A study of the effects of PVAC on works of art on paper and wood: pH and colour change

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ABSTRACT This paper presents the preliminary findings of pH and colour measurements carried out on artworks on paper and on wood that had been treated with a poly(vinyl acetate) (PVAC) based adhesive in the 1980s. In both cases, areas treated with PVAC proved to be less acidic than untreated areas. Contrary to expectations, the conservation treatments have not, as yet, increased acidity levels in the objects under study. Colour measurements of the works on paper showed that those that had been backed with a cotton fabric using a mixture of methylcellulose and PVAC were less yellow than those from the same print run that had not been backed. This finding suggests that the backing somehow prevented the natural degradation of the support. In view of these preliminary results, further research is clearly needed. This study forms part of a broader ongoing project to assess the role of PVAC in the conservation of a range of cultural assets.

KEYWORDS PVAC, adhesives, works of art, posters, panel paintings, pH, colour, alterations

Introduction

Poly(vinyl acetate) (PVAC) based emulsions have been used widely in conservation in Spain since their introduction in the 1950s, and are still used today in many conservation treatments (Robson 1993; Quandt 2002).

In the early 1990s, neutral pH PVAC emulsions specially designed for use in conservation started to be distributed in Spain and today many commercial brands of PVAC emulsions are available for general use. However, as PVAC is known to give off acidic vapours when it ages (Down *et al.* 1996) its suitability for conservation purposes is questionable.

The preliminary findings presented in this paper are part of a broader research project (Spanish Ministry of Education and Science; HUM2006-05345). This work is a follow-up to previous research, which found that PVAC causes alterations to transferred mural paintings, especially when inadequately applied (Campo *et al*. 2005; Nualart 2007). Our current project aims to identify the possible effects of PVAC on different types of artworks such as archival materials, paintings on wood and canvas, ceramics and transferred mural paintings. The findings will then be used to suggest suitable PVAC removal procedures for each type of support, if required.

This paper focuses on pH and colour change in PVAC treated objects on paper and on painted wood.

Case studies

All of the 23 works of art selected for this study (Table 1) come from well-known public collections in Spain: the Museu Nacional d'Art de Catalunya (MNAC), the Museu Episcopal de Vic (MEV) and the Museu-Monestir de Pedralbes (MMP-MHCB). To ensure that the study sample was homogeneous, works were selected that had received PVAC conservation treatment during the 1980s in the Barcelona area. The works selected were posters on paper containing mechanical pulp and paintings on wood; all but two specimens (both posters) contained lignin.

The works on paper are nine pairs of original posters, produced between 1905 and 1923. Each pair includes two works printed from the same plate and in the same edition, one of which has never been backed and one of which was backed during the 1980s, a common procedure in paper conservation (Lladó Buisán and Centeno 2005). The sample set thus comprises nine backed and nine unbacked posters. All the pieces are the property of the MNAC and are examples of one of the most prolific periods in the history of posters in the Western world. All were printed in lithographic workshops in Barcelona and were designed by prominent artists such as Casas, Llimona, Brunet, Elias and Canals. They are all lithographs containing three or more colours on chemical and mechanical pulp paper. In the period between their purchase by the Junta de Museus in 1932 and 2002 (Quílez 2007) the posters were stored in an upright position in wooden storage cabinets without any protection from acidic vapours.

Table 1 List of selected works studied from the MNAC, the MEV and the MMP-MHCB.

Registration number	Title	Artist	Date	Materials description	Year of the treatment	Conservation treatment carried out
MNAC-00429-C	D. Carles Exhibition	Canals	1914	Lithography. Mechanical, thermomechanic and bleached pulp	unrecorded	Backed with cotton fabric, PVAC and MC
MNAC-00429-C1	*D. Carles Exhibition*	Canals	1914	As MNAC-00429-C	–	Not backed
MNAC-00438-C	*Art Exhibition. Spring of 1919*	Labarta	1919	Lithography. Mechanical, chemical pulp (kraft process) and bleached pulp	1986	Backed with cotton fabric, PVAC and MC
MNAC-00438-C1	*Art Exhibition. Spring of 1919*	Labarta	1919	As MNAC-00438-C	–	Not backed
MNAC-00439-C	*Furniture Internatl Exhibition, 1923*	Elías	1923	Lithography. Bleached pulp with mechanical pulp	1980	Backed with cotton fabric, PVAC and MC
MNAC-00439-C1	*Furniture Internal Exhibition, 1923*	Elías	1923	As MNAC-00439-C	–	Not backed
MNAC-00443-C	*Art Exhibition. Spring of 1918*	Cardunets	1918	Lithography. Mechanical, chemical pulp (sulphite process) and bleached pulp	1987	Backed with cotton fabric, PVAC and MC
MNAC-00443-C1	*Art Exhibition. Spring of 1918*	Cardunets	1918	As MNAC-00443-C	–	Not backed
MNAC-00451-C	*Festes de Barcelona. 1905*	Brunet	1905	Lithography. Bleached pulp	1987	Backed with cotton fabric, PVAC and MC
MNAC-00451-C1	*Festes de Barcelona. 1905*	Brunet	1905	As MNAC-00451-C	–	Not backed
MNAC-00453-C	*Jocs Florals Barcelona. 1908*	Casas	1908	Lithography. Mechanical, thermomechanic and bleached pulp	1980	Backed with cotton fabric, PVAC and MC
MNAC-00453-C1	*Jocs Florals Barcelona. 1908*	Casas	1908	As MNAC-00453-C	–	Not backed
MNAC-00458-C	*IV Internal Art Exhibition, 1911*	Climent	1911	Lithography. Bleached pulp with traces of mechanical pulp	1980	Backed with cotton fabric, PVAC and MC
MNAC-00458-C1	*IV Internal Art Exhibition, 1911*	Climent	1911	As MNAC-00458-C	–	Not backed
MNAC-00460-C	*V Internatl Art Exhibition, 1907*	Llimona	1907	Lithography. Bleached pulp with traces of mechanical pulp	1984	Backed with cotton fabric, PVAC and MC
MNAC-00460-C1	*V Internatl Art Exhibition, 1907*	Llimona	1907	As MNAC-00460-C	–	Not backed
MNAC-00652-C	*Barcelona. Grans festes. 1910*	Brunet	1910	Lithography. Bleached pulp with traces of mechanical pulp	1982	Backed with cotton fabric, PVAC and MC
MNAC-00652-C1	*Barcelona. Grans festes. 1910*	Brunet	1910	As MNAC-00652-C	–	Not backed
MEV-556	*Altar frontispiece Sant Pere de Ripoll*	Anonymous	second half 13th century	Relief on white poplar, gilded and polychromed	unrecorded	Gluing of the new dust guard
MEV-10738	*Flagellation of Saint Eulalia*	Bernat Martorell	between 1427 and 1437	Wood panel in red pine, egg tempera polychromy	1982–1988	Panels glued with PVAC: excess adhesive visible on recto
MEV-10739	*Martyrdom of Saint Eulalia*	Bernat Martorell	between 1427 and 1437	Wood panel in red pine, egg tempera polychromy	1982–1988	Panels glued with PVAC: excess adhesive visible on recto
MMP-MHCB 115.051	*Saint Bernard of Siena*	Anonymous	16th century	Carved wood panel, gilded and oil polychromed	1989	Panels glued with PVAC. Joins also filled with a mixture of PVAC and sawdust
MMP-MHCB 115.052	*Saint Eulalia of Merida*	Anonymous	16th century	Carved wood panel, gilded and oil polychromed	1988	Panels glued with PVAC. Joins also filled with a mixture of PVAC and sawdust

It is known that both PVAC and methylcellulose (MC) were used in the backing process. Documentary sources (Albiol and Roda 1980) report that the poster *Cartell dels Jocs Florals de Barcelona: Festes del Cinquantenari* by Ramon Casas was backed at the MNAC in the 1980s by applying 'general use' PVAC adhesive and MC in two stages. First, the backing cotton fabric was impregnated with PVAC, then, once the PVAC was dry, the fabric was glued to the poster using MC. However, two conservators working at MNAC during the period have reported that the two adhesives (a commercially obtained PVAC emulsion and a 4–5% MC solution) were always first blended together and the resulting mixture was then used to glue the fabric to the paper by soaking the fabric well in the adhesive mixture. The excess adhesive would then be removed by wringing out the fabric, which would be tensioned and the moistened poster placed on top of it, making sure that there was good contact between the two. Future cross-section analyses may help to clarify which of the two procedures was used in the posters under consideration.

The works of art on wood chosen for the study belong to the MEV and the MMP-MHCB. In both cases, documentary evidence shows that PVAC had been applied in past conservation treatments.

Commercial PVAC was rapidly introduced into the practice of wood conservation. Among its advantages were the facts that the adhesive is ready to use, there is no need to heat it in a water bath, it keeps well for a long time and it dries quickly. As a result, traditional collagen glues were almost entirely replaced by PVAC in the 1960s, both for the construction and for the conservation of wooden objects. In wood conservation PVAC has three main uses. The most important is as an adhesive to glue parts of the support, the second is to consolidate the ground or paint layers and the third is as a binding medium to prepare a mixture with sawdust to fill cracks or holes in the support.

Finding works of art on wood with documentary evidence of PVAC use in gluing together the support was difficult because the operation was often regarded as simple 'repair work' performed by non-specialists and was not recorded in conservation reports. It was easier to locate works with documentary evidence of the use of PVAC to consolidate the ground and paint layers. However, the problem here is that most of the PVAC treated areas have subsequently undergone infilling with coloured retouchings and accessing these areas would damage the inpainting. Since our works of art are on permanent display, this was not an option. Finally, we decided not to study cases in which PVAC had been used to consolidate the paint layers, but to study only the few documented cases in which it had been used to repair the wooden structures.

During the selection process for this study, the presence of PVAC was confirmed in two ways. In the case of the works of art on wood, it was not possible to take samples, and so the adhesive was identified by means of visual inspection under white and ultraviolet (UV) light and through the application of a tiny drop of Lugol reagent (iodine-iodide) (Sadao *et al.* 1970, 1972) to a specific area (see Figure 1).

In the case of the posters, samples were taken from the backing adhesive of each backed specimen and analysed using Fourier transform infrared (FTIR) spectroscopy. The presence

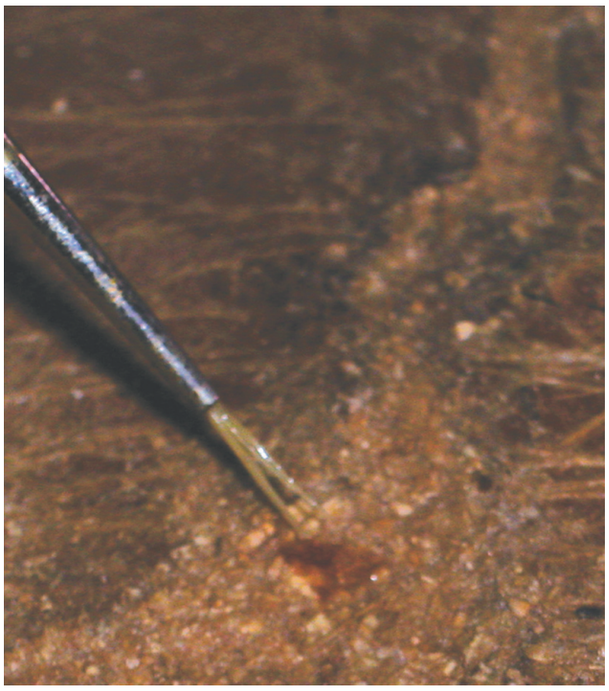

Figure 1 Positive Lugol test on a sawdust and PVAC mixture used to fill a crack on a wooden support.

of PVAC as a backing adhesive was confirmed in all cases. The presence of MC (a cellulose ether) could not be identified using FTIR, since the presence of cellulose from the cotton backing masks it. To corroborate the presence of MC in the backing procedures performed at the MNAC during the 1980s, other posters backed during the same period and by the same conservators were analysed. The backings were removed from some of these posters in 2006 and the MNAC provided nine fragments of the backing fabric. A dry residue was extracted from these fabrics for FTIR examination by placing a 25 cm^2 fragment of each backing fabric in ethanol for two days. The fabric was then removed and left to dry. After this, the sample was placed in water for two days. The fabric was then removed, the water left to evaporate and the dry residue analysed by FTIR. The spectra produced all contained the characteristic bands for methylcellulose and differed from those obtained

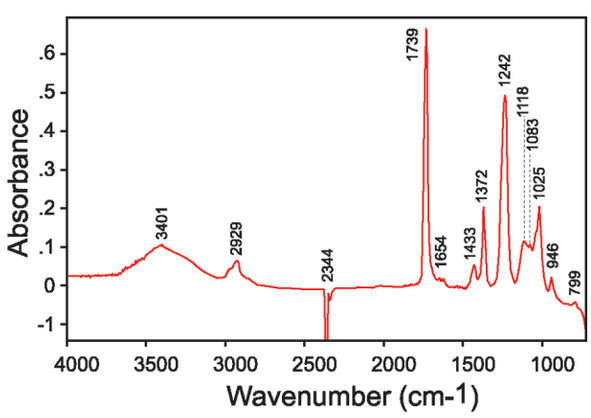

Figure 2 FTIR Spectra of a sample from the backing adhesive of the poster MNAC-00438-C. Note the presence of PVAC.

by using FTIR directly on the backing adhesive. To further ensure that there is no interference from the cotton fibres in these results, analysis using matrix-assisted laser desorption/ionisation time-of-flight (MALDI-TOF) mass spectrometry of these samples is being carried out.

Once the presence of PVAC had been confirmed, the objects were examined visually. The backed posters were compared with the unbacked copies from the same print run. For the works of art on wood, PVAC treated areas were compared with untreated areas. Our present work focuses on the pH and colour differences.

Experimental details

The pH was measured on PVAC treated and untreated areas of all the selected works using a contact Crisol PH 25 pH meter with a 52–07 surface electrode. In most cases, several different measurements were taken and an average value was obtained. In all cases a drop of distilled water was placed on top of the area to be analysed, left for one minute to allow the water to penetrate the substrate and the measurement then made. The analysed area corresponds to that of the electrode, a circle of 0.8 cm in diameter. In the case of works of art on wood, surface pH measurements were taken on a flat area of the PVAC between the glued joints and on an untreated area of the wooden support nearby, with the object placed horizontally.

For the posters, pH was measured on the backed and unbacked specimens. In each case, two measurements were taken from representative points on both the verso and the recto. For the backed posters, because of the backings, measurements taken on the verso are therefore measurements of the backing fabric in contact with the paper support, rather than the paper. Since the backings are larger than the posters it was possible to also take two measurements on solely the backing fabric where it was not in contact with the paper. In all cases when taking the readings, areas without ink were chosen in order to avoid interference. Areas with local problems such as foxing, stains or tears were also avoided.

In the unbacked posters, no differences were observed between the way the verso and recto absorbed the drop of water. Generally, the drop was able to wet the area in 10–15 seconds. This time differed depending on the pulp composition of the paper, as well as the sizing and the superficial dirt present. In the backed posters it was observed that water had more difficulty in wetting the verso of the poster. This is not surprising as in the backing process the backing fabric had been impregnated with the PVAC-MC mixture. However, one minute was long enough to wet the canvas and to obtain reliable surface pH measurements. Water absorption time was similar on the recto of the backed and unbacked posters.

Colour was measured using a S2000 Ocean Optics spectrophotometer between 410 and 750 nm. Eight readings were taken for each object. The different measurements were overlaid to confirm the reliability of the instrument; the graphs matched in most of the cases. Measurements were taken on the recto of the backed and unbacked posters. The criteria for selecting the area to be measured were the same as those used in the case of pH (ie ink and locally degraded areas were avoided).

Colour differences between PVAC treated and untreated areas were not studied for the works of art on wood for two main reasons. First, since wood does not usually have a homogeneous colour across its surface, different colour readings may merely reflect natural differences in colour (ie areas with different degrees of lignification). In addition, the presence of tannins and other elements that colour the wood (which are usually water soluble) might have dyed the PVAC and caused misleading colour changes.

Results and discussion

pH

Results of the pH measurements are given in Table 2. Perhaps contrary to expectations, comparison of the pH values of the backed and unbacked posters shows less acidic levels in the

Table 2 pH measurements of all the works of art studied. Sample numbers match those in Table 1.

Registration number	pH of the recto	pH of the fabric	pH of the verso	Observations
MNAC-00429-C	6.18	6.50	6.18	pH less acidic in the fabric. pH less acidic than the unbacked poster
MNAC-00429-C1	4.80		4.90	Similar pH in the recto and in the verso
MNAC-00438-C	5.20	5.90	6.17	pH less acidic in the fabric and the verso. pH less acidic than the unbacked poster
MNAC-00438-C1	5.20		4.20	pH less acidic in the recto
MNAC-00439-C	5.80	6.35	6.37	pH less acidic in the fabric and the verso. pH less acidic than the unbacked poster
MNAC-00439-C1	5.10		4.90	Similar pH in the recto and in the verso
MNAC-00443-C	5.00	6.35	6.00	pH less acidic in the fabric and the verso. pH less acidic than the unbacked poster
MNAC-00443-C1	4.30		3.90	pH slightly more acidic in the verso
MNAC-00451-C	5.50	5.80	4.40	pH less acidic in the fabric. pH less acidic than the unbacked poster
MNAC-00451-C1	4.48		4.20	Similar pH in the recto and in the verso
MNAC-00453-C	4.80	5.50	5.00	pH less acidic in the fabric. pH less acidic than the unbacked poster

cont'd

Registration number	pH of the recto	pH of the fabric	pH of the verso	Observations
MNAC-00453-C1	4.10		4.00	Similar pH in the recto and in the verso
MNAC-00458-C	5.29	5.40	5.20	Similar pH in the recto and in the verso. pH less acidic than the unbacked poster
MNAC-00458-C1	4.50		5.10	Similar pH in the recto and in the verso
MNAC-00460-C	5.95	5.90	5.80	Similar pH in the recto and in the verso. pH less acidic than the unbacked poster
MNAC-00460-C1	4.80		4.60	Similar pH in the recto and in the verso
MNAC-00652-C	5.60	5.70	5.80	Similar pH in the recto and in the verso. pH less acidic than the unbacked poster
MNAC-00652-C1	4.44		4.20	Similar pH in the recto and in the verso

Registration number	pH of wood support	pH of PVAc on the joint	Observations
MEV-556	-	-	
MEV-10738	5.12	6.30	pH less acidic in the PVAC in the joint
MEV-10739	5.50	6.18	pH less acidic in the PVAC in the joint
MMP-MHCB-115.051	4.64	4.00	pH less acidic in wood
MMP-MHCB-115.052	4.83	5.02	pH less acidic in the PVAC in the joint

backed specimens. For the works of art on wood, with one exception we also found the PVAC to be less acidic than the wood. The exception was for an area where sawdust mixed with PVAC had been used to fill in gaps in the support; here the mixture was more acidic than the wood (pH 4.00 as opposed to 4.64).

pH values were also similar on the recto and verso of most of the unbacked posters, although there were a few exceptions. The causes of this are still to be determined. Although no records of the backing treatments are available, the conservators working at the time all agree that the posters did not receive any treatment such as cleaning or deacidification prior to backing. Conservators from the MNAC also confirmed that the posters had not undergone any conservation treatment after the backing treatment in the 1980s.

These preliminary results suggest that, in the case of posters, the presence of the backings or the process of applying the backings, has prevented the acidity of the supports from increasing.

Colour

Examples of colour measurements on posters are included in Figure 3. Each graph shows the colour readings on a pair of posters, comparing the backed posters (black line) with their unbacked counterpart (red line). The wavelengths are shown on the x-axis (400–750 nm) and reflectance on the y-axis (0–100%).

Comparison of the colour measurements showed that the backed posters have less discoloration than the unbacked ones. This can be seen in the data for the pair of posters MNAC00439C and MNAC00439C1 in Figure 3. The reflectance in the blue region of the backed poster and the unbacked poster is similar. However, progressing through the spectra the difference between the two increases in the yellow-orange-red regions and is much higher for the unbacked posters.

Backed posters also have a greyer tone (generally lower light reflectance throughout the spectra) than unbacked posters. This effect is less noticeable in the posters with high lignin content, due to their yellowing.

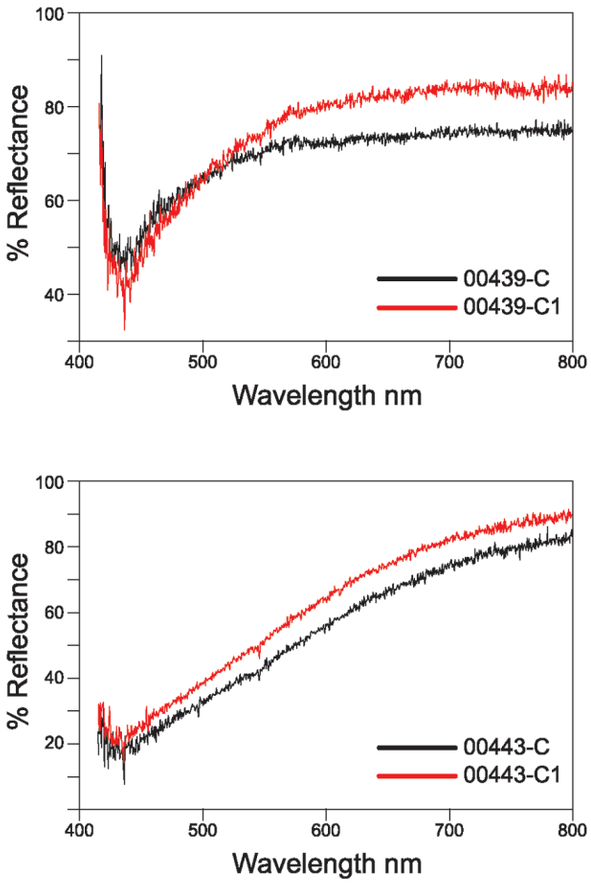

Figure 3 Colour measurements of pairs of backed and unbacked posters. Black lines = backed posters: red lines = unbacked.

These two results confirm the results of the visual inspection. The fact that the backed posters appear to be less yellow than those that are unbacked is also contrary to expectations, since PVAC is known to yellow when ageing (Down *et al.* 1996). However, the presence of the MC and the cotton fabric in the backings appears to have somehow prevented the paper support from yellowing.

The generally greyer tone of the backed posters may be due to the fact that the surface picks up dirt more easily if PVAC has been applied, as this adhesive has a low glass transition temperature. Alternatively, the humidity of the backing treatment may have carried surface dirt into the paper support, giving it its present grey tone.

Conclusions

Although the project is still at an early stage, the overall results obtained so far and described in this paper indicate that the treatments reported are unlikely to have increased the acidity in the two substrates studied (paper and wood). The pH measurements were around one pH unit more acidic in the unbacked posters than in the backed ones, and in general the wooden supports were more acidic than the adhesive tested in the same object. As PVAC gives off acidic vapours when ageing, these results are unexpected. Further research will be carried out to study if the treatments used on these pieces are likely to cause degradation in the future. For the backed posters, the possible buffer effect of the MC and the cotton fabric on the PVAC adhesive and the posters themselves will also be studied in greater depth.

As regards colour, the unbacked posters showed more yellowing than the backed posters. This is especially noticeable in cases in which the paper has a high proportion of mechanical pulp. Again, it seems that some feature of the backing treatment has prevented the degradation of the paper. However, PVAC-backed posters were found to have acquired a greyer tone.

In the case of the wooden supports, we have not yet observed any evidence of change in the pieces studied that might be attributable to PVAC. Further studies are needed to determine whether PVAC has harmful effects on wood. In the case of paper, further studies are also required to shed light on the interactions between the PVAC and the paper supports and to determine why the backed posters are less acidic, less yellow, and greyer.

Forthcoming studies will include characterisation of the three types of PVAC commonly used in conservation in Spain and an analysis of their effects on wood and paper mock-ups. Both the adhesives and the mock-ups will be artificially aged in the dark under controlled heat and humidity conditions. The pH of the surface and of a cold extract will both be measured.

Composition of the adhesives will be analysed using FTIR, gas chromatography–mass spectrometry, Raman and scanning electron microscopy. It is hoped to publish the results of these tests in the near future.

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