development of appropriate cleaning methods for acrylic emulsion paint films have also been made, including the evaluation of common and potential cleaning systems through practical workshops (Courtauld Institute of Art, London; Cologne Institute for Conservation Sciences (CICS), Cologne; and *Cleaning Acrylic Painted Surfaces* at the Getty Conservation Institute (GCI), Los Angeles); as well as the ongoing collaboration between The Dow Chemical Company, the GCI and Tate, which involves the assessment of relative cleaning solution efficacy with high-throughput technology (HTP).

Over the course of the project the TAAMPP team have delivered over 30 presentations nationally and internationally, and by the end of 2010, will have produced over 25 publications; including the 6 monthly TAAMPP newsletters, websites, as well as public and academic papers in international conservation and scientific journals (see *TAAMPP publications: 2006 - 2010*). The TAAMPP newsletters have been distributed in over 25 countries; which we celebrate as a great dissemination success and thank everyone very much for their support! Consistent interest has also been shown by artists' paint manufacturers (Winsor and Newton, Golden Artist Colors) regarding research findings and regular requests for information and advice continue to be received from conservators and conservation educators.

The TAAMPP team and research outcomes have benefited from the collaboration and input of many individuals and institutions; hence a heart-felt thank you also goes to: Maureen Cross, Courtauld Institute of Art, London; Tom Learner, Alan Phenix and Michael Schilling, Getty Conservation Institute, Los Angeles; Joyce Townsend, Christopher Lewis, Ruth Findlay, Helen Beeckmans, Nigel Llewellyn and Marcella Leith, Tate, London; Jacob Thomas, Eric Hagan, Nicky White and Amanda Cropper, formerly Tate, London; Bamber Blackman, Imperial College, London; Paul Gardener and Elizabeth Reissner, London; Mindy Keefe, The Dow Chemical Company, Midland; Costanza Miliani and MOLAB (now Charisma), Perugia; Simone Musso, formerly Politechnico di Torino, Turin; Stefan Zumbühl, University of Applied Sciences, Bern, Switzerland; Gunnar Heydenreich and Petra Demuth, CICS, Cologne; Frank Hoogland and Jaap Boon, AMOLF, Amsterdam; Richard Wolbers, University of Delaware, Delaware; Golden Artist Colours, New York; Ian Garret and Peter Waldron, Winsor and Newton, UK; Talens, The Netherlands; Stuart Croll, North Dakota State University, Fargo; Jonathan Stephenson, London; Crosby Coughlin, New York; John Hoyland and Bernard Cohen, London. In addition to the generous grant from AXA Art; Tate and the GCI have also supported this research. Bronwyn would particularly like to thank Dr. Ulrich Guntram, Frances Fogel and Tom Wessel of AXA Art for their sustained interest and support throughout the TAAMPP and the brilliant, hard-working members of the TAAMPP team (at Tate and beyond) for an enormously rewarding 3+ years!

For future events and information regarding Tate research please contact Bronwyn Ormsby (bronwyn.ormsby@tate.org.uk); or visit the Tate TAAMPP and Modern Paints websites:
http://www.tate.org.uk/research/tateresearch/majorprojects/conservation_modernpaints.htm
http://www.tate.org.uk/research/tateresearch/majorprojects/conservation.htm.

For information regarding the *AXA Art Research Grant* and/or AXA Art in general, please contact Frances Fogel of AXA Art UK (frances.fogel@axa-art.co.uk); or www.axa-art.co.uk.

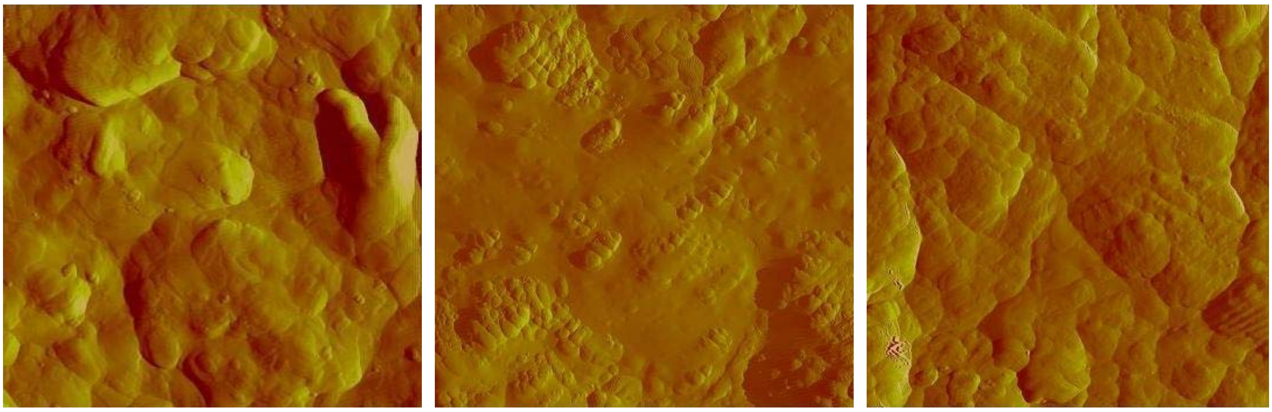
The following sections summarise the main findings of each of the 5 aspects of the TAAMPP in more detail. This is followed by a list of publications arising from the TAAMPP and related research.

Stream 1: general paint properties

Investigations into acrylic paint properties carried out during the TAAMPP have included several pilot studies into: paint swelling (Getty Conservation Institute), Atomic Force Microscopy of the paint surface (Imperial College), comparing titanium white paint with priming formulations; and FTIR-based studies of paint surfaces.

Swelling: The swelling behaviour of paint films is one of the most important aspects to consider when using any form of liquid solvent on paint films as part of a conservation process. The swelling behaviour of acrylic emulsion paint films has not been explored to any great extent, and was investigated as part of the TAAMPP using Thermo-mechanical analysis (TMA) and microscopy at the GCI. Experiments carried out on test free-films cast from two paint brands (Liquitex and Winsor and Newton) demonstrated that Shellsol A (aromatic hydrocarbon solvent), acetone, and high pH aqueous solutions tended to cause the most paint swelling and that the organic pigmented test films tended to swell more than either the gesso or titanium white (inorganic pigmented) films. All test films tended to soften when immersed in aqueous solutions with a pH above 6.0 or 6.5, and lower pH solutions tended to swell/soften films to a lesser extent. The relationship between swelling and cleaning solution conductivity (ionic strength) requires further exploration. Swelling at the surface of a painting was noted during cleaning tests with aqueous solutions at a pH of 8.0 to 8.5 (*case study 1*). With respect to paint brand, the Liquitex paint test samples tended to swell more than the Winsor and Newton films tested, which reflects differences in formulation. Accelerated light ageing (about 50 years equivalent display in museum conditions) produced a slight decrease in swelling capacity when compared to unaged equivalents; suggesting that paint films may become less vulnerable to swelling with time. This study will be submitted for publication in 2010.

Paint surface morphology: Imaging the surfaces of acrylic emulsion test paint films – for example, using Atomic Force Microscopy (AFM) – has enhanced our understanding of the nature of the surface of these paints - particularly with respect to the presence of surfactant materials on the paint surfaces (originating from the paint film) and how this can vary with paint brand, exposure to cleaning treatments and accelerated ageing. Small canvas samples removed from the reverse of the Andy Warhol painting (*case study 2*) were also imaged and a portable AFM system, accessed through MOLAB (July 2007), was piloted on the Warhol, Liberman (*case study 3*) and Hoyland (*case study 4*) paintings. Where present in reasonable quantities, surface surfactant layers appear as large, smooth, round 'hill-like' structures on a micro-scale (*see left-most image*). The removal (or partial removal) of surfactant from test free-film and canvas samples after light ageing and/or aqueous cleaning was also successfully imaged. It was noted that the removal of surfactant (where present) through cleaning with water resulted in the enhanced visibility of the pigment/extender clusters and polymeric features (*see centre image*).

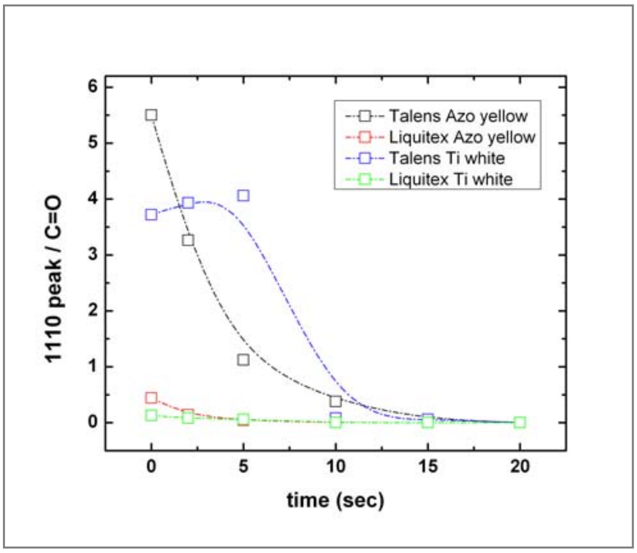


AFM image (10 x 10µm) of Talens titanium white test film (high levels of surface surfactant).
(L): control (untreated): (C) water swabbed for 1 minute: (R) mineral spirits swabbed for 1 minute. © Tate 2009.

Surface surfactant remained visible on all mineral spirit (non-polar) solvent-swabbed samples after treatment (*see right image*), with evidence for the disturbance of this layer from the mechanical action of cleaning. Where surfactant was not present however; the surface of the mineral spirits-swabbed samples appeared roughened, which requires further investigation. Some topographical differences were also observed between test paint films made with different pigments; for example the synthetic organic pigmented films had smoother surfaces with smaller features reflecting smaller pigment particle sizes and lower pigment volume concentrations. The inorganic pigmented test films were characterised by larger particulate aggregates (seen in central image). This research has been submitted to *Studies in Conservation* and is expected to be published in 2010.

Tracking surface surfactant behaviour: Investigations into the chemistry of the surface of test paint films and painting surfaces spanned the length of the TAAMPP project, involving three different Fourier Transform IR-based techniques (ATR, transmission FTIR and MOLAB accessed portable reflectance mid IR spectroscopy). The most abundant materials identified on the surface of test paint films, paintings and in aqueous extracts of paint films were polyethylene oxide (PEO)-type surfactants, such as Triton X-405 (known to be used in paint formulations).

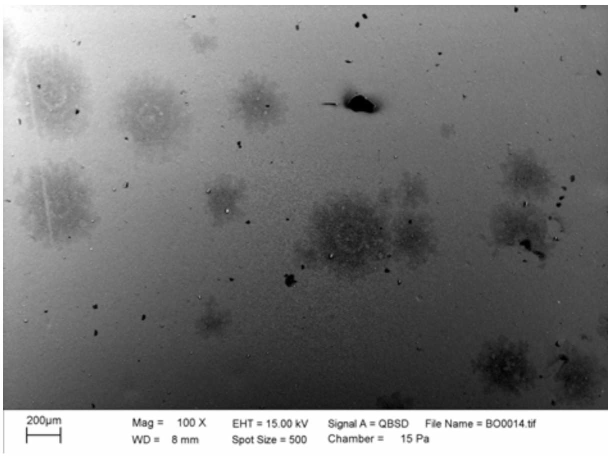
Limitations due to instrument detection limits, interference from pigments and extenders included in the paint, residual water, similarities in the structures of PEO-based surfactants and the presence of other paint additives prevented the exact characterisation of surfactants using these methods. Nonetheless, these techniques proved particularly useful for quantifying differences in surfactant presence and abundance with respect to: paint brand; pigment type; substrate type; accelerated ageing regime; changes induced by surface by cleaning treatments - including differentiating responses to aqueous/aliphatic solvent systems - and tracking the re-exudation of surfactant after cleaning treatments and light ageing. In addition, the speed at which surfactant can be removed from paint films was tracked using ATR, proving that in some cases surfactant could no longer be detected after only 5s of aqueous swabbing (*see image on next page*). The portable IR reflectance system provided vital information on the presence and abundance of PEO surfactants on case study painting surfaces and confirmed that short exposures to aqueous swabbing treatments will at least partially remove surface surfactant. As was the case for the AFM study - the use of mineral spirits resulted in the disturbance and partial removal of surface surfactant where present. This information was published in the *ICOM-CC Triennial Conference* in India (2008) and the IRUG8 meeting proceedings in *e-Preservation Science* (2009).



Monitoring the aqueous removal of PEO-based surfactants from the surface of four test acrylic emulsion films on canvas with FTIR-ATR spectroscopic analysis. Liquitex and Talens titanium white (PW6) and azo yellow (PY3) test films. © Tate 2009.

Comparing priming formulations and titanium white paints: A comparative study of the properties of acrylic emulsion-based titanium white and ground (also known as priming and gesso) films was carried out during the TAAMPP with input via a concurrent Tate and Imperial College (London) modern paints project carried out by Dr. Eric Hagan. Acrylic emulsion ground (priming) formulations and titanium white paints are formulated with the same components, namely: acrylic latex binder (p*n*BA/MMA or pEA/MMA), TiO_2 pigment, chalk/clay/talc fillers, and additives. Analysis has shown that the relative volume of pigment within ground formulations is generally higher than in the titanium white paints tested. Mechanical testing carried out by Eric revealed that the ground formulation of each brand was stiffer than the equivalent TiO_2 paint, which is primarily due to the different pigment loadings; and that the least flexible ground formulation with the highest solids volume (amount of solids in a given volume of paint) contained chalk and kaolin in addition to the titanium white pigment. This increased stiffness imparted primarily by the higher solids volume partly explains why acrylic priming formulations are more prone to cracking than acrylic paint films. The effect of other factors such as the shape of filler particles and the level/type of additives requires further investigation.

Ambient temperature was shown to have a more pronounced effect on the physical properties of these paints than either relative humidity or the rate of any applied force (such as an impact) – this is due to the close proximity of the acrylic binder glass transition temperature (T_g) to room temperature conditions. Imaging of surface surfactant present on test samples demonstrated that it can appear as isolated rounded crystals (see image on next page) or as semi- or fully-coherent films, which are generally less visible to the naked eye than the round crystal structures. Less surfactant was detected on the ground formulation samples than the titanium white paint equivalents from each brand and some ground formulations were inherently more yellow than the TiO_2 paints, presumably resulting from the inclusion of filler materials. Simulated surface cleaning treatments were carried out, which demonstrated that the surface surfactant is (at least partially) removed with aqueous treatments. Changes in colour and gloss showed similar trends to all other paint types (*discussed later*).



A back-scattered electron scanning electron microscopy (BSE-SEM) image (100x) of the surface of a Winsor and Newton titanium white test paint film.

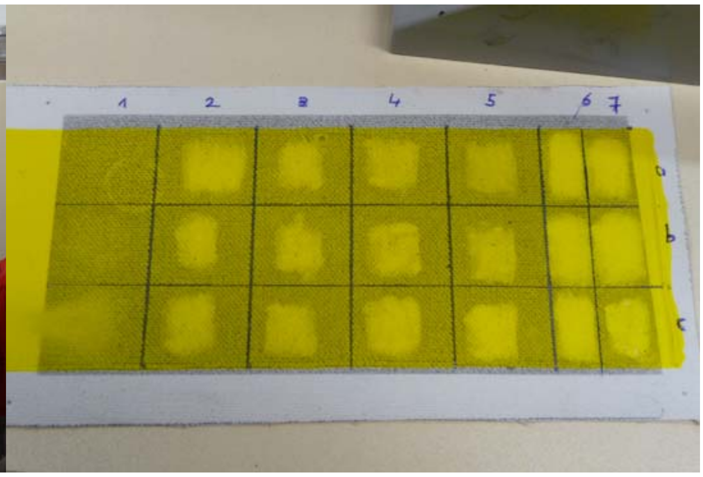
The dark round spots illustrate the early phase of surfactant migration and crystallisation on this paint film. Depending on how much surfactant is present in the film; the surfactant can eventually form a coherent layer across the paint surface.

© Tate 2007.

Stream 2: cleaning system efficacy (removal of soiling)

This aspect of the TAAMPP spanned the entire project and will extend into 2010 through internships at Tate and ongoing research collaborations. For this, artificially soiled samples (*right image*) were created using formulations adapted from similar soils used by Richard Wolbers (University of Delaware) and Alan Phenix (GCI). Data on the relative cleaning efficacy of various common and some novel cleaning solutions were generated from workshops at the Courtauld Institute, London, the *Cleaning Acrylic Painted Surfaces* colloquium at the GCI, Los Angles and the Cologne Institute for Conservation Sciences (CICS), Cologne (*left image*).

CICS conservation students at Cologne University during a cleaning acrylic paints workshop delivered by Bronwyn Ormsby, November 2009 © Tate 2009.



Test azo yellow paint sample with a sprayed coating of artificial soiling; divided into squares. Each square has been cleaned using common or novel cleaning systems. © Tate 2009.

Cleaning tests indicated that paint brand, pigment type and soiling type influence the efficacy of soiling removal and that any additions/adjustment to cleaning solutions such as surfactants, pH adjustment, ionic strength (conductivity) and chelating agents needed to be balanced against risks such as cleaning system residues, swelling capacity, gloss change, abrasion and colour pick up. Of the commonly used cleaning solutions tested, saliva (high conductivity) often cleaned more effectively than pure deionised water, with some pigment loss noted for several organic pigmented films. Carbonated water, deionised water with 1% ethanol v/v. and the combination of 1% w/v. di- or triammonium citrate and 1% v/v. Triton X-100 tended to clean paints quickly.

The soiled primed canvas samples (a commercially applied ground layer only) proved to be difficult to clean due to the increased roughness/tooth of the surface. High aromatic content hydrocarbon and ketone-based solvents (e.g. acetone) tended to remove pigment. It was also noted that if water droplets were left to sit on the soiled paint surfaces and left to dry in ambient conditions, that the underlying soiling became embedded in the paint film and was impossible to remove (thereby emphasising the need for protection against water-damage and high relative humidity environments). On the whole, sponges and dry methods were rated as poor to moderate in terms of their cleaning efficacy – but tended to produce better results when slightly dampened with water. Some dry methods were noted as appearing to push the dirt into the paint film and tending to burnish paint surfaces.

This aspect of the TAAMPP has been enhanced by a collaboration set up in 2008 between the Dow Chemical Company, the GCI and Tate involving the use of high throughout technology to assess soiled acrylic emulsion paint test samples with several cleaning solutions simultaneously. The paint samples and soiling types used are based on Tate preparations and the cleaning solutions initially assessed were based on TAAMPP research. This collaboration will ultimately result in the introduction of new cleaning systems to the conservation profession, with a particular emphasis on enhancing the efficacy of aliphatic hydrocarbon solvents, which tend to be poor performers. Some Dow materials were piloted in cleaning workshops in 2009 and current progress is being reported through AIC conferences (*2009 and 2010*), with detailed papers to follow in 2010.

Stream 3: passive soiling of acrylic emulsion paint films

In order to explore the soiling of acrylic emulsion paint films, a group of painted test canvases including both Talens and Liquitex titanium white and phthalocyanine green acrylic emulsion paints were created with the aim of observing the passive soiling process over time. Equivalent samples were created using oil (Rowney Artists' Oil Colour), alkyd (Winsor and Newton Griffin) and water mixable oil (Winsor and Newton Artisan) paints, to help establish whether acrylic paints become soiled more quickly than other modern paint types.

To assess whether surface cleaning can also affect the re-soiling of cleaned paint films, some of the acrylic samples were cleaned with deionised water (clearing surface surfactant), 60-80 BP 0% aromatic content mineral spirits (does not clear surface surfactant) or Groom Stick®. Other acrylic samples were cleaned with water loaded with NaCl so that residual ions were left on the surface and others were coated with either: Renaissance wax, Golden soft emulsion gel, MS2A varnish (+ Tinuvin 292) or Golden soft gel with the addition of an experimental conducting polymer - Panipol®. Loading the paint surface with residual ions may determine whether a lightly charged paint surface repels soiling; alternatively, the Panipol polymer was added to assess whether surface charge dissipation (the removal of surface charge) affects re-soiling rates. NB: the addition of Panipol to a varnish rendered the applied coating green(!), hence its use in this study was purely experimental.

Test canvases for the TAAMPP soiling study on the wall of the paintings conservation studio.

One section of each sample was covered with clear Mylar as a control (unsoiled) area. Samples had 10 months exposure on this wall and were then moved to the science lab for further soiling. This study is ongoing.

Initially the canvas samples were hung vertically in the paintings conservation studio at Tate (*see above image*), which proved to be too clean! After the first assessment period (10 months) little change was noted in the samples apart from some expected colour changes in the paint films (which were predictably more pronounced for the oil and alkyd samples) and small changes in gloss. The samples were then moved and laid flat for a further 6 months exposure (16 months total) in the organic materials analysis laboratory.

The assessment of the paint surfaces after this time (surface chemistry, conductivity, UV and visible imaging, colour and gloss measurement) revealed that the surface conductivity of the alkyd and oil samples was generally lower than the acrylic samples and that at this stage, there was no clear relationship between surface conductivity and soiling (although the cleaned samples had slightly lower conductivity; which was also noted for the case study paintings (*see case studies)*. No significant changes in surface surfactant were noted. By this stage, dust was however beginning to accumulate and differences could be seen in the size of the dirt particles deposited. For example, the alkyd and oil samples had larger particles and fibres deposited on the surface; and the acrylic samples tended to have uniform layers consisting of smaller sized particles. In general, there were also small decreases in gloss where the soiling had accumulated. Colour measurements taken after 16 months exposure once again indicated that the oil and alkyd samples exhibited greater colour change than the acrylics. This group of samples will be re-evaluated again in 2010 and again on a yearly basis. When the trends in soiling accumulation become more clearly defined, a paper will be published outlining general findings and any recommendations arising from the research.

Stream 4 – varnishing acrylic emulsion paint films

Another important stream of the TAAMPP was the varnish study; developed in response to questions from Collectors about how best to protect their acrylic works of art from the risks associated with soiling accumulation. This involved the assessment of several commercial and conservation varnishes for their suitability as protective coatings for acrylic emulsion paints. The test samples include a similar group to those used for the soiling study, created with two brands (Talens and Liquitex) of titanium white and phthalocyanine green acrylic emulsion paint. The materials used include acrylic solution, acrylic emulsion, hydrocarbon and ketone resins as well as microcrystalline wax (*see images below*). The coatings were applied according to manufacturer's directions or accepted conservation standards. Some of the solution (solvent carried) coatings immediately produced uneven films and developed adhesion problems (which may in part reflect problems with our application procedures). Each coated sample was accelerated light aged for 6 months in a UV-free daylight tube chamber with controlled relative humidity and temperature to an equivalent of 100-150 years display in a museum environment (assuming reciprocity). Samples were evaluated after the 6 month exposure period for surface chemistry, surface conductivity, UV and visible light imaging, colour, gloss and solubility. Surface conductivity readings after ageing revealed very little change. Colour change was also minimal with E^{94} values of less than 2.0 units with some exceptions (the green samples registered greater colour change than whites samples). Gloss values tended to decrease with light ageing – with some exceptions. Where surfactant was detected on the sample surface (i.e. either migration through the coating from the paint film or contributed by emulsion-based coatings), it was found to have degraded after 6 months light exposure. On the whole, the varnishes tended to act as barriers to the migration of surfactant from the paint film to the coating surface, with the exceptions of the ketone and wax-based coatings.

Varnish removeability tests using water-based and hydrocarbon solvents revealed that the emulsion varnishes – as expected – were not able to be fully removed. The solution-based varnishes responded differently to the range of aliphatic and aromatic solvents tested. The 100% aromatic solvent had the most damaging effect on the underlying paint layers (also noted in the cleaning efficacy study); resulting in pigment loss; which was also occasionally observed with the use of Stoddard (18% aromatic content) solvent. The light aged varnishes required increasing numbers of swab rolls for effective removal, indicating that a slight change in solubility had occurred after ageing. The solution varnishes also proved difficult to clear completely (residual varnish was visible through the microscope), as many tended to gel and were difficult to control. The wax coating attracted surface dirt, although it was successfully removed with low % aromatic content hydrocarbon solvents (with some exceptions). The green paints were more sensitive to colour loss than the whites and the Talens samples were the most prone. Regalrez® was the easiest solution varnish to remove however the associated adhesion problems resulted in an unsatisfactory visual result. At this point it is not possible to recommend any of the varnishes tested, as each was affected by either optical, pigment loss, handling or removal issues. This information will be augmented by further varnish removal treatments at Tate in 2010, including an assessment of the underlying paint surfaces after complete removal.

Patricia Smithen, Head of Paintings Conservation (now Head of Conservation, Programs), Tate (left) and Maureen Cross, Lecturer, Courtauld Institute of Art (right) applying varnishes to the acrylic painted primed canvas samples for the TAAMPP varnish study. © Tate 2007.

Stream 5: case study conservation treatments of paintings from Tate's collection

Approach to the evaluation of case study paintings:

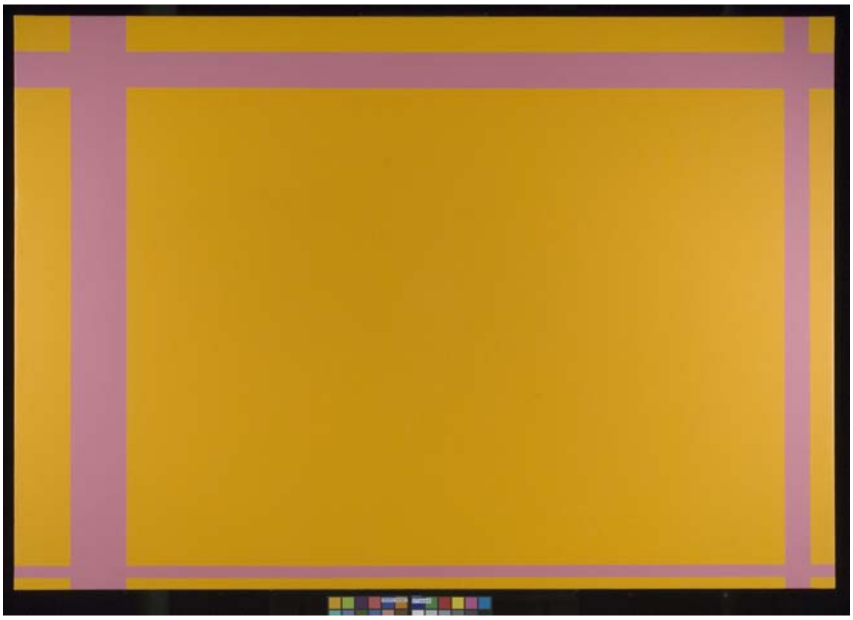
The case studies formed a vitally important part of the TAAMPP research; where the results of the myriads of assessments carried out on test samples were compared and contextualised with those gained from the study of naturally aged, lightly soiled works of art dating from 1962 to 1973. After a thorough examination of each painting, the cleaning systems used on the case studies were chosen from a group of commonly used systems, with variations introduced through controlling pH, solution conductivity, solvent choice and the addition of cleaning action enhancing materials such as non-ionic and anionic surfactants, potentially azeotropic solvents such as ethanol, as well as gelling and chelating agents. Due to a lack of research into the presence and effects of cleaning system residues on acrylic emulsion paints, non-gelled, volatile systems were used where possible. Where wet cleaning was required, the effects of water were minimised by drying off swabs before applying them and blotting the cleaned paint surface immediately after application. Some dry cleaning methods were also employed and novel methods were introduced where appropriate. The materials used are summarised under each painting heading below.

As stated, each case study painting was evaluated prior to and after conservation in order to characterise any changes induced by the surface cleaning treatment. For this, a number of established conservation examination methods as well as standard and novel scientific tools were employed to characterise paint film constituents and paint surfaces. These included: photography and microscopy using ultraviolet, infra-red and visible light; visual observation; as well as colour and gloss measurement. Surface chemistry was characterised via FTIR (Fourier Transform Infra-Red) spectroscopy, FTIR-ATR (Attenuated Total Reflectance) spectroscopy, portable mid-IR spectroscopy, Electrospray Ionisation – Mass Spectrometry (ESI-MS) of swabs taken from painting surfaces and surface conductivity. Paint constituents were identified via: Pyrolysis Gas Chromatography – Mass Spectrometry (PyGC-MS); Direct Exposure-Mass Spectrometry (DEMS), transmission FTIR (Fourier Transform Infra-Red) spectroscopy, EDX (Energy Dispersive X-ray analysis) and ED-XRF (Energy Dispersive – X-Ray Fluorescence). Surface topography was explored through light microscopy, portable Atomic Force Microscopy (AFM), bench-top AFM and Back Scattered Electron - Variable Pressure Scanning Electron Microscopy (BSE-VP-SEM).

Several collaborative partners were involved in the evaluation of these paintings including the Getty Conservation Institute (GCI) via their sponsorship of the Atomic Force Microscope (AFM) analysis carried out at Imperial College London. *In-situ* non-invasive reflectance FTIR and portable AFM was made available through the transnational access MOLAB - 6th Framework Programme (Contract Eu-ARTECH, RII3-CT-2004-506171). The ESI-MS analysis of cotton swabs was carried out by Frank Hoogland at the FOM Institute for Atomic and Molecular Physics (AMOLF), Amsterdam, supported by the approved FOM programme 49 granted by FOM (Utrecht), a subsidiary of the Dutch Organisation for Scientific Research NWO (The Hague).

Jeremy Moon: Untitled 2/72 (1972)

Jeremy Moon's painting *Untitled 2/72* (*see image on next page*) was the first cleaning treatment carried out as part of the TAAMPP. This painting exhibited some of the common problems associated with acrylic emulsion paintings including an overall dust and grime layer; embedded dirt; a fine grey-white surface layer and drip marks which are believed to have occurred while the painting was stored in the artists' leaky studio. The paint media was confirmed as a p(EA/MMA) (ethyl acrylate/methyl methacrylate) copolymer which is consistent with the early form of acrylic emulsion paint. Pigments were identified as cadmium orange and quinacridone red (PV19), with some titanium white and barium sulphate added as an extender. Analysis of the surface revealed that the surface conductivity was generally low, with the dried drip accretions having higher conductivity due to the deposition of material. Surface analysis also revealed that the pink (PV19) passages were more surfactant rich than the cadmium orange passages. The cleaning solution used for this painting was a 2% v/v. ethanol solution in deionised water, adjusted to pH 7.5 with ammonium hydroxide, as it removed more of the drip mark accretions and surface dirt than any other system tested. It was also noted during testing that the paint film began to swell when using aqueous solutions of pH 8.5 and above. The treatment was monitored with microscopy and UV light examination. The after treatment assessment revealed that there had been no significant colour change to the surface and that a slight increase in gloss resulted from the removal of the combined surface dirt and surfactant layers. After treatment, the painting was more vibrant and Moon's subtle brushwork was visible. This painting formed part of a display of Moon's works at Tate Britain in 2007. Details of the treatment and evaluation approach were published in a paper presented at the Australian Institute for the Conservation of Cultural Materials (AICCM), National Conference in 2007.



After treatment photograph of Jeremy Moon's Untitled 2/72 (1972).

Photo: Tate 2007
© Jonathan Stephenson courtesy Rocket Gallery, London.

Andy Warhol: Portrait of Brooke Hayward (1973)

Andy Warhol's painting *Portrait of Brooke Hayward,* painted in 1973, was selected as the second acrylic painting to be cleaned as part of the TAAMPP. It was lightly soiled, with substantial amounts of residual cotton fibres left on the surface from a previous wet-cleaning treatment which needed to be removed to prevent them becoming embedded in the paint film with time. The painting is made up of four separate pieces consisting of both silk-screen ink and acrylic emulsion paints applied to a white priming layer. Warhol created this work by transferring a photographic image of Brooke Hayward to a silkscreen. The commercially prepared canvasses were laid flat and the acrylic emulsion paints were brushed onto the surface. A different colour was used for each of the main elements of the image: the background, skin, lips, irises, eyelids, and eyebrows. The paint was carefully applied within the outlines of these features, but loosely brushed in other areas, with variable thicknesses, incorporating air bubbles. Next, the silkscreen was placed over the acrylic paint and a black printing ink was forced through the screen with a squeegee, transferring the image to the surface with characteristic dots. The screen was re-used for each of the four pictures and sometimes the positioning of the image did not coincide exactly with the paint.

As for all of the case study paintings, the constituents of the paint films were identified through analysis. The coloured (non-black) paint layers were confirmed as an ethyl acrylate/methyl methacrylate p(EA/MMA) acrylic copolymer. The silk screen (black) areas were all identified as an alkyd medium (an oil-resin binding medium commonly used in house paints and inks). The off-white priming layer was also identified as an alkyd medium. Warhol's palette included titanium white, cadmium yellow/orange with associated barium sulphate, cobalt blue, chromium oxide green, possibly some Mars red, with calcium sulphate and chalk extenders. The black pigment used in the silk screen ink is probably carbon black and the pink and red paints were identified as containing the synthetic quinacridone red pigments PR122 and PR207/PV19.

After a thorough examination and evaluation of the surface, it was decided that dry cleaning systems were required for this painting. FTIR and ESI-MS analysis confirmed that there was no accumulated surfactant on the surface (possibly due to the previous wet-cleaning where it may have been removed) and cleaning tests showed that both the light soiling layer and cotton fibres were removed using a combination of dry brushing and Groom Stick® - using ultraviolet light examination on a regular basis to track the removal of the cotton fibres. In addition, the light scuff marks noted around the painting edges were found be small areas of abrasion and/or paint accretions. The after treatment assessment determined that there were no significant changes resulting from the cleaning treatment. The surface conductivity of this painting was low when compared to the Moon painting (due to previous cleaning treatments) however it was very slightly reduced by this cleaning treatment. The painting was displayed after cleaning in 2008, and is regularly on display at Tate Modern.

Alexander Liberman: Andromeda (1962)

The third TAAMPP case study painting was Russian-American artist Alexander Liberman's (1912-1999) *Andromeda* (1962), presented to Tate by the Montargent Foundation in 1964 and loaned in 2002. Liberman's paintings of 1961-2 were abstract, geometric and hard-edge. *Andromeda* has been described as having 'circles (that) stretch from the top to the bottom edge of the canvas while gigantic arcs (sections of circles) sweep across the picture plane..' (James Pilgrim in exhibition catalogue *Alexander Liberman*, Corcoran Gallery of Art, Washington, DC, 1970). It is currently the earliest confirmed acrylic emulsion painting in Tate's collection and is painted on a circular canvas of dimensions: 1650 x 1650 x 40 mm.

The painting consists of four areas of uniform colour – black, lilac, dark purple and dark green which were in relatively untouched condition as the surface had only ever been brushed in preparation for the 2002 loan. The medium for each colour was confirmed as a p(EA/MMA) acrylic emulsion copolymer, which is appropriate for the date of the painting. The pigments were identified as: titanium white, Mars black, a synthetic organic purple dioxazine pigment PV23, chromium oxide green, and calcium sulphate as the main extender pigment. Crosby Coughlin, a representative of the artist's estate, visited Tate in October 2007 to discuss the materials, techniques and ageing characteristics of Liberman's paintings and *Andromeda* was acknowledged to be in excellent condition - marred only by the obscuring layer on its surface. Crosby related that Liberman usually worked with Liquitex acrylic paints through this period, which is consistent with the analytical results and early use of acrylic emulsion paints in the United States.

The painting surface was obscured by a layer of fine soiling combined with the whitish bloom characteristic of surfactant build up, which was particularly visible during cleaning (see *during treatment image below*). Cleaning tests consistently revealed a more saturated and vibrant surface once this layer had been removed. Accumulated surfactant on the painting surface was confirmed via several analytical techniques and appeared to be thicker in some areas. The presence of substantial surfactant layers suggested that *Andromeda* would benefit from a water-based cleaning treatment to recover colour saturation and to ensure the efficient removal of the soiling layer, which had become intermingled with the surfactant. In addition, while dry cleaning methods resulted in a partial cleaning of the surface, they did not produce a visually satisfactory result. This painting differed from previous case studies in that the paints contain little or no titanium white (apart from the lilac area) and *Andromeda* also consists of large areas of synthetic organic pigmented paint, which can be more sensitive to pigment loss and swelling during wet cleaning than inorganic pigmented films.

The aqueous cleaning solution used was a 2% v/v. ethanol solution in deionised water adjusted to pH 6.0. Each section was carefully cleaned with two to three successive (blotted) cotton swab applications, resulting in an overall even surface. The aliphatic systems tested - even with the addition of surfactant - removed very little surface dirt. As for the Moon and Warhol paintings, the final stage involved reassessing the painting surface for changes. In this case, the gloss data indicated that a slight increase had resulted from the removal of the soiling and surfactant layer, which concurs with results from other case studies and experiments carried out on test paint films.

Alexander Liberman's Andromeda, during surface cleaning treatment.

The darker, more saturated areas have been cleaned; the lighter areas have a layer of soiling and surfactant on them.

Photo: Tate 2008.

John Hoyland: 25.4.69 (1969)

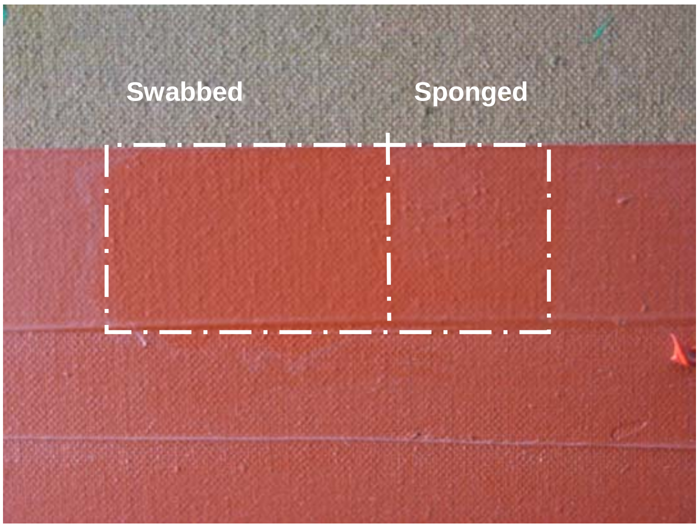
John Hoyland's *25.4.69 (*see *image below)* is a skilful example of an acrylic emulsion painting on canvas with multiple surface qualities. With this painting Hoyland began to test the limits of acrylic emulsion paints through paint dilution and wet-in-wet techniques. The upper section consists of layered veils of diluted paint with spatters of impasto and the lower section consists of several areas of palette knife applied impasto in a variety of colours. Analysis of the painting revealed that the paint binder is a p(EA/MMA) acrylic emulsion co-polymer. The pigments include: cadmium red, cadmium yellow, Mars red, umber, and the organic pigments PY3, PR3 and PV19, with barium sulphate as the main extender. Analysis also confirmed that surfactant was present on the surface of several paints in the lower impasto section (suggesting that the presence of surfactant may in part be dependent on the thickness of acrylic paint films); including on the surfaces of the umber, Mars red, PR3 red, and the organic PY3-containing green paint; with trace amounts possibly present on the cadmium passages.

The before treatment paint surface conductivity was moderate (0.1 to 0.9 mSiemens/cm) with the impasto areas having higher values than the upper more dilute section. The gloss values in the lower section were higher than the upper section. The lower section was affected by a light grey hazy surface layer similar to those noted on both the Moon and Liberman paintings – consisting of deposited soiling as well as migrated surfactant and inorganic materials from the paint film. Cleaning tests with a range of aqueous and organic solvent systems revealed once more that the removal of this layer resulted in an increased saturation of the paint and more vibrant colour. As this painting has two distinct paint textures, the surface cleaning treatment was tailored accordingly. The upper, dilute section was sponge-cleaned using an extremely lightly water-wetted Conservators sponge (Preservation Equipment Ltd, UK), applied using gentle, slow, broad strokes across the surface, taking care to avoid discrete impasto areas. The sponged surface was then dry cleaned with Groom Stick (Preservation Equipment Ltd, UK) using a rocking motion to remove any loose soiling remaining on the surface. Each paint colour in the lower section was tested separately and observations were made on how efficiently the soiling layer was removed, noting any colour transfer onto the swab, surface swelling and the possible appearance of blanching and gloss changes after treatment.

Left: John Hoyland's 25.4.69 (1969) after cleaning. Photo Tate 2009.

Below: Detail of aqueous cleaning tests (swabbing and sponging) on the iron-oxide red section of the lower portion of Hoyland's 25.4.69. The paint surface is more saturated in the swab cleaned section (within white box, on left).

Photos: Tate 2009. © John Hoyland.



After extensive testing, the lower impasto section was cleaned with a 1-2% v/v. solution of ethanol in deionised water with the pH adjusted to 6.0. As was the case for the Moon and the Hoyland paintings, this solution offered the most efficient removal of surface soiling with minimal effect on the paint surface. In most cases two swab applications were required and any occasional light pigment transfer onto the swab decreased with subsequent swabbing. Interestingly, the green organic pigment (PY3)-containing paint was prone to significant pigment transfer, possibly resulting from higher quantities of surfactant and/or other water-soluble materials in the paint (during cleaning it also frothed the most). This was minimised through adjusting the relative saturation of the cotton swab and by limiting solvent exposure. As was the case for the Moon and Liberman paintings the removal of the light-scattering soiling layer was achieved more efficiently using an aqueous system (see *right image on previous page*), resulting in significant increases in colour saturation after treatment. Once again gloss changes were minimal, with small increases noted for most paint passages after treatment. Colour change was also minimal, although in some cases slightly higher than other case studies, due to the greater variations in colour and texture of this paint film.

Bernard Cohen: Painting with Three Spots, One Blue and Two Yellow (1970)

The final case study was British artist Bernard Cohen's (b. 1933) *Painting with Three Spots, One Blue and Two Yellow* (T01538) painted in 1970 and purchased by Tate in 1972. Cohen created his spot paintings by inter-layering sprayed dots of coloured acrylic paint with brushed coats of white acrylic emulsion paint. Throughout this period Cohen used Bocour paints and avoided using priming products, preferring the flexibility and surface quality of artist's professional quality titanium white paint instead. This painting is a good example of the large, monochrome surfaces typical of acrylic emulsion paintings. There were some light finger marks and scuffs around the edges, as well as an overall fine layer of deposited surface soiling. This is a particularly large painting (1524 x 3962 mm), with an expanse of evenly applied white paint, with a wax-based artist-applied (probably brushed) coating added to help protect the paint layer.

London-based conservator Paul Gardener test cleaning the edge of Bernard Cohen's 'Painting with Three Spots, One Blue and Two Yellow' (T01538).
Photo: Tate 2009 © Bernard Cohen.

During treatment image of Bernard Cohen's 'Painting with Three Spots, One Blue and Two Yellow' (T01538). The vertical cleaning line and variations in surface gloss can be seen in raking light (source from left).
Photo: Tate 2009 © Bernard Cohen.

The materials Cohen used were relatively uncomplicated; the paint medium was identified as p(EA/MMA) acrylic emulsion copolymer (in at least two discernable layers) and the pigment was identified as titanium white with no extenders present. The coating was tentatively identified as beeswax, however the blue and yellow pigments forming the three spots could not be identified due to the overwhelming presence of titanium white pigment. The surface conductivity of this painting was very low, presumably due to the presence of the surface coating; with all readings falling below 0.05 mSiemens/cm. Similarly, no surface surfactant was detected on the paint surface, which is relatively matte. The after treatment evaluation revealed that the conductivity had decreased by a small amount; and that the surface gloss had increased between 0.1 and 2.3 units. This reflects inherent gloss differences in the brushed wax coating across the painting as well as the removal of soiling, as can be seen in the raking light image (see *right image on previous page*) where the vertical cleaning line is also visible.

Mineral spirits and other hydrocarbon solvents could not be used on this painting surface for soiling removal without risking the removal of the wax coating. Therefore a number of aqueous and dry cleaning systems were tested in discrete areas along the edges to assess how the coating, paint film and deposited soiling layers responded (see *left image on previous page*). The treatment commenced with an overall light clean with a smoke sponge (Preservation Equipment, UK) to remove any loose particulate material; which did not affect the gloss or appearance of the wax layer. Areas of ingrained soiling and light fingerprints were lightly wet-cleaned using deionised water swabs; followed by localised dry cleaning using a Staedtler Mars Plastic® eraser once the wetted areas had dried. Further cleaning of remaining marks was achieved using cotton swabs dampened with deionised water. Some accretions were then removed using a cotton swab and saliva, and cleared with deionised water. Water was also introduced to the paint film using a brushed on gel system consisting of 1% w/v. Pemulen TR2 (Noveon Inc, Ohio) in deionised water (pH 6.0) to assess whether the controlled introduction of water would aid in the removal of residual fingerprints. The gel was left on the surface for one minute, swabbed gently with a dry swab and cleared with a deionised water swab. This worked extremely well in reducing the overall greyness of these areas and did not affect the surface appearance of the coating and paint film. Dry superfine disposable micro brushes (Microbrush® International) were also used to reduce scuffs and marks along the top edge. To finish, a final overall surface clean was carried out using a lightly water wetted Conservators Sponge (Preservation Equipment, UK).

It appears that the wax coating, may have contributed to the success of this cleaning treatment – i.e. the removal of the more stubborn marks and ingrained soiling may not have been possible were it not present. However, it was also noted that the coating had yellowed slightly and that some of the surface dirt may have become embedded in the coating – thereby preventing it from being easily lifted. Considering this painting consists of a vast expanse of matte titanium white paint, the wax coating in this case appears to have protected the paint film from some of the problems associated with embedded soiling. However, as it was not necessary at this stage to remove the wax coating, the removal process is unlikely to be free of associated risk.

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