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Conservation Concerns for Acrylic Emulsion Paints: A Literature Review

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Detail from John Hoyland's Saracen 1977, acrylic emulsion on canvas, taken in raking light from the right. © John Hoyland/Bridgeman Art Library

Acrylic emulsion artists' paints were received with much fanfare and excitement in the 1950s and 1960s. They embodied the characteristics that many artists had been searching for at that time, affording a means of expression that was distinct from oil painting and its associated history and traditions. As Kenneth Noland described it, 'there was an urge to loosen painting. [These colours] released new kinds of tactile qualities'.¹ These synthetic paints produced films of great clarity and phenomenal elasticity, were easy to manipulate, could be painted directly onto supports, dried quickly, were thinned with water and exhibited high resistance to ultraviolet degradation. John Hoyland recalled, 'I remember reading articles in magazines. They talked about the radiance of [acrylic paint] and the fluidity of it and that it would never yellow. It seemed exciting in the way people got excited about the use of plastics, aluminium and other industrial materials'.² Helen Frankenthaler, who switched from using oil paints to acrylic emulsions in the early 1960s, said:

I changed to acrylics for a number of reasons. Once, I was told that they dry faster, which they do, and that they retain their original colour, which they do. I would say durability and light and the fact that one can use water instead of turpentine: all that makes it easier given the abstract image. As painting needed less and less drying time, depth, and so forth, the materials came along that made that more obvious.³

In spite of their outstanding mechanical and aging properties, acrylic emulsion paintings do suffer damage, often through external influences. Within the conservation profession, concerns were soon raised as some of these newly painted works began to require cleaning and repair.^{4 5} Similar themes were discussed in the following decades.⁶⁷⁸

Essentially, three fundamental problems were identified. The first was that most conservation treatments had been designed for traditional paintings in oil and were found unsuitable for acrylic emulsion paintings,

due in particular to the high sensitivity of these synthetic paints to the majority of organic solvents and heat. The second was the complete lack of knowledge about acrylic emulsion systems, especially the complexity and constant changes to the formulas, with insufficient information coming from the manufacturers of both raw materials and artists' paints. The third was that damage may be especially noticeable in colour field or monochromatic paintings, disrupting the delicate surface texture, colour or gloss, ^{1 8 9} all of which are often integral to the artists' intent and can be altered by even the slightest contact. Even small damages can therefore soon become 'unacceptable'. Since remedial treatment is so difficult with acrylic paintings, preventive conservation is crucial.¹⁰

In general, very few studies of the conservation of acrylic emulsion paintings have been published. Instead, concerns tend to be communicated through informal discussion. The intent in this paper is to review the majority of available information from the conservation literature and to encourage further discussion and research by conservators, conservation scientists, paint manufacturers and artists. It should be stressed that this review only takes into account publications in the English language. Naturally, a broader understanding of the subject would be possible from surveying material written in other languages, in particular German texts by Röhm, who first reported the production of a solid acrylic polymer in 1901 and developed a commercial synthesis of acrylate esters in 1927.¹¹ ¹² The authors also do not review the incredible developments that have taken place with organic and inorganic pigments, although good accounts by de Keijzer and Marontate, for instance, already exist.¹³ ¹⁴

The conservation concerns with acrylic paint media tend to fall into four categories and will be presented as such, beginning with the development of waterborne acrylic artists' paints, and followed by paint properties, aging properties and issues associated with cleaning.

The development of waterborne acrylic artists paints

Henry Levison, a chemist-turned-paint maker, founded the company Permanent Pigments in 1933, which produced the first line of waterborne acrylic emulsion paints called Liquitex[®] in 1954.¹⁴ He often supplied artists in exchange for soliciting their advice, occasionally hiring them as consultants or staff. The development of Liquitex[®] came not long after the introduction of the first artists' acrylic paint, Magna[®], by the paint makers Leonard Bocour and Samuel Golden in 1947. Magna[®] acrylic paints were solution paints and quite distinct from waterborne emulsion paints. In practical terms, Magna[®] dried quickly by evaporation of an organic solvent; it remained resoluble in many hydrocarbon solvents as well as further layers of paint and could be blended with oil paint.^{7 15 16} In contrast, the drying process of emulsion paints involves a complicated coalescence of emulsified polymer spheres after an initial evaporation of water. These paints become insoluble in water – and further layers of emulsion paint – after they have dried.

Confusingly, many terms are used to refer to waterborne acrylic paints, such as acrylic emulsions, latex, and polymer colours. In fact, technically, they are dispersions rather than 'emulsions', because they are composed of tiny beads of solid, amorphous polymer suspended in water. The fact that these paints could be diluted and thinned with water, instead of mineral spirits, made them – and continues to make them – very appealing to artists. The raw polymer emulsions used by artists' colourmen and paint makers were frequently those from Rohm and Haas' Rhoplex[®] series of products (known as PrimalTM in Europe), such as AC-22, AC-33, AC-234 and AC-634. Rhoplex[®] AC-33 first became available in 1953. All of these emulsions were copolymers, utilizing the harder methyl methacrylate (MMA) and softer ethyl acrylate (EA) to create the required working properties, such as flexibility as well as durability for house paints, satisfying their primary market. Since the end of the 1980s many of the resin formulations have changed to a poly (*n*-butyl acrylate/methyl methacrylate) copolymer, such as Rhoplex[®] (or PrimalTM) AC 235. In the form of a paint film these tend to be slightly tougher and more hydrophobic than the poly(EA/MMA) resins, making them more durable to outdoor exposure. Styrene has sometimes replaced, either partly or entirely, the MMA component to save on manufacturing costs.¹² 17 18

Additives

Acrylic emulsions contain a multitude of additives that determine the performance properties of the paint, from shelf life, application and longevity, to properties affecting health and safety. ¹⁸ ¹⁹ ²⁰ ²¹ ²² Additives are introduced at two distinct stages of production: during the manufacture of the emulsion polymer and during the formulation of the paint itself. With the exception of a few volatile additives (see below), all additives remain in the dry paint film. Research into their interaction with the binder is therefore necessary for a complete understanding of the aging properties and effects of treatment on acrylic emulsion paints. However, almost nothing has been achieved towards this, either analytically or from manufacturer's information, on their precise identity. While the paint formulator knows the basics of these materials, the additives themselves contain proprietary materials and are constantly changed to meet the needs of the large coatings industry.²⁰ ²³

Additives in the emulsion binder

- Initiators are used as a source of free radicals to initiate the polymerisation process, in which monomers condense to form the polymers. These are most often persulfates, eg. potassium persulfate,²⁴ which thermally decompose to form free radicals. The polymer manufacturer may also use a redox system, adding ferrous and thiosulfate along with the persulfate salts, to allow for room temperature reaction.²⁵
- Chain transfer agents are incorporated to aid in controlling/limiting molecular weight (MW) during polymerisation, eg. dodecyl mercaptan.²⁶
- *Buffers*, typically ammonia, are added to maintain a pH between 8 and 10, for maximum dispersion stability of the acrylic polymer.
- Surfactants are a critical group of components, necessary to create the micelles for particle formation and long-term particle stabilisation. Common surfactants are non-ionic (eg. alkyl phenol ethoxylates) and anionic (eg. sodium lauryl sulfate or dodecylbenzene sulfonate) that are typically added at 2 to 6% by weight (%/wt).25 These provide stability through electrostatic and steric hindrance mechanisms.
- Protective colloids also contribute to steric stabilisation and are water-soluble natural or synthetic polymeric emulsifiers such as hydroxyethylcellulose and polyvinyl alcohol, added in 1 to 10%/wt.
- Preservatives are generally added in low doses (less than 1%/wt) to protect against the growth of microorganisms, commonly methyl benzisothiazolinones, chloromethylisothiazolinones, barium metaborate and formaldehyde donors, such as 1-(3-chloroallyl)-3,5,7-triaza-1-azoniaadamantane chloride.
- *Residual acrylic monomers* are also present at 50 to 1000 parts per million or so, resulting from incomplete polymerisation.

Additives utilised by paint formulators to achieve the intended performance properties

- Wetting and dispersing agents are added to wet pigment surfaces, allowing pigment agglomerates to break apart a critical process in developing colour strength and providing steric and/or electrostatic stabilisation of the pigments. Typical wetting agents include alkyl phenol ethoxylates, acetylenic diols, alkylaryl sulfonates and sulfosuccinates.²⁷ These are similar to the surfactants used during polymerisation. Dispersing agents are typically polyphosphates (generally calcium or potassium salts of oligophosphates with two to six phosphate units) or polycarboxylates (sodium and ammonium salts of polyacrylic acids, 2,000 to 20,000 MW).²⁴
- Coalescing solvents are added to ensure film formation under varying atmospheric conditions. They are slow evaporating solvents with some solubility in the polymer phase. They act as a temporary plasticiser, allowing film formation at temperatures below the system's glass transition temperature (Tg) for the system,²⁵ after which they slowly diffuse to the surface and evaporate, increasing the hardness and block resistance of the film. Typical coalescents are ester alcohols, e.g., *Texanol*[®] (Eastman Chemical Co.), benzoate esters such as *Velate*[®] (Velsicol Chemical Co), glycol ethers, glycol ether esters and *n*-methyl-2-pyrrolidone.

- Defoamers are necessary to reduce the inherent tendency of emulsions to foam, a consequence of incorporating surfactants. Typically these are mineral oils or silicone oils, the latter (polydimethylsiloxanes) are much more efficient and active, but more likely to produce film defects (craters, fisheyes, etc.). The mechanism by which defoamers function is not fully understood, but these very hydrophobic materials are thought to move to the air/liquid interface, allowing the air to release.24 25
- Preservatives, although typically included in acrylic emulsions, are supplied in additional quantities and are introduced to avoid dilution as water and other components are added.
- Thickeners and rheology modifiers are required to achieve the desired viscosity and flow properties. Thickeners function through multiple hydrogen bonds to the acrylic polymer, thereby causing chain entanglement, looping and/or swelling which results in volume restriction. The most common group is that of cellulose derivatives, including hydroxyethylcellulose, methylcellulose and carboxymethylcellulose. Also important are alkali-swellable polyacrylate emulsions, which add considerable viscosity upon neutralisation with an appropriate base (such as ammonia). Polysaccharides such as xanthan and guar gums are also used. A relatively new group of organic rheology modifiers – altering rheological properties more than building viscosity – is that of hydrophobically-modified ethoxylate urethanes (HEURs). Inorganic thickening agents can also be used, such as forms of bentone clays, including the bentonites, smectites and attapulgites, and fumed silicas.
- Freeze/thaw stabilisers are added to prevent the freezing of a waterborne paint, avoiding the formation of ice crystals that would disrupt the dispersion stability and causing permanent damage through polymer coagulation. The incorporation of 2 to 10% ethylene or propylene glycol ensures that water, surfactants and protective colloids will return to the acrylic emulsion surface in an orderly way.²⁶

Identification and analysis

There is a need for conservation-driven research, publications and interviews with artists about their chosen materials, reasons for using them and thoughts on the conservation of their work. Several papers have presented the history of the manufacture of artists' acrylic paints and their commercial introduction to artists.^{2 7 14 28} Marontate presented in-depth interviews with paint manufacturers and examined their early concerns for the durability of the materials, and participation in groups such as the American Society for Testing and Materials.14 Lodge and Barclay presented concise reviews of the history of synthetic paints in the hands of artists.^{7 28} In addition to charting the manufacturing history of synthetic paint media. Crook and Learner conducted detailed studies of several artists, their materials and the construction of their paintings.²

Several museums have established programs of artists' interviews either on audiotape or video, or through written questionnaires about specific artworks, typically upon their acquisition. Many issues can complicate the gathering of such information, for instance, the artist may not recall the exact materials or may provide contradictory information.^{29 30 31 32 33 34} All of these issues were extensively considered and a methodology of interviewing artists proposed in the symposium and publication, Modern Art-Who Cares?^{31 34 35} The importance of using scientific analysis to confirm an artist's recollections has been stressed.²

Several papers have now appeared on methods of scientific analysis and chemical characterisation of acrylic emulsion paints. Essentially, it is now possible to identify the major components in an acrylic paint, e.g. binder, pigment and extenders. The three main techniques have been Fourier transform infrared (FTIR) spectroscopy,¹² 17 22 36 37 38 39 40 41 42 pyrolysis - gas chromatography (Py-GC)²² 43 44 and pyrolysis gas chromatography – mass spectrometry (Py-GC-MS).^{12 17 36 38} In addition, direct thermally-resolved mass spectroscopy (DTMS) has been shown to be effective at identification of acrylic binders and the majority of pigments.^{12 46} However, the use of ultraviolet (UV) fluorescence microscopy staining gave inconsistent results for layers of acrylic in cross-sections,²² perhaps an inevitable consequence for such

complex formulations. The analysis of additives, however, is very scarce; with the exception of recent FTIR studies, which have identified polyethylene glycol (PEG)-type surfactants.^{47 48} This may support the presence of alkyl phenol ethoxylate surfactants, which are common in the coatings industry.

Other characteristics of acrylic emulsions have also been studied. The relative proportion of each monomer in copolymer emulsions was measured by nuclear magnetic resonance (NMR)⁴⁹ and thermomechanical analysis (TMA).12 Molecular-weight distributions of the soluble component and an estimate of the degree of cross-linking in dried films were made by size exclusion chromatography (SEC) and thermogravimetric analysis (TMA).^{47 48} Scanning electron microscopy (SEM) has also been used to document film coalescence and topography.^{19 50 51}

Paint properties

Film formation

The basic process of film coalescence has been described frequently in the conservation and paint industry literature, though authors acknowledge the over-simplification of this model and the need for further research 51 52 53 54 55 56 57 58 Acrylic emulsions are composed of particles of amorphous polymer suspended in water. The two-phased system is held in suspension by surfactants and/or other surface stabilisers. During drying, water evaporates to draw the spherical polymer particles closer, which then meld together to form a 'honeycomb' network. A coalescing-solvent additive ensures that the polymer particles remain malleable during – and after– this process, to produce more complete compaction, even after the water has evaporated. Eventually, the boundaries between particles become barely detectable and the film is considered continuous. However, it has been shown that pores or micro-voids are often left within the film, readily seen with light microscopy and SEM.²² 51 59 60 61 62 63

The degree of coalescence is dependent upon a variety of conditions, including the ambient conditions during drying, the Tg, which is approximately 10 C for poly(EA/MMA) emulsions,¹² ¹⁸ minimum film formation temperature (MFT), modulus of elasticity and viscosity of the resin, as well as the function of additives such as coalescing agents.⁶ ⁵⁴ ⁵⁷ Paints left to dry slightly below their Tg and MFT will result in films of higher porosity. A paint drying significantly below its Tg will form a loose, powdery layer.

Film porosity and pin-holes

The porosity of acrylic emulsions was exploited early on in the coatings industry. Acrylics were ideal as coatings for wood because they allowed water vapour to pass through them, reducing the risk of delamination.^{54 67}, However, porosity in an artwork coating has obvious conservation implications: dirt and air pollution may become trapped, making removal difficult and providing a haven for biological growth.⁶⁸ 69 70

Similar concerns have been raised about pin-holes, or craters.^{20 22 54 59 61 67 71} These defects are often produced in emulsion paints as a result of the foam created during both manufacturing and application,^{20 22} although this phenomenon can occur in other types of paint, even oil-based media. It has also been suggested that voids may trap conservation cleaning agents through capillary action, possibly causing long-term damage.⁷¹ In the case of outdoor murals, efflorescence of the substrate or the formation of ice crystals can occur, causing a build-up of material on the surface or between the coating and substrate.^{54 59 61 68}

Haziness

A phenomenon sometimes observed in clear acrylic emulsion films is haziness. Under natural and accelerated aging conditions, haziness was observed in young films of Liquitex[®] Acrylic Gloss Medium.⁴⁸ The haziness was composed of microscopic spherulitic crystals on the surface of the acrylic film, as characterised by light microscopy. These water-soluble crystals formed as the temperature and relative humidity (RH) to which the films were exposed increased. FTIR revealed that the crystals contained

compounds similar to those found in PEG of about 1500 MW. It was predicted that crystals might develop if the temperature was between the melting point of the crystalline material and the Tg, of the polymer. At that point, the PEG-type material would be free to migrate through the film and crystallise. Proposed temporary solutions were either to raise the temperature of the film, melting the crystals once formed, or to keep the film temperature below its Tg, eg. to prevent crystal formation. The risks associated with both techniques were mentioned.

A different type of haziness or cloudiness has also been reported, which can occur during the drying process before all the water has evaporated or when coalescence is incomplete, leaving pores or micro-voids within the film.^{51 59 60 61 62 63}

Thermoplasticity

The temperature sensitivity of acrylics can be problematic, especially while paintings are in storage or transit. Their low Tg makes them rubbery at room temperature, attracting dirt and airborne pollution. High temperatures and RH can cause packing materials to stick to the surface. In one reported instance, ⁷² an acrylic painting on paper became adhered to its PerspexTM glazing, although separation was possible through localised applications of a heated spatula to the front of the PerspexTM.

Low temperatures and RH are particularly damaging, as they can cause a significant decrease in elasticity of the paint film and consequent cracking of the paint upon flexing, as demonstrated by Erlebacher et al.⁷³⁷⁴ Emulsion films were exposed to various temperature and RH combinations and their strength, modulus and elongation at break were measured. In general, the strength and stiffness of the films increased as the temperature and RH decreased, particularly under conditions of 40 to 50% RH at 15 °C and below. However, at very cool temperatures, such as -3°C, the strength actually began to decrease, as well. At 40% RH, brittleness occurred in some colours at 5 °C, but at 5% RH this figure could rise to as high as 11°C. The warning was clear: cold temperatures and low RH, conditions that are feasible in winter, make acrylic emulsion paintings brittle and susceptible to cracking.

Conversely, a warm, humid environment, even if only experienced during shipment, can encourage mould growth, as reported by Gatenby.⁷⁰ In this case, loose mould and dirt were removed by dry brushing and vacuuming and then with distilled water and non-ionic surfactant. However, this treatment was complicated further by the matte and powdery nature of the paint; the mould left black stains in some areas of the paint.

Properties of additives

Although most additives remain to be studied in-depth, recent attention has been focused on the effect of the surfactants. These have been located in dried films, especially within the subtle boundaries among the coalesced polymer beads.^{53 56 57 59 75 76} It has also been suggested that surfactants (and other additives) migrate to both the surface of the film and the film/substrate interface.^{48 55 57 63 76 77 78 79 80 81 82 83} The migration occurs at several stages: first, during application of the paint to the substrate, as a way of breaking the surface tension and allowing the paint to wet-out the substrate,^{80 81} because porous substrates can absorb surfactant; ^{66 84} second, during drying of the paint film when capillary action forces water and water-miscible additives to the film surface; ^{61 85} and third, after drying upon elongation of the film.⁸¹ Surfactants on the film surface may change its gloss, both in degree and uniformity, may cause adhesion failure of varnish²¹ and may harbour dirt and biological growth.⁸⁶ Surfactants are also likely to foam and be susceptible to removal during surface cleaning.^{21 77 78} The effect of a surfactant on the mechanical properties of the dried film has only recently been investigated.⁸⁷

Ageing properties

Yellowing/discoloration

Clear acrylic paint media were observed to yellow or discolour slightly in three studies. In the first, an artist

had observed yellowing of Golden[®] clear acrylic medium in one of his paintings, prompting a joint research project between Golden Artist Colors, Inc. and the Buffalo State College Art Conservation Program.⁸⁸ A variety of non-pigmented artists' acrylic media were subjected to both natural and accelerated aging. Discoloration was noticed in the samples applied to cotton and linen supports, more so than in those applied to glass. The discoloration appeared shortly after the samples had dried naturally; accelerated aging did not significantly increase yellowing. The discoloration was attributed to the migration of components from the support into the medium during drying. The water in the media dampened the support and components within, such as size, dirt and degradation products, and, upon evaporation through the film surface, pulled the decolourants into the media. This support-induced discoloration (SID) can be avoided by thoroughly washing the canvas or linen with water before use.

Yellowing of clear acrylic emulsion media was also noticed during another study.⁸⁹ The samples of clear acrylic media, supported on glass plates, exhibited slight yellowing (and an increase in UV fluorescence) after natural aging in the dark, after light aging and after oven-aging. The yellowing was more intense in the thickest areas of the film and not confined to the surface. During the aging process, the films were submitted to periodic solvent extraction to monitor changes in MW through viscosity. The increase in yellowing coincided with a decrease in solubility. Naturally aged films became increasingly insoluble in benzene two weeks after application, exhibiting partial swelling instead, and after 60 days the samples became so insoluble that elevated temperatures were necessary for dissolution. The yellowing was attributed to slight cross-linking of the film. It was proposed that even though chromophores are not present in the initial formulation of the acrylic, their development may be catalysed by other reactions within the film.

Finally, in an additional study by Whitmore et al.⁹⁰ the yellowing of clear acrylic films in the dark was explored, providing evidence that they can be bleached in the light, to varying degrees, as can oil paint; films with SID are less susceptible to light-bleaching.

Cross-linking and oxidation

Cross-linking in waterborne acrylic emulsions can occur at three stages: during the polymerisation/production of the raw polymer resin; during drying/coalescence of the paint film; and during aging (both natural and accelerated) of the dried film. Acrylic emulsions can be formulated to undergo varying degrees of cross-linking during drying, depending on the end use of the product, using additives called cross-linkers. However, these are not thought to be present in artists' emulsion paints.^{19 56 91} Instead, the high MW of the polymer is enough to provide high film strength from chain entanglement.^{54 56} It has been reported that during aging, a film can cross-link and oxidise as a result of photo-degradation and from the effect of residual surfactant.⁶⁶ However, while Chiantore detected cross-linking in sample films, both before and after aging, oxidation products were not found.⁷⁷ The principal consequences of cross-linking are an increase in brittleness and hardness,^{66 94} which may actually improve the film's resistance to dirt pick-up and abrasion.

Effect of pigments

Inclusion of pigments tends to stabilise the binder, as they are often effective UV absorbers. Inorganic pigments tend to offer improved durability in comparison to the organics. Titanium dioxide is probably the most studied pigment. Of the two different crystalline forms, rutile, rather than anatase is appropriate for exterior paints because it is far less reactive to ultraviolet radiation. Anatase, which is highly reactive to ultraviolet radiation, can form radicals and degrade the polymer.²⁴

Cleaning

Recently, Klein conducted a census to 'determine the most commonly used methods and materials used by painting conservators in their treatment of acrylic paintings'.⁹⁶ Out of 190 surveys sent to paintings conservators in North America, only 31 were completed. In addition, 41 letters of refusal were returned, citing reasons such as insufficient experience in treating acrylics and lack of time or staff to fill out the

survey. It was confirmed that many conservators treat acrylic artwork with products and techniques developed for traditional paintings and more conservators considered themselves 'self-taught' in the treatment of acrylic paintings as opposed to being trained through their university program. By far the most common treatment problem encountered on both unvarnished and varnished paintings was some form of cleaning, typically requiring the removal of dirt or marks from vandalism. A wide range of cleaning materials and methods were identified, principally dry methods, such as brushes and erasers, and aqueous methods, e.g. saliva or water, often with small additions of ammonia, surfactants or triammonium citrate, or even baby wipes. However, a range of organic solvents and solvent gels were also cited. Some of the major concerns of the participants were the difficulty of grime removal, the sensitivity of the paint, leaching during aqueous cleaning, identifying the specific components of the media, the application and future removal of varnishes and the protection of unvarnished paintings from deterioration.

Affinity for dirt pick-up

Frequently mentioned in the literature, yet rarely analysed, is the tendency of an acrylic emulsion paint film to imbibe surface dirt. Dirt can come into contact with the painting through airborne pollutants,⁹⁷ handling (eg. fingerprints) and accidents or vandalism. It has been suggested that indoor air pollution, accumulating gradually on a painting surface, may take approximately 50 years to become perceptible to the human eye.⁷⁸ ⁹⁸ The principal factors thought to affect the attraction of dirt to acrylic paintings mentioned in the literature include:

- Tg, MW, MFT and softening point of the acrylic resin. If all are low, then the resulting film exhibits a low hardness at room temperature, forming a tacky 'trap' for incidental dirt.⁶ 7 99 100
- static charge. Acrylic paint films are non-conductors and therefore can accumulate a static charge, attracting dust from the air.³⁸
- pigment concentration. It has been suggested that high pigment load can block dirt pick-up.¹⁰¹
 However, it is likely that the uneven surface resulting from a paint of high pigment load would trap dirt mechanically and therefore significantly increase the difficulty of dirt removal.
- hydrophilic additives, such as surfactants. Such additives located at the film surface can attract and imbed dirt particles.¹⁰²

Sensitivity to solvents

The sensitivity of acrylic emulsion paint films to organic solvents clearly limits a conservator's choice of cleaning techniques, consolidants, inpainting materials and options for varnishing and varnish removal. There is difficulty in removing imbedded grime without disturbing the surface texture, colour and gloss. Mechanical cleaning, such as with eraser crumbs or a molecular trap like Groomstick!TM are sometimes used before testing wet-cleaning techniques,^{70 87} and have been investigated by Saulnier.¹⁰³

Solubility tests have been proposed as a simple form of analysis/identification preliminary to more complex instrumental techniques.³⁸ 10⁴ Nielsen discussed such solubility tests during forensic investigations.¹⁰⁴ Small quantities of unknown samples to be identified were exposed to solvents to view the following phenomena: bleeding of organic pigments, swelling, dissolution of the film, and effervescence from carbonate extenders and other additives. The reactions were compared with the reactions of control samples for initial characterisation before further tests were conducted. The necessity of building a library of identified standards is often stressed.²² 38 104

Sensitivity to water

Even water or water-based cleaning methods can impact the paint surface. Acrylic emulsion films can remain soluble in water up to a week and beyond after application. Upon drying, they become less soluble in water. ^{51 54 57 75 85} However, it is widely known among conservators of modern paintings that acrylic emulsion films remain sensitive to swelling by water. A recent study by Murray et al tested the effect of

several water-based cleaning agents on the dimensions and mechanical properties of acrylic emulsion paint films.⁸⁷ Sample films of cobalt blue paint were submersed in water-based cleaning agents for either one minute or one hour and then left to dry. One percent solutions of Orvus[®] WA Paste and Aerosol[®] OT (both anionic surfactants), TritonTM X-100 (a non-ionic surfactant) and triammonium citrate (a chelating agent with a pH of 7.2) were tested, all commonly used and visually effective cleaning agents. Immersion, though not a conservation cleaning technique, is a repeatable test that may indicate the effect of multiple cleanings on a painting and/or any residual cleaning agent left in the film, as well as results from disaster conditions.

An interesting conclusion was that samples immersed for one minute showed weakened mechanical properties compared to those immersed for an hour. It was concluded that in one minute, only limited penetration of the cleaning solution into the paint sample was possible, causing expansion of the outer surface, but not the core, stressing the sample prior to mechanical testing. However, an hour's immersion allowed the solution to reach and react with all parts of the sample, leaving the sample uniform in condition and in reaction to mechanical testing. After the minute-long immersions and subsequent drying, the sample volumes had increased, mostly due to an increase in thickness, however, after the hour-long immersions the samples returned to the original volume; indications were that after longer immersion times the thickness and volume would decrease further.

Conclusion

Although discussion about the conservation of these paintings has taken place almost since the introduction of artists' acrylic paint, there is clearly a lack of information on these materials and works of art that is relevant to conservation. It is important to continue research and to share the information among conservators, conservation scientists, artists' materials manufacturers and artists. In terms of future research, a fuller understanding in two broad areas is needed: 1) the structure and components of acrylic paints, in and of themselves, including the individual properties of additives and their interactions, and 2), the effect of outside influences on the film, such as aging, abrasions, dirt pick-up and dirt location within the film strata, wet and dry conservation cleaning techniques, as well as the paint film's interaction with other materials such as priming and varnish.

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