An evaluation of selected retouching media for acrylic emulsion paint

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AN EVALUATION OF SELECTED RETOUCHING MEDIA FOR ACRYLIC EMULSION PAINT

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In this study, polar and non-polar retouching media were analyzed to assess their applicability and reversibility on acrylic emulsion paint films (Golden and Schmincke acrylic paints). Acrylic emulsion paints are very sensitive to a variety of solvents. Only water, short-chain alcohols and aliphatic hydrocarbons are considered suitable for their treatment. Therefore, the retouching media used in this study were chosen for their solubility in each of these solvents. Distilled water and ethanol were used in order to test the reversibility of the polar retouching. Noctane, n-hexane and diethyl ether, which offer weak dispersive interactions but different vapor pressures, were employed for swab removal of the non-polar retouching. Extraction tests with different polar and non-polar solvents, showed which components were leached out of the acrylic paint film sample during swab removal of retouching media. Gloss measurements and photomicrographs taken of the paint film samples before and after the application of the retouching displayed variations when compared to untreated reference samples. Both measurements were taken again after reversibility tests in order to demonstrate any changes in morphology and gloss of the paint film samples.

KEYWORDS: *Acrylics, Retouching, Painting, Acrylic Emulsion, Modern, Reversibility Tests, Solvents, Vapor Pressure*

1. INTRODUCTION

In spite of their many advantageous properties, acrylic emulsion paintings do suffer damage, often through external influences (Jablonski et al. 2003; Pastor Valls and Del Carmen Perez Garcia 2007; Learner 2009). When it comes to treatments such as cleaning, filling, and retouching, conservators soon realize that approaches designed for traditional oil paintings cannot be applied to acrylic emulsion paintings (Klein 2000; Smithen 2007). The most significant difference between oil and acrylic emulsion paint lies in the high sensitivity of the latter to organic solvents and water. Liquid action rapidly leads to changes in optical and mechanical properties of acrylic emulsion paints. The penetration capacity of liquids on acrylic emulsions is very fast as there is good permeation along the surfactant channels that form in between the rhombic structure of the latex particles (Kittel 2001, 140; Jablonski et al. 2003, 6; Zumbühl and Scherrer 2010, 82). Since acrylic emulsion paint layers are sensitive to different outside influences it is important to focus not only on material properties but also on reversibility when evaluating products for conservation treatments.

1.1 SENSITIVITY TO WATER

Water can have an impact on acrylic emulsion paint films. The sensitivity of acrylic emulsions to water is determined by thickeners, extenders, wetting agents, coalescing agents, and other water-soluble additives. The ability of these substances to build hydrogen bonds with water molecules causes swelling of the paint film when immersed in or swabbed with water (Murray et al. 2002, 7; Ormsby, Learner, Forster et al. 2007, 195; Ploeger et al. 2007, 202; Zumbühl et al. 2007, 259). For the same reason, aqueous treatments leach surfactants[1] and other water-soluble additives at and near the paint surface (Digney-Peer et al. 2004, 205; Ormsby et al. 2006, 143, 2009, 191). There are changes in the mechanical properties of the paint film (Murray et al. 2002, 7; Hagan and Murray 2005, 45) as well as an alteration of the hygroscopic properties (Zumbühl and Scherrer 2010, 83). Furthermore, after aqueous swab rolling a slightly higher glass transition temperature (T_g) has been detected (Ormsby, Learner, Forster et al. 2007, 194). Other consequences of water action are optical changes of the paint film (Ploeger et al. 2007, 205). Nevertheless, aqueous swabbing treatments showed minimal changes in gloss and

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color overall (Ormsby, Learner, Forster et al. 2007, 198). All these visual and mechanical changes are referred to as moderate and aqueous cleaning has developed to be an accepted conservation treatment.

1.2 SENSITIVITY TO ORGANIC SOLVENTS

Previous findings indicate an enormous swelling capacity of acrylic emulsion paints in organic solvents over a broad range of the polarity scale (Seuffert 1993; Simmert 1995; Attanasio 2005; Ormsby, Learner, Forster et al. 2007; Zumbühl et al. 2007). Maximum swelling is produced by contact with solvents inducing strong dispersive interaction, such as chlorinated solvents, as well as solvents containing polarizable molecules such as aromatics (Zumbühl 2011, 2003–2016). Through the paint's high swelling capacity, surfactants are extracted, which results in an inter-diffusion of latex particles, whereby the morphological structure of the paint film is irreversibly altered (Attanasio 2005, 51; Zumbühl and Scherrer 2010, 81–83). The solvents with minimal swelling action are found near the upper and lower ends of the polarity scale. Highly non-polar solvents such as aliphatic hydrocarbons and very polar solvents such as short-chain alcohols are the substances that show the least swelling action on acrylic emulsion paint (Attanasio 2005, 52; Zumbühl et al. 2007, 259). Concerning the action of alcohols on acrylic emulsion paint, it is not possible to make categorical statements. According to recent studies every paint product reacts differently to the action of alcohol (Attanasio 2005, 55; Zumbühl et al. 2007, 259). Aliphatic hydrocarbons that are free of aromatic compounds are the only organic solvents that show no significant changes to acrylic emulsion paints (Seuffert 1993, 50; Attanasio 2005, 50; Ormsby, Learner, Forster et al. 2007, 194, Ormsby, Learner, Smithen et al. 2007, 291; Zumbühl et al. 2007, 259). Samples treated with aliphatic hydrocarbons showed only minor decreases in gloss and no changes visible to the eye were produced. However, it was noticed that non-polar solvents exhibit an increased tendency to remove organic pigments from paint films (Ormsby, Learner, Forster et al. 2007, 197–198). These findings influenced and limited the solvents and thus the binding agents selected for the ensuing test series.

1.3 STATE OF KNOWLEDGE REGARDING RETOUCHING MEDIA FOR ACRYLIC EMULSIONS

At this time, there are few studies related to retouching acrylic emulsion paints. However, some findings referring to cleaning or other treatments, such as Wolbers' (1997) reflections about varnishing acrylic emulsion paints, can be applied to retouching acrylic emulsion paints. In his article, Wolbers suggests that additives can be extracted and/or re-deposited from the acrylic paint film by applying a varnish. He also states that soluble paint film components can mix with the applied coating and accordingly change its stability and aging properties. Moreover, the porosity of acrylic emulsion paint films promotes physical inclusion of any substance applied and therefore makes the reversibility of any varnish problematic (Wolbers 1997, 274). Considering the potential risk that lies in applying a binding agent dissolved in an organic solvent, both varnishing and retouching seem to present similar difficulties. As acrylic emulsion paints are highly sensitive to most solvents, suitable retouching media are severely limited. Sims et al. (2010) recently published a preliminary study on retouching media for acrylic paintings. Based on recommendations from practitioners, the authors chose several different paint media for testing. The publication by Sims et al. concentrates on aesthetic criteria such as color and gloss matching, reversibility, and handling properties of binding agents and thus gives initial insights into the applicability of the media tested. These findings give valuable information that contributes to the goal of modifying treatments for acrylic emulsion paints. However, further investigations in the field of retouching acrylic emulsion paint are required.

The outcomes of cleaning studies (Attanasio 2005; Ormsby, Learner, Forster et al. 2007; Ploeger et al. 2007; Zumbühl et al. 2007; Zumbühl and Scherrer 2010) suggest changes in morphology and composition of acrylic emulsion paint occur when applying or removing retouching media, and this is a factor that has not been taken into account in any study so far. Differing from other investigations, this study examines the morphology of acrylic emulsion paint films in greater depth. Furthermore, the applicability of non-polar products and solvents is evaluated.

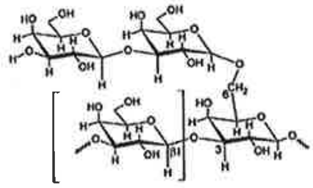
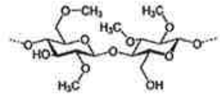
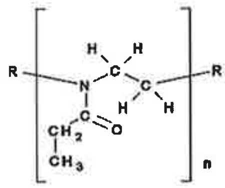
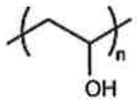
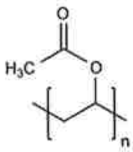
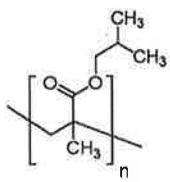
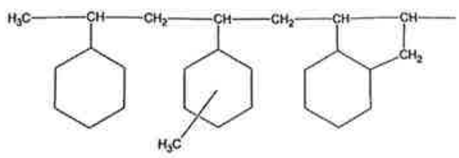
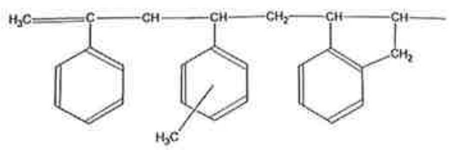
2. Experimental Setup

2.1 SAMPLE PREPARATION

Two commercially available artist's paint systems were used as samples of acrylic emulsion paint films that were to be retouched. In order to receive equally level paint film samples, the paints had to be diluted before application as follows:

- GOLDEN Fluid Acrylics (GAF) by Golden was applied undiluted;
- GOLDEN Heavy Body Acrylics (GAHB) by Golden was diluted with 40% distilled water (w/w);
- AKADEMIE Acryl color (SAF) by Schmincke was diluted with 20% distilled water (w/w);
- AKADEMIE Acryl color extra heavy body (SAHB) by Schmincke was diluted with 30% distilled water (w/w).

TABLE 1 BINDING AGENTS USED TO FORMULATE RETOUCHING PAINTS. INFORMATION TAKEN FROM MATERIAL DATA SHEETS, FIGURES TAKEN FROM HORIE (2010) AND MATERIAL DATA SHEETS.

	Name	Group	Molecular weight (M_W)	Glass transition temperature (T_g)	Structure
Polar	Gum Arabic	Polysaccharide	200,000–800,000 g/mol	–	
	Methocel™ A 15 LV	Cellulose derivate	86,000 g/mol	–	
	Aquazol® 200	2-Ethyl-2-oxazoline	200,000 g/mol	69–71°C	
	Mowiol® 4-88	Poly(vinyl alcohol)	31,000 g/mol	38–45°C	
	Mowilith® 20	Poly(vinyl acetate)	25,000 g/mol	30–40°C	
Non-polar	Degalan® PQ 611	Iso(butyl methacrylate)	100,000 g/mol	32°C	
	Regalrez™ 1094	Hydrogenated hydrocarbon resin	850 g/mol	40°C	
	Kristalex™ 7030	Hydrocarbon resin	1050 g/mol	32°C	

The paint samples were drawn down onto two different substrates including silicone-coated PET foil (Hostaphan foil RNT 36) and cleaned glass slides to a wet thickness of 300 µm using a paint film applicator (Erichsen GmbH). At the time of experimentation, each sample had dried in ambient conditions protected from dust for at least 2 months. Since acrylic paint films change only minimally through aging (Whitmore and Colaluca 1995; Learner et al. 2002; Smith 2007) it was decided to let the paint samples cure under ambient conditions with a room temperature of 65–75° F, above the paints, minimum film formation temperature (Berndt 1987, 18–19; Simmert 1995, 82; Kittel 2001, 140; Jablonski et al. 2003, 6).

Fourier transform infrared spectroscopy (FT-IR) was employed to identify the acrylic emulsions used in both of the paint formulations. FT-IR data were collected with a Perkin Elmer System 2000 µ-FT-IR spectrometer. Each spectrum was the average of 16 scans collected at 4 cm^{-1} resolution and a range from 4000 to 580 cm^{-1}. The spectra indicated that the Golden paints are based on a p(nBA/MMA) copolymer whereas the Schmincke paints are based on an acrylic–styrene copolymer.

Black paint film samples simplify gloss measurements. Additionally, black is a difficult color to retouch, leading to the conclusion that if a good color-match is gained on a black surface then the media used will most likely work with other hues, too. Golden acrylic paint in carbon black consists of carbon (PBk 7) only, whereas Schmincke's acrylic paint in lamp black consists of iron oxide (PBk 11) and carbon (PBk 7).

2.2 EXTRACTION TESTS

Extraction tests were performed to see which components are likely to leach out of the paint samples during the removal of the retouching with polar and non-polar solvents and distilled water. Extraction tests were carried out with 8 cm-long strips of both paint samples. The free paint films were immersed in distilled water, ethanol, *n*-hexane, or diethyl ether for 12 hours and then removed. The extraction solutions were then pipetted onto clean cavity slides and left to dry in an oven at 40°C for 48 hours before analysis. Solid residues from each sample were analyzed by transmission µ-FT-IR spectroscopy. FT-IR data were collected with a Perkin Elmer System 2000 µ-FT-IR spectrometer. Each spectrum is the average of 16 scans collected at 4 cm^{-1} resolution and a range from 4000 to 580 cm^{-1}.

2.3 APPLICATION OF RETOUCHING

For this study, the retouching media were chosen by considering their expected solubility in highly polar or non-polar solvents for reasons that are addressed above. Further important criteria were the composition and T_g of the binding agents as well as their durability. For a complete list of all selected binding agents see table 1. The solubilized binding agents were mixed with pigments directly on the palette (for solution percentages see table 2). To mimic the application of retouching as done in conservation practice, the paint was applied to the samples with a brush. The most common damages that occur on acrylic emulsion paintings are abrasion, glossy patches, or handling marks. As total loss occurs only rarely (Klein 2000, 24; Ormsby, Hackney, Smithen et al. 2007, 11; Pastor Valls and Del Carmen Perez Garcia 2007, 293), the retouching was applied directly onto the paint samples without previously mimicking any degree of loss. All samples were protected from dust and allowed to dry for one week in ambient conditions,[3] before measurements and observations were made.

TABLE 2 COMPOSITIONS OF RETOUCHING PAINTS APPLIED TO GOLDEN AND SCHMICKE ACRYLIC EMULSION PAINT SAMPLES.

Binding agent	Solution for Golden paint samples	Solution for Schmincke paint samples	Solvent used
Gum Arabic (Schmincke HORADAM® Gouache)	50% (w/w)	50% (w/w)	Distilled water
Methocel™ A 15 LV	3% (w/w) + PBk 7	2% (w/w) + PBk 7, PBk 11	Distilled water
Aquazol® 200	10% (w/w) + PBk 7	10% (w/w) + PBk 7, PBk 11	Distilled water
Mowiol® 4-88	10% (w/w) + PBk 7	10% (w/w) + PBk 7, PBk 11	Distilled water
Mowilith® 20	10% (w/w) + PBk 7	10% (w/w) + PBk 7, PBk 11	Ethanol
Degalan® PQ 611	20% (w/w) + PBk 7	10% (w/w) + PBk 7, PBk 11	*n*-Heptane
Regalrez™ 1094	20% (w/w) + PBk 7	10% (w/w) + PBk 7, PBk 11	*n*-Heptane
Kristalex™ 7030	20% (w/w) + PBk 7	10% (w/w) + PBk 7, PBk 11	*n*-Heptane/1-butanol (9:1 mol/mol)

TABLE 3 SELECTED SOLVENTS USED FOR THE SWAB REMOVAL OF APPLIED RETOUCHING PAINTS. INFORMATION IS TAKEN FROM FUESERS (2006) AND REICHARDT AND WELTON (2011), AND DATA SHEETS FROM MERCK CHEMICALS, APRIL 2011. IMAGES ARE TAKEN FROM WIKIPEDIA.ORG, APRIL 2011.

Solvent	Chemical formula	Structure	Properties
Water	H_2O		Category: non-solvent Vapour pressure: 23.4 hPa (20°C) Interactions: active and passive hydrogen bond forces
Ethanol	C_2H_5OH		Category: alcohol Vapour pressure: 59 hPa (20°C) Interactions: active and passive hydrogen bond forces
n-Octane	$CH_3(CH_2)_6CH_3$		Category: aliphatic hydrocarbon Vapour pressure: 14 hPa (20°C) Interactions: dispersive forces
n-Hexane	$CH_3(CH_2)_4CH_3$		Category: aliphatic hydrocarbon Vapour pressure: 160 hPa (20 °C) Interactions: dispersive forces
Diethyl ether	$(C_2H_5)_2O$		Category: ether Vapour pressure: 587 hPa (20°C) Interactions: dispersive forces

2.4 REMOVAL OF RETOUCHING

The removal of the retouching was conducted using sterile medical cotton swabs (15 × 7 mm) produced by Applimed SA, Switzerland. The cotton swabs were dipped in the respective solvent for five. partially dried by rolling on blotting paper for two seconds. Reversibility was tested by swabbing for one and a half minutes, replacing the swabs every 30 seconds. All samples were protected from dust and allowed to dry for one week in ambient conditions, before measurements and observations were made.

All retouching paints formulated with polar media were removed with distilled water except those made with Mowilith 20 which were removed with ethanol. According to previously performed solubility tests (Engel 2011), vapor pressure proved to be an important parameter when considering the solubility of varnish materials (Zumbühl et al. 2014). Therefore, it was decided to test three non-polar solvents, offering varying vapor pressures but comparable interaction forces, to remove the non-polar retouching paints (see table 3). This physical value is of relevance, since the

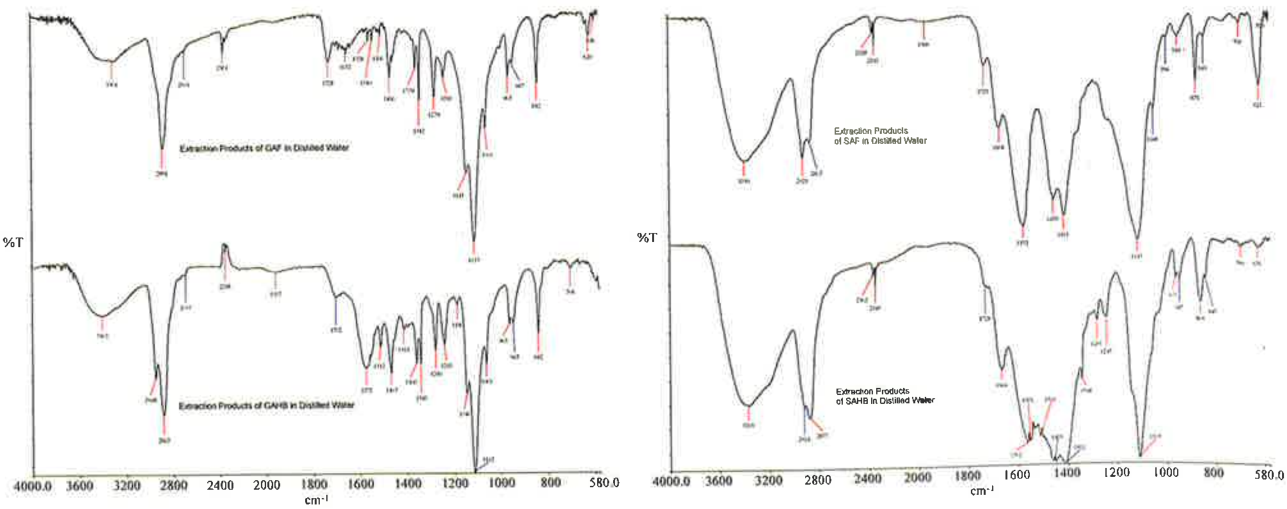


FIG. 1. The FT-IR spectra on the left show extraction products from both Golden paint samples immersed in distilled water. The spectra obtained suggest that polyethylene glycol (PEG) has leached out of the Golden paint films. Due to superposition, other compounds could not be detected. The FT-IR spectra on the right show extraction products from both Schmincke paint samples immersed in distilled water. Here, the spectra suggest polar, hygroscopic compounds, which are not totally assignable. Reference spectra (Hummel and Scholl 1981) suggest a mix of PEG and ionic surfactants.

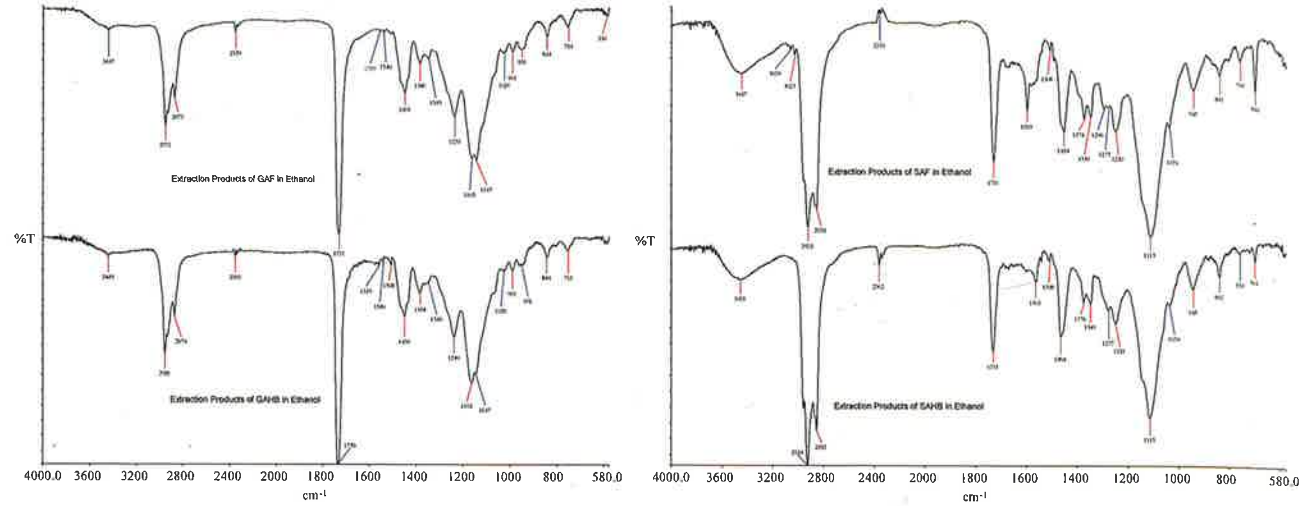


FIG. 2. The FT-IR spectra on the left show extraction products from both Golden samples immersed in ethanol. All of the peaks indicate the extraction of the methacrylate-copolymer. Strong absorption of the ester group suggests an acrylate ($\nu C{=}O \approx 1730$ cm^{-1}, $\nu_a C{-}O{-}C \approx 1240$ cm^{-1}, and $\nu_s C{-}O{-}C \approx 1150$ cm^{-1}). The characteristic pattern of $\nu C{-}H$ with strong $\nu_a CH_3$-absorption ≈ 2955 cm^{-1} indicates a methacrylate. The FT-IR spectra on the right show extraction products from both Schmincke samples immersed in ethanol were the main components extracted are PEG-stearates (see reference spectra 5181, 5182 in Hummel and Scholl 1981). Furthermore, small amounts of the acrylic-styrene copolymer were leached.

entropy change of dissolution is related to the cohesive energy of the liquid (Zumbühl et al. 2014). Non-polar retouching paint was removed with *n*-octane, *n*-hexane, and diethyl ether. For a complete list of all selected solvents, see table 3.

Gloss measurements (see Appendix), as well as photomicrographs (see Appendix), were taken of the acrylic paint film samples before and after the application of retouching. The same measurements were repeated after swab removal of the retouching in order to show changes in morphology and gloss of the paint film samples.

3. RESULTS AND DISCUSSION

3.1 EXTRACTION TESTS

Extraction tests were performed in order to characterize the quantitative change in the paint layers caused by solvent action. Leaching behavior of both Schmincke and Golden paint film samples in distilled water confirmed published findings regarding aqueous cleaning issues (Owen et al. 2005; Ormsby et al. 2006, 2009; Ploeger et al. 2007; Kampasakali et al. 2011). As anticipated, different water-soluble additives, including polyethylene oxide (PEO)

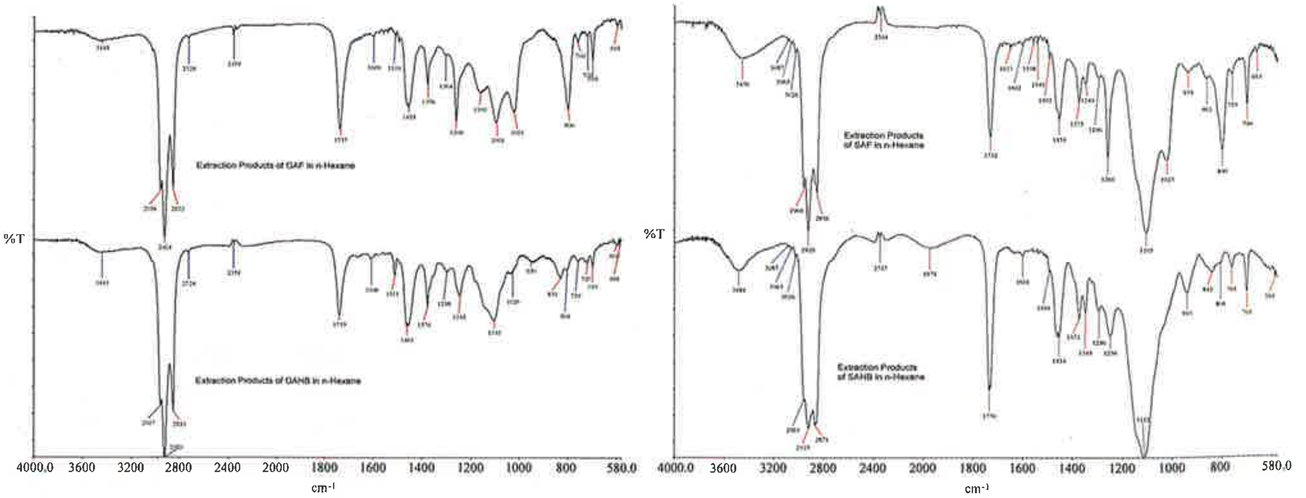


FIG. 3. The FT-IR spectra from the extraction products of both Golden (left) and Schmincke (right) samples immersed in *n*-hexane show peaks related to different components extracted in different proportion. Absorbtion bands of the CH_3-group ν_a-$CH_3 \approx 2958$ cm^{-1} and $d_s CH_3 \approx 1376$ cm^{-1} indicate short-chain components or branched-chain components with methyl substituents. Furthermore, nonionic surfactants such as PEO were leached out. Extractions of GAF and SAF both show absorption bands at 1260, 1095, 1020, and 800 cm^{-1}, which are characteristic for non-polar silicone components.

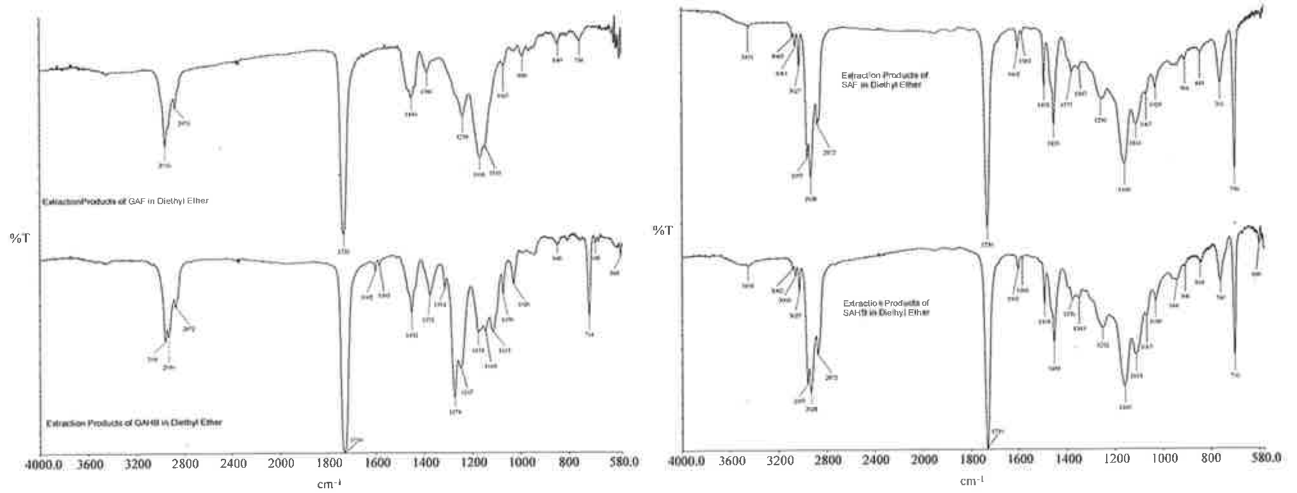


FIG. 4. The FT-IR spectra from the extraction products of both Golden (left) and Schmincke (right) samples immersed in diethyl ether appear very similar to the spectra from extraction products immersion in ethanol. The main component extracted is the acrylic copolymer for the Golden samples and the acrylic-styrene copolymer for the Schmincke samples.

derivatives, were leached out of the paint film samples in distilled water (fig. 1). Immersion in ethanol showed that the main component extracted from all samples was the acrylate polymer binder as well the PEG additive in varying amounts for the different paints (fig. 2). For both Golden paint samples, the peaks indicate p (nBA/MMA) copolymer, whereas the extracts of both Schmincke paint films were identified as PEG and acrylic–styrene copolymer. These findings related to ethanol agree with Attanasio's (2005) results, which showed that even short-chain alcohols can dissolve the acrylic binder in paints. It was also noted that PEG additives are not only soluble in highly polar solvents, but also in non-polar solvents. The spectra from the paint samples immersed in *n*-hexane indicate different hydrocarbon compounds containing PEG in different quantities (fig. 3). Similar to other related compounds used in paint manufacture, the PEG-stearate contains long hydrocarbon chains and therefore is readily dissolved by dispersive interactions with *n*-hexane (NCBI 2011). Extracts from paint samples immersed in diethyl ether suggest that not only additives, but also the paint binder itself, were dissolved in large amounts (fig. 4). These results agree with previous findings, which indicated that the paint's morphology can be changed irreversibly through solvent action (Attanasio 2005; Learner 2007; Ormsby, Learner, Forster et al. 2007; Ploeger et al. 2007; Zumbühl et al. 2007; Zumbühl and Scherrer 2010).

3.2 REVERSIBILITY TESTS

A further aspect of this study focuses on reversibility of different retouching media that can be used on acrylic paint substrates. Here, particular attention was given to optical changes in the acrylic paint layer after removing the different retouching media. The findings obtained in the present study support previous statements about the different reaction of each acrylic emulsion paint to solvent action, indicating that each manufacturer includes different additives in its paint (Attanasio 2005, 55–56; Owen et al. 2005, 23).

Overall, there were only a few binding agents that were not considered suitable as retouching media for acrylic emulsion paints. Gouache did not sufficiently interact with the paint samples and shrank while drying. This led to cracks forming in the retouching layer as well as in the paint sample beneath. Furthermore, the removal of the Mowilith 20 retouching with ethanol resulted in a changed morphology for all paint samples. This was not surprising, as the extraction tests performed showed that ethanol was able to leach out the p(nBA/MMA) or acrylic–styrene copolymer from the paint film. In conclusion, there was no difference between heavy body sample paints or the fluid sample paints when examining effects caused by swabbing.

3.2.1 GLOSS MEASUREMENTS

With regard to the gloss measurements carried out, no trend could be seen in the results given by both Golden paint samples (fig. 5) whereas both Schmincke paints indicate a more definite trend. The removal of non-polar retouching from both Schmincke samples led to an increase in gloss which seems to relate to the vapor pressure of the solvent used for swab removal (fig. 6).

Overall, the retouching on the Golden paint samples showed much higher differences in gloss than the

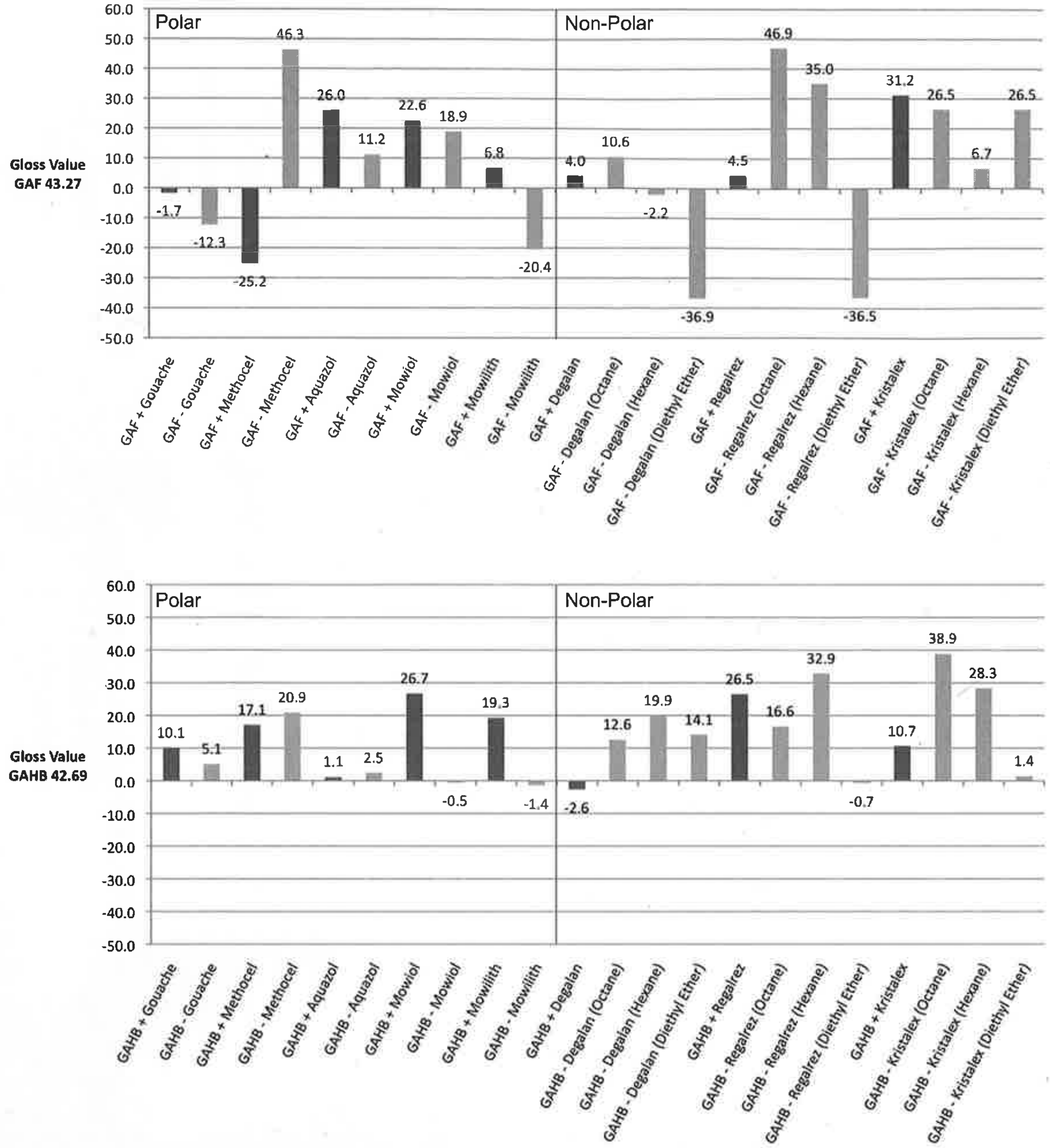


FIG. 5. The total change in gloss of the Golden paint samples. The dark columns (▮) represent the gloss values of the applied retouching and the light columns (▮) indicate the gloss values after removal of the retouching.

retouching on the Schmincke samples. Good gloss results were achieved using Methocel A 15 LV and Aquazol 200 as retouching media. From the total change in gloss demonstrated by the Schmincke samples where retouching was applied, as well as removed, the retouching removal mostly led to an increase in gloss (fig. 6). This can be attributed to the removal of low molecular compounds from the surface of the paint film. The outcomes of different cleaning studies have demonstrated that surfactants are removed from acrylic emulsion paints by aqueous swabbing (among others: Digney-Peer et al. 2004; Attanasio 2005; Owen et al. 2005; Ormsby, Learner, Forster et al. 2007; Ormsby et al. 2008; Kampasakali et al. 2011).

The non-polar retouching layers could not be removed as easily as the polar retouching layers, which had a notable impact on morphology of both Schmincke and Golden paint samples. The non-polar resins Degalan PQ 611 and Regalrez™ 1094 proved to be good retouching media for both the Golden and the Schmincke samples. Furthermore, it was observed

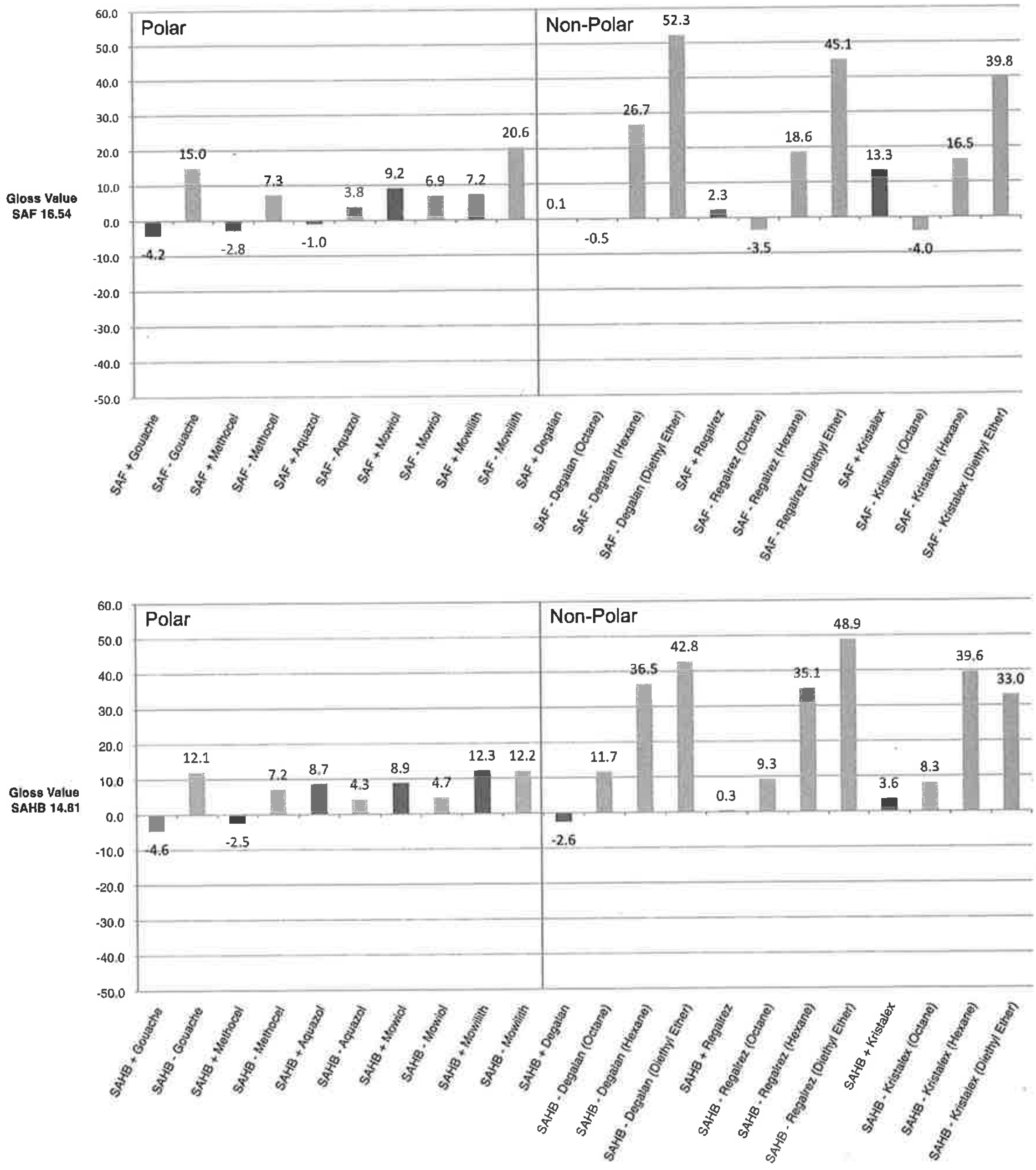


FIG. 6. The total change in gloss of the Schmincke paint samples, with the dark columns (▮) representing the gloss values of the applied retouching and the light columns (▯) indicating the gloss values after removal of the retouching. With both Schmincke samples, especially with the non-polar retouching, one can see the tendency of gloss increase after swabbing. There also seems to be a correlation of the increase in gloss and the increase in vapor pressure of the non-polar solvent used for swab removal.

that removing the retouching with a swab and *n*-octane led to the smallest changes in gloss. Treatments with *n*-hexane however, showed a large increase in gloss, which was exceeded by the results from samples treated with diethyl ether. Variation in gloss is a direct result of the different properties of the solvents. Solvent-induced coalescence leads to a loss of microscopical latex structure and to a smoother, more reflective surface. These findings correspond to what could be expected from the results given by previous solubility tests (Engel 2011, 24–30) and strengthen the conjecture that the vapor pressure of a solvent has a crucial impact on solubility processes. This is due to the reduced cavitation energy of the solvent, which increases the entropy of dissolution and in consequence, the speed of the solvent action (Zumbühl et al. 2014).

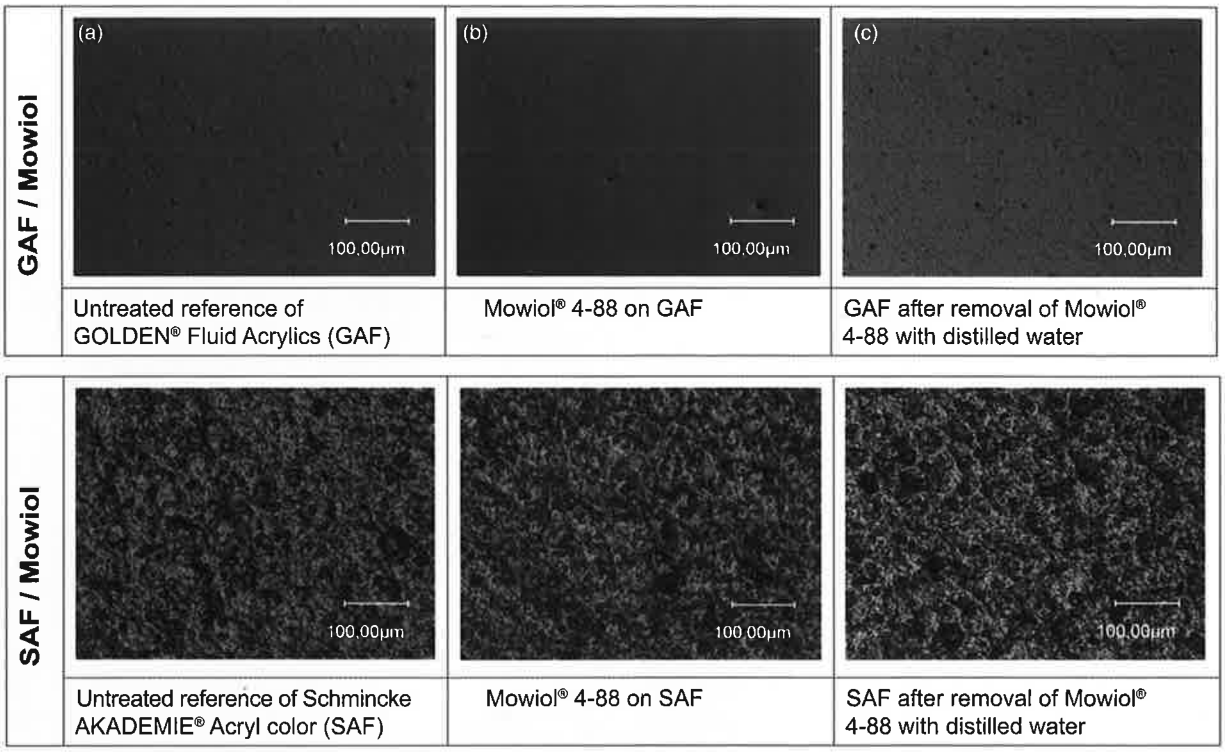


FIG. 7. Photomicrographs of an application and removal cycle of a GAF sample (top) and a SAF sample (bottom). Both paint samples show an increase in pinholes on the surface after swab removal of the Mowiol® 4-88 retouching.

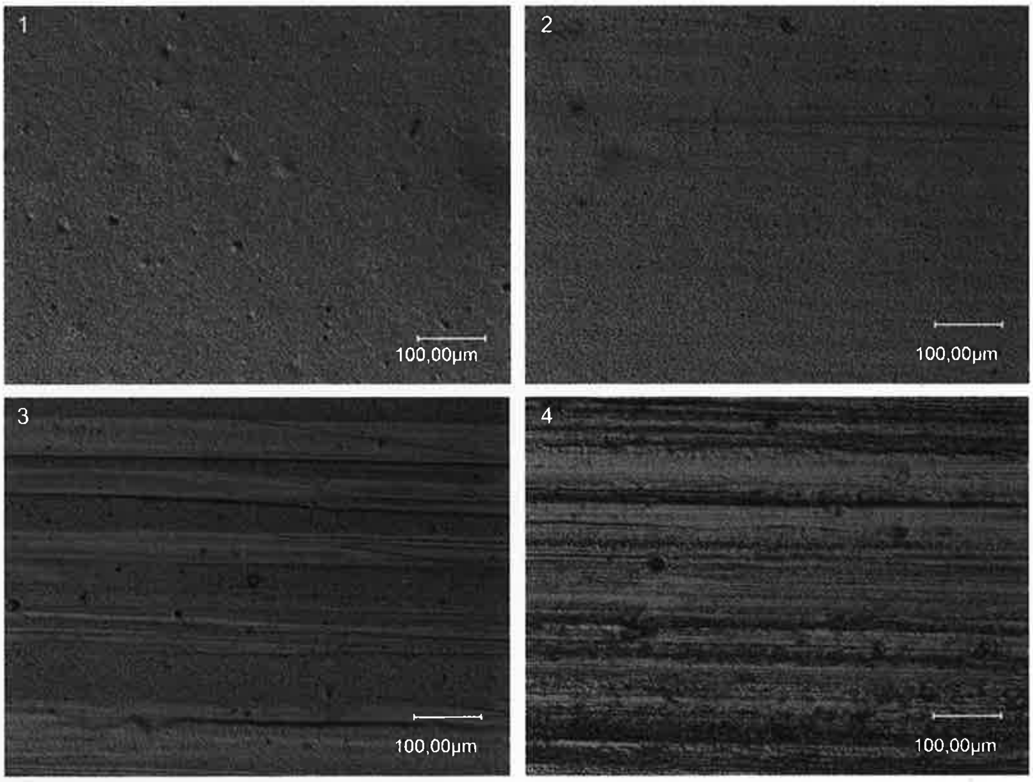


FIG. 8. Photomicrograph of: 1) the untreated GAF paint sample; 2) the GAF paint sample after the removal of Degalan® PQ 611 with *n*-octane which led to an increase in pinholes on the surface; 3) the GAF paint sample after the removal of Degalan® PQ 611 with *n*-hexane. Here, evidence of abrasion and interference colors can be seen; and 4) the GAF paint sample after the removal of Degalan® PQ 611 with diethyl ether which led to an altered texture.

3.2.2 Photomicrographs

Microscopical observations do not entirely correspond with the results from gloss measurements. Photomicrographs revealed that all aqueously treated samples showed a minimally increased roughness due to more pinholes in the paint surface. This was also observed by Ploeger et al. (2007) and is attributed to the removal of surfactants and other water-soluble additives from the surface. Mowiol 4-88 showed the best visual results as a retouching medium on all samples, and its removal with distilled water changed the samples the least (fig. 7). Treatment with ethanol however, left friction marks on all of the samples. The extraction tests indicated that ethanol not only dissolved the Mowilith 20 retouching, but also the acrylic copolymer in the paint film. Therefore, marks were left on the paint sample surface and the structure of the sample was changed.

Non-polar reversibility tests showed poorer visual results. Samples from which Degalan PQ 611 was removed remained the most comparable to the reference sample (fig. 8) and treatment with *n*-octane showed the least alteration. However, all Golden samples treated with *n*-hexane revealed distinctive thin-film interference (fig. 8). This probably derived from a component that was leached out of the paint film and sparsely spread on the surface of the sample by swabbing. All of the samples treated with non-polar high vapor pressure solvents showed signs of abrasion caused by swab rolling. Mechanical action can be held responsible for abrasion even more if a solvent with high vapor pressure is used to remove a retouching with a swab. If the solvent evaporates too quickly, the cotton swab will start to abrade the paint surface.

4. Conclusions

By analyzing the data obtained from solubility tests of several binding agents (Engel 2011, 24–30), as well as performing the reversibility tests on non-polar retouching with *n*-octane, *n*-hexane, and diethyl ether, it is clear that apart from chemical interaction, the vapor pressure of these solvents (see table 3) was crucial to the solubility process and to physical changes in the paint samples. This observation is highly important as aliphatic hydrocarbons are believed to be a reasonable alternative to polar solvents when treating acrylic emulsion paint surfaces. Attanasio (2005), Zumbühl et al. (2007), and Zumbühl and Scherrer (2010) found that aliphatic hydrocarbons do not destroy the latex particles of acrylic emulsion paint films and therefore cause no visible changes in morphology. However, the severe damage caused by diethyl ether and *n*-hexane cannot fully be attributed to fast chemical interaction. In fact, mechanical action plays an important role in the process of removing retouching layers from acrylic emulsion paints. As the solvent works as a lubricant during the reversibility procedure, the speed of its evaporation rate while swabbing is crucial. Since diethyl ether evaporated very quickly, abrasion caused by the mechanical action of the swab increased. Previous studies about cleaning acrylic emulsion paint surfaces confirm this as changes to the surface morphology were detected after cleaning with cotton swabs (Seuffert 1993, 66; Simmert 1995, 95).

In conclusion, one can say that no perfect retouching medium for acrylic emulsion paints exists. Nevertheless, this study was able to identify a number of media suitable for retouching acrylic emulsion paintings. It was pointed out that acrylic paint layers are very sensitive to a number of solvents and therefore it is crucial to select a suitable retouching medium by taking the paint's susceptibility to solvents into account.

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Appendix

Gloss measurements were taken at three different stages during this investigation. The first measurements were taken a little more than two months after sample preparation, then again after the retouching was applied and finally after reversibility tests were performed. Gloss measurements were taken with a three angular micro-TRI-gloss device by BYK Gradener (USA). The micro-TRI-gloss device was calibrated prior to measuring using the zero standard integrated in the instrument holder. Seven readings per measuring point were obtained using 85° geometry for both of the matte Schmincke AKADEMIE® Acryl color samples, 60° geometry for the satin GOLDEN® Heavy Body Acrylics samples and 20° geometry for the glossy GOLDEN® Fluid Acrylics samples. A cardboard template was constructed to allow measurements to be taken at the same spot before and after applying and removing the retouching. For each sample, the average value of seven readings per point was used. To show how much variation, the standard deviation from the average of each test series was calculated. The results are reported to 95% confidence level. These data were processed using

Microsoft Excel 2008 software. A gloss unit value smaller than the reference's value indicates a decrease in surface gloss, and a value higher than the reference's indicates the opposite. The maximum acceptable difference between reference and retouching on GOLDEN® Fluid Acrylics samples was set at ±6.4 gloss units, for retouching on GOLDEN® Heavy Body Acrylics samples, the maximum acceptable difference was defined at ±3.5 gloss units and ±7.2 gloss units was stated as the maximum for both Schmincke samples. These maximum values were determined according to the different geometry used for measurements (cf. Saulnier 2002, 25; Owen et al. 2005, 11–12).

Analogous to the gloss measurements, photomicrographs were performed at three different stages during this investigation. The first measurements were obtained from untreated samples, a little more than 2 months after sample preparation. Photomicrographs were taken again after application of the retouching and finally after performing reversibility tests. Photomicrographs were taken using a VHX-1000D 16-bit resolution digital microscope by KEYENCE with a VHZ-100R real zoom lens and an integrated digital camera at 300x magnification with objective illumination.

Notes

1 Major leached additives are non-ionic surfactants such as polyethoxylates (PEO) and polyethylene glycols (PEG) (Ploeger et al. 2007, 202; Ormsby et al. 2008, 873).

2 H. Schmincke & Co. GmbH & Co. KG do not provide acrylic emulsion paints in pure carbon black (PBk7).

3 The room temperature was set at 65–75°F and the relative humidity was set at 45%–55%.

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Sources of Materials

AKADEMIE® Acryl Color Lamp Black
AKADEMIE® Acryl Color Extra Heavy Body Lamp Black
HORADAM® Gouache ivory black
Pigments PBk 7 and PBk 11: H. Schmincke & Co. GmbH & Co. KG
Otto-Hahn-Strasse 2, 40699 Erkrath
Germany

Methocel™ A 15 LV: The Dow Chemical Company
Enorica GMBH

Hans-Boeckler-Ring 47, 22851 Norderstedt
Germany

Aquazol® 200: ISP Technologies Inc.
Lindenstrasse 10, 6340 Baar
Switzerland

Mowiol® 4-88: Kuraray
Omya (Switzerland) AG
Industriestrasse 10, 5745 Safenwil
Switzerland

Mowilith® 20: Hoechst, Kremer Pigments GmbH & Co. Hauptstr. 41–47, 88317 Aichstetten
Germany

Degalan® PQ 611: Röhm (Switzerland) GmbH
Ruchstuckstrasse 8, 8306 Brüttisellen
Switzerland

Regalrez™ 1094 and Kristalex™ 3070: Eastman, Keyser & Mackey Switzerland
Badenerstrasse 587, 8048 Zürich, Switzerland

GOLDEN® Fluid Acrylics and GOLDEN® Heavy Body Acrylics: Golden Artist Colors, Inc.
188 Bell Road, New Berlin, NY 13411–9527
USA

Solvents: Merck Switzerland
Chamerstrasse 174, 6300 Zug, Switzerland.

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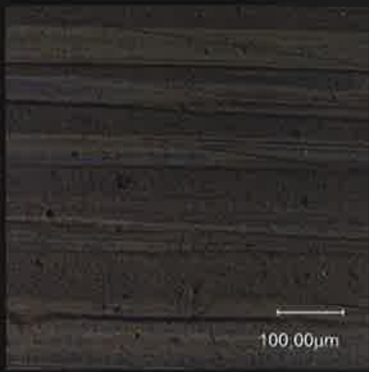

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