Sensitivity of Oil Paint Surfaces to Aqueous and Other Solvents

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ABSTRACT. This paper investigates the sensitivity of modern commercially produced artists’ oil paints to the use of aqueous and other solvents for cleaning. Water sensitivity has been observed in oil paintings where the paint has been used to create a great range of surface effects. It was reported in paint that exhibits efflorescence where fluctuations in environmental conditions or former treatments may have accelerated migration of degraded components to the surface of the paint film. The colored passages most frequently cited as problematic included ultramarine, cadmium yellows, chromium oxide green, and cobalt violet. Oil paint films, based on twentieth-century manufactured paints, with known proportions of pigments, stearates, aluminum hydroxide, hydrolyzed linseed oil, and hydrogenated castor oil in linseed oil were prepared and cured. After artificial aging, the paints were tested for water sensitivity. Ultramarine paints were the most sensitive to water applied by swab, followed by chromium oxide, whereas raw sienna was the least sensitive. The inclusion of linseed fatty acids and aluminum hydroxide increased the sensitivity of the paints to water. Aluminum stearate-containing paints swabbed with aqueous solvents exhibited localized stearic acid efflorescence. Ultramarine stearate-containing paints formed a paint-medium skin that was initially resistant to swabbing with water but contained water-sensitive paint beneath.

INTRODUCTION

The water sensitivity of modern paintings produced with commercial artists’ oil paints is a phenomenon commonly encountered by conservators of twentieth-century paintings. Sensitivity to the use of aqueous and other solvents typically applied with a cotton wool swab during cleaning affects well-bound oil paint and can also occur in paint that has been applied straight from the tube, with no modifications, or in tube paints with artists’ additions of materials such as non- or semidrying oils, waxes, or resins. The problem has been reported in passages of large, unvarnished, and unglazed modern oil painting, including Jasper Johns’ Untitled, 1964–1965 (Stedelijk Museum, Amsterdam; Burnstock et al., 2007; Wijnberg et al., 2007), Karel Appel’s Les Animaux, 1961 (Collection of the Netherlands Institute for Cultural Heritage [ICN]; Mills, 2008; Mills et al., 2008), and paintings by Robyn Denny, dating from the 1960s, at the Museu Calouste Gulbenkian, Lisbon (Gayler et al., 2008). Related case studies and technical analysis of water-sensitive oil paintings from the 1950s and 1960s are discussed in depth in a recent Courtauld Institute of Art student project (Tempest, 2009).

Dirt deposition may be patchy or even and can be particularly disfiguring on modern paintings, which may have no layer of protective varnish, a varied surface texture, different degrees of porosity in different areas, or a significant degree of impasto to trap surface.
Test paints, replicating basic formulations of modern manufactured artists’ oil paints on the basis of present knowledge (technical information was obtained from Harding, Colart, and Old Holland), were prepared from raw materials and painted out in early 2008. The materials used were cold-pressed and alkali-refined linseed oil (combined in a ratio of 4:1), powdered pigments, hydrogenated castor oil (1%–10%), linseed fatty acids (2%–5%), aluminum hydroxide (5%–30%), aluminum stearate (2%–30%), and zinc stearate (2%–30%; in ultramarine only). Additives were incorporated into test paints at a range of proportions recommended for use in tube paints, from 2%–5% of aluminum stearate (Tumosa, 2001) to 20%–30%, which is significantly higher than generally found in commercial paints in order to identify trends in sensitivity and to test analytical detection limits.

Three pigments were chosen for the study on the basis of their various degrees of sensitivity as observed in dried oil paint films: ultramarine (three different shades: two fine and one coarse), chromium oxide green, and raw sienna. All materials were provided by Old Holland (http://www.oldholland.com) except for aluminum hydroxide and aluminum or zinc stearate, which were obtained commercially. Proportions of most powdered additives were measured by weight as a percentage of the dry content; in the case of linseed fatty acids and hydrogenated castor oil, stock solutions of a linseed oil mixture with 2% and 5% linseed fatty acids and 2%, 5%, and 10% hydrogenated castor oil by weight were substituted as the binding medium. All of the paint samples were mixed with an automatic muller provided by Old Holland, which mimics the action of the industrial three-roller steel mill used in factories. The oil content was varied with the aim of achieving a “buttery” consistency where possible (Figure 1).

Ultranarine oil tube paints were painted out and aged, including a selection of Winsor & Newton, Michael Harding, Haagsche Kunsthildersverven Fabriek (no longer available), and Old Holland paints. Ultramarine, chromium oxide green, and raw sienna tube paints were modified with additives, combined in the automatic muller mixer, and painted out on thick Melinex and commercially prepared cotton canvas with chalk- and titanium white-containing acrylic priming. Each sample comprised a section of both flat and impasto paint, applied using a brush on canvas, a draw-down bar with a fixed clearance of 25µm for the flat area on Melinex, and a palette knife to create the impasto. After three months of curing, artificial aging with fluorescent light tubes (36W Philips Color 96, in combination with Lexan polycarbonate sheets to filter out ultraviolet) of test paint films was carried out at about 44% RH and 25°C. The samples received the calculated equivalent of 25.2 years of museum lighting (200 lux, eight hours a day, assuming reciprocity). The samples were then stored under ambient conditions until testing at various times.

The paint films were tested for solvent sensitivity using the same procedures as in Mills et al. (2008). Tests were carried out after 6, 18, and 24 months of storage following artificial aging by three independent evaluators. The paint films were tested by swab rolling, applying minimal pressure, using deionized water, saliva, and iso-octane. Assessments were visually aided by light microscopy. The sensitivity criteria were categorized as follows: ++++, very sensitive, pigment or paint removed within 5 swab rolls; ++, sensitive, paint removed within 10–20 swab rolls; +, moderately sensitive, paint removed within 30 swab rolls; –, not sensitive.
Cross sections were taken from test paint films and embedded in Polypol resin and dry polished. Elemental analysis was carried out with a scanning electron microscope with energy dispersive spectrometry (SEM-EDS) or X-ray microanalysis, and imaging was carried out in a variable-pressure SEM (VP-SEM). X-ray fluorescence was carried out with a portable instrument. Both X-ray diffraction and Fourier transform infrared (FTIR) analysis were carried out. The latter was also combined with an attenuated total reflection (ATR) system. Details of the equipment and operation conditions are given at the end of the paper.

RESULTS AND DISCUSSION

Conservators’ Interviews

Interviews were conducted with conservators of modern paintings, including a survey that identified examples of water-sensitive oil paintings that ranged from unspecified paintings by Kandinsky and Malevich dating from the 1910s to works from the 1990s by John Murphy (P. Young, private practice, London, personal communication). The survey suggested that most of the water-sensitive paintings date from the 1950s and 1960s.

From the first decades of the twentieth century onward, paint formulations began changing, and numerous additives were being incorporated into manufactured oil paints for the first time (Tumosa, 2001). The limited number of documented occurrences of paintings sensitive to aqueous cleaning may be due to the application of protective varnish coatings to many paintings made before 1900. The peak in the noted occurrence of water sensitivity in paintings from the 1950s and 1960s may also relate to the recent treatment of the works in response to contemporary demands on the works for loan and display. Oil paintings from more recent decades may exhibit equal, or higher, degrees of sensitivity on aging; the extent to which they do may not be fully appreciated until they are brought into conservation studios in larger numbers in 20 or 30 years’ time.

Unmixed tube colors were most frequently cited as problematic, for example, cadmium and chrome yellows and reds, ultramarine, cobalt blue, chromium oxide green, and purple pigments, such as cobalt violet (L. Wijnberg, Stedelijk Museum, personal communication; L. van der Loeff, Kröller-Müller Museum, personal communication; J. Krueger, National Gallery of Art, personal communication; S. Digney-Peir, Metropolitan Museum, personal communication; M. Basto, private practice, Lisbon, personal communication; Young, pers. comm.). Although water sensitivity is not usually noted in paints containing earth pigments, conservators tend to approach these passages with caution (Wijnberg, pers. comm.). Water sensitivity has been observed in oil paint films with a great variety of surface effects and application techniques; it is therefore very difficult to draw up diagnostic guidelines based on topography. However, there are some characteristic physical manifestations such as paint films with efflorescence that have been linked to water sensitivity (Basto, pers. comm.; Young, pers. comm.). In these cases, fluctuations in environmental moisture (or possibly previous cleaning campaigns) may have accelerated the migration of degraded components to the surface of the paint film. In other instances, sensitivity has been associated with unusually tacky paint; this commonly coincides with the modification of tube paints with artists’ additions of other media but may also be associated with the plasticizing effect of metal stearates, as well as the low pigment volume concentration enabled by the inclusion of stearates.

Test Paint Films: Tests for Solvent Sensitivity

A summary of the test results with saliva are presented in Table 1. Tests with deionized water showed less sensitivity than those with saliva.

The most influential variable with regard to water sensitivity was found to be the pigment used for the test paints. Ultramarine films on canvas were consistently highly sensitive to deionized water and saliva (+++, +++). The sensitivity of paints containing chromium oxide green depended on the batch and the admixtures with other materials (+++, +, −), and raw sienna paints were the least sensitive (+, −). Chrome green and ultramarine paints on canvas showed a higher level of water sensitivity than the same films on Melinex. This may be attributed to the absorption of some of the oil binding medium and the formation of a less well bound paint film that was more susceptible to the mechanical action imparted by swabbing of the green and blue paint films. Conversely, raw sienna paint on Melinex showed moderate sensitivity (+) and was mostly insensitive on the canvas support (−). This difference in sensitivity was noted in the second set of tests that were carried out 18 months after the first.

In general, saliva was found to affect sensitive paint more quickly than deionized water. This may be due to the slightly higher pH (deionized water has pH 5.5; saliva has approximately pH 7.5), its surfactant properties, or its greater ionic strength. For ultramarine, the difference between water and saliva was less apparent than for the green and earth paints. The sensitivity of the paint films to iso-octane was generally low, but there was a consistent decrease in sensitivity of the chrome green and the raw sienna paints between 6 and 24 months after artificial aging, probably reflecting the further drying of the paint.

Ultramarine test paints in oil medium on canvas without additives were found to be very sensitive to saliva and water (+++, ++), and the commercial tube paints were invariably similarly sensitive. This relates to the hydrophilic nature of the pigment and the exacerbation of sensitivity through absorption of medium by the support that left the films more leanly bound. The addition of aluminum stearate to ultramarine and oil seemed to have little or no discernible effect on the sensitivity of the paints; the addition of zinc stearate reduced the sensitivity, especially in the second series of tests. Interesting, the combined addition of aluminum stearate and aluminum hydroxide produced films that were also more sensitive to saliva and water than the unmodified paints.
that were more resistant to saliva and water, most notably on Melinex (−). The addition of zinc stearate in combination with aluminum hydroxide had a similar but less pronounced effect.

Ultramarine on canvas with added aluminum hydroxide, linseed fatty acids (LF), and hydrogenated castor oil (HC) were significantly water sensitive (+++) also after prolonged aging. In contrast, on Melinex supports ultramarine paint without additives and films with added LF or LF and HC were significantly less sensitive (+, −) to saliva than the other ultramarine paints (+++, +).

The three grades of ultramarine behaved differently. Test paints combining the two finer grades of ultramarine (36 and 37), oil, and 10% aluminum hydroxide produced paint films of closely similar appearance, with an even midlevel gloss and saturation in flat areas and saturated, slumped, and wrinkled impasto. The same recipe with ultramarine 244 resulted in a streaky flat area with distinct phase separation and a paint-medium skin (Figure 2), with slumping and wrinkling in the impasto and slight bloom in the interstices. In paints of the same recipe that substituted the three ultramarines, the coarser grade (244) was more sensitive to aqueous solvents but less sensitive to iso-octane than ultramarines 36 and 37.

Ultramarine has a high level of oil absorption, poor drying properties, and extreme hydrophilicity. Larger particle size is associated with more extreme phase separation and increased sensitivity to polar solvents. However, phase separation in the samples was linked to a reduction in the water sensitivity of the paint on aging. Reduced sensitivity to water in the impasto areas could be explained by the protective function of the skin of organic material of the hydrophilic pigment in relation to polar solvents.

Paints containing zinc oxide, anatase titanium dioxide, and ultramarine have been associated with water sensitivity in paintings (Tempest, 2009). Zinc oxide and ultramarine are hydrophilic and may facilitate the disruption of the surface of the paint during swabbing with aqueous solvents. A separate mechanism in which oil paint films become more accessible to polar solvents on aging may involve the breakdown of stearate additives, perhaps in synergy with other hydrophilic components.

Paints incorporating chromium oxide green on canvas without additives or with aluminum stearate had negligible sensitivity to aqueous solvents (−, +), whereas a higher sensitivity to saliva was observed when mixed with aluminum hydroxides (+), LF (2% and 5%), and HC (only at 10%; ++). Combinations of 10% metal stearates and 10% aluminum hydroxide resulted in a lower water sensitivity (−). Raw sienna paints on canvas were not affected by polar solvents (−), whereas samples on Melinex showed slight sensitivity to saliva (+) after aging.

The swab tests showed varying interactions with the paint surfaces that seemed to be generally related to the hydrophilicity or hydrophobicity of the surface. Chrome green and ultramarine paints with high oil content, especially on Melinex supports, were relatively unaffected by swabbing. Paints containing high percentages of added stearates were at first resistant to swabbing with any solvent and would suddenly break up and yield pigment from the underlying paint that remained vulnerable and was not fully cross-linked.

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**Table 1.** Results of the cleaning tests with saliva after 6 and 24 months storage at ambient conditions after artificial aging. The results are mean category values of all tests carried out. No distinction is made between the different ultramarine pigments used since their sensitivities were similar. Symbols and abbreviations are as follows: ++++, very sensitive, pigment or paint removed within 5 swab rolls; +++, sensitive, paint removed within 10–20 swab rolls; +, moderately sensitive, paint removed within 30 swab rolls; −, not sensitive; AS, aluminum stearate; AH, aluminum hydroxide; LF, linseed fatty acids; HC, hydrogenated castor oil; NT, not tested. An asterisk (*) indicates lower sensitivity at higher concentrations.

<table>
<thead>
<tr>
<th>Pigment</th>
<th>Support</th>
<th>Testing time (months)</th>
<th>No additive</th>
<th>Al stearate</th>
<th>Zn stearate</th>
<th>Al hydroxide</th>
<th>AS/AH</th>
<th>LF</th>
<th>HC</th>
<th>LF–HC</th>
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<tr>
<td>Chrome green</td>
<td>Melinex</td>
<td>6</td>
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<td>Melinex</td>
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<td></td>
<td>Canvas</td>
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<td>–</td>
<td>+/-</td>
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<tr>
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<td>Raw Sienna</td>
<td>Melinex</td>
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<td>+/-</td>
<td>–</td>
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The method for assessing the sensitivity of the paints did not account for the extreme behavior of the ultramarine-containing paint films; however, there was a close similarity to the reported behavior of ultramarine paints in paintings undergoing surface cleaning in previous studies (Wijnberg et al., 2007). The effect of excess stearate addition, linked with the formation of an incompletely cross-linked skin of medium and possibly the retardation of cross-linking of the underlying paint, produced the anomalous results in water sensitivity tests in this study. Further analysis is required to confirm this observation and to examine the skin of the medium in more significantly aged samples, which could present more oxidized or hydrolyzed surfaces and therefore be more hydrophilic. Degradation of the stearate additives may play an important role in the distinctive behavior of metal stearate-containing paint as it ages since this process will result in free fatty acids and aluminum hydroxide, which is hydrophilic. This effect may be particularly pronounced in films with a high oil content (such as ultramarine paints). The pH of the paint may also play a role, where the alkaline character of some films favors the formation of water-soluble soaps from free fatty acids or liberated by hydrolysis.

**Test Paint Films: Surface Phenomena**

Efflorescence was observed shortly after swabbing with aqueous solvents on the surface of water-sensitive chromium oxide green and ultramarine paints containing aluminum stearate on Melinex (Figure 3). It increased in density with increasing stearate content. Elemental aluminum remained distributed within the paint film, and FTIR of the bulk paint confirmed the presence of aluminum stearate (Figure 4). Although no increase in sensitivity was observed with additions of aluminum stearate in raw sienna paints, similar localized efflorescence was visible on samples on Melinex. The FTIR spectra for efflorescence on a variety of samples containing different pigments are characteristic of long-chain carboxylic acid (Figure 5). The SEM imaging shows planar, shardlike crystalline surface features that are present in abundance in areas of efflorescence and are absent, or

**FIGURE 2.** (A) Ultramarine 244 + 10% aluminum hydroxide, showing streaky surface appearance and slumped, glossy impasto. (B) Back scattered electron image of cross section of ultramarine 244 + 10% aluminum hydroxide, showing a paint-medium skin below the top layer of pigment particles.

**FIGURE 3.** Localized efflorescence on (left) chromium oxide green + 20% aluminum stearate and (right) Winsor & Newton Winton French ultramarine + 20% aluminum stearate.
present only in low concentration, in areas where aqueous solvents have not been applied to the surface (Figure 6).

Other structures, distinct from fatty acid efflorescence, were observed using SEM on the surface of samples of water-sensitive oil paint films (Figure 7). The structures are visually similar to those containing magnesium and carbon observed by Mills et al. (2008) on the surface of Talens ultramarine, raw sienna, and cadmium yellow and red paint films (Figure 8). As there were no
magnesium-containing additives in the test paints, this indicates that some surface structures previously linked with degradation of certain additives, such as magnesium stearate or magnesium carbonate, can form in the absence of these additives.

**CONCLUSIONS**

Tests for water sensitivity by swab rolling after aging of linseed oil-bound test paint films indicated that additions of aluminum hydroxide and linseed oil fatty acids (also in combination with hydrogenated castor oil) enhanced the water sensitivity of the paints made using all pigments. Samples containing combinations of aluminum hydroxide and aluminum stearate generally reduced sensitivity to water. The evaluation criteria did not account for the phenomena observed in the ultramarine-containing paints with added stearates that formed a skin of medium on the surface that was initially resistant to swabbing with polar solvents. However, the paint beneath the skin was sensitive to polar solvents, and these samples responded to water in a manner very similar to that reported during the treatment of ultramarine passages in modern paintings.
It is proposed that metal stearates can both plasticize the paint and retard the drying process in oil-bound films. Free fatty acids, either as an integral additive (impurity associated with the metal stearates) or as a product of hydrolysis of the metal stearates, may migrate to the paint surface during drying or degradation of the film under normal environmental conditions, and in some films this process may be enhanced by cleaning treatments using water. Aluminum stearate-containing paints swabbed with aqueous solvents exhibited localized stearic acid efflorescence, whereas aluminum compounds remained distributed within the paint film. This may be associated with the breakdown of the metal stearates to form free fatty acids. The incorporation of aluminum hydroxide in addition to metal stearates appears to reduce both these tendencies, thus acting as a stabilizer.

The properties of pigments play a defining role in the characteristics of dried paint films and only certain combinations of pigment and additive result in water sensitivity. There is a relationship between the inclusion of metal stearates in oil paint and the occurrence of water and other solvent sensitivity. The presence of pigments that are poor driers, combined with the low pigment volume concentration enabled by the inclusion of metal stearates, can lead to a soft sticky film that may never fully polymerize, resulting in an open polymer network susceptible to swelling by polar solvents.

Future studies will look into the aging properties as well as the specific behavior of additives. Stearate (nondrying) fatty acids in cheap paints may turn into surfactants in alkaline environments. It is known that surfactants have been used in oil paint manufacture and are still used for lower-quality paints. Surfactants such as Duomeen, Empigen, and Empilan (P. Waldron and I. Garrett, Winsor & Newton, personal communication) may increase solvent swelling by polar solvents.

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REFERENCES


