

Multitechnique Approach to Evaluate Cleaning Treatments for Acrylic and Polyvinyl Acetate Paints

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ABSTRACT. A multitechnique approach was applied to two types of commercial paints, Liquitex (acrylic) and Flashe (polyvinyl acetate) to evaluate cleaning treatments carried out with water and a selection of organic solvents having different polarities. The analysis included weight loss and water absorption-desorption tests; pyrolysis–gas chromatography–mass spectrometry, Fourier transform infrared spectroscopy, UV-Vis spectrophotometry, light microscopy, scanning electron microscopy, atomic force microscopy, voltammetry of microparticles, mechanical tests, and microtensile tests. The study showed, among other results, differences in the mechanical behavior of both types of paints after exposure to water and other organic solvents. These differences correlate well with content changes of additives and pigments after cleaning. Morphological changes after cleaning can also be correlated with compositional changes in the film depending on the solvent used.

INTRODUCTION

Until some years ago, conservation treatments aimed to solve the problems presented by centuries-old paintings. These depended on the polymerization, cross-linking, and/or hydrolysis reactions that the paint might have experienced, the films' drying times, and the internal stresses that could have developed within the painting structure as a consequence of the many intrinsic and extrinsic variables that could have changed over the years.

The industrial development during the twentieth century led to the progressive development of synthetic media and paints. Because of the complexity of these products, whose composition and formulation are not known, the interactions of pigments, media, and all kind of “enhancers” in the behavior of the resulting films have yet to be characterized as these will affect their aging characteristics and stability over time.

Presently, the problems presented by the conservation of modern and contemporary paintings make essential the knowledge of these synthetic formulations. The lack of the time perspective makes understanding how polyvinyl acetate (PVAc) and acrylic paint films form, what determines their stability, and how they interact with both the environment and the materials and methods used by conservators crucial for the development of appropriate conservation treatments.

The study of the effects of cleaning treatments on the physical and chemical properties of artists' materials has increasingly attracted the attention of researchers in the field of conservation science since the 1990 IIC Brussels Congress "Cleaning, Retouching and Coatings" (Mills and Smith, 1990). In particular, a significant number of papers focus on the effects of cleaning of modern materials such as acrylic media (Ormsby and Learner, 2009).

Alternative cleaning methods to swabbing (with water, pure solvents, or their mixtures to obtain specific polarities) include the use of gels, emulsions, surfactants, and chelating agents, among others, which apart from their low toxicity, aim to minimize the penetration and retention action of solvents as well as to control their effectiveness. This is particularly true for the case of gels and emulsions.

Gels are helpful in avoiding the rapid penetration of water and solvents into the paint layers.

Emulsions allow the formulation of stable cleaning mixtures from nonmiscible solvents by adding a surfactant as an emulsifier. In particular, water-in-oil emulsions allow water to be in contact with water-sensitive surfaces that cannot be exposed directly to it. This is helpful in the case of waterborne acrylic and PVAc paints. The resulting emulsion mixture can then be applied with a brush, bringing the micro-particles of emulsified water in contact with the surface of the acrylic film. Finally, surfactants and chelating agents can be designed to act selectively on specific materials that need to be removed.

A multitechnique approach to evaluate different cleaning methodologies was applied to a selection of both acrylic and PVAc paints in an attempt to provide practical understanding of the effects of cleaning with water and solvents and therefore the consequences that a conservation treatment might have on an artwork. Insights into the following questions, among others, were sought:

- How are these paints affected by water and/or solvents?
- To what extent does the application methodology significantly influence the resulting action of water and/or solvents (in terms of both effectiveness and potential damage risks)?
- Are gels and emulsions a valid solution in terms of effectiveness and limitation of risks associated with retention and residue issues?

EXPERIMENTAL METHODS

COMMERCIAL PVAc AND ACRYLIC PAINTS

The PVAc paints tested were Flashe paints (supplied by LeFranc & Bourgeois). The colors studied included oriental red, green armour, Senegal yellow, and burnt umber. The acrylic paints tested were Liquitex (Heavy Body) phthalocyanine blue, red oxide, Hansa yellow, cadmium yellow, Mars yellow, burnt umber, raw umber, titanium white, naphthol red, and Liquitex

gloss medium and varnish. Talens Studio raw sienna, Talens glossy medium, and Talens gel medium were also tested.

PREPARATION OF TEST SPECIMENS

Film specimens were prepared by casting the paints onto Mylar sheets and allowing them to dry for 1 to 2 years before testing. The resulting films exhibited an average thickness of 0.15 mm.

IMMERSION TESTS

Samples weighing approximately 0.4–0.5 g were immersed in deionized water or solvent (ethanol, acetone, white spirit, or ligroin) for 10 minutes, 20 minutes, and 12 hours. In the case of pure binding media, such as Talens glossy medium and Talens gel medium, water immersion for 90 minutes was carried out. The films were then removed, dried from the excess of water or solvent, weighed, and analyzed. An aliquot of the resulting liquid extract was preserved, and another aliquot was dried at 50°C in a laboratory oven and then analyzed.

GEL AND EMULSION CLEANING METHODS

Vanzan gel (a xanthan gum with a high molecular weight water-soluble polysaccharide thickener) was prepared by mixing 1 g of Vanzan in 50 mL of deionized water.

Klucel G gel (a nonionic cellulose ether) was prepared by mixing 2g of Klucel G in 50 mL of deionized water.

A ligroin in water (water in oil, W/O) emulsion was prepared by first mixing 10 mL of water with 4 mL of Brij 30 (a nonionic polyoxyethylene surfactant) and then adding 90 mL of ligroin. Both gels and emulsions were applied by brushing. After a specified time, they were removed with a dry cotton swabs, and then the surface was swabbed with water.

INSTRUMENTATION

The analytical techniques applied are the following; the working conditions for the instruments and procedures for sample preparation were similar to those of previous studies: (1) weight measurements of water absorption-desorption and weight loss tests performed with a Precisa XT 120-A precision balance, (2) pyrolysis–gas chromatography–mass spectrometry (Py-GC-MS; Osete-Cortina and Doménech-Carbó, 2006; Silva et al., 2010), (3) Fourier transform infrared spectroscopy and UV-Vis spectrophotometry (Doménech-Carbó et al., 2006b:156), (4) light microscopy (Doménech-Carbó et al., 2006a:162), (5) scanning electron microscopy (SEM) and atomic force microscopy (AFM; Doménech-Carbó et al., 2006b:156), and (6) mechanical tests and microtensile tests (Silva et al., 2010). Mechanical and microtensile tests were carried out on the films after they had been dried for 1 month at laboratory conditions (23°C and 55% RH) after treatment.

RESULTS AND DISCUSSION

WATER IMMERSION OF TEST FILMS

Waterborne acrylic and vinyl paints are not soluble in water but are highly sensitive to liquid water. The sensitivity of these products has been tentatively attributed to the presence of additives included in the paint formulations (Juhué and Lang, 1993; Kientz and Hall, 1993; Juhué et al., 1995; Belaroui et al., 2003).

Figure 1 shows the water absorption curves obtained by a 20 minute immersion of Liquitex Heavy Body (HB) acrylic paint

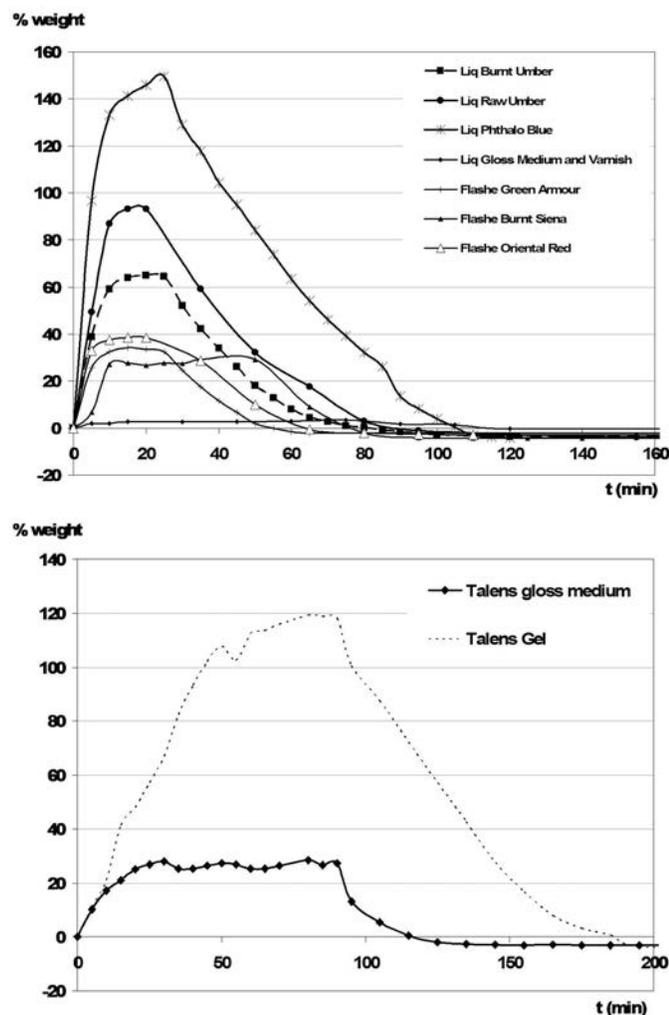


FIGURE 1. (top) Water absorption and drying curves for acrylic Liquitex Heavy Body and PVAc Flashe paint films (average thickness of 0.15 mm) after a 20 minute immersion of deionized water. Note that the acrylic paints phthalocyanine blue and naphthol red showed practically the same behavior, and this also occurred for the oriental red and the Senegal yellow. (bottom) Equivalent curves for the Talens gel and Talens gloss medium after 90 minute immersion.

films in deionized water. The specimens tested (average thickness of 0.15mm) were nearly fully penetrated in this time, whereas they took about 2 to 4 hours to dry, although complete drying may require days. All colors exhibited weight loss due to the extraction of water-soluble additives present in the bulk film.

The acrylic paints showed a variable water uptake, depending on their color, that ranged between 60% and 200% weight in the first 20 minutes of immersion. Interestingly, synthetic colors such as naphthol red and phthalocyanine blue exhibited the highest water absorption and visible swelling when compared to earth colors and other inorganic pigments. Likewise, the synthetic colors also exhibited more weight loss. This result indicates that the formulations are *tailored* by the manufacturers to stabilize the emulsion as a function of pigments and additives, which will clearly affect the overall water sensitivity of the dried film. In contrast, Liquitex acrylic medium and varnish films were unaffected by the water exposure during immersions, showing low weight gain and minimum swelling.

After a 90 minute immersion, Talens acrylic glossy medium and Talens gel medium showed extensive water absorption and swelling, and this behavior differs significantly from that of the Liquitex binding medium. The gel absorbed far more water than the glossy medium, indicating the presence of additives that affect the water sensitivity of the final product. The analysis of these products by Py-GC-MS revealed that both products, the glossy and the gel medium, are ethyl acrylate-methyl methacrylate-butyl acrylate polymers.

The PVAc Flashe paints contain a high pigment volume concentration and behave as brittle paints when compared to the acrylic paints described previously. The immersion tests performed for these paints (Figure 1) showed that most colors exhibited similar water absorption-drying profiles, with the exception of the earth colors. Most of the earth color films lost cohesion when subjected to the immersion tests, which is probably related to the expansion of the clay minerals in the film. The absorption-drying profile for burnt sienna and green armour reveal higher water retention after the immersion test that can be attributed to the presence of clay minerals from the earth pigment.

EFFECT OF WATER IMMERSION ON THE MECHANICAL PROPERTIES OF TEST FILMS

Figure 2 shows the stress-strain plots of the acrylic Liquitex HB burnt umber and phthalocyanine blue films after a series of water or solvent immersions. The curves for the burnt umber are representative for all acrylic and the PVAc Flashe paint films.

From these curves, it becomes evident that the effect of the immersion on the mechanical properties of the acrylic films requires some 20 minute immersions to become significant. This may be related to the fact that it took water this amount of time to fully penetrate into the film, promoting the leaching of additives and inducing changes in the lattice structure. Consequently, it can be considered that for a short exposure to water these films are almost unaffected.

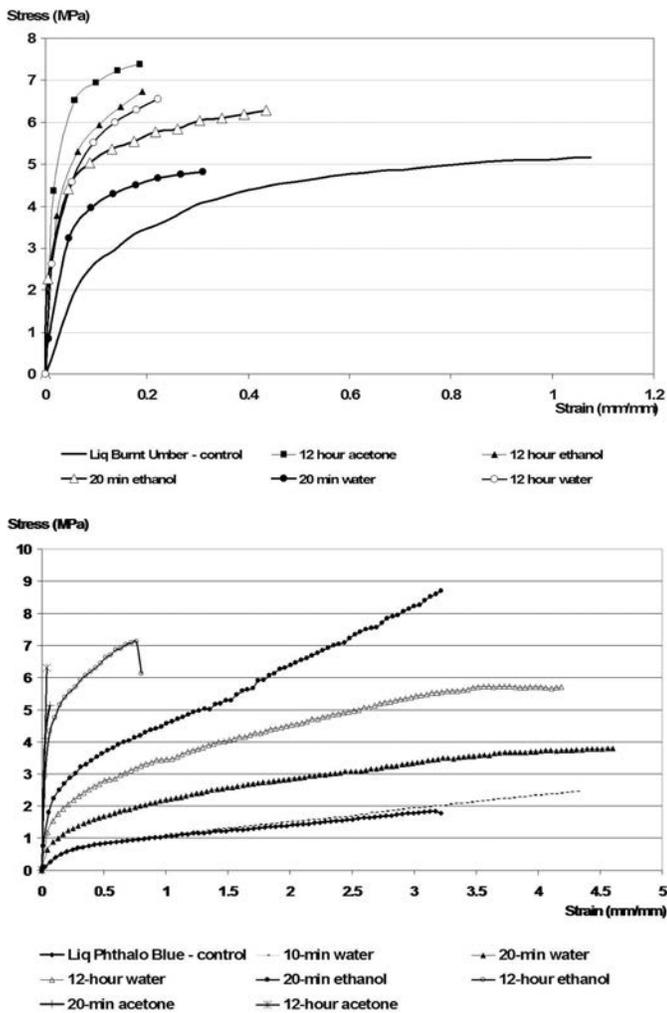


FIGURE 2. Stress-strain plots of (top) the acrylic Liquitex HB burnt umber paint film and (bottom) phthalocyanine blue paint film for the control test and after immersion in water or solvent for different times. The behavior of the burnt umber paint reflects that of the acrylic and PVAc paints in general.

All paint films tested, i.e., acrylic and PVAc, except for the phthalocyanine blue, showed an increase in stiffness and a decrease in the elongation-at-break values after 20 minute and longer immersion times in water, ethanol, or acetone. As shown in Figure 2, acetone dissolves the polymer chains much faster than ethanol, making the paint film far more brittle, as shown above for the 20 minute and 12 hour immersions in acetone. The 12 hour exposure to ethanol embrittles the paint film far more than the equivalent water immersion. Interestingly, the phthalocyanine blue films showed an increased plastic deformation capacity for the case of water.

Bar charts illustrating the weight loss for both these paints as a function of immersion time in water are shown in Figure 3.

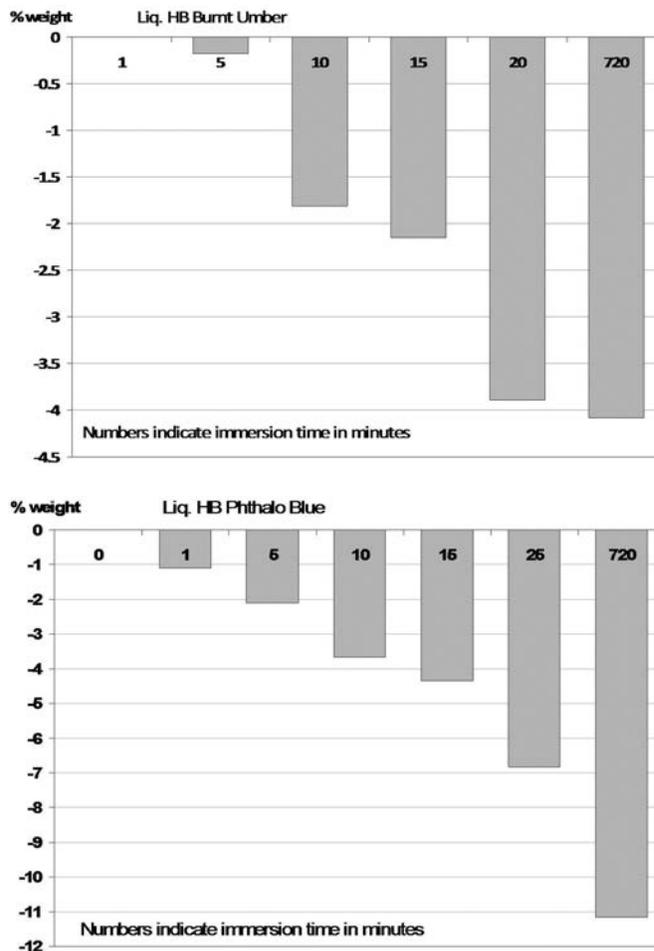


FIGURE 3. Weight loss as a function of water immersion time for the acrylic Liquitex HD (top) burnt umber and (bottom) phthalocyanine blue paint films.

The extraction of minor compounds present in the bulk films can be readily measured in the first few minutes of immersion, particularly for the phthalocyanine blue, explaining the different mechanical properties of these films when exposed to water immersion longer than 20 minutes.

The examination of both acrylic and PVAc paints by SEM clearly showed that water immersion creates micropores in the structure of the film (Figure 4). Complementary data collected with a microtensile strength tester coupled to a light microscope showed that these micropores were the starting points for cracking of these films when subjected to stress.

MECHANICAL PROPERTIES OF ACRYLIC FILMS AFTER WATER IMMERSION AND SWABBING TESTS

The mechanical properties of acrylic Talens raw sienna films were evaluated after 5 and 20 minute water swabbing or water

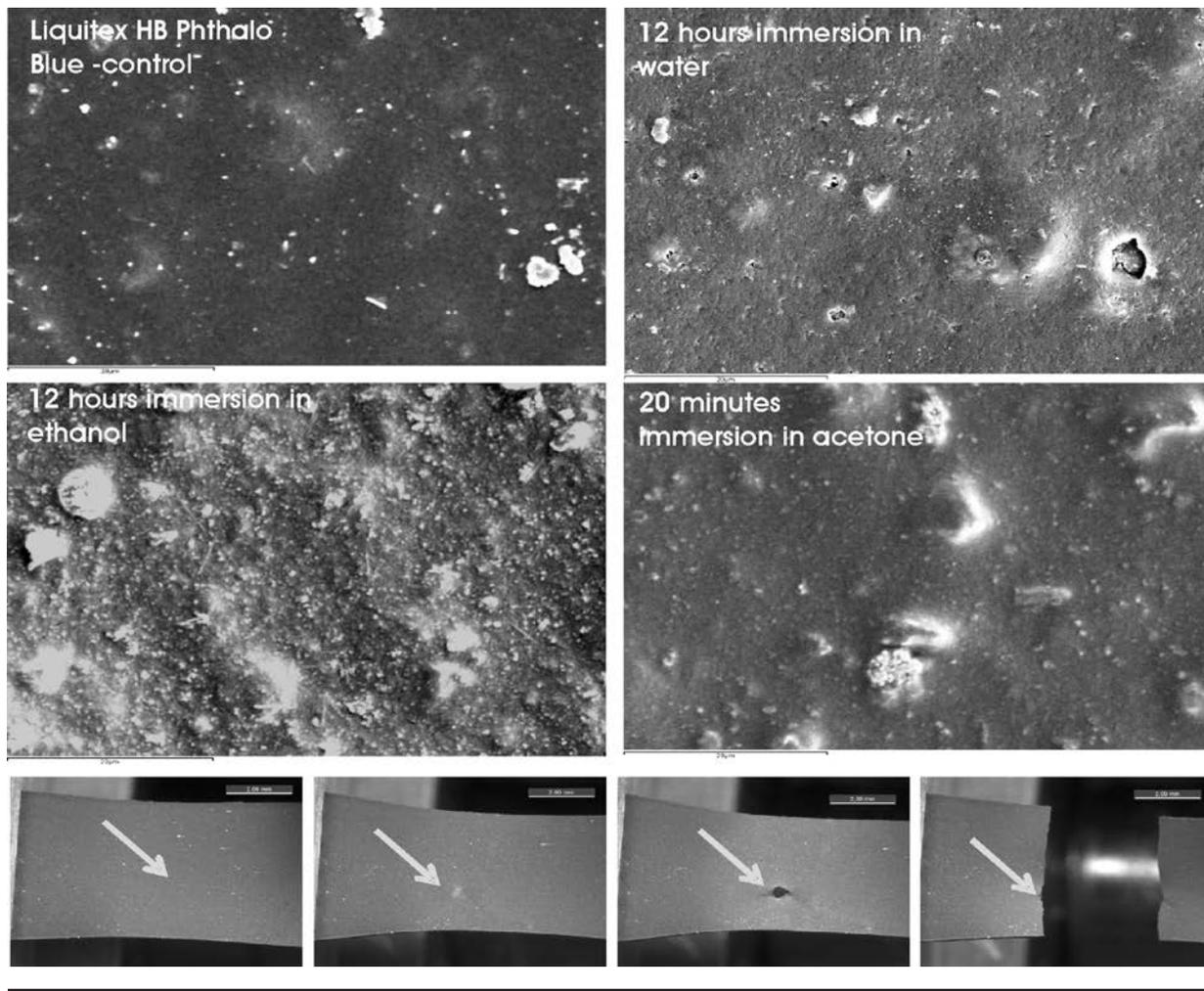


FIGURE 4. The SEM photomicrographs of acrylic Liquitex HB phthalocyanine blue films before and after immersion in water (12 hours), ethanol (12 hours), and acetone (20 minutes). The photos below show light microphotographs taken during micro-tensile testing, where the starting points for the mechanical failure are the micropores.

immersion tests. The stress-strain curves are presented in Figure 5 and show that these samples, similar to most acrylic ones, underwent an increase in stiffness and elongation-at-break values within 5 minutes for both immersion and swabbing. It is evident that in the first few minutes, the immersions affect the paint's mechanical properties more dramatically. However, after 20 minutes of water exposure, both immersion and swabbing present similar stress-strain curves, indicating that water swabbing for longer periods of time may have mechanical effects on paints similar to those obtained with water immersion.

EFFECT OF SOLVENT IMMERSION ON TEST FILMS

In general, the exposure of acrylics and PVAc paints to solvents resulted in the dissolution of polymer chains and extraction of additives. The AFM images presented in Figure 6 show a PVAc

Flashe Senegal yellow paint film before and after immersion in acetone. The exposure of these films to solvents with lower polarity than water, such as acetone and ethanol, resulted in an increase in the roughness of the surface at micro- and nanoscales as the grains of pigment become more evident. This shows not only that additives are being removed but also that large amounts of polymer chains are being extracted, which affects directly the overall properties of the films.

As mentioned, acetone affects the paint films by dissolving the polymer chains much faster than ethanol. As a consequence, the samples readily became stiff and brittle and almost impossible to test. Ethanol, on the other hand, affects the mechanical properties of the film in the first 20 minutes after immersion, but it takes a longer exposure time to embrittle the sample.

On the other hand, both acrylic and PVAc paints showed less susceptibility to nonpolar solvents such as ligroin and white

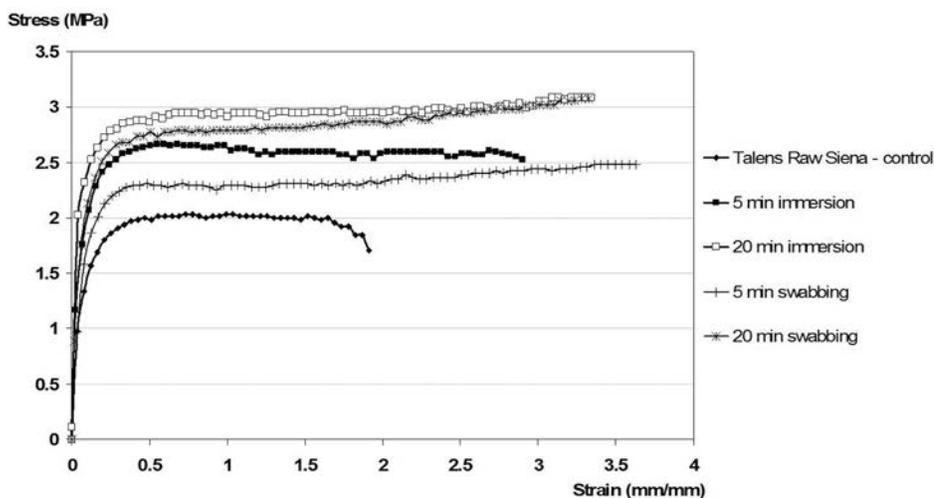


FIGURE 5. Mechanical properties for Talens raw sienna films after 5 and 20 minutes of water swabbing or immersion.

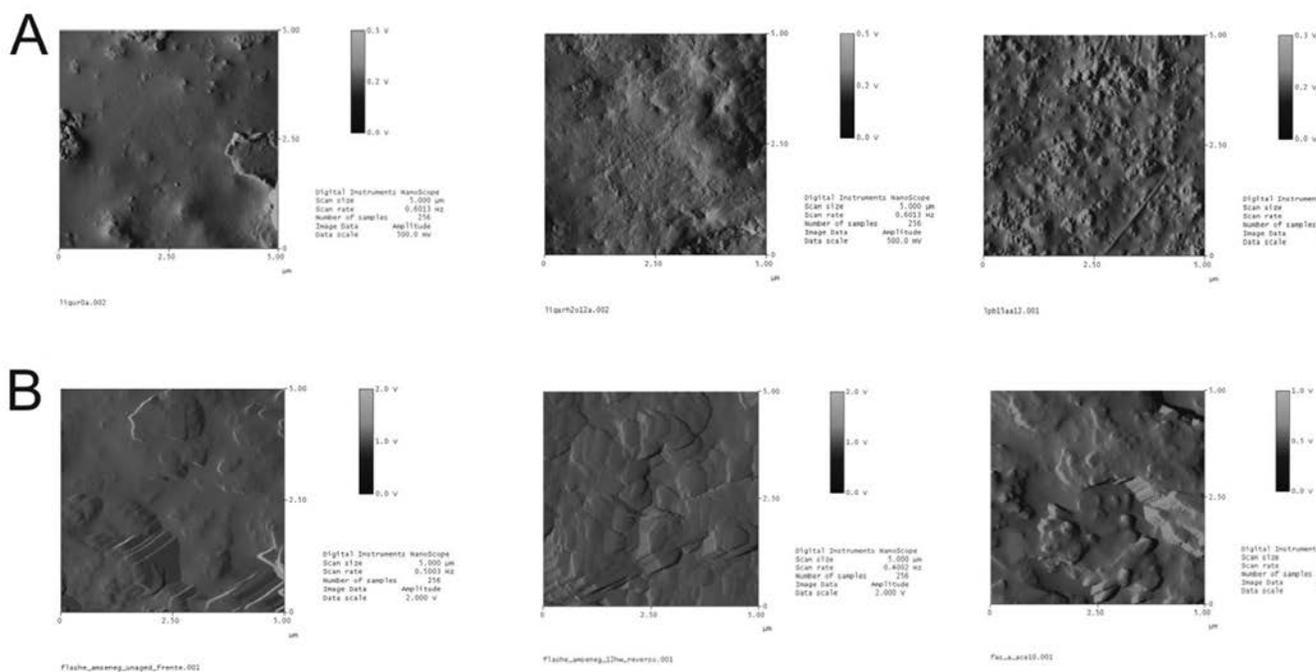
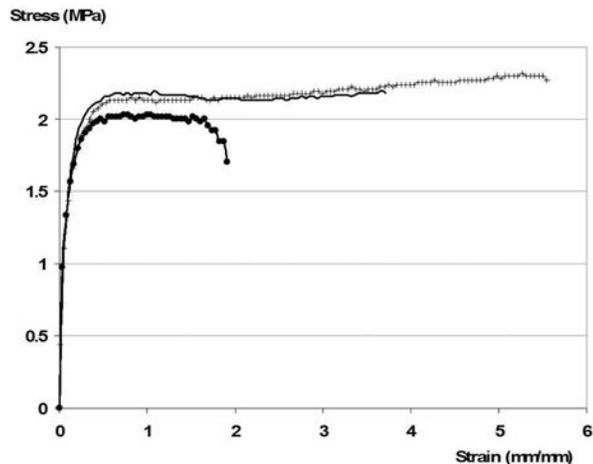


FIGURE 6. The AFM images of PVAc Flashe Senegal yellow paint film (A) before and (B) after immersion in acetone. (left) Unaged films, (middle) 12 hour water immersion, and (right) 20 minute acetone immersion.

spirit, as discussed in prior studies (Zumbühl et al., 2006). Aliphatic solvents did not produce an evident swelling effect in any of the paint films tested. Nevertheless, it was interesting to note that the samples retained these solvents for a long time, resulting in a plasticizing effect of the paint films, which is shown by an increase in the elongation-at-break values (Figure 7). It is important to mention that there was a slight increase in the stiffness of Talens raw sienna specimens after 30 minute immersion in either ligroin or white spirit. Furthermore, the SEM surface examination of the same test specimens, as well as those treated with

water, revealed alterations in their micromorphology, including the appearance of microfissures visible at very high magnification (Figure 8).

Interestingly, the 12 hour water immersion of PVAc Talens raw sienna severely affected the paint film; the whitish aspect of the SEM image is due to the migration of calcite and clay minerals from the core to the surface of the film (Wedin and Bergström, 2005). This is likely related to the swelling of these particles with water and consequent migration in the water-swollen latex.



— 30-min immersion Ligroine
 + 30-min immersion White Spirits
 x Talens Raw Siena - control

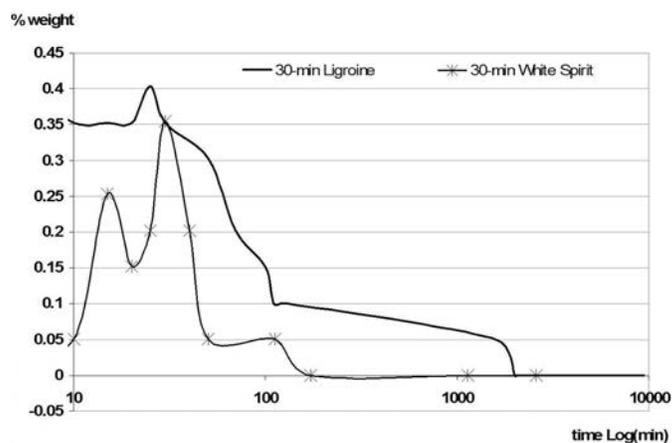


FIGURE 7. (top) Stress-strain plots for Talens raw sienna paint films before and after 30 minute immersion in either ligroine or white spirit. (bottom) Weight increase and loss for the samples during and after 30 minute immersion in white spirit or ligroine.

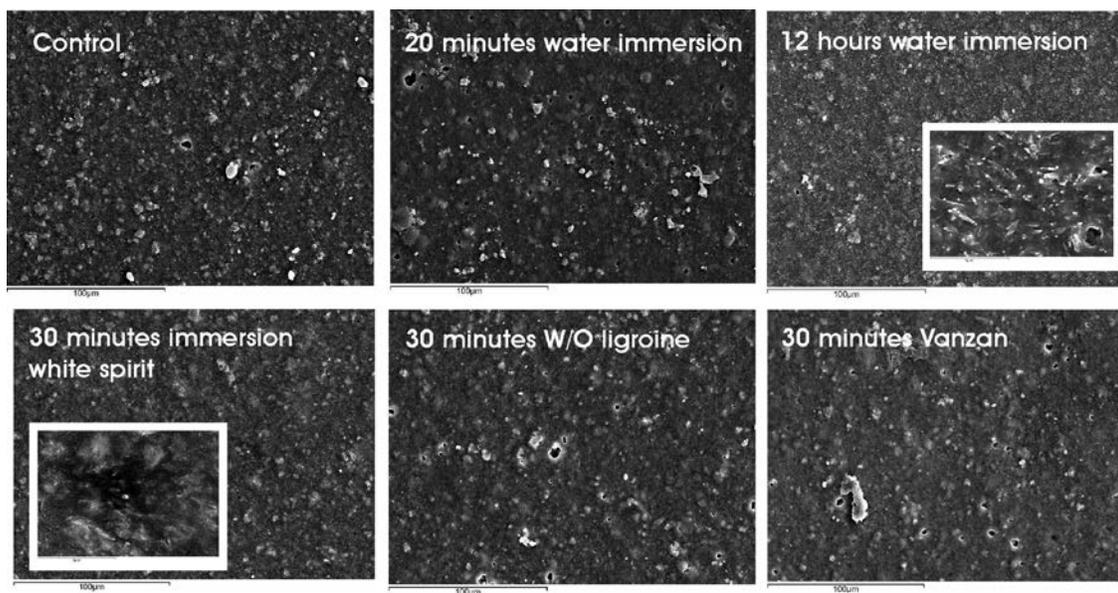


FIGURE 8. The SEM photomicrographs of Talens raw sienna paint films. Top row: (left) before treatment, (middle) after 20-minute water immersion, and (right) after 12-hour water immersion. Bottom row: (left) 30-minute white spirit, (middle) 30-minute ligroine W/O emulsion, and (right) 30-minute Vanzan gel. Details magnified at 10,000x.

IDENTIFICATION OF ADDITIVES

The UV-Vis spectrophotometry and Fourier transform infrared spectroscopy confirmed the presence of nonionic polyethoxylate surfactants as the major component of the aqueous extracts from both PVAc and acrylic paints. Interestingly, in the PVAc aqueous extracts there were also noticeable IR absorption bands ascribed to a cellulose ether-type compound that is commonly used as a paint thickener.

Further analysis of the dried aqueous extracts of PVAc paints by means of Py-GC-MS enabled the identification of other minor additives, such as a phosphate-type compound (flame retardant), methenamine (preservative), and styrene and methacrylic acid (Silva et al., 2010). The presence of these compounds reflects the complex formulation of these paints. In this case, a small amount of an acrylic emulsion was probably added in order to improve the final properties of the paint. Additionally, in the extracts of solvents with lower polarity, such as acetone or ethyl acetate, a small amount of pigment was identified in paints where a synthetic organic pigment was used. For example, a characteristic UV absorption band associated with an organic pigment was identified in a burnt umber-based color. This suggests the addition of an organic pigment to enhance the optical properties of the paint.

ALTERNATIVE METHODS FOR CLEANING ACRYLIC FILMS: GELS AND LIGROIN W/O EMULSIONS

A similar approach to that previously described for water immersion was used for gels and ligroin in water emulsions (W/O) used as cleaning methods of acrylic films. Talens raw sienna film specimens were exposed to Vanzan and Klucel G gels for different amounts of time: 5, 10, 20, and 30 minutes. Another set of samples was exposed to a ligroin in W/O or immersed in ligroin for 30 minutes. The water absorption-drying data were obtained, and the mechanical properties were measured after drying the specimens for 1 to 2 months under laboratory conditions (23°C and 55% RH).

The weight increase and loss curves for Talens raw sienna films exposed to water immersion and swabs as well as in contact with different gels for 5 or 30 minutes is shown in Figure 9. This figure illustrates that the use of Vanzan gel reduces significantly the amount of water absorbed into the acrylic films compared to the immersion and swabbing data also presented. At 30 minutes, the gel is still able to provide water to the surface but significantly reduces the water penetration and swelling of the acrylic paint film. Similar results were obtained for Klucel G gels.

Four main points can be observed from these curves. First, the amount of water absorbed at a specific time is nearly the same whether the film is immersed in water or swabbed. Second, the amount of water absorbed from a gel is significantly reduced compared to immersion or swabbing, and this amount is not proportional to the time the gel is applied to the film. A 5

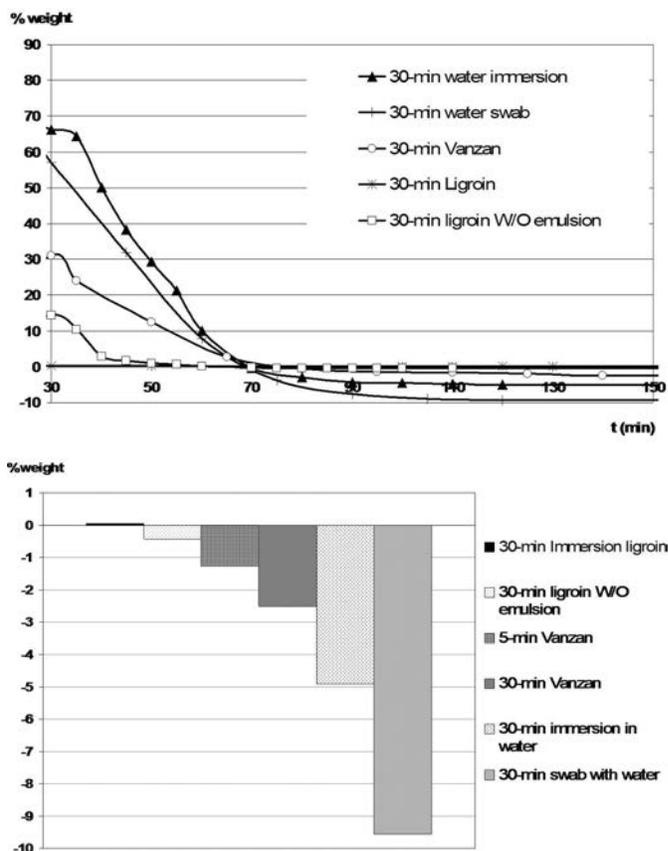


FIGURE 9. (top) Weight loss upon exposure of Talens raw sienna films to water immersion or swabbing, application of Vanzan gels, immersion in ligroin, and treatment with ligroin W/O emulsion for specified times. (bottom) Weight loss of the test paint films after application of these treatments.

minute application results in half the amount of water absorbed compared to a 30 min application.

Third, that 30 minute immersion in ligroin does not change the weight of the paint film significantly as this solvent is barely absorbed into the Talens acrylic films. However, it remains trapped inside the polymer chains for long periods of time, as shown by the measured weight increase. This results in a plasticizing effect of the paint film, as shown in the stress-strain curves in Figure 7. Last, that application of a ligroin W/O emulsion for 30 minutes reduces the amount of water absorbed to about half of that supplied by a gel in the same amount of time, and additive leaching was significantly reduced, as reflected by the low weight loss.

The SEM photomicrographs presented in Figure 8 clearly show that the surfaces of the test specimens were less affected when treated with gels, such as Vanzan, than when subjected to water immersion. This means that surface cleaning can be adjusted to control the risk of leaching and removal of additives using gel systems based in water.

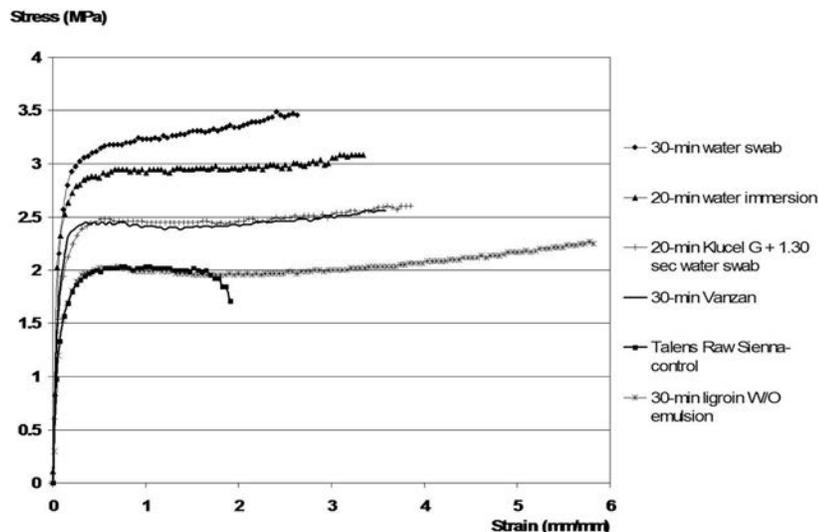


FIGURE 10. Stress-strain plots for acrylic Talens raw sienna paint films subjected to water immersion, water swabbing, Klucel G gels with and without rinsing, Vanzan gels, and ligroin W/O.

The effects of these gels on the mechanical properties of these acrylic paint specimens are illustrated in Figure 10 using the example of the Talens raw sienna. The use of the Vanzan gel on the paint film surface did not significantly affect its mechanical properties until 30 minutes of exposure to the gel had been reached. After this, the specimens started to exhibit a slight increase in stiffness, even though there was no alteration in the elongation-at-break values. Specimens treated with Klucel G gel showed a similar behavior.

It is also evident that 30 minute water swabbing affects the films more than 20 minute water immersion. The application of the ligroin W/O emulsion did not result in any significant change in the mechanical properties of the film as there was a lower extraction of paint additives.

It is important to highlight that some acrylic colors such as Liquitex Heavy Body phthalocyanine blue and naphthol red showed high sensitivity to the W/O emulsion cleaning treatments because of the presence of a surfactant in the emulsion. A simple solubility test showed that ligroin with a surfactant was able to dissolve the paint film, and that this solvent plus surfactant mixture gave the solvent the power observed with the ligroin W/O emulsion system. These points are important to bear in mind when performing the solubility tests prior to the cleaning treatment itself.

CONCLUSIONS

This study has shown that, in general, the acrylic and PVAc paints tested readily absorbed water during the immersion tests. The water absorption and swelling were evident within the first few minutes of immersion. For longer immersion times, both 20 minute and 12 hour tests, the absorbed water took roughly 2 to 4 hours to dry, and the residual water required at least 1 to 2 days for complete elimination. Some paint films, such as the

PVAc Flashe burnt sienna, exhibited longer water retention times that could be attributed to the presence of clay minerals in the paint films.

For the same commercial brand, the absorption of water and the swelling effect were dependent on the pigments, fillers, and, especially, the additive content present in each color formulation. In general, synthetic colors were more prone to water absorption than inorganic ones. All films lost weight after complete drying. This could be related to the extraction of water-soluble additives, which has been shown to be a time-dependent process. Consistently, the films that exhibited more weight loss were those that absorbed more water. This was evident for Liquitex Heavy Body and also Talens colors.

The analysis of the water extracts from the immersion tests revealed the presence of different additives depending on the type of paint. In the case of the acrylics studied, a nonionic surfactant and, to a lesser extent, an anionic polyethoxylate surfactant were the major components of the extracted materials. This mixture of surfactants and an ether cellulose-type thickener were the major compounds found in PVAc Flashe paints.

Water cleaning results in the dissolution of additives, and long exposure times to water have been shown to affect the polymer lattice. This effect should be taken into account when considering the probable repeated exposures to water as a result of successive cleaning interventions over time. On the other hand, cleaning with solvents of lower polarity readily enables the dissolution of polymer chains and additives, especially if combined with mechanical action, e.g., swabbing. The solubilization of polymer chains and additives severely affected the mechanical properties of the paint films, making them far more brittle and thus more susceptible to damage and loss.

As an alternative to the more general water and solvent cleaning methods, a preliminary study on the effects of gels such as Vanzan and Klucel G as well as ligroin W/O emulsions was also carried out. The use of water gels reduced the overall effects

of water in the paints tested (absorption into the bulk film, increase in stiffness, and decrease of flexibility). The same was true for the water in oil emulsion system tested. The use of these products as cleaning alternatives to pure water appears to be a fruitful field to explore for cleaning modern materials.

It should be of interest to broaden the test sample matrix since it became clear that for different paint brands, and even for different colors within each brand, there was a variable sensitivity to the different treatments applied. In cleaning modern paints the phrase “each painting is unique” is definitely applicable, and cleaning tests should be conducted before using any of the cleaning products discussed here.

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