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On the study of oil paint adhesion on optically transparent glass: Conservation of reverse paintings on glass

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1.0 – Abstract

Reverse painting on glass is a technique which consists of applying a cold paint layer on the reverseside of glass. The main challenge facing these artworks is the fragile adhesion of the pictorial layer – a simple movement can modify the appearance of the painting. This paper details a study into the adhesion parameters of pigments on glass and the comparison between different pigments. The relationships between the binder (linseed oil) with pigments and the glass with or without the use of an adhesive are studied. Physical analyses by surface characterisation have been carried out to better understand the influence of the pigment. The use of a sessile drop device, optical microscopy, scanning electron microscopy (SEM), a surface 3D profiler and a pencil hardness scratch tester were necessary to establish a comparison of the pictorial layer adhesion. A comparison of the effect of two adhesives; namely ox gall and gum arabic, has shown that the adhesion is not only linked to the physical parameters but that possible chemical reactions can influence the results. Finally, a treatment based on humidity-extreme storage has shown the weakness of some pictorial layers.

Keywords: Reverse painting; art conservation, adhesion, wettability, glass.

2.0 – Introduction

In the art of painting, many kinds of support can be used. For example, wood, canvas and stone have all been utilised in the past. One other such support is glass. Glass has been used and manufactured since Antiquity and is produced by melting a mixture of silica with alkaline and a stabilizer. The evolution of the composition of glass has led to optically transparent glass which has contributed to the development of various painting techniques [1]. From this, two techniques have arisen: fired paintings and cold paintings. In the case of fired paintings, the pigments are applied on the surface of glass with a vitreous material and then fired until the melting temperature is reached to fix the decoration [2]. Cold painting on glass has been conducted since the Roman era by applying lacquer and oil paint on to the glass surface. Due to the speed of deterioration from oxidative processes and the effects of humidity, the technique of reverse painting on glass has been further developed over time with the glass being utilised, simultaneously, as a protective varnish and a support. These paintings are directly executed on to the back of the glass in a reverse manner. That is, first, the details and shadows are painted and then the background. The different colours can be applied one after the other, once the previous layer has dried, or can even be applied before drying by implementing thinner layers [3-5]. The presence of a black background (e.g. paper, wood) is necessary on account of the optical nature of the reverse paintings as they are viewed using reflected light rather than the traditional transmitted light. Having said that, some glass paintings have been used as a filter in front of projected light but this has only been seen in special cases [1]. One of the unique features of reverse painting on glass is that it gives a particular unique brightness to the piece of art compared to competing techniques [6]. This is on account of there being no an air gap between the glass and the painting for reverse painting on glass. During the 18th century Arnaud Vincent de Montpetit invented the Eludoric painting technique, which consisted of painting with an oil binder under a thin layer of water. The painting was then covered with a glass panel pasted with an adhesive [1]. Contrary to this technique, reverse paintings on glass were directly applied to the glass and the technique was considerably developed during the 16th and 18th

centuries in Europe and China. The 18th and 19th centuries saw the evolution of this popular technique in Europe [3]. Damage to these specific types of artwork can derive from the glass, the frame, the backboard or from the binding, the medium and the paint layer [6]. As a result, many museums and art galleries prefer to retain these paintings in storage due to preservation and conservation issues. In addition to the development of reverse painting on glass, throughout history, there is currently a significant drive towards the study of such art to improve and enhance current conservation techniques [3, 7-9].

The evolution of the glass industry in Europe gave rise to the increased use of transparent properties of glass. For instance, in the 15th century, Venice developed a transparent and flat glass called Cristallo. In France, the Lorraine region became a production centre for glass during the 16th century. Many exchanges between these locations led to the development of the reverse painting on glass technique [1]. Concerning the pictorial layer, many recipes and solutions have been used and, as a result, conservation difficulties are linked to the mixture of many pigments and binders [1, 4, 9, 10]. The lack of standard conformity in the technique of reverse painting on glass provides many challenges today regarding conservation and restoration of these kinds of artworks. What is more, in addition to pigments, silver and gold are also present on reverse paintings on glass, leading to further conservation and restoration implications [6].

Damage to the paint layer can derive from a number of factors, ranging from the way in which the pigments and media are used to storage and handling conditions. These damages generally arise through the detachment of paint layers, loss of colour and fragmentation, and can be strongly linked to the painting technique, the preparation of pigments and the use of media. These factors are necessary to be taken into account when considering preserving the painted artwork [4]. Sometimes, observed glass deterioration (e.g. broken glass, corrosion) can be indicative of decay within the colour layers beneath. Indeed, the study by Neelmeijer [7] shows the necessity to not only understand the deterioration mechanisms of the paint layers but also the interactions between the paint and the glass itself.

The paint layer can also be damaged through photochemical reactions as a result of chemical instability. Furthermore, the penetration of water can create significant deterioration, with the development of microorganisms and the separation between hydrophilic and hydrophobic materials. The failure of adhesion, due to the oxidation of the paint or the effect of light and heat, can lead to powdering, blistering or peeling of the colour layer. What is more, poor restoration techniques can also increase the deterioration [6, 10] highlighting the crucial necessity for managing the deterioration of the paint layer for successful conservation.

Storage considerations of reverse paintings on glass are complicated because of the sensitivity of the materials used and also because of the non-standard mixtures implemented by the artist. This is why reverse paintings on glass are less often seen in museums than other paintings. Best practice is to keep these paintings in their frames with the glass side placed face down. The use of acid-free tissue paper is recommended for wrapping the painting before storing in a sealed box, resistant to air and water vapour. This, along with the implementation of an air circulation and filtration system, removes the possibility and likelihood of air pollution. Finally, current recommendations for conserving these artworks are to maintain a stable, optimised environment (T=18–20 °C; RH=50–55 %) [6, 7].

Artworks conservation is heavily linked to the understanding of the materials present. Interactions between the materials and the environment, inter-material reactions and long-term behaviour must be studied to gain a more in-depth understanding of the issues that arise during restoration. The adhesion parameters of a material are heavily linked with the wettability characteristics of that material. As such, considerable amounts of research over a large range of applications have been conducted in the area of adhesion and wettability characteristics [11-16].

This work is focused on material interactions of specific relevance to the oil-based painting technique of reverse painting on glass, and is aimed at making inroads to informing conservation and restoration practice for these rarely studied artworks. The determination of adhesion parameters of pigments on glass is presented and the inter-comparison of different pigments. The effect of adhesive coatings and the relationships between the binder (linseed oil), pigments, glass and adhesive are also investigated.

3.0 – Experimental Technique

3.1 Pigments

Nine pigments (L. Cornelissen & Son) were used for this study. Table 1 summarizes the pigments and their chemical characteristics [17-20]. The pigments were chosen to implement different particle shapes and sizes in order to observe the influence on the adhesion of the pictorial layer on glass.

3.2 Binder and adhesives

Cold pressed linseed oil was implemented in this study as a binder in the technique of reverse painting on glass. It should be noted here that only one binder was selected to focus on the specific influence of the pigments and adhesives [21].

Adhesives in the technique of cold painting on glass are essential to reinforce the durability of the artwork and as such two were selected for this study: gum arabic and ox gall (Winsor & Newton), both of which were commonly used during the 18th century [22, 23]. The gum arabic adhesive was mixed with water (1:1 vol) whereas the ox gall adhesive was used as-received. Both adhesives were applied to the surfaces of glass slide samples and left to dry in air prior to the application of the pigments.

3.3 Support Glass

To ensure that the same type of glass was used throughout the experimentation, soda lime glass samples measuring 75 mm² and with a thickness of 1.5 mm were used. These samples were cleaned using isopropanol (99.7%; Sigma Aldrich Co.) in an ultrasonic bath for 10 minutes before any experimentation was carried out.

3.4 Sample Preparation for Pigment Application

Each pigment given in Table 1 was mixed with the binder to obtain a homogeneous paste. In order to compare each pigment, the maximum quantity of oil absorbed by 1 gram of pigment was added to create the pigment paste.

The homogenous pastes were applied to the glass slides in three sets:

Set 1: The pigment pastes were directly applied to the soda lime glass samples.

Set 2: The pigment pastes were applied to the soda lime glass samples which had previously been prepared with the mixture of gum arabic and water adhesive.

Set 3: The pigment pastes were applied to the soda lime glass samples which had previously been prepared with the ox gall adhesive.

Four slides prepared with each adhesive were also used as a control and for the wettability characteristics and topography analyses.

3.5 Accelerated Ageing

Accelerated ageing treatments were conducted on those samples which included the presence of the adhesives, in accordance with the procedures detailed by Feller [24]. The treatments were done by using a controlled environmental chamber (MLR-351-H, Sanyo). Three treatments were undertaken on the selected of samples and are summarized in Table 2.

3.6 Wettability Analysis

In accordance with the procedure detailed by Rance [25] the samples were ultrasonically cleaned in isoproponal (99.7%; Sigma Aldrich Co.) for 3 minutes at room temperature before using a sessile drop device to determine various wettability characteristics. This was to allow for a relatively clean surface prior to any contact angle, θ , measurements being taken. To ensure that the sample surfaces were dry, a specimen dryer was employed to blow ambient air across the samples. A sessile drop device (OCA20; Dataphysics Inc.) was used with relevant software to allow the contact angle, θ , for triply distilled water and θ for diiodomethane to be determined for each sample (as-received soda lime glass, gum arabic adhesive and ox gall adhesive). By starting with a droplet of volume of 5.00 µl, the advancing θ were achieved by adding 0.25 µl, respectively, for each measurement. Thereafter, the surface energy of the samples. For the two reference liquids, the DROPimage Advanced software calculated the total surface-free energy of the samples. It should be noted here that ten values of θ , using two droplets in each instance, were recorded to achieve a mean θ for each liquid and surface.

In addition to the water (Premium Quality; Sigma Aldrich Co.) and diiodomethane (99%; Sigma Aldrich Co.), the contact angle for every pigment (mixed with linseed oil) on the glass samples (with and without adhesives) were obtained to give an indication of the relationship between the pictorial layer and the surface.

3.7 Surface Topography Analysis

The topography of the soda lime glass samples with and without the adhesives was determined by implementing a white light interferometer (WLI) (NewView 500; Zygo Ltd). The WLI was set-up using a x2.5 objective with a numerical aperture of 0.075. This allowed the topography and the global shape of the surface to be studied. This system also allowed Ra roughness parameters to be determined for each sample. Where Ra can be defined as the arithmetic average of the absolute values along a single specified direction.

3.8 SEM-EDX Analysis

Scanning electron microscopy (SEM) (Inspect S; FEI Inc.) was implemented in the backscattered electron (BSE) mode to make precise observations on pigments by using the physical contrast in the secondary electron mode. In order to obtain the measurements, an EHT range of 2 kV to 8 kV was implemented at magnifications ranging from x500 to x3000. Energy-dispersive X-ray analysis (EDX) (Inca x-ray spectrometer; Oxford Instruments Ltd.) was also combined with the SEM to carry out chemical analysis on the pigments used during this study.

3.9 Scratch Testing

A pencil-hardness testing device was manufactured and used to scratch the paint layers using pencils with a range of hardness values. Indeed, the hardness value of each paint layer was determined to be between the first pencil hardness creating a scratch in the paint, and the previous pencil hardness which did not affect the surface of the paint. During manufacture, the ISO15184 standard for pencil scratch tests, and established standards for film hardness assessment of soft coatings such as paint and varnishes, was followed in accordance with Atkins [26] and Chen [27].

The scratch tests were carried out at a constant angle of 45° +/- 1° to the paint layer with a vertical load of 750 g +/-10 g. The scratch testing device's mass was also taken into account for the loading. During the scratching tests, the experimentation was conducted with a velocity between 0.5 mm/s and 1 mm/s over a distance of at least 7 mm. In order to control these parameters, a rule was used with a vertical indicator to show when the machine was manually pushed above the surface. A chronometer was used to measure the time of displacement. Finally, a level was implemented to control the flattening of the machine during the test.

The pencils used were Graphite pencils (Derwent). The standard specifies the use of 20 pencils from the same distributor. The hardness of each pencil was known and is represented in Figure 1. No cuts or damages were observed on the tip of each pencil prior to experimentation. Furthermore, before

any experimentation was carried out, each pencil was sharpened delicately with a blade to remove the wood section without affecting the lead. Then, the surface of the lead tip was polished using abrasive paper (400 grit) to create a smooth and flat-surfaced tip.

The temperature ($\pm 0.063^{\circ}$ C) and relative humidity ($\pm 0.04\%$) was recorded during 24 hours, at intervals of 1 hour, in the laboratory where the tests were carried out using an ibutton (Signatol SL54TH). The tests were carried out with a constant temperature of 23° C +/-2°C and a constant relative humidity level of 55% +/- 5%. Initial scratch creations in the paint were checked by visual observation, but a microscope (comparative microscope Projectina Heerbrugg with PIA6000 software) was used to further observe the profile of each scratch. Finally, the location of breakage (for the slides with two interfaces (glass/adhesive – adhesive/paint)) was obtained by an optical microscope (Nikon Elipse e800; Nikon Corp.) implementing two levels of light (Ph1-6 and Ph1-3), x10 filter NCB11 lenses and x10 objective lenses.

4.0 – Results and Discussion

4.1. Effects of Adhesives

The first comparison was to study the behaviour of adhesives (gum arabic mixed with water (1:1vol) and ox gall) on glass by comparing their contact angle to those obtained for water (see Figure 2). The visualisation of liquid droplets on glass showed that ox gall gave rise to a smaller contact angle when compared to the gum arabic and water mixture, implying that ox gall resulted in improved adhesion characteristics. It should be noted, however, that the homogeneity of the dried adhesive on glass could at times disturb this initial observation. On account of this, it was essential to understand the physical aspect of the support used during this study. The means and standard deviations were obtained with five measurements on five successive drops on the support (glass slide). The contact angle values for the glass slide with no adhesive and the glass slide with the gum arabic were equivalent, implying that the adhesion characteristics are somewhat similar.

From Figure 3 it can be seen that the glass slide substrates, free from adhesive, were relatively smooth compared to the other samples and had the smallest difference in height which was approximately 0.6 μ m. The glass slide covered with gum arabic (mixed with water (1:1 volume)) was also determined to be relatively smooth but the peak heights were determined to be higher at approximately 3.7 μ m. It is believed that this was due to the effect of the brushes during the adhesive application. Concerning the ox gall glass slide, the profile was different in comparison. This was due to no large undulations being present; however, the sample did give rise to the highest difference in height (approximately 13.0 μ m). Furthermore, rough lines were easily seen on a macroscopic scale and were clearly visible upon normal inspection viewing of the sample. These correspond to the tool (a brush) used to put the adhesive on to the glass substrate. It is expected that the ox gall was not homogeneous on the surface and that the adhesion of paint was likely to have been affected by this dispersion.

The third step in the analysis of adhesive effects was to compare the surface free-energy of glass slides with and without adhesives. The surface free-energy gives information on the compatibility between the support and the applied layer. The adhesive behaviour is linked to the surface capacity

to make a strong relationship with the paint layer, in this case. The results obtained during this experimentation are presented in Figure 4, where it can be observed that the glass slide sample covered with ox gall adhesive had the highest value of surface free-energy, with specific regard to adhesion. Furthermore, it can be seen from Figure 4 that the application of adhesives (gum arabic or ox gall) increased the surface free-energy implying that the two studied adhesives should give rise to improved adhesion characteristics. This is due to the fact that gum arabic is a hydrocolloid, containing numerous hydroxyl groups which gives rise to liquid binding characteristics [28]; whereas ox gall acts is a surfactant and has been used many times as a wetting agent. These substances give rise to enhanced adhesion characteristics and, in this instance, gave rise to an increase in the surface free-energy.

With these three steps of analysis, ox gall appeared to be the best adhesive, in terms of improving the adhesion characteristics, because the contact angle of the liquid on glass was the smallest and the surface free-energy of the samples covered with dried ox gall was the highest. Taking this in to account, the adhesion at the glass/paint interface was enhanced for the gum Arabic coating, based on the wettability analysis. As expected, the glass slide without adhesive had the worse adhesion parameters, with the lowest surface free-energy and highlights the need for the implementation of an adhesive for any future reverse painting on glass artwork. The slides surface profile given by the application of adhesives on glass could affect the adhesion but also improve the attachment of oilbased paintings. As can be seen from Figure 3, the dried adhesives have modified roughness profiles, and as such, would also have a likely impact upon the physical adhesion of paint to the samples.

4.2. The pictorial layer

The paint was produced from different pigments mixed with linseed oil, and as such, the shape and size of pigment can significantly modify the adhesion characteristics. It is widely known that adhesion characteristics can be modified using physical and chemical relationships. Physical adhesion of the surface roughness was likely due to the relationship between the pigment's grains, the binder (cold pressed linseed oil) and the surface as all of these parameters are likely to have an effect on the adhesion characteristics. The chemical relationship between the pigments and the binder is also a parameter which could modify the adhesion properties. As a result of this, linseed oil, which can be used as a binder, was also tested for sessile drop measurements on the three kinds of supports (glass slide, glass slide with gum arabic and glass slide with ox gall). Figure 5 shows that linseed oil had an improved adhesive behaviour on the glass slide with the ox gall adhesive, compared to the glass slide with the gum arabic adhesive and the glass slide without adhesive. This is due to the fact that ox gall is a well-known surfactant and wetting agent, lowering the interfacial tension between the oil and the surface of the glass slide.

Twenty-five measurements were also carried out for each of the paint mixtures, using the sessile drop device, on the three kinds of support. Figure 6 shows the difference in pigments in relation to the contact angle they made with each of the substrate supports. The presence of adhesives had an enhanced wetting effect when compared to the glass slide substrates with no adhesive present. Having said that, it was generally found that the presence of pigments varied the liquid-surface interaction to the point where the contact angle was larger than the contact angles determined when using the linseed oil. For Prussian blue, vermilion, dragon's blood and red ochre, ox gall was

found to be the best surface for an enhanced adhesive contact. The pigments green earth, indigo and yellow ochre all exhibited better adhesion characteristics with a smaller contact angle arising on those glass slide substrates covered with gum arabic adhesives. For malachite, the results obtained on the two adhesives were close, but had a better adhesion on the glass slide only.

Prior to the scratch testing, which was destructive, the sample cross-sections (dried paintings on glass after treatments) were observed for pictorial layer thickness (on the side of polished glass slides with 400 grit silicon paper) under the comparative microscope. Figure 7 shows the mean value obtained for one pigment on three glass slides. For Prussian blue, green earth, vermilion, lead white and yellow ochre, the thickness of the pictorial layer was directly linked to the size of pigments. But for malachite, red ochre and indigo, the pigment size was higher than the thickness of the pictorial layer. The measurements of pigments were carried out on agglomerates and big particles. It is believed that the mixture with oil eliminated the agglomerates or that the reaction between the pigment and the binder (linseed oil) was enough to reduce the size of large particles. Concerning the case of dragon's blood, it was observed that the standard deviation was much larger compared to the other pigments.

4.3. Scratch Testing

Considering the glass slides with no adhesive present, green earth, red ochre and vermilion based pictorial layers were harder than the others, but the differences were only approximately 1 pencil hardness. It was observed that adhesives increased the hardness in some cases, whereas for dragon's blood, indigo, green earth and yellow ochre nothing notable was observed. Contrary to what was expected, gum arabic seemed to be the best adhesive for four pictorial layers: malachite, Prussian blue, red ochre and vermilion. An improvement of the adhesion was observed with ox gall for malachite, Prussian blue, vermilion, but lead white was the only pigment which seemed better with ox gall adhesive than with gum arabic.

The scratch profile was determined under optical microscopy by observing the profile of the edges. The cracking and the delamination are two parameters described by Atkins [26] used in this study and are given in Table 3. These scratch failure modes are linked to the localization of the applied scratch. Indeed, for the two layered slides (slides with adhesives), the scratch test was conducted between the glass and the adhesive or between the adhesive and the pictorial layer. Every slide was observed under optical microscopy and the slides were classified with their localization of scratch (see Table 4). The differences observed on the localisation of the rupture are linked to the pictorial layer cohesion and to the possible reaction between the adhesive and the painting layer. Whereas ox gall was first considered the best adhesive, the scratch tests showed that gum arabic is better for most of the pigments. This can be explained by the inhomogeneity of the ox gall and the chemical link between this adhesive and the pictorial layer having a major impact upon the adhesion characteristics.

4.4. Ageing Effects

The accelerated ageing treatments, consisting of exposure to extreme levels of humidity for three sets of slides, had an influence on the pictorial layer adhesion. First, the slides with adhesives, but without pictorial layer, were observed under optical microscopy after the cyclic treatments (see Figures 8 and 9).

The humidity treatments were very destructive for the glass slides only covered with adhesives. With the humidity treatments, a circular structure was visible which became more randomised with the level of treatment. For ox gall, the dendritic structure observed prior to treatment was removed, leaving the glass surface with no structure after three cycles of treatments. These physical modifications gave rise to a change in the physical adsorption properties and physical interlocking of the pictorial layer, having an impact on the pictorial layer adhesion on glass.

Vermilion remained the hardest pictorial layer among the others, but the effects of treatments on glass slides without adhesive reduced the hardness to a non-measurable level with the pencilhardness test. For the resistant pigments (vermilion, red ochre, Prussian blue) it was found that there the hardness was further improved on gum arabic when compared with ox gall. The microscopic observations of the profile of scratch are similar to those obtained without treatment. Only one pigment showed a particular good behaviour after treatment: yellow ochre (see Figure 10). That is, the painting layer behaved like a solid and elastic film, with a better cohesion than adhesion on glass. Concerning the examination of slides after the scratch test, the results are completely similar to those obtained without treatment. The rupture seems to be essentially linked to the lack of cohesion of the pictorial layer comparing to the adhesion phenomenon.

It should be noted that, although some accelerated aging has taken place, more research is required to fully understand the effects of ageing on the adhesion characteristics of materials from the 16th and 18th Century. Having said that, it has been observed, following the ageing processes, that the use of adhesives gave rise to a more stable pictorial layer. This is significant as it implies that careful consideration of the restoration techniques should be undertaken, especially for those artworks that did not involve the use of an adhesive layer. Restoration of such artwork is usually very difficult as the repair is usually required on an unexposed surface, between the glass and the paint. As a result of this and the work that has been carried out here, it has been evidenced that the use of a suitable binder and adhesive is necessary to support and restore any reverse paintings on glass, where delamination has occurred.

From a conservation point of view, antique reverse painting on glass artworks could be displayed, in a specific environment, following careful consideration to the effects of that environment on the adhesive which enables the pictorial layer to be more stable. As binders/adhesives are present in many reverse paintings on glass humidity and oxidation rates would be critical to ensure the quality of the binder and, ultimately, the adhesiveness of the pictorial layer. In addition to this, contact with the pictorial layer would have to be reduced to a minimum to ensure that the adhered layers are not compromised by scratching, wear and fatigue. Exposure to UV light (e.g. sunlight) would also, as with any antique artwork, need to be kept to a minimum to slow the rate of fading and reduce any effects of the UV light on the adhesion characteristics of the pictorial layer.

Even with adhesives making the pictorial layer more stable, it is highly likely that antique reverse painting on glass artwork would be extremely more fragile than what has been observed here and as such highlights the need to protect and sufficiently restore and conserve the pictorial layers. With all

of this in mind, owed to the fragility of adhesion of the pictorial layers, great consideration of the glass-adhesive-pictorial interface is crucial before implementing any chemical or physical restoration/conservation.

5.0 – Conclusions

It is crucial to gain an in-depth understanding of a material's behaviour in its environment in order to follow a good campaign of restoration. The present study has shown that pictorial layers on glass must be in a good equilibrium to keep a good cohesion and adhesion. The size of pigments and their relationship with the binder not only affect the cohesion of the paint layer, but also the adhesion characteristics. It has also been evidenced through this work that the addition of an adhesive can modify the adhesion characteristics to the point where these characteristics are improved. But, their behaviour in extreme environmental conditions of storage can weaken the adhesion and the cohesion of the paint layer due to possible chemical reactions. This particular study was focused very much on the physical parameters, but the impact of the chemical evolutions of the pictorial layer during the drying process or during the treatment would also have a likely major impact upon the adhesion characteristics.

From all pigments studied, vermilion was the easiest to observe with a large evolution of the hardness especially with the addition of adhesives. It was evident that even if ox gall had better parameters or behaviour on glass (small contact angle, glass slides with ox gall with the highest surface free energy), in most cases, the results show that the pictorial layer was more adherent on gum arabic. That is, the homogeneity of the adhesive layer and the interactions between the paint and the adhesive were ultimately more enhanced with respect to the adhesion characteristics, with the application of gum arabic. This is highly significant as it highlights the great need for a homogenous adhesive layer when undertaking, conserving and restoring reverse painting on glass artworks.

6.0 - References

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Pigment Name	Chemical Formula/Name	Layer thickness (µm)
Prussian Blue	Iron (III) hexacyanoferrate (II) 32	
Malachite	Basic copper (II) carbonate 27	
Green Earth	Basic copper (II) carbonate	47
Indigo	Natural vegetable pigment	40
	$C_{16}H_{10}N_2O_2$	
Vermilion	Mercury (II) sulphide	17
Dragon's blood	Plant resin : cinnabarone 104	
	$(C_{32}H_{32}O_7)$ with flavonoids	
Red Ochre	Iron (III) oxide (clay, silica)	34
Yellow Ochre	Goethite, clay, silica	79
Lead White	Lead (II) carbonate	27

Table 1 – Summary of pigments with their chemical characteristics.

Treatment Number	Ageing Treatment	
1	1 run of [a)22h 80%RH (23°C +/- 2°C) b)22h 50% RH (23°C +/-	
	2°C) c)1 week drying]	
	Followed by 25h under UV lamp	
2	2 runs of [a)22h 80%RH (23°C +/- 2°C) b)22h 50% RH (23°C +/-	
	2°C) c)1 week drying]	
	Followed by 25h under UV lamp	
3	3 runs of [a)22h 80%RH (23°C +/- 2°C) b)22h 50% RH (23°C +/-	
	2°C) c)1 week drying]	
	Followed by 25h under UV lamp	

Table 2 – The three cycle treatments used for the ageing study.

 Cracking: Forward chevron tensile cracks Delamination: Recovery spallation 	 Cracking: Forward chevron tensile cracks Delamination: Wedge spallation 	 Cracking: Forward chevron tensile cracks Delamination: Buckling spallation
Prussian blue Malachite Green Earth Dragon's blood Yellow ochre	Vermilion Lead white	Indigo

Table 3: Scratch failure modes of the pictorial layer during the pencil hardness scratch test.

	Scratch between	Adhesive	Scratch in the
	adhesive and the	partially	pictorial layer
	pictorial layer	scratched	
Slides with Arabic gum adhesive	Prussian blue	/	Red ochre
	Malachite		Lead white
	Green Earth		
	Indigo		
	Vermilion		
	Dragon's blood		
	Yellow ochre		
Slides with Ox gall adhesive	Indigo	Prussian blue	Vermilion
	Dragon's blood	Malachite	Red ochre
	Yellow ochre	Green Earth	
	Lead white		

Table 4: Localisation of scratch for the slides with two interfaces.

9B / 8B / 7B / 6B / 5B / 4B / 3B / 2B / B / HB / F / H / 2H / 3H / 4H / 5H / 6H / 7H / 8H / 9H Softer Harder

Figure 1: Hardness scale implemented with the pencil hardness test.



Figure 2: Comparison of the wetting by water on glass slides with the two adhesives (Arabic Gum/water and Ox gall.



Figure 3: (a) 3D surface profiles and (b) line profiles for the (1) glass slide, (2) glass slide with Arabic gum adhesive and (3) glass slide with ox gall adhesive.



Sample Type

Figure 4: The surface free-energy for the glass supports with and without adhesives with the standard deviation.



Figure 5: The contact angle of linseed oil on the glass substrates with and without adhesives with the standard deviation.



Figure 6: The contact angle for every pigment mixture studied on the three variations of glass substrate (glass slide, glass slide with Arabic gum adhesive and glass slide with ox gal adhesive) in comparison with the contact angle obtained with linseed oil including the standard deviations for each sample.



Figure 7: Comparison of the thickness of the paint for every pigment including the standard deviation.



Figure 8: Arabic gum on glass slides OM x100 of ageing treatments. (a) No treatment, (b) 1 cycle, (c) 2 cycles and (d) 3 cycles.



Figure 9: Ox gall on glass slide OM x100 of ageing treatments. (a) No treatment, (b) 1 cycle, (c) 2 cycles and (d) 3 cycles.



Figure 10: Scratch test of yellow ochre on glass substrate (with ox gall adhesive) following (a) no treatment and (b) 2 cycles of ageing treatment.