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Retouching unvarnished acrylic emulsion paintings, a comparative study

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Abstract: Acrylic films have specific characteristics such as sensibility to polar organic solvents (and in some extent water) and are prone to accidental superficial alterations. Most of the necessary retouching caused by accidental alterations is directly on the film so the notion of reversibility is crucial. This is why this study is focused on retouching media that are already proven to be suitable for acrylic paintings. Those materials are then soluble in either water or aliphatic hydrocarbons. The tested materials are Aquazol® 200 and 500, Klucel® G, gum Arabic, and Regalrez® 1094 mixed with pigments. Ready to use materials (Aquacryl®, QOR®, and Winsor & Newton® watercolours) were also tested. Various criteria were examined: first, all the materials were tested unpigmented and mixed with titanium white. Then, their gloss and colour change were measured, to see which material is more prone to produce matte films. A set of samples were then exposed to artificial light aging, and another set exposed to high relative humidity in order to isolate the impact of light and humidity on the gloss and colour of the resins (like yellowing) and observe how the retouching could behave in poor conservation conditions. Empirical tests were also conducted: the resins were mixed with five different pigments to see difference in opacity and saturation between materials. Most importantly, the materials were tested on naturally aged acrylic paintings, to see which material(s) are easier to use. The aim of this study was not to find the best retouching material, but rather to validate and enlarge the possibilities for the retouching of acrylic painting.

Keywords: Acrylic paintings, QOR®, Regalrez® 1094, Aquazol®, Gum Arabic, Klucel® G.

Reintegración de pinturas de emulsión acrílicas sin barnizar, un estudio comparativo

Resumen: Las películas acrílicas tienen características específicas como la sensibilidad a los disolventes orgánicos polares (y en cierta medida al agua) y son propensas a alteraciones accidentales superficiales. La mayor parte de las reintegraciones necesarias, provocadas por alteraciones accidentales, se realiza directamente en la película, por lo que la noción de reversibilidad es crucial. Por eso, este estudio se centra en aglutinantes que ya han demostrado ser aptos para pinturas acrílicas. Estos materiales son entonces solubles en agua o en hidrocarburos alifáticos. Los materiales probados son Aquazol® 200 y 500, Klucel® G, goma arábiga y Regalrez® 1094 mezclados con pigmentos. También se probaron materiales listos para usar como Aquacryl®, QOR® y acuarelas Winsor & Newton®. Se examinaron varios criterios: primero, todos los materiales se probaron sin pigmentar y mezclados con blanco de titanio. Luego, se calculó su brillo y cambio de color, para ver qué material es más propenso a producir películas mate. Posteriormente se expuso un conjunto de muestras a envejecimiento por luz artificial, y otro conjunto expuesto a alta humedad relativa con el fin de aislar el impacto de la luz y la humedad en el brillo y color de las resinas (como el amarilleamiento) y observar cómo podría comportarse la reintegración cromatica en malas condiciones de conservación. También se realizaron pruebas empíricas: las resinas se mezclaron con cinco pigmentos diferentes para ver la diferencia de opacidad y saturación entre los materiales. Lo más importante es que los materiales se probaron en pinturas acrílicas envejecidas naturalmente para ver qué materiales son más fáciles de usar. El objetivo de este estudio no fue encontrar el mejor aglutinante de reintegración, sino validar y ampliar las posibilidades de reintegración de la pintura acrílica.

Palabras clave: Pintura acrílica, QOR®, Regalrez® 1094, Aquazol®, goma arábiga, Klucel® G.

Reintegração de pinturas de emulsão acrílica sem envernizar, um estudo comparativo

Resumo: A pintura acrílica tem características específicas, como a sensibilidade a solventes orgânicos polares (e, em certa medida, à água) e é propensa a alterações acidentais superficiais. A maioria das reintegrações cromáticas necessárias, causadas por alterações acidentais, são feitas diretamente sobre a tinta, por isso a noção de reversibilidade é crucial. O foco deste estudo são os aglutinantes que já se mostraram adequados para pinturas acrílicas. Estes materiais são solúveis em água ou em hidrocarbonetos alifáticos. Os materiais testados são Aquazol® 200 e 500, Klucel® G, goma-arábica e Regalrez® 1094 misturado com pigmentos. Também foram testados materiais prontos a usar como o Aquacryl®, QOR® e aquarelas Winsor & Newton®. Vários critérios foram examinados: primeiro, todos os materiais foram testados sem pigmentação e misturados com branco de titânio. Em seguida, foi medido o brilho e a alteração de cor, para se perceber qual

o material mais propenso a produzir peliculas mates. Posteriormente, um conjunto de amostras foi exposto ao envelhecimento por luz artificial, e outro conjunto exposto a alta humidade relativa, a fim de isolar o impacto da luz e da humidade no brilho e na cor das resinas (como o amarelecimento) e observar como a reintegração cromática se pode comportar em más condições de conservação. Também foram feitos testes empíricos: as resinas foram misturadas com cinco pigmentos diferentes para ver a diferença de opacidade e saturação entre os materiais. Os materiais foram testados em pinturas acrílicas envelhecidas naturalmente para ver quais dos materiais são mais fáceis de usar. O objetivo deste estudo não foi encontrar o melhor aglutinante de reintegração, mas validar e ampliar as possibilidades de reintegração da tinta acrílica.

Palavras-chave: Pinturas acrílicas, QOR®, Regalrez® 1094, Aquazol®, goma arábica, Klucel® G.

Introduction

—The issues in the retouching of acrylic paint films

The cleaning acrylic paintings has been the subject of numerous research; however, there are only a few studies concerning the retouching of acrylics. Retouching acrylics starts with understanding the material, its chemical and physical properties, and alterations that can and should be retouched.

Acrylic paints have been manufactured since the 1950's, and have been popular among artists since the 60's. This synthetic binding media has a few particularities that differ from traditional oil paintings such as:

- Acrylics are soluble in water, and dry fast because of film coalescence. This allows the paint film to be dry on the surface very quickly. This is one factor that can appeal to artists: this type of painting dries fast, is easy to use and is less toxic for its user. Monochrome surfaces are therefore easier to obtain with acrylics, even in large formats.

- Acrylics possess a low glass transition temperature (Tg) which is close to room temperature. The Tg of acrylics is between 17°C and 22°C (Learner, 2000) depending on the polymer or copolymer of the paint. This low Tg allows the paint film to remain flexible. Acrylics are then less prone to cracking than oil paintings, but more susceptible to dust attraction, and accidental alterations of the surface.

The alterations of acrylics paint films are also different from traditional paintings. As said before, acrylics are less prone to cracking, so the alterations that need to be retouched are often done during handling and transportation of the paintings. The most recurrent alterations are fingerprints, local polishing (abrasions) and scuff marks. Complete deterioration of acrylics is quite rare but can occur during an accident or due to technical incompatibility from the artist's technical process. Most of these paintings are not varnished, which makes the retouching process even more complex. It should be noted that most of these alterations could be avoided if preventive conservation measures were systematically applied. As acrylics paints are porous films, even if a retouching is reversible, the retouching media is most likely to leave residues in the paint layer after removal. That is why reversibility and stability are a crucial issue.

— Choosing a suitable material

As alterations are all directly on the paint layer, the notion of reversibility is key. Acrylics have different sensitivity to solvents than traditional oil paintings: acrylic paintings are soluble in organic polar solvents, and in some extend swell in the contact of water (Dillon, Lagalante and Wolbers, 2014; Ormsby, Learner, 2009). Aliphatic hydrocarbons have less interactions with acrylic paint films.

Beside reversibility, aesthetical criteria are essential. Acrylic paintings are less likely to be varnished, so the retouching media should ideally directly have the same level of gloss as the painting. Acrylic films tend to be matte, sometimes slightly glossy, depending on the brand, additives in the composition of the paint, and the pigments used. The level of gloss required is therefore dependant on the alteration which needs retouching (if the alteration is polished, or scuffed, the retouching material should be more or less matte). Another criterion is the opacity that can be obtained with the retouching media: if fingerprints, lacunas, or stains are retouched, the required opacity will differ.

A retouching media suited for acrylics should be soluble in either water, or aliphatic hydrocarbons, reversible, and should be matte to slightly glossy. It should also be light-stable as there is no varnish to protect it.

Several retouching media tested in previous studies (Engel, Zumbuhl, 2015 ; Sims, Cross, Smithen, 2010 ; Santois, 2012) were selected considering their solubility and reversibility. The aesthetic criteria were then examined (gloss and colour change) as well as their chemical and physical stability. It is important that the retouching remains reversible, but mainly stable, so these paintings will be restored as little as possible. The products tested in this study are listed in Table 1.

It should be noted that the aim of this study is to find a panel of suitable retouching medias, rather than one perfect product. The materials were tested according to different parameters: light, humidity, and film-forming qualities. For the light and humidity evaluation, gloss and colour stability of the products were measured.

Table1.- List of selected materials

	Nature of the product	Name of the product
Soluble in water	Poly(2-ethyl-2-oxazoline)	Aquazol® 200
		Aquazol® 500
	Polysaccharide	Arabic gum
	Hydroxypropylcellulose	Klucel G®
Commercial products soluble in water	Poly(2-ethyl-2-oxazoline)	QOR®
	Polysaccharide (+ additives) Full composition unknown	Watercolors Winsor & Newton™
	Copolymer BA/MMA Full composition unknown	Aquacryl®
Soluble in hydrocarbons	Hydrogenated hydrocarbon	Regalrez® 1094

Table 2.- List of proportions for the unpigmented and pigmented samples

	Product	Unpigmented	Pigmented
Prepared products	Aquazol® 200	5%, 10%, 15% in water	5%, 10%, 15% in water 1v solution/1v pigment
	Aquazol® 500	5%, 10%, 15% in water	5%, 10%, 15% in water 1v solution/1v pigment
	Arabic gum	10% in water	10% in water 1v solution / 1v pigment
	Klucel® G	1% in water	1% in water 1v solution/1v pigment
	Regalrez® 1094	5%, 10%, 15% in Shellsol D40	5%, 10%, 15% in Shellsol D40 1v solution/1v pigment
Commercial, ready-to-use products	QOR®	Ready to use Ready to use with drops of synthetic ox gall	Ready to use Ready to use with drops of synthetic ox gall
	Winsor and Newton watercolors	/	Ready to use Ready to use with Acematt HK125
	Aquacryl®	/	Ready- to use

Materials and methods

— Sample making

The samples were made on acrylic paint films applied on a commercially prepared cotton canvas. Two different types of acrylic paints were chosen: Liquitex Heavy Body titanium white, and Golden titanium white. These paints were chosen because of their difference in gloss: Golden paint produces a matte film, whereas Liquitex are slightly glossy. This difference in gloss can be explained by the difference in composition (more or less additives, and addition of extenders like clay could perhaps form films which are more matte).

All the retouching materials were applied on the samples using a film applicator. The obtained films of retouching media were 200 microns thick. Each selected material was prepared and applied both unpigmented and pigmented (see Table 2), to see to the

behaviour of the resin, and how it is influenced by the presence of pigments. Only the Aquacryl wasn't applied unpigmented. For the pigmented medias, 1 gram of resin solution was mixed with 1 gram of titanium white pigment (Kremer). The pigment was immerged in the solution for 24 hours, and then mixed with a spatula, in order to properly wet the pigment particles. Some products were tested in different concentration in order to evaluate different levels of gloss.

— *Testing methodology and measurements*

Gloss and colour change were the two main criteria tested, in different light and humidity settings. Three sets of samples were made for this study, in order to separate the impact of light and humidity.

One set of samples was artificially aged for 500 hours in a Q-Sun Xe-1-S Xenon Light Chamber, at the Meurice Institute, in Brussels. The samples were exposed through a Daylight Q Filter, so the wavelength of the light was between 290 and 800 nm. In average, the temperature inside of the chamber was 48°, due to the heat of the light, and 15% relative humidity. The settings of the Q-Sun Chamber were 0,60 w/m2 and 340 nm. The wavelength chosen is similar to a previous study done on Aquazol (Wolbers et al, 1998). The samples were rotated frequently so the samples were exposed to the Xenon light homogeneously. A Blue Wool Scale placed in the chamber with the samples allowed us to make a parallel between 500 hours of exposure and 100 years. Because of the heat and low humidity, the conclusions made about the impact of light are indications rather than certainty.

Another set was tested in high relative humidity (RH). This set of samples was put in a humidity chamber, where RH was maintained to 90% with a saturated saline solution of potassium chloride also present in the chamber. The samples were left in this high RH for 12 consecutive days.

The last set was kept in the dark for the whole duration of the study as an untouched control.

Concerning the gloss, a PCE-GM 60Plus glossmeter (PCE Instruments) was used, with an angle of 60°. And for measurements of colour, a colorimeter Minolta CR-221 was used. The measures with the colorimeter were done according with the CIE standard (Illuminant D65, and 2° angle). For each sample, 20 measurements were made (10 with the glossmeter, and 10 with the colorimeter), and averaged (combined with standard deviation). All the measurements were also compared visually.

Concerning the film forming qualities and reviews, a panel of painting conservation students from the ENSAV La Cambre school evaluated and gave their opinions concerning saturation, opacity, and about the easiness to use the products.

Results and discussion

— *After artificial light aging*

Prior to the measurements, it was noted that there was a more or less visible change in most of the samples. If the difference in colour, before and after artificial light aging was visible during the visual appreciation, the gloss changes, in most cases was harder to quantify.

• *Gloss evaluation*

After measurements, it was clear that all samples had a decrease in gloss for the unpigmented media. The main results for the unpigmented media were that the Aquazol samples (200, 500 and QOR) were the samples with the most notable decreased gloss (decrease of up to 16 gloss units). This may be explained by a degradation of the resin with UV light, which was also noted in previous studies (Engel, Zumbuhl, 2015). Regalrez 1094 samples also had an important gloss reduction (and higher the concentration, higher the decrease). Unpigmented Gum Arabic and Klucel G samples also had a decrease, but it was a similar reduction than the unretouched samples of acrylic.

For pigmented samples, there was, in general, a good stability of almost all retouching materials. The addition of the pigment lowers the proportion of the resin, so the decrease in gloss was less noticeable, even with a glossmeter. Commercial products were the samples that had the biggest difference in gloss before and after artificial light aging, but this was not visible without instrumental measurements. The only exceptions were the QOR samples, with or without synthetic ox gall (up to a 9 gloss unit decrease). For pigmented samples, Aquazol 200, 500, Regalrez 1094 and Klucel G showed very good results. However, Regalrez samples were difficult to apply (see 3.3. below). Aquazol and Klucel G were most stable in time when applied pigmented, in opaque films. The slight decrease of gloss for commercial products may indicate a degradation of the unknown additives of these paints. Samples of Aquazol and gum Arabic mixed in the studio had a tendency to be more stable. However, the disadvantage of preparation in the studio meant that the pigments were less finely grounded, and this process was more time-consuming.

• *Colour evaluation*

For unpigmented samples, the difference of colour before and after artificial aging was measured with Delta E values. As such, there was an important yellowing of all

Aquazol samples (200, 500 and QOR). Regalrez samples also yellowed significantly, and it was increasing with the concentration of the resin. Gum Arabic and Klucel G yellowed as well, but it was not visible without a colorimeter. The yellowing of unpigmented Aquazol and Regalrez samples was significative and thus discouraging to use in unpigmented, or transparent retouching. Gum Arabic or Klucel G are then more suitable for transparent, thin retouching.

Pigmented samples generally had a good stability in colour. We can then conclude that the addition of pigment lowers the yellowing of the retouching, which is very encouraging for opaque retouching on acrylics. However, for commercial products, some were changes visible, for example, on the QOR samples, which did not yellow very much but remained tacky, and attracted dust (see more in 3.2 below). Winsor & Newton samples had a greyish aspect after artificial aging, which could be a consequence of the alteration of additives, or maybe an interaction between additives, pigment, and acrylic. In comparison, the sample of Arabic gum mixed in the studio, did not have this aspect after light exposure, and was rather stable. For pigmented samples, Aquazol, gum Arabic and Klucel G mixed in the studio showed the best results, and all three products offer a large range of gloss suitable for acrylics. Klucel remains matte, and gum Arabic and Aquazol can be matte to slightly glossy.

—After exposition under high relative humidity

The samples were exposed under very high relative humidity (up to 90% RH). The colour of the retouching materials (pure, or pigmented) did not change, either with measurements with the colorimeter or with visual observations. However, some of the retouching materials did have some noticeable changes.

For the unpigmented samples, some were very sensitive to humidity. The most sensitive samples were the ones made with Aquazol (Aquazol 200, 500 and QOR). All of them were reactive (when a cotton swab was applied on it, it was still sticky). That was no difference between Aquazol 200 and 500, but QOR was even more reactive. This sensibility to humidity was problematic to some extent because these samples attracted dust. However, when those samples were out of the humidity chamber and placed in a room with a relative humidity of 50%, in less than an hour, the samples were not sticky anymore (no attraction of dust, no residues when swabbing with a cotton swab).

The gum Arabic samples had a little tendency to crack under high humidity when unpigmented. This alteration was visible under microscope on all samples, and on some samples, it was even visible with regular observation. Klucel G was the least reactive water-based medium. The Regalrez samples (5%, 10% and 15%), as expected, were not reactive to humidity, which is normal considering the fact that the resin is soluble in hydrocarbons and insoluble in water.

The samples that were mixed with pigments however had better results: Aquazol samples (Aquazol 200 and 500) did not attract dust at all. When a cotton swab was applied on those samples, it was less tacky than the unpigmented samples.

However, QOR samples attracted dust, and where also tacky. Gum Arabic and Klucel G samples had good results, and had no particular alterations due to the high relative humidity.

Pigmented Regalrez samples were not sensitive to humidity, but the adherence of those films was considered weak, and the retouching was flaking in all Regalrez samples.

— Film forming qualities

During the making of all the samples, some materials had some noticeable traits. To confirm them, we asked a panel of students in painting conservation to use the different products.

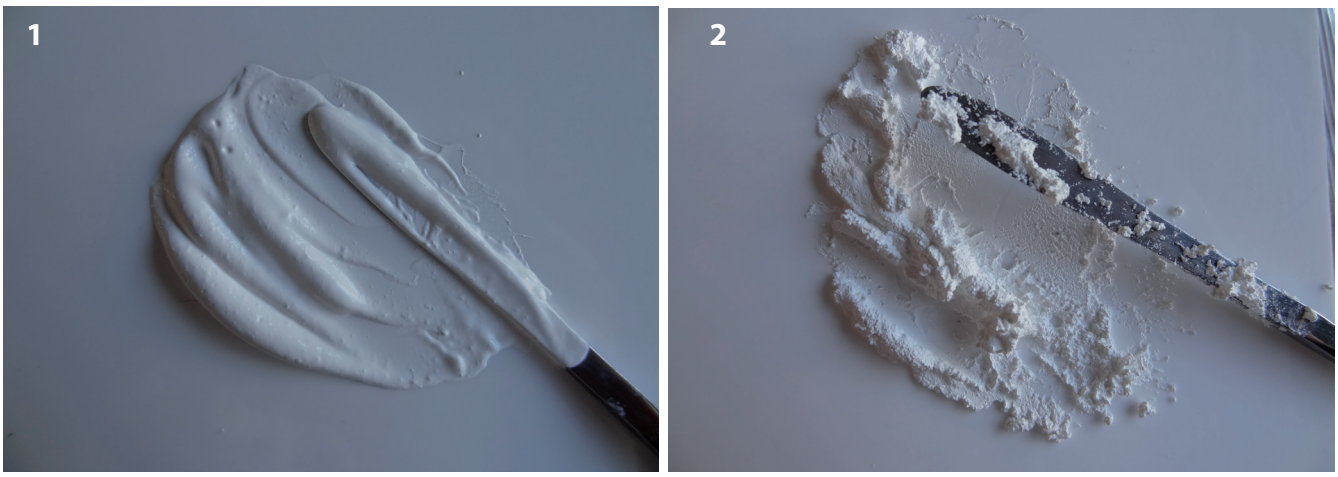
All participants had the same remarks concerning the handling of the retouching materials:

- Regalrez 1094, although promising on paper, is the hardest retouching material to use. Tested in Shellsol D40, the unpigmented resin has a tendency to diffuse very quickly on the paint layer, as well as in filling materials. When pigmented, the Regalrez did not mix well with the pigment particles. An uneven final aspect was obtained, and, in the worst cases, a weak adherence of the retouching to the paint film when the pigment/resin ratio was too low. This was already perceptible when mixing the resin solution with the pigment, as seen in Figure 1 and 2 below.

- Klucel G in 1% in water was the easiest material to use. It was easy to apply on the paint layer, and presented a good pigment dispersion in the medium. At this concentration, it was not too viscous. The obtained film was however very matte, and less saturated than another media.

- Retouching with Aquazol 200 (as well as Aquazol 500) produced less matte films. Like Klucel G, there was a god dispersion of the pigment particles in the medium. Retouchings with Aquazol were more saturated than with Klucel G.

- Gum Arabic and Winsor & Newton watercolours were very easy to use. The retouching was less matte than with Klucel G. The saturation level of gum Arabic and Aquazol is very similar.



Figures 1-2.- Mixing Aquazol 200 with titanium white pigment (on the left), mixing Regalrez 1094 with titanium white pigment (on the right). We can see on the right picture that the mix obtained with pigment and Regalrez is hard to mix, and to apply. On the left picture, mixing pigment and Aquazol is really smooth.

Figure 3.- Mixing some of the materials with various pigments. From top to bottom: Regalrez 1094 (10% in Shellsol D40), Klucel G (1% in water), Arabic Gum (10% in water), Aquazol 200 (10% in water), Aquazol 500 (10% in water), QOR medium solution mixed with pigments. We can clearly see the difference of light and saturation between the retouching materials, especially in darker colors. .

Conclusions

The results of this study show that there is no perfect retouching material, but rather a panel of materials than can be used. All the tested materials were reversible after light artificial aging.

The different characteristics of each material highlights how they could be used. For example, Aquazol (200, 500 and QOR) are more reactive to water, and light. Aquazol tends to yellow when unpigmented. Therefore, Aquazol could be used preferably for less matte acrylics, in opaque retouching rather than transparent tones.

For thin, transparent retouching, gum Arabic seems more suitable, as thicker layers of gum Arabic are more prone to cracking, especially in high relative humidity. In thin layers, the pigment is also easily dispersed, and yellows less in time than Aquazol films.

Klucel G is recommended for very matte retouchings that are also less saturated. Even if it was the most promising retouching medium on paper because of its solubility in aliphatic hydrocarbons, Regalrez 1094 was very difficult to use. Although it does not react to high humidity, it yellows when unpigmented, and is hard to apply when pigmented. It also diffuses on the surface, which makes it difficult to control on small areas.

However, more research should be conducted on retouching acrylics with Regalrez 1094, as it was the only medium soluble in aliphatic hydrocarbons (and therefore potentially the least problematic toward acrylic paint films). Other solvents could be used, and maybe restrains the diffusion of the resin on the paint layer.

During this study, the products soluble in water were done with deionized water, however, maybe a buffered water with proper conductivity could be interesting to solubilize Aquazol, Klucel and Gum Arabic, especially if the paint layer is sensitive to water. In all cases, the removal of previous retouching soluble in water should be done with water with proper pH and conductivity to avoid the swelling of the acrylic painting. Other factors such as penetration in the acrylic paint film could be investigated, and the impact of the residues after removal of retouching with these materials.

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