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The Effects of Water Exposure on Surface Characteristics of Acrylic Emulsion Paints

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As acrylic emulsion paint is a relatively new artistic medium, much about its properties and conservation remains unknown. The low glass transition temperature of acrylic paints causes the paint surface to be soft and slightly tacky at room temperature, thereby attracting dirt and dust which can become embedded. The cleaning of acrylic paintings continues to be a subject on which there is little consensus, with conservators using a variety of dry and wet techniques. This study, as part of an ongoing project, focused on the effects of water on the surface of the paint film. Colour and gloss measurements, visual examination, light microscopy and scanning electron microscopy were used before and after exposure of the samples to water to characterize the surface and the effects of contact with water. Different paint colours (titanium white, black, burnt umber, ultramarine blue and alizarin crimson) from different manufacturers were swabbed or immersed for either one minute or 24 hours in distilled water. As formulations from different manufacturers continually change, the object of the study was to identify trends, rather than results that would remain constant over time. The swabbed samples showed very little or no colour change, but gloss changes were measurable. For all manufacturers, titanium white samples showed the least amount of colour change after swabbing and immersions and ultramarine blue samples showed the greatest. In this experiment, swabbing or immersing the samples did not cause components of the paint to appear on the surface, but in some instances, did disperse or remove materials already on the surface.

La peinture acrylique en émulsion est un médium artistique encore relativement nouveau, et encore assez méconnu du point de vue de ses propriétés et de ses méthodes de traitement en restauration. Puisqu'elle a une température de transition vitreuse peu élevée, à température ambiante la peinture acrylique demeure tendre et légèrement poisseuse, ce qui fait que la poussière et la saleté qui s'y déposent y adhèrent facilement. Il y a encore peu de consensus parmi les restaurateurs au sujet des meilleures techniques de nettoyage pour ce genre de peinture, et donc une variété de méthodes à sec et à l'aide de solvants sont utilisées. Cette étude, qui fait partie d'une plus vaste recherche sur le nettoyage des peintures acryliques, avait pour objet de déterminer les effets de l'application d'eau sur des feuillets de peinture acrylique. Des échantillons avant et après leur exposition à de l'eau ont été évalués à l'aide de mesures de couleur et de lustre ainsi que d'examen visuels et aux microscopes optique et électronique à balayage, afin de caractériser la surface ayant été exposée à de l'eau et d'évaluer les effets du contact avec de l'eau. Des peintures de diverses couleurs (blanc de titane, noir, terre d'ombre calcinée, bleu d'outremer et cramoisi d'alizarine) et provenant de divers manufacturiers ont été mis à l'essai de trois façons : les échantillons ont été soit humectés en y roulant à leur surface un coton-tige imbibé d'eau distillée, soit totalement immergés dans de l'eau distillée, et ce, pendant soit une minute, soit 24 heures. Le but de l'étude était d'identifier des tendances plutôt que de fournir des recommandations fixes concernant les produits soumis à l'étude, car il faut s'attendre à ce que les manufacturiers changent la composition de leurs produits dans un avenir non lointain, comme ils ont l'habitude régulière de le faire. Les échantillons qui ont été humectés à l'aide d'un coton-tige ont fait preuve de peu ou pas de changement de couleur, mais il a été possible de mesurer une différence de leur degré de lustre. Parmi tous les produits des divers manufacturiers, les peintures blanches au titane ont démontré le moins de changement de couleur après tous les trois types de contact avec l'eau, alors que le bleu d'outremer était, au contraire, le plus sensible. En tenant compte des limites de cette expérience, aucun des trois types d'applications d'eau n'a causé la migration d'éléments de la peinture à sa surface; cependant, dans certains cas, des matériaux déjà présents à la surface ont été déplacés ou enlevés.

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Introduction

The abundance of synthetic paints developed for industry in the 20th century caught the attention of artists such as David Hockney and Helen Frankenthaler who experimented with these paints first in the 1960s.¹ Synthetic resin house paints became especially popular with artists because of low cost, easy availability, and quick drying time.² Artists' colourmen developed paints using synthetic resins, such as polyvinyl acetate (PVA), acrylic resins, and acrylic emulsions as the binding medium, instead of the traditional oil binder. Acrylic emulsion paints, in particular, soon became "the most important type of synthetic paint developed for artists' use".³ Widely used by artists today, acrylic emulsion paints owe their popularity to the

fact that the diluent is water and not toxic organic solvents. In addition, the paint film dries very quickly, being touch-dry in a matter of minutes; this feature, so different from the long drying process required by traditional oil paints, allows artists to add layer upon layer with little intervening drying time. The flexible nature of the acrylic polymer paint film is also attractive to artists. Little is known, however, about the conservation of acrylic emulsion paintings and the effects of conservation treatments on them.

Rohm and Haas first introduced acrylic emulsions for a range of applications, including exterior house paint, in 1953. Commercially, several companies then started manufacturing acrylic emulsion paints specifically for artists, with Liquitex, by

Permanent Pigments Inc. of Cincinnati, Ohio, being the first, in 1954. An early emulsion sold by Rohm and Haas, called Rhoplex AC-33 (Primal in the U.K.), is reported to have been used for the Liquitex emulsion paint.⁴ Other artists' colourmen soon responded with their own lines of acrylic emulsion paints: Grumbacher with Hyplar and Bocour with Aqua-tec. Today, many companies, such as Golden, Grumbacher, Liquitex, and Winsor & Newton offer an extensive line of acrylic emulsion paints and products.

The fast drying time and flexible surface that made acrylics so attractive to artists result from the physical characteristics of an acrylic polymer emulsion that serves as the vehicle or binder for the paint. Acrylic emulsion paint has been defined as "paint containing a stable aqueous dispersion of polymers or copolymers of acrylic acid, methacrylic acid, esters of these acids or acrylonitrile; sometimes termed latex, acrylic latex, or polymer emulsion paint."⁵ Although commonly referred to as emulsions, acrylics are actually dispersions (emulsions are suspensions of small droplets of a liquid in another liquid, while dispersions are suspensions of a solid in a liquid). The acrylic polymer is present in the solid state in water;⁶ however, to avoid confusion with current literature, the acrylic water-borne polymer and the paint made from it, will be termed emulsions for the purposes of this paper. The acrylic emulsion is a high molecular weight acrylic polymer with polymer chains entangled into spherically shaped particles, dispersed in water, with an average particle size distribution of 100 to 500 nanometers.⁷ The emulsion is initially prepared by "emulsion polymerization." The monomer and a polymerization surfactant are added to the water, followed by a catalyst to initiate the reaction and polymerize the monomer. The result is an emulsion of very small particles of polymer suspended in water.⁸

The paint may also contain a variety of additives: "surfactants, preservatives, defoamers, glycols, solvents and thickeners" with many functions, "to achieve aging stability, to control foaming, to ensure freeze-thaw stability, film coalescence, and to obtain a desired consistency."⁹

The solubility of the components must be identified when wet cleaning. Acrylic emulsion paint films are partially soluble in organic solvents, such as acetone, toluene, and xylene, as the paint films are sensitive to, and readily swollen by, the solvents. Although the acrylic polymer itself is not soluble in water, some of the additives in the paint may be.¹⁰ It has been suggested that the distribution of these water-soluble additives throughout the paint film could render the entire paint film water-sensitive.¹¹ Studies have also shown that the film-air interface can be rich in water-soluble surfactant, which can be washed off with distilled water.¹²

Polyethylene glycol (PEG) type surfactants have been found to be especially important with respect to surfactant migration and solubility. PEG type surfactants have been extracted with water immersions¹³ and have also been found on the paint surface of acrylics.¹⁴ Studies in the polymer coatings industry have shown that the location and concentration of the surfactant

are influenced by the surface tension of the substrate. Latex films prepared on glass, mercury, and polytetrafluoroethylene (PTFE) showed different concentrations of surfactant at both the substrate-film and film-air interface.¹⁵ In another case, when dried Liquitex paint samples were prepared on glass slides and compared with samples on commercially prepared canvas, many more additives were seen by eye to have migrated to the surface of the paints applied to glass slides.^{16, 17}

Other additives, such as ammonia, often used as a pH buffer, evaporate out of the paint film during drying, but others can remain in the paint film.¹⁰ Dispersants, used to prevent pigment flocculation, can be water-sensitive. If they remain in the dried acrylic emulsion paint film attached to the pigment particles, they could be sensitive to aqueous cleaning treatments.¹⁰ Conservators have reported foaming of the paint layer during aqueous cleaning. This suggests that components are being leached out of the paint film.^{18, 19}

Temperature plays an important role in the formation and performance of an acrylic emulsion film. During film formation, the resin particles merge and create a continuous film; however, below a certain temperature, known as the minimum film-forming temperature (MFT), the particles cannot coalesce and create a stable film.²⁰ The MFT is especially important for artists' acrylic emulsion paints because the temperatures in artists' studios or storage areas can vary considerably,²¹ and the final coalescing of the paint film can occur months after the paint film is applied. The implications for conservation of acrylic emulsion paint are significant, in that a poorly formed film is much more susceptible to water and, therefore, to aqueous cleaning.²²

Related to the MFT is the glass transition temperature, T_g , the point above which the resin is pliable, soft and somewhat tacky and below which the polymer becomes hard, brittle, and glassy. The T_g can directly affect the performance and physical characteristics of the paint film.²³ As the T_g of many acrylic paints is close to room temperature, this results in soft paint films that can easily become embedded with dirt and dust. This makes their cleaning by conservators difficult.²⁴ Below the T_g , the paint is brittle and vulnerable to physical stress.²⁵ Plasticizers and some stabilizers can affect the T_g . The T_g can also be adjusted by copolymerization with harder acrylic monomers, such as methyl methacrylate.²⁵

The critical pigment volume concentration, CPVC, is very important, as is the pigment volume concentration, PVC, for the appearance and performance of the acrylic emulsion paint film. The CPVC "expressed as the percentage of pigment volume to total volume of the film is that point at which there is just sufficient binder to wet and fill the voids between the particles".¹⁸ The resistance of the paint film to abrasion is related to the CPVC. If the CPVC is surpassed and voids are present, the pigment particles are not tightly bound in the film and can easily be abraded.²⁶ It has been shown that "a sharp break occurs in the resistance of a latex film to scrubbing at the CPVC point of the paint. Also tensile strength appears to peak at this critical pigment concentration."²⁷

The appearance of the acrylic emulsion paint film has several characteristics that distinguish it from that of oil paint. Pinholing, which occurs during the drying of the paint, is the result of air bubbles in the paint film.²⁸ These leave voids within the paint film, some of which can be seen without magnification. Smaller pinholes or voids can be discerned only with the microscope. The appearance of the dried paint film can be distinctly more matte than that of oil or solvent based paints, partly as a result of the inclusion of some additives.²⁸

Conservators use a variety of techniques, both wet and dry, to clean the surface of acrylic emulsion paints. The effects of these treatments are still being assessed. The cleaning of acrylic emulsion paints has become a focus of research at Queen's University over the past several years.^{16, 17, 19, 29, 30} Also, a review article on the cleaning of acrylic emulsion paints has recently been published.³¹ In an earlier part of the present study, mechanical and tensile testing was used to quantify the effects of aqueous treatment. Immersion in five different solutions, for different periods of time, resulted in changes in dimension, mass, and mechanical properties.³⁰ The following research, as part of the ongoing study of acrylic emulsion paints, will address the effect of aqueous cleaning on the surface characteristics of acrylic emulsion paint films. Visual aspects of any work of art are integral to its meaning and impact; thus, any conservation treatment should be evaluated according to its effect on the surface of the object.

Experimental

In order to determine the effect of water exposure on the surface characteristics of acrylic emulsion paints, sets of samples of four inorganic paint colours, one set from each of three manufacturers, were swabbed with distilled water, or immersed for one minute, or for 24 hours, in distilled water. Three additional sample sets were chosen for the same experiments: one of the inorganic paints from one of the manufacturers, from a different batch, cast later; and two more sets of the same organic paint colour but from two different manufacturers. Immersion is not considered a possible conservation treatment, but it is a repeatable test that is used to evaluate the effects of cleaning treatments. As well, it may be used to simulate the effects of repeated aqueous treatments or disaster conditions such as flooding. Chroma meter and gloss meter measurements, light microscopy, scanning electron microscopy, and visual observations were used to study the surface characteristics, before and after exposure to water.

Samples

The acrylic emulsion paints evaluated were Golden Heavy Body Acrylics, Grumbacher Academy, Liquitex Basics, and Winsor & Newton Finity. For each of the first three manufacturers, four different paint colours were examined: black, titanium white, burnt umber and ultramarine blue. For Grumbacher and Winsor & Newton, alizarin crimson was also tested. The three black paints examined did not all have the same composition, so the results cannot be directly compared. The pigment in the Golden

“bone black” paint is Pigment Black 9 (carbonized bone); the pigments in the Grumbacher “mars black hue” paint are a mixture of Pigment Black 9 (carbonized bone) and Pigment Black 7 (carbon black); and the third sample, Liquitex “mars black,” is Pigment Black 11, a synthetic iron oxide. The alizarin crimson samples also had different compositions; the Grumbacher sample was Pigment Red 83 (1,2-dihydroxyanthraquinone), while the Winsor & Newton sample was a mixture of Pigment Red 177 (4,4'-diamino-1,1'-dianthraquinonyl) and Pigment Violet 2 (phosphotungstomolybdic acid salt of Rhodamine 3B ethyl ester). The composition and Color Index (CI) numbers for the pigments are given in **Table I**.

The paint colours selected were chosen for several reasons. First, they are all commonly found in artists' palettes and are likely to be found in many works of art. Secondly, the pigments for most of the colours within the same colour group are the same. Finally, extensive work has been done on the mechanical and chemical behavior of the paints in other parts of the Queen's University acrylics project. The results from this portion of the study provided information on the accompanying change, or lack thereof, in the surface characteristics of the different paint films.

All these paint samples were cast in 1999. In addition, a new tube of titanium white sample was tested that was cast in 2001. A total of 15 paints were tested. Samples were all tested in 2003.

Sample Preparation

All the paint samples were cast on Mylar in February 1999 at the Smithsonian Institution in Washington D.C., except for the Golden 2001 titanium white samples which were cast at Queen's University in Kingston, Ontario in February 2001. The samples were made by putting down layers of electrical tape on the Mylar, thus creating a well for the paint, and drawing down the paint with a microscope slide or the flat-edge of a piece of metal, thus forming a uniform wet thickness that then dried to an approximate thickness of 0.11 mm for the 1999 samples and 0.25 mm for the 2001 samples. The samples were tested in April and May of 2003. The samples were cut to approximately the same size of 10 mm x 60 mm with a scalpel and metal straight edge. The alizarin crimson samples were a slightly larger size: 15 mm x 60 mm; this was because these samples were tested last, after it was discovered that a slightly larger sample size would better accommodate the gloss meter. The samples were handled with latex gloves at all times during the study. Three samples were prepared for each colour and testing technique; in addition, three untreated samples for each colour from each manufacturer were used as the controls. In order to reduce stress to the paint film, the Mylar was removed from the paint film prior to testing rather than vice versa. The samples were temporarily mounted on glass slides for viewing with the light microscope before and after testing.

Analysis

The paint samples were analyzed before and after exposure to

Table 1: Pigments and Colour Index Names for the Different Manufacturers' Paint Colours. The source of the data on the paint composition was provided on the paint tubes or from verbal information from the manufacturer.

Colour	Golden	Grumbacher	Liquitex	Winsor & Newton
Titanium White (cast 1999)	Pigment White 6 (titanium dioxide)	Pigment White 6 (titanium dioxide)	Pigment White 6 (titanium dioxide)	Not Tested
Titanium White (cast 2001)	Pigment White 6 (titanium dioxide)	Not Tested	Not Tested	Not Tested
Black	"Bone Black": Pigment Black 9 (carbonized bone)	"Mars Black Hue": Pigment Black 9 (carbonized bone) and Pigment Black 7 (carbon black)	"Mars Black": Pigment Black 11 (synthetic iron oxide)	Not Tested
Burnt Umber	Pigment Brown 7 (calcined natural iron oxide with manganese)	Pigment Brown 7 (calcined natural iron oxide with manganese)	Pigment Brown 7 (calcined natural iron oxide with manganese)	Not Tested
Ultramarine Blue	Pigment Blue 29 (sodium aluminum sulfate)	Pigment Blue 29 (sodium aluminum sulfate)	Pigment Blue 29 (sodium aluminum sulfate)	Not Tested
Alizarin Crimson	Not Tested	Pigment Red 83 (1,2-dihydroxyanthroquinone)	Not Tested	Pigment Red 177 (4,4'-diamino-1,1'-dianthroquinonyl) and Pigment Violet 2 (phosphotungstomolybdic acid salt of Rhodamine 3B ethyl ester)

water, testing both visually and with instruments. Visually, the samples were observed in both incident and raking light and their colour, surface gloss and texture were noted. The viewing conditions were under northern sky daylight. Data on colour, gloss and surface characteristics were collected using a chroma meter, a gloss meter, light microscopy, and scanning electron microscopy.

Colour Measurements

The reflective colour of surfaces was measured using a tristimulus Minolta Chroma Meter CR-300, and CIE (1976) $L^*a^*b^*$ colour space was used for data analysis. Measurements were at three different locations on the samples following the ASTM D 2244 standard. A template of Mylar and off-white matboard was constructed to ensure that the same three locations (top, middle, and bottom) were tested on every sample. Calibration was performed on a white ceramic tile standard. The L^* , a^* , b^* chromaticity coordinates were recorded for each sample, and an average E^* was calculated from these measurements with Microsoft Excel software. The L^* corresponds to the lightness or darkness, a^* refers to the red-green value, and b^* to the blue-yellow value. The ΔE^* , the total change in colour, is calculated using the formula: $\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$. A difference of 0.5 units in L^* , a^* , or b^* was chosen to be the value that may be perceptible by the average viewer in ideal conditions, and a ΔE^* of 1.0 or more in

the same conditions.³² The average ΔE^* results are given in chart form, but the change in L^* , a^* , or b^* are mentioned in the text only if they were greater than 0.5 units. In all charts and discussions, the results of the measurements at the three locations on a sample were averaged and a confidence level of 95%, shown by the error bar, was used for the ΔE^* values. For the control samples, the colour was measured in the three locations on two separate trials. The colour differences tabulated for the controls are the average differences between the two trials.

Gloss Measurements

Gloss meter measurements using a BYK Gardner micro-TRI-gloss were taken for each sample, following ASTM D 523.³³ Measurements at three different locations on the sample were recorded before and after aqueous treatment for the geometries 60° and 85°, the two geometries most relevant for matte and semi-gloss paint surfaces. Preliminary testing had indicated that the change in gloss did not warrant the 20° angle used for highly reflective surfaces. The results for 85° presented in this paper as gloss values under 30 gloss units, as is the case in this study, are best differentiated with this geometry. Positive or negative changes in gloss were taken from the difference in the before and after treatment measurements. A higher reading, or positive change indicates an increase in surface gloss and a negative change indicates a decrease. The maximum acceptable difference for two results was set at a tolerance level of 7.2 gloss units as

this is the value quoted in ASTM D 523 as the limit of reproducibility between laboratories for the mean value of three determinations.³³ The 7.2 unit value may or may not correspond to a visible change depending on the quality of the surface being evaluated and the observation conditions. Again, a confidence level of 95%, shown by the error bar, was used for the average measurements for the three locations. As in the case of the colour measurements, the gloss of the control samples was measured in three locations on two separate trials. The gloss differences tabulated for the controls are the average differences between the two trials. The gloss meter and chroma meter measurements were taken at the same time to reduce handling of the samples; therefore, the template was constructed to fit both the chroma meter and the gloss meter. It is important when measuring the gloss of paint films to follow the direction of the method of application, so all samples were cut accordingly.

Light and Scanning Electron Microscopy

After the colour and gloss measurements were completed, the samples were characterized by light microscopy and visual examination. The samples were temporarily mounted on glass microscope slides and observed with transmitted and incident light using a Nikon SFG-Kt light microscope at 50x magnification. Voids, pigment particle density, surface texture and dust or dirt were observed for each sample. Some titanium white samples cast in 1999 and 2001 were also examined using a JSM-840 JEOL scanning electron microscope after coating the sample with gold to avoid charging.

Exposure to Water

Swabbing Tests

The swabbing tests were carried out to replicate the actual techniques of conservators when cleaning acrylic emulsion paintings. Prepared cotton medical swabs, from Fisher Scientific, with 6 inch wooden applicator sticks, were used for the tests. The swabs were moistened with 120 μ l of freshly distilled water and then rolled back and forth along the length of the samples five times, exerting minimal pressure on the paint film. The samples were placed on screen drying racks and allowed to dry for 72 hours, before the measurements and observations were made.

Immersion Tests

The immersion test procedure was based on ASTM D 543, "Standard Practices for Evaluating the Resistance of Plastics to Chemical Reagents."³⁴ Pyrex dishes were filled with 250 mL of freshly distilled water and samples were immersed for one minute or 24 hours. The samples were removed after immersion, dabbed with Kimwipes to remove any excess water, and allowed to dry for 72 hours on mesh screens before measurements and observations were made. The immersion tests were done one colour at a time, so that comparisons could be made immediately between paints originating from different manufacturers.

Results

In this research, visual and microscopic examinations revealed that exuded materials, such as glossy spots, were present on the surface of some paints before exposure to water. Recent studies using infrared spectroscopy have shown that the exuded material contains nonionic surfactants of the Triton X-405 type.³⁵ In addition, before exposure to water, there were white crystals on the surface of all of the paint samples, which are also believed to be surfactants. These results are consistent with previous researchers' findings where surface materials consisted of additives such as surfactants.^{13, 14} As well, before exposure to water, pinholes were found to be present on the surface of all samples.

Titanium White

The titanium white samples measured less colour change than any of the other samples. **Figure 1** shows the total colour change for the titanium white samples. The error bars indicate a confidence level of 95%. As seen in **Figure 1**, the ΔE^* measurements were less than 0.6, far below a ΔE^* of 1.0, the instrumental tolerance for selecting colour matching. All the swabbed samples were the same as their controls or even measured less colour variation, shown by the confidence intervals; the exception was the Grumbacher sample which had more colour change after being swabbed, though its ΔE^* was still less than 0.3. The immersed samples for the Grumbacher and Liquitex paints measured more change than their controls, while still having a ΔE^* of less than 0.6. The Liquitex one-minute and 24-hour samples visually appeared bluer; from the measurements, the Δb^* for the one-minute sample was only -0.22, but for the 24-hour sample it was -0.48, which is very close to the perceivable level of -0.5. The Golden control samples measured greater colour changes (although they were still under 0.6 units) than the treated samples did. The swabbed Golden samples from 1999 and 2001 both had a ΔE^* of less than 0.2 units. When comparing the Golden 1999 and 2001 samples, the magnitude of colour change was the same for the different types of treatments.

As seen in **Figure 2**, the Liquitex samples had very similar gloss measurements before and after swabbing, with the small confidence interval indicating very little variability. In general, the Liquitex samples had a matte surface paint, with a rough and very uneven appearance under magnification, although the titanium white samples were the smoothest of these Liquitex samples. There was a significant measured increase in gloss for the swabbed Grumbacher samples but this did not equate to a perceptible visual change. The Golden 1999 samples showed no significant change in gloss measurements after swabbing or one-minute immersions, whereas the Golden 2001 samples did significantly increase in gloss. The Golden 2001 samples immersed for 24 hours were similar to the Golden 1999 samples; considering the confidence interval, the Golden 1999 samples had a just perceptible decrease in gloss after the 24-hour immersion. More testing should be done to determine if this was truly significant. These samples were not deformed after being

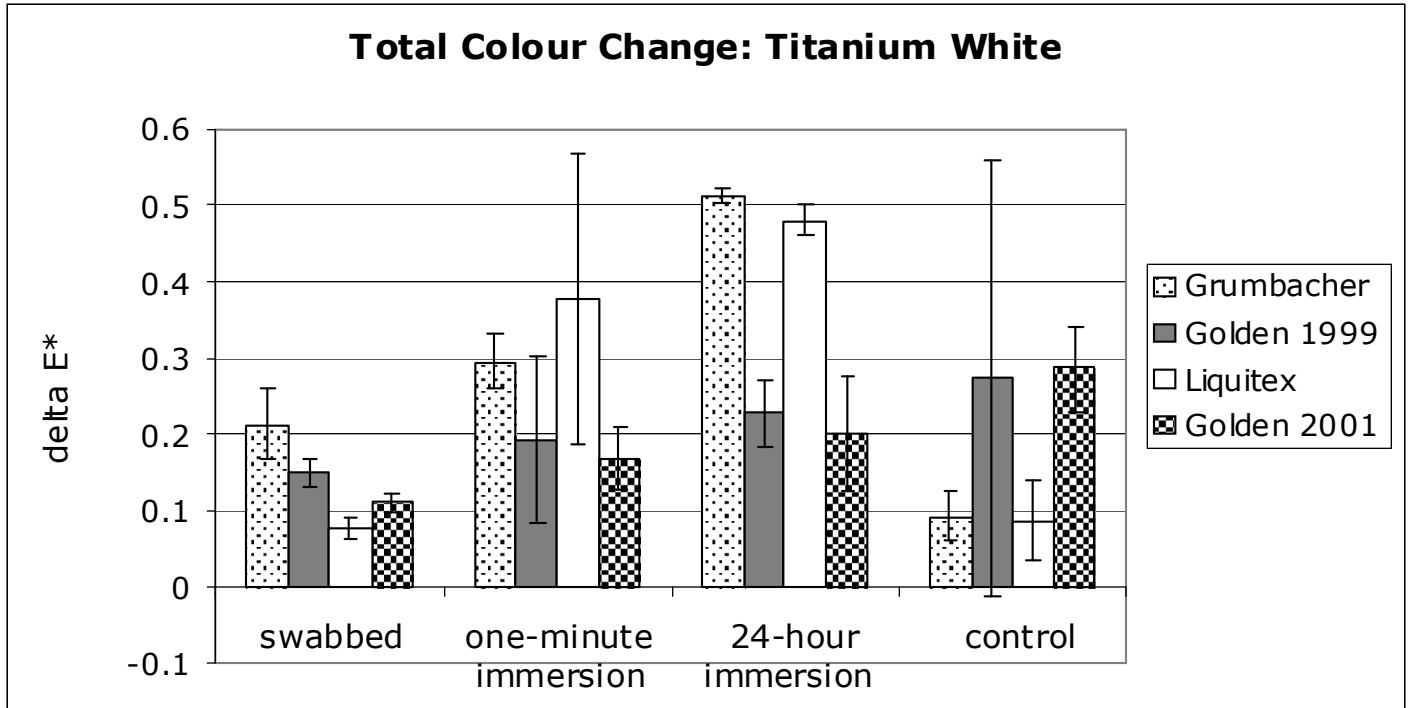


Figure 1. Total colour change (in ΔE^*) for titanium white samples. The error bars show a confidence level of 95%.

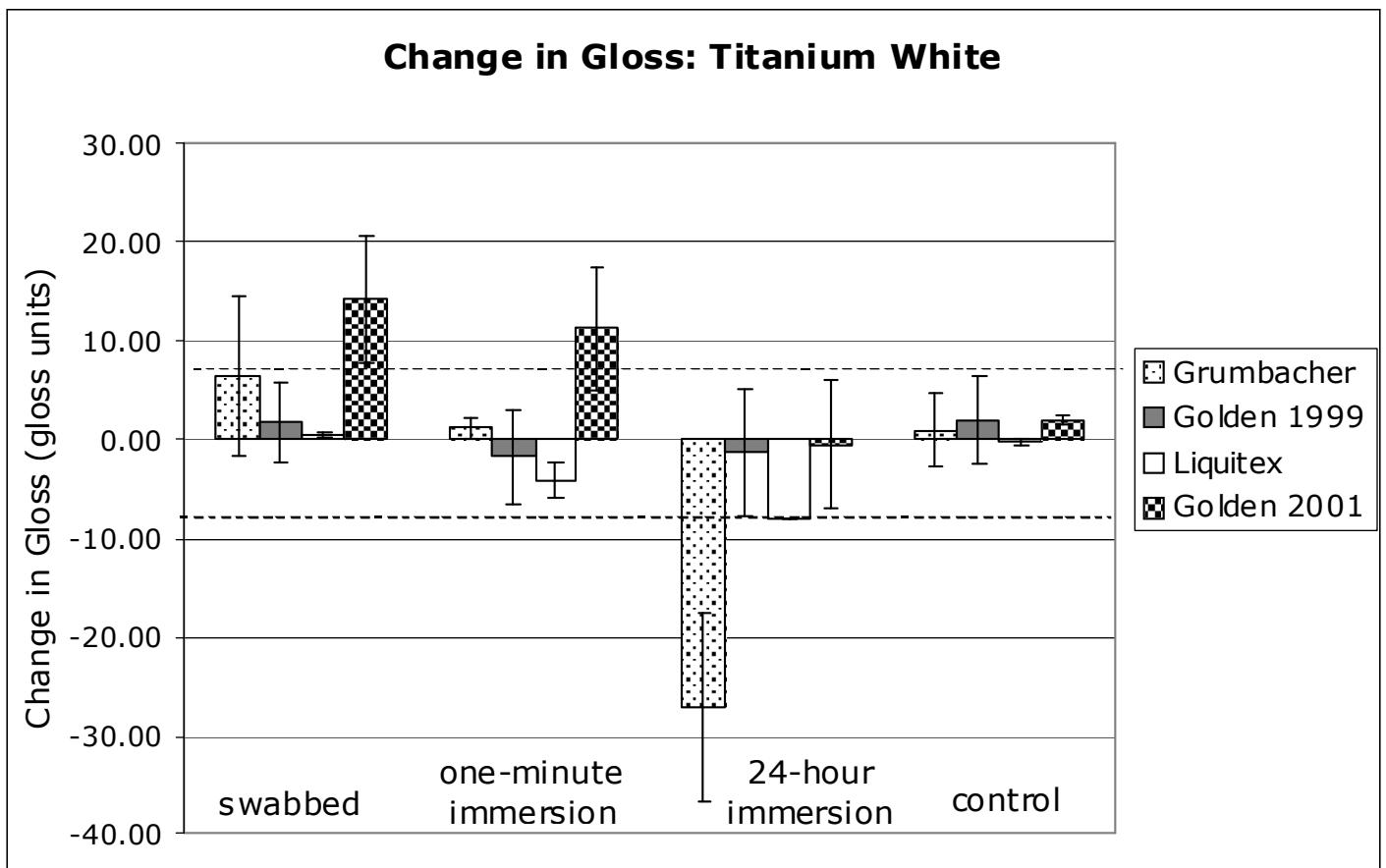


Figure 2. Change in gloss (in gloss units) for titanium white samples. The error bars show a confidence level of 95%. The dashed lines indicate a tolerance level of 7.2 gloss units, set by ASTM D 523 to be visually the maximum acceptable gloss change.

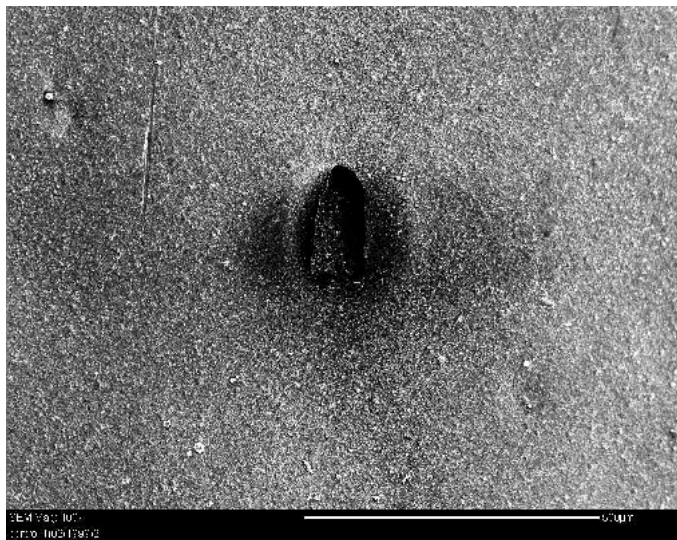


Figure 3. Scanning electron micrograph of a control titanium white sample (cast in 1999), at 100x magnification. The pinhole is shown in the centre. Scale: 1 cm = 125 μ .

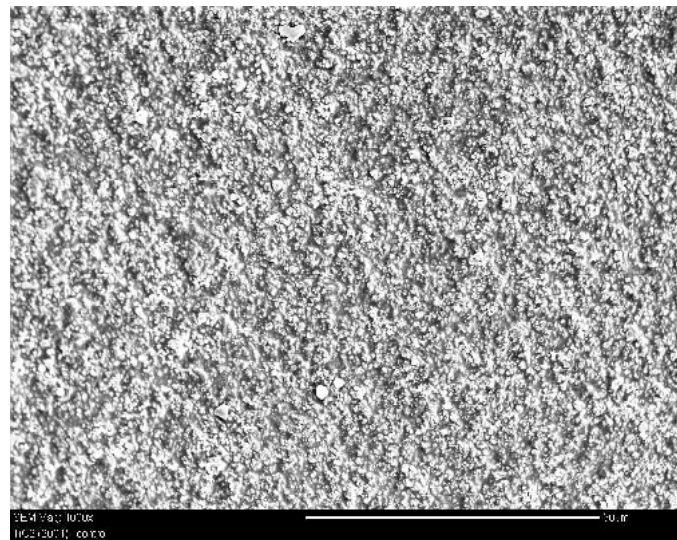


Figure 5. Scanning electron micrograph of a control titanium white sample with no additives (cast in 2001), at 1000x magnification. Scale: 1 cm = 12.5 μ .

immersed. The significant decrease in gloss for the Grumbacher and Liquitex samples that were immersed for 24 hours may be partly explained by the fact that the Grumbacher samples showed slight deformation and the Liquitex samples showed cockling and wrinkling. The Grumbacher samples did visually appear slightly glossier after being immersed for 24 hours.

From visual and microscopic observations, the Golden 2001 samples appeared less uniform in gloss than the 1999 samples. The 2001 samples before treatment had yellowish white, opaque and waxy rings that were visible at 4x magnification, probably indicating that additives are present on the surface. **Figure 3** shows an SEM image of the 1999 sample (also showing a pinhole) and **Figure 4** shows the 2001 sample. At higher

magnification of the 2001 sample, **Figure 5** shows an area free of additives, while **Figure 6** shows an area with additives. After swabbing, there were no rings, but very glossy spots appeared at the top and bottom edges of the samples (**Figure 7**); this corresponded to an increase in measured gloss. The placement of the spots at the edges and the disappearance of the rings suggest that the additives were water-soluble and were redistributed with swabbing. Similar visual effects have been seen during swab cleaning of actual acrylic paintings, possibly from the same mechanism of displacing components of the paint to the edges. This effect is said to be avoided with use of a sponge.³⁶ After both sets had been immersed, there were no spots or rings, suggesting that the additives had been washed from the paint film. This can be seen in the SEM image of the 24-hour sample

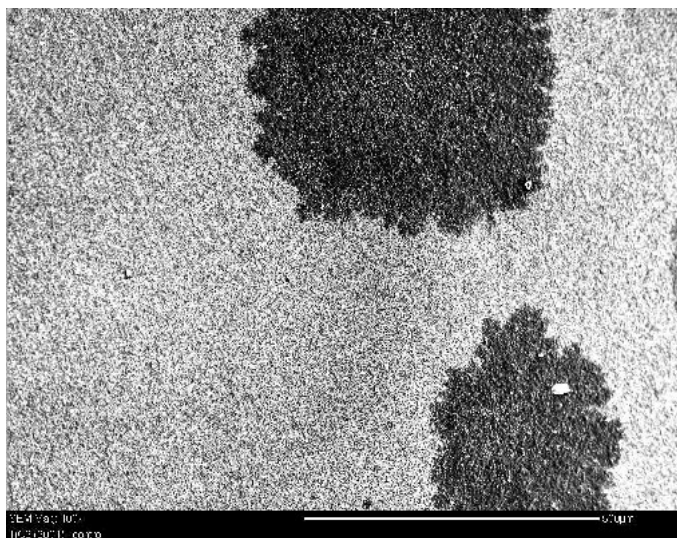


Figure 4. Scanning electron micrograph of a control titanium white sample with areas of surface additives (cast in 2001), at 100x magnification. Additives are the two round areas. Scale: 1 cm = 125 μ .

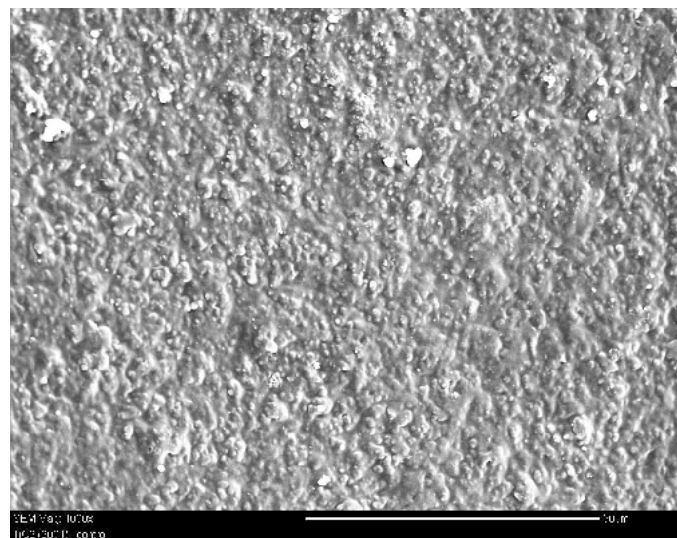


Figure 6. Scanning electron micrograph of a control titanium white sample completely covered with surface additive layer (cast in 2001), at 1000x magnification. Scale: 1 cm = 12.5 μ .



Figure 7. Scanning electron micrograph of swabbed titanium white sample with areas of displaced additives (cast in 2001), at 100x magnification. Scale: 1 cm = 125 μ.

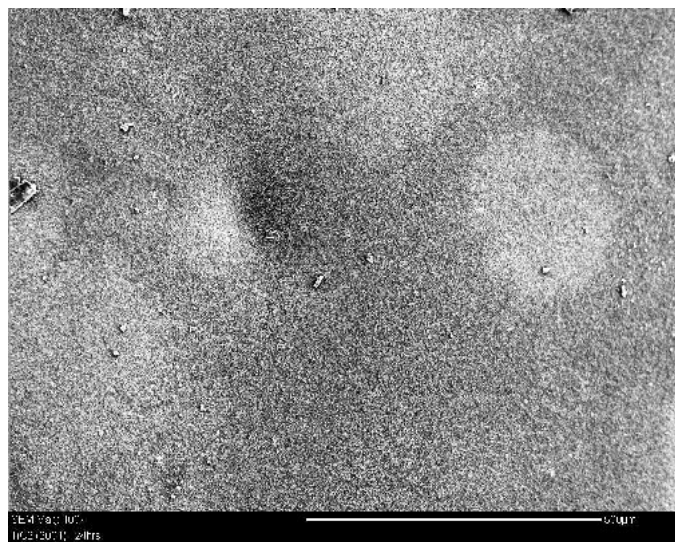


Figure 8. Scanning electron micrograph of immersed titanium white sample with possibly leached areas (cast in 2001), at 100x magnification. The samples were immersed in distilled water for 24 hours. Scale: 1 cm = 125 μ.

(**Figure 8**). After the 24-hour immersions, the change in measured gloss was very small (although the confidence interval showed that the measurements could be both more and less glossy). This is a decrease from the higher gloss changes measured for the swabbed and one-minute samples. As the Golden 2001 and 1999 samples were very similar after the 24-hour immersion, it can be concluded that surface additives were washed off leaving quite similar paint surfaces in both samples.

Black

As shown in **Figure 9**, the Grumbacher black samples had a measured colour change with $\Delta E^* > 1$ for all treatments; i.e., swabbing, one-minute immersion and 24-hour immersion. The mean value for the swabbed sample was the smallest value and fell beneath the 1.0 value at 0.91, but with the confidence interval the measured colour difference was greater than 1.0.

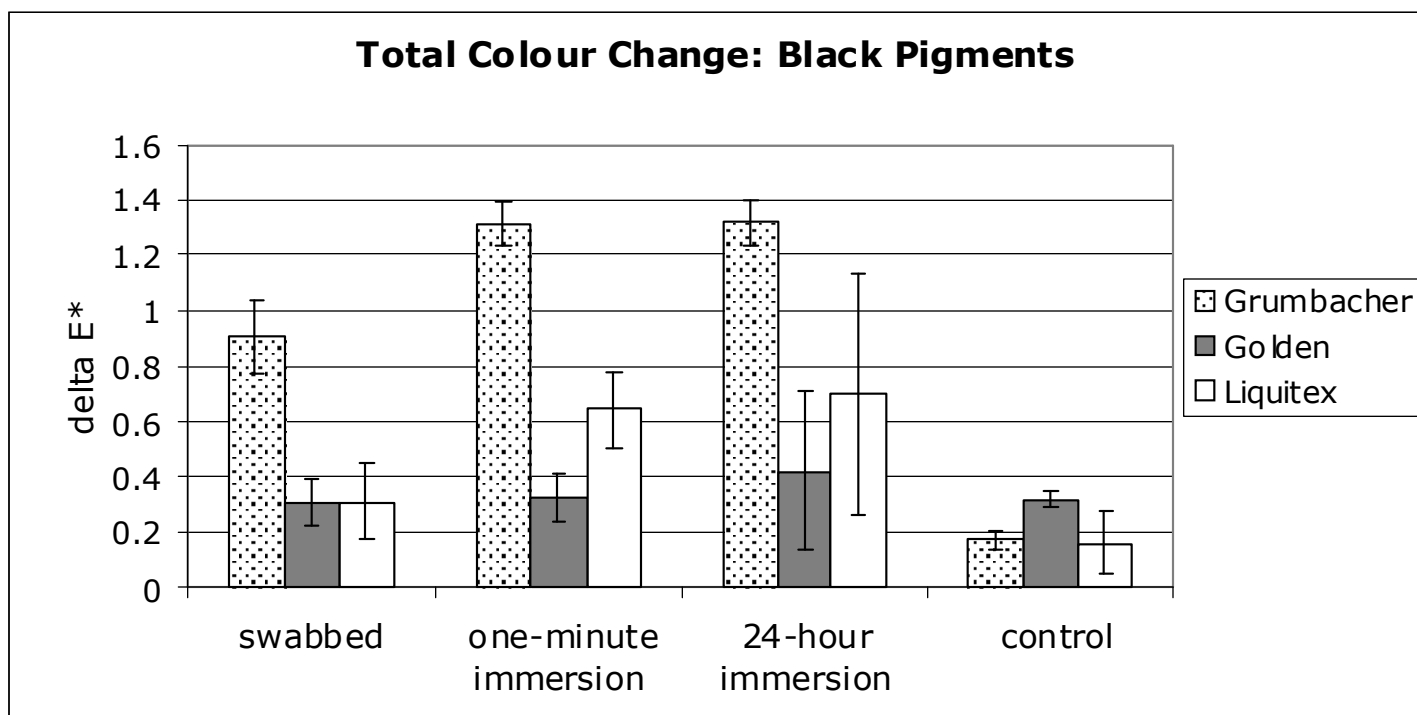


Figure 9. Total colour change (in ΔE^*) for samples of mars black (Liquitex), of bone black (Golden), and of a mixture of bone black and carbon black (Grumbacher). The error bars show a confidence level of 95%.

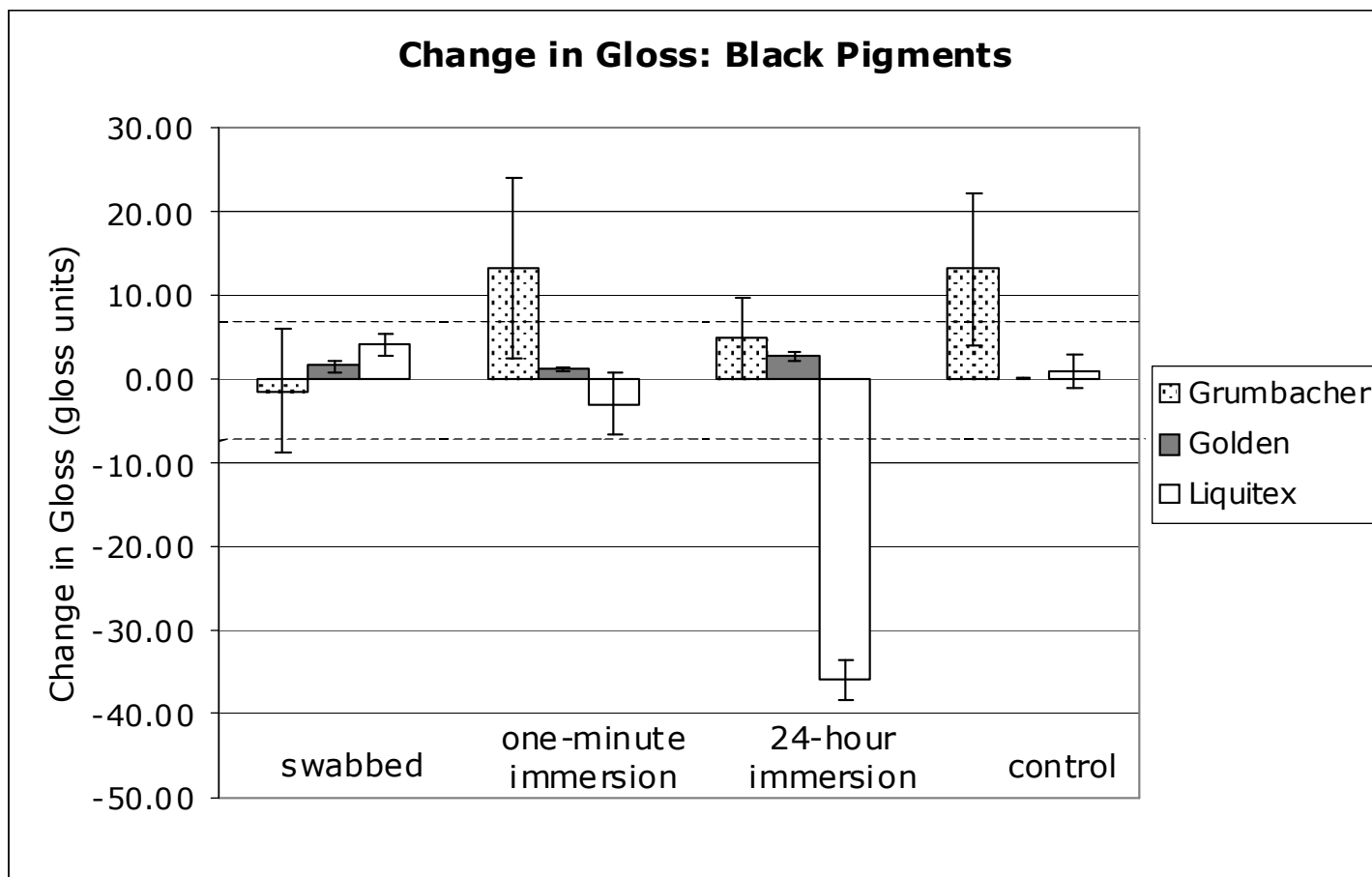


Figure 10. Change in gloss (in gloss units) for black samples. The dashed lines indicate a tolerance level of 7.2 gloss units, set by ASTM D 523 to be visually the maximum acceptable gloss change.

This meant that a discernable colour change was measured in the Grumbacher black samples, even with a very limited contact with water. For all treatments, these samples had a Δb^* greater than 0.5 and were, therefore, measured as being more yellow. The Golden bone black samples and the Liquitex mars black samples, after all treatments, were well below the limit of observable change, except for the Liquitex 24-hour immersion sample. The pigment in the Liquitex mars black samples is synthetic iron oxide, the pigment in the Golden bone black is carbonized bone, and the pigments in the Grumbacher mars black hue are carbonized bone and carbon black, and so direct comparisons cannot be made. The Golden and Liquitex 24-hour immersion samples showed a large variability in measured colour change, as indicated by the large confidence intervals. For all samples, the colour change, compared with the control, was significant after swabbing, greater after short immersion, and greater still after longer immersion. This shows that colour change is occurring with exposure to water, although the rates are different for the different manufacturers. No obvious colour changes were observed with the naked eye, even though the measured colour change was over 1.0 in some cases.

With respect to measured gloss changes (**Figure 10**), the

Grumbacher samples showed a significant amount of variability, especially with the control samples and the samples that were swabbed and immersed for one minute. There was a significant decrease in measured gloss for the swabbed Grumbacher samples (taking into consideration the confidence interval), but an increase in gloss for the Grumbacher samples that were immersed for one minute. The 24-hour sample was over the instrumental tolerance level, but the control varied to an even greater degree. The Liquitex samples immersed for 24 hours showed a decrease in measured gloss, probably because the samples were extremely deformed and wrinkled. Visual and microscopic observations showed that the Grumbacher samples had a network of glossy spots and agglomerates before treatment; the gloss was uneven with matte, darker spotty areas. After swabbing, there were glossy round spots near the top and bottom edges of the samples; this showed that the action of swabbing appeared to move additives to different locations on the surface. The glossy network became more prominent and distinct. After immersion, the network of gloss was present, but the high gloss spots were absent; the samples immersed for 24 hours were less glossy than the samples immersed for one-minute. Some of these observations concurred with the gloss measurements. First, the gloss of the samples did vary. The gloss meter measured a

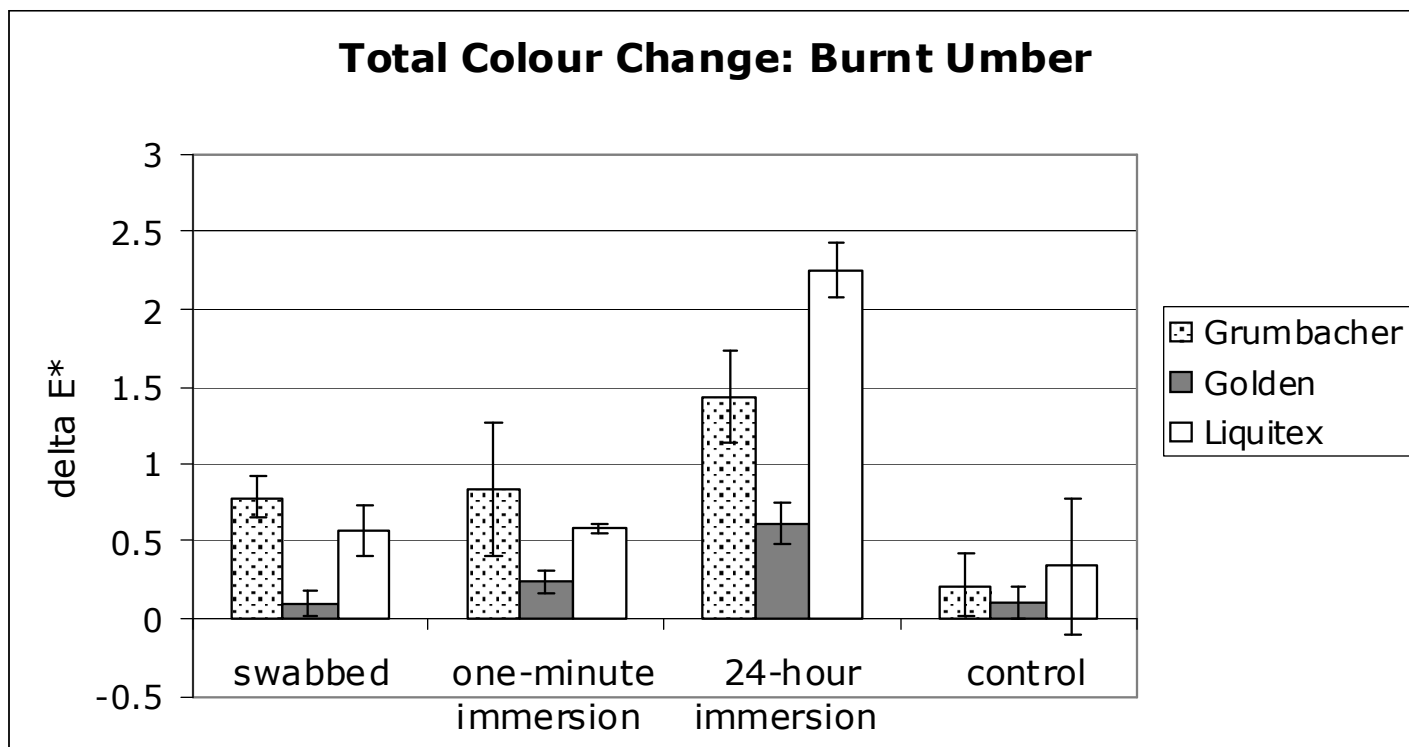


Figure 11. Total colour change (in ΔE^*) for burnt umber samples. The error bars show a confidence level of 95%.

decrease in gloss with swabbing, but with a high variability shown by the large confidence interval. The one-minute immersed samples had a significant increase in measured gloss, corresponding to their network of more prominent gloss, while the control samples had high variability that was both measured and visually observed. The visual observations and gloss meter measurements showed that the samples immersed for a longer period of time (24 hours versus one minute) became less glossy.

Burnt Umber

Overall, the burnt umber samples generally showed slightly more change in measured colour than the black samples and much more than the titanium white samples. As shown in **Figure 11**, all the swabbed burnt umber samples had a total colour change of less than 1.0 unit, with only the Grumbacher samples changing more than the control after swabbing. The samples that registered a ΔE^* of over 1.0 were the Grumbacher one-minute and 24-hour samples and the Liquitex 24-hour samples. The samples subjected to one-minute immersion showed results similar to those of the swabbed samples, but the 24-hour immersion samples showed more measured colour change: the Grumbacher samples became darker and more yellow, the Golden samples became lighter, and the Liquitex samples became lighter and more yellow. When observed visually only the Liquitex samples immersed for 24 hours became lighter. Overall, the Golden samples showed the least amount of change or sensitivity to water.

Gloss measurements, shown in **Figure 12**, indicated that the Golden and Liquitex swabbed samples showed little change compared with the control. The Grumbacher samples had large variability with the control and after exposure to water, while Golden and Liquitex samples did not. Only the Grumbacher samples registered a perceptible change in gloss, with an increase after swabbing, a decrease after 24-hour immersion, and a huge variation after one-minute. However, because the control also had a large confidence interval, only the decreases after one-minute and 24-hour immersions can be considered significantly different from the control. These samples were also cockled, which helps to explain the large decreases in gloss. The Liquitex samples after 24-hour immersion were also cockled.

Visual and microscopic observations showed the Grumbacher burnt umber control samples to be slightly mottled and to have a faint network of glossy additives. Immediately after swabbing, the additives became much more visible, with lighter, glossier spots forming a loose network over the matte paint. After drying for 72 hours, the additives were not as visible, but were still more distinct than on the unswabbed samples. This caused the gloss to measure an increase, although the change was still less than the confidence interval of the control. After being immersed for one minute, the samples were more mottled, a fact that was also shown by the highly variable measurements. The samples immersed for 24 hours had a very pronounced additive network that covered over 80% of the surface and consisted of irregularly shaped agglomerates.

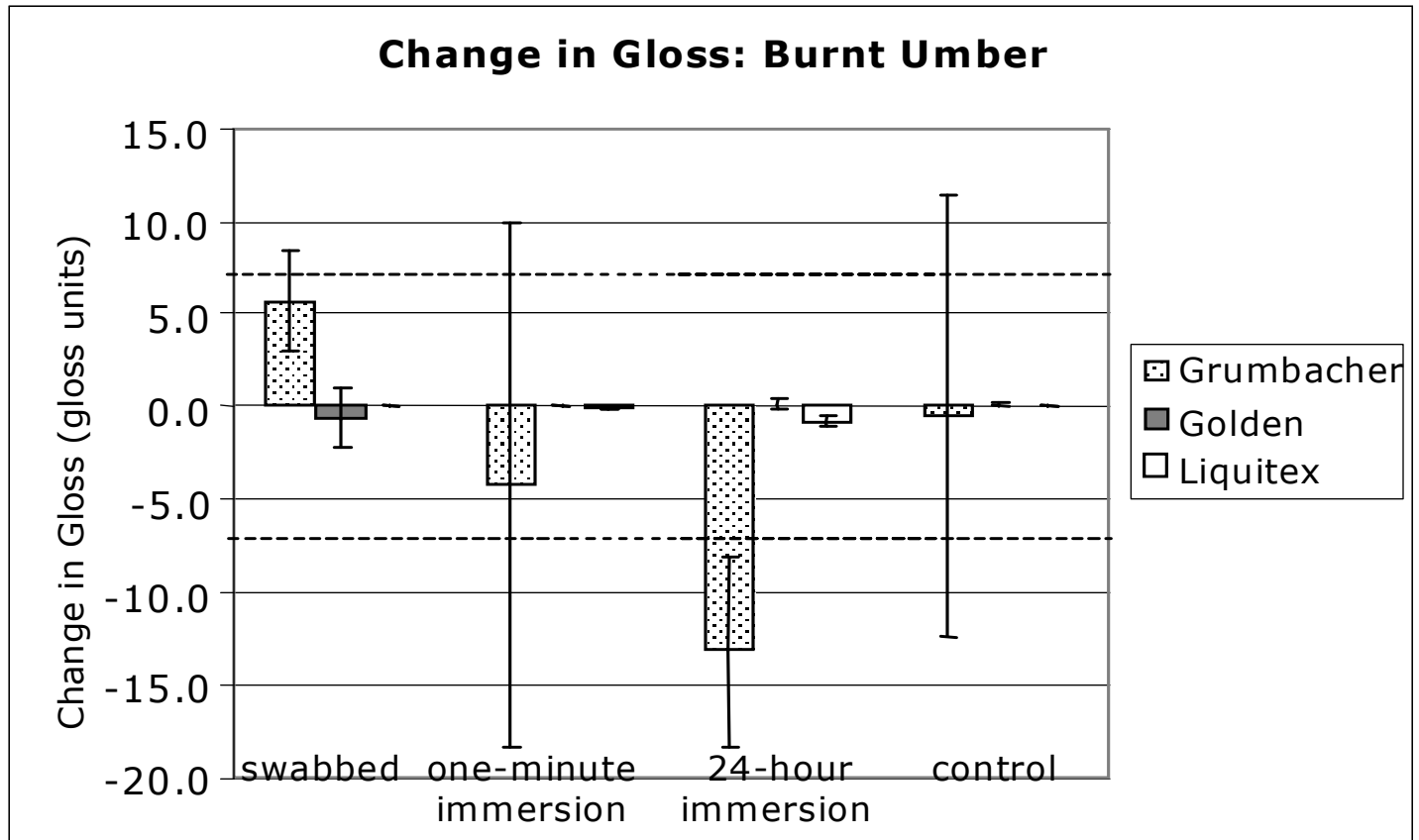


Figure 12. Change in gloss (in gloss units) for burnt umber samples. The dashed lines indicate a tolerance level of 7.2 gloss units, set by ASTM D 523 to be visually the maximum acceptable gloss change.

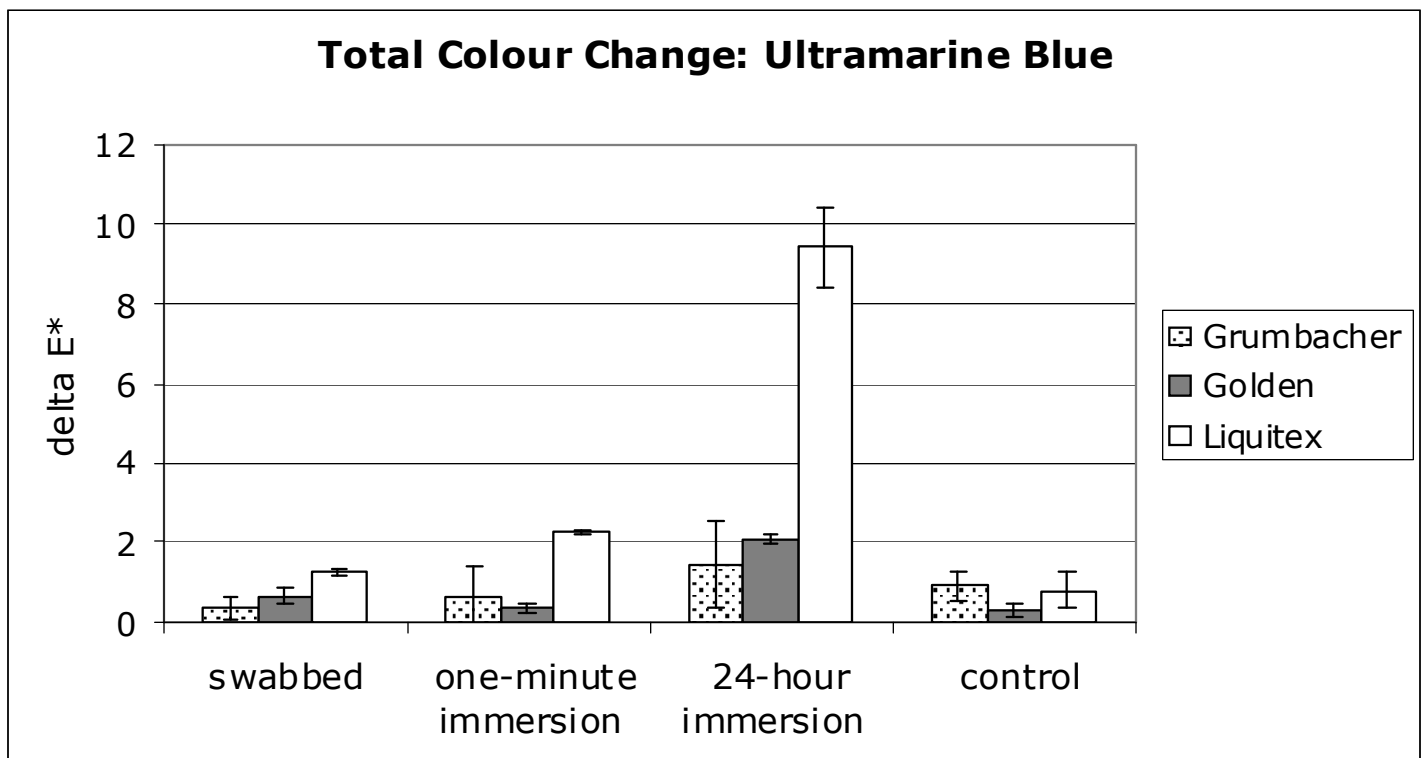


Figure 13. Total colour change (in ΔE^*) for ultramarine blue samples. The error bars show a confidence level of 95%.

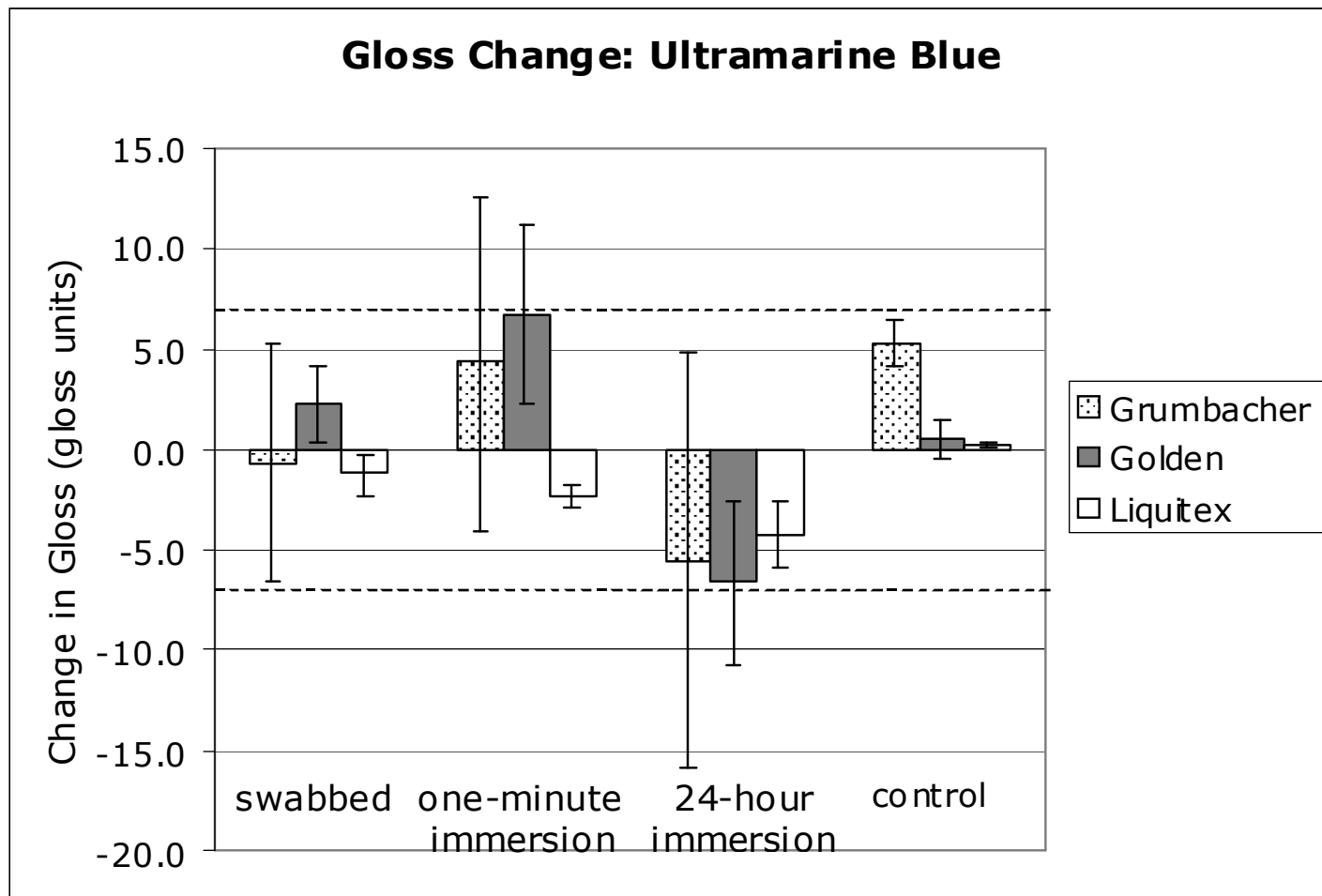


Figure 14. Change in gloss (in gloss units) for ultramarine blue samples. The dashed lines indicate a tolerance level of 7.2 gloss units, set by ASTM D 523 to be visually the maximum acceptable gloss change.

Ultramarine Blue

As seen in **Figure 13**, only the swabbed samples for Liquitex had a ΔE^* over 1.0 (measured as being lighter and more yellow), although with the variability of the control samples, the change in colour is very close to that of the control. For all treatments, Liquitex had the largest measured colour changes with ΔE^* values ranging from greater than 1.0 to over 9.0 units. The changes to one-minute immersions were measured to be over 2.0. Samples measured lighter, greener, and more yellow and were visually observed to be bluer. The Liquitex samples immersed for 24 hours showed the greatest colour change, with a ΔE^* over 9.0 (samples measured lighter, redder and bluer). Visually the samples became lighter and bluer after exposure to water. The number of bumps on the surface of the samples greatly increased after immersion. After 24-hour immersion, these bumps were more prominent and appeared to have lost pigment, now being light blue to white. The Golden and Grumbacher samples were not observed visually to have changed colour, but changes in colour were measured. The Golden 24-hour immersion samples had a ΔE^* over 2.0, with change in

measured colour toward red and blue. All the Grumbacher samples after immersion were over 1.0 unit (the 24-hour samples were measured to be bluer and greener), as was the control.

From the gloss measurements, given in **Figure 14**, it can be concluded that swabbing caused no perceptible change. The mean gloss values of both the Grumbacher and Golden samples increased in measured gloss after the one-minute immersions and decreased after 24-hour immersions. The large confidence interval of the measured gloss values for the Grumbacher samples exposed to water indicated that the values were extremely variable. The Liquitex samples decreased steadily after swabbing, one-minute immersions, and 24-hour immersion, but the changes were under 7.2 and were therefore not perceptible. The Liquitex samples, again, showed less variability (indicated by the smaller confidence interval) than samples from other manufacturers. All the samples were deformed after 24-hour immersions, an important reason for the decrease in gloss.

Visual and microscopic observations showed that the Grumbacher control samples were slightly mottled and had an

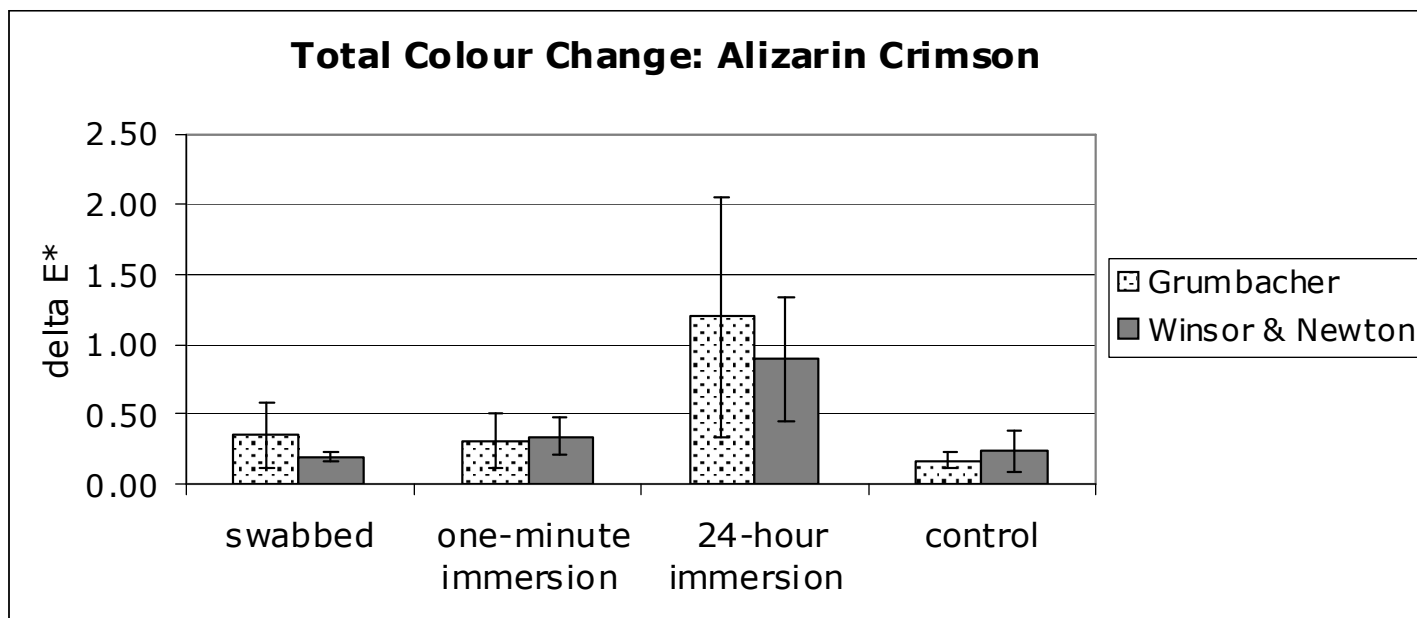


Figure 15. Total colour change (in ΔE^*) for alizarin crimson samples. The Grumbacher sample is Pigment Red 83; the Winsor & Newton sample is a mixture of Pigment Red 177 and Pigment Violet 2. The error bars show a confidence level of 95%.

uneven gloss in raking light. After swabbing, the samples became more matte and had spots with angular shapes and with some glossier round additives at the top and bottom edges. Post immersion, the matte additive spots became very prominent and the glossy spots disappeared. The variability that this caused to the gloss can be confirmed by the large confidence interval for all the samples exposed to water.

The Golden ultramarine blue samples had the most irregular surface of the four colours of Golden paints. The samples had light, glossy, round additive spots that could be seen in raking light. These were found individually and in agglomerates. After swabbing, where the water had been easily absorbed into the paint, there were matte additive spots over 40% of the surface. The spots were discrete or formed agglomerates, but did not form a network. These changes did not cause a perceptible difference in the measured gloss. After the immersions, there were fewer glossy spots, indicating that the additives had been leached from the paint surface; however, for the one-minute immersions, there was an unexplained increase in gloss.

Alizarin Crimson

After the alizarin crimson samples were swabbed or immersed for one minute, the colour change was measured to be less than 1.0 (**Figure 15**). Indeed, the samples had changed only very slightly in some cases and not at all in others, compared with the control samples. Both sets of samples did measure a perceptible colour change after 24-hour immersions. There was large variability in the results for these samples indicated by the large confidence intervals. Interestingly, the Grumbacher samples were light pink after 24 hours of immersion. As they dried, the colour returned to that of pre-immersion. There was no visible

colour difference for any of the samples after treating and drying. As discussed in the experimental section, the Grumbacher and Winsor & Newton samples cannot be directly compared as they were made with different pigments.

As shown in **Figure 16**, there was a perceivable decrease in gloss after the 24-hour immersions; however, these samples also showed a distortion that would affect the gloss measurements.

Visually, all samples before treatment were smooth, regular, and had a relatively even gloss and colour. Some samples had scratches and marks that were only visible when viewed under the microscope. The Grumbacher samples had fewer white crystals on the surface, while the Winsor & Newton samples had a few blue and orange-gold crystals, in addition to the white crystals. After swabbing there was no change except for some scuffmarks, smearing of crystals on the surface, and some additional scratches.

Discussion and Conclusions

Colour Measurements

Swabbing did not usually cause a significant colour change ($\Delta E^* < 1$). Exceptions to this were: Liquitex ultramarine blue (it should be noted, though, that this colour change was very close to that of the control when the confidence interval is considered) and Grumbacher black (the mean value was not over 1.0, but with the confidence interval there was a measured colour change).

For the immersed samples (both one minute and 24-hour immersions, unless otherwise stated), the following were true:

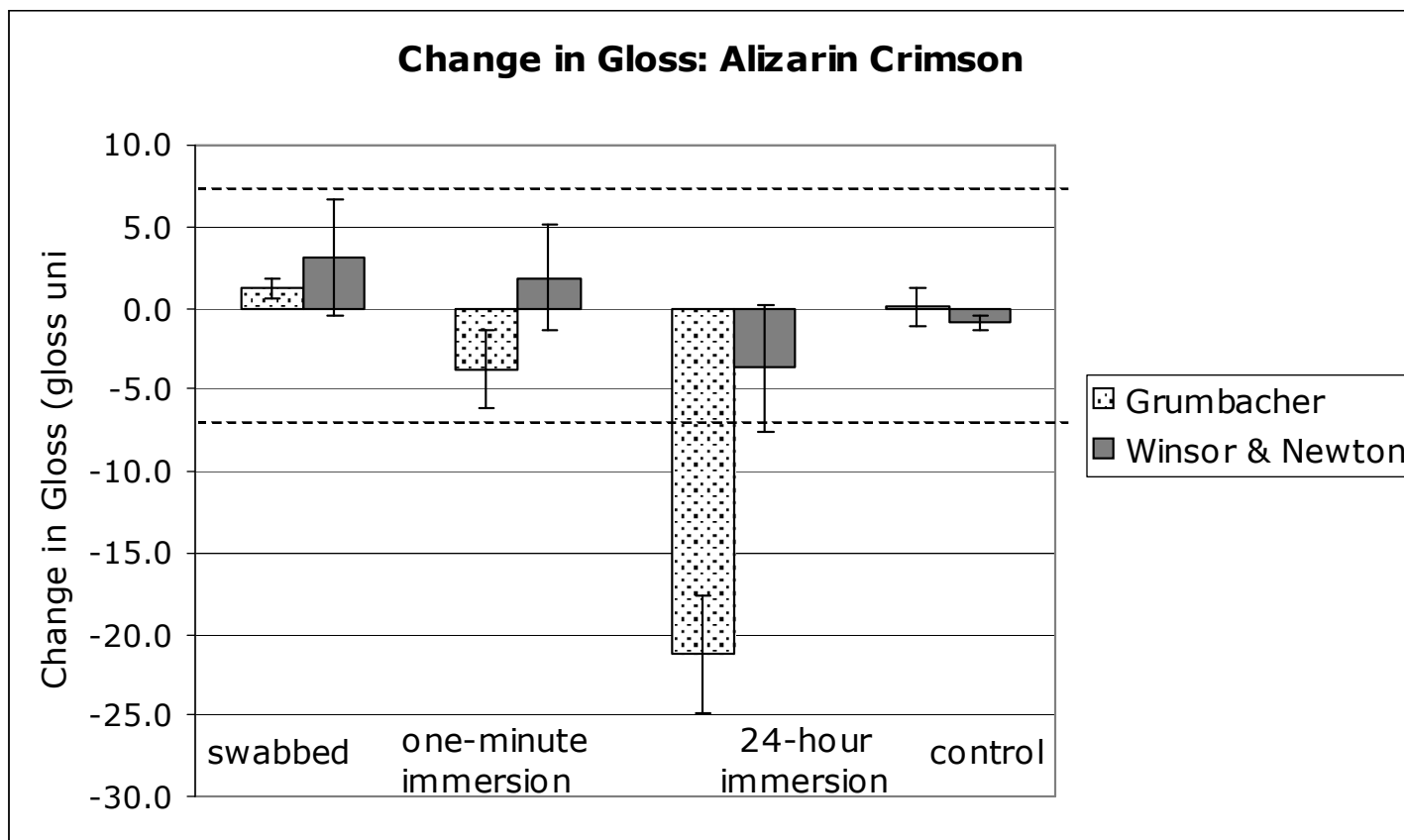


Figure 16. Changes in gloss (in gloss units) for alizarin crimson samples. The dashed lines indicate a tolerance level of 7.2 gloss units, set by ASTM D 523 to be visually the maximum acceptable gloss change.

1. All the titanium white samples had a ΔE^* less than 1.0.
2. The most sensitive colour was ultramarine blue, for all manufacturers; five out of six immersions had measured colour changes greater than 1.0 after treatment.
3. The most extreme measured colour changes were for Liquitex ultramarine blue, that had a total colour change over 9.0.
4. Alizarin crimson samples immersed for 24 hours had a measured, perceptible colour change with a ΔE^* over 1.0. It is important to note that the two manufacturers did not use the same pigments to make these paints.
5. All the Liquitex samples immersed for 24 hours had measurable colour changes, with ΔE^* over 1.0, except for the titanium white samples.
6. Only the following Liquitex paint colours were perceived visually to have undergone colour change after the paint samples were immersed: titanium white, burnt umber, and ultramarine blue.
7. All the Grumbacher samples had colour changes greater than 1.0, except the titanium white samples and the one-minute immersed alizarin crimson samples.
8. All the Golden samples had a ΔE^* less than 1.0, except for ultramarine blue immersed for 24 hours.

Gloss Measurements

The high variation in the gloss of some paints (for example, Grumbacher), as indicated by the large confidence intervals of the controls, meant that some measured gloss changes to samples after treatment could not be taken as significant. The large decrease in measured gloss after immersion, usually after the 24-hour immersion, is, in large part, due to the considerable deformation of the samples, though it is impossible to know to what extent the immersion is responsible. Bearing these points in mind, only the following samples definitely showed measured gloss changes beyond the threshold 7.2 value: for swabbing, Grumbacher black (only due to the large confidence interval), Grumbacher titanium white, and Golden titanium white (cast 2001); for one-minute immersions, Grumbacher black, Grumbacher ultramarine blue (due to its confidence interval), Golden titanium white (cast 2001) and Golden ultramarine blue; and for the 24-hour immersions, Golden titanium white (cast 1999; only due to its confidence interval). The Liquitex paints showed the least change in measured gloss after swabbing and immersions.

The variability in measured gloss was indicated by the confidence interval. All colours of Liquitex paints generally

Table II: Visual Observations of Additives on the Surface of Paint Films.

Treatment	Observations	Grumbacher ultramarine blue	Golden ultramarine blue	Grumbacher black	Golden titanium white (2001)	Grumbacher burnt umber
Control	Slightly mottled	yes				yes
	Uneven gloss	yes			yes	
	Glossy spots		yes			
	Faint glossy network*			yes		yes
	Darker matte spots			yes		
	Rings				yes	
Swabbed	Matte spots	yes	yes			
	Glossy spots at top and bottom	yes		yes	yes	
	Agglomerates		yes			
	Glossy network*			yes		yes
	Rings				no	
Immersed	Prominent matte spots	yes				
	Fewer or no glossy spots	yes	yes	yes		
	Glossy network*			yes		
	Rings				no	
	Agglomerates					yes

*The term “glossy network” is used to describe an irregular pattern of joined glossy spots.

showed little variability. Grumbacher samples consistently showed a large variability in gloss, before and after treatments. The Golden samples had little variability for the bone black and burnt umber samples, but had large variability for the titanium white and ultramarine blue samples. The variability could change with different supports. Samples that visually showed additives on the surface were also samples that showed large variability in gloss.

Visual and Microscopic Observations

Surface effects, such as matte spots, glossy networks of spots and other phenomena were observed on many samples. These are described in **Table II**. These surface effects are probably caused by the presence of additives in the acrylic paint that have migrated to the surface. Swabbing sometimes caused the additives to be displaced to the edges of the samples. Only samples where additives existed on the surfaces before treatment visually showed additives post treatment. This was true for Grumbacher black, burnt umber, and ultramarine blue, and for

Golden ultramarine blue, and titanium white (2001). Conservators may find this reassuring when treating acrylic paintings, although chemical changes may still have taken place. It is interesting to note trends. For example, only the ultramarine blue paints from Golden and Grumbacher had similar matte spots after swabbing. It appeared that only the organic paint samples of alizarin crimson had scratches before and, subsequently, had more scratches after swabbing. This needs to be examined further. Interestingly, only two sets of samples foamed slightly during swabbing: Grumbacher burnt umber and Golden titanium white which was cast in 2001.

The paint samples were all cast on Mylar. The migration of additives in the paint film was probably influenced by the substrate, as has been shown by other work.³⁷ Given the non-porous nature of the Mylar, it is probable that more additives came to the surface than would have if a porous substrate such as a commercially prepared acrylic gessoed canvas were used.^{16,17} The results presented here may, however, give some indication of trends that might be seen with paint on a more

porous support. The behaviour of these additives, even in small concentrations, could significantly affect the surface of the paint film.

Different Paint Batches

Different paint batches can result in different surface characteristics due to changes in formulation. The 1999 and 2001 Golden titanium white samples had different visual characteristics and gloss measurements. The films cast in 2001 had ring-shaped, yellowish white, opaque, and waxy additives that were absent from films cast in 1999. The gloss measurements for the two sets of paint samples were different, except for the 24-hour immersion samples where the additives from the 2001 samples had been leached away giving it a similar gloss measurement to its 1999 counterpart. The only known compositional change was that a “more durable” titanium white pigment was used in the 2001 samples, although the raw materials that the paint company used could have changed without them knowing.³⁸ It should be noted that films made by Golden at the time of paint production do not show the surface additives seen on the 2001 samples.³⁸ As the samples from these experiments were the only ones to have these specific visual characteristics, further investigation is warranted.

Overall Trends and Future Work

This work has shown that acrylic paints can react very differently to aqueous treatments. This is indeed understandable as each manufacturer includes different materials in their paint. Although formulations can change, it is hoped that this work indicates trends that could be important in the cleaning of acrylic paints. For the paints tested, swabbing caused little or no colour change (both visually and by measurement). Swabbing did, however, cause some measured gloss changes that were significant for some colours from some manufacturers. For these experiments, when additives were visually observed before swabbing, they were also seen afterwards; however, if no additives were seen before treatment, none appeared after. Swabbing was sometimes found to displace additives to the edges of the sample. For a paint colour from one manufacturer, samples from different batches and cast in different years were tested; the results did show that there was variation between batches.

The surface characteristics of a painting are integral to its aesthetic. This research will be integrated with results from mechanical, physical, and chemical testing of acrylic paints, thereby leading to a fuller understanding of the issues involved in the safe and effective cleaning of acrylic paint surfaces. Future work will test older paint films and films on substrates other than Mylar.

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Materials

Acrylic emulsion paints; Golden Heavy Body Acrylics, Grumbacher Academy, Liquitex Basics and Winsor & Newton Finity; local art suppliers.

Mylar (polyethylene terephthalate film): Carr McLean, 461 Horner Avenue, Toronto, ON M8W 4X2, 1-800-268-2123.

Kimwipes: Fisher Scientific Limited, 112 Colonnade Road, Ottawa, ON K2E 7L6, 1-613-226-7658.

Cotton medical swabs: Fisher Scientific Limited.

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