ISSUES ASSOCIATED WITH ADHESIVES USED ON ARCHAEOLOGICAL POTTERY

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Abstract: *The aim of this investigation was to identify issues associated with the use of adhesives used on archaeological pottery. This involved asking Australian conservators and archaeologists what adhesives they use. Based on their responses, control adhesive samples were acquired. An analysis methodology that involves UV fluorescence, chemical spot tests and FTIR was tested on these control adhesive samples. Surprisingly this revealed formulation changes in two commercial products that have not been noted by the conservation profession. This demonstrates the importance of monitoring formulation change in order to identify issues that may affect adhesive performance and thus require further investigation. Next the adhesive analysis methodology was tested on adhesive samples that were removed from Cypriot pottery artefacts. Four out of the five samples were successfully identified. Identification served to illustrate issues associated with the ageing of CN.*

Keywords: *Adhesives, analysis, archaeological pottery*

INTRODUCTION

The preservation of archaeological pottery for future generations often involves the introduction of an adhesive to the vessel. Conservation criteria require that the adhesive should be of appropriate strength, reversible and have good ageing properties (*Cronyn 1990*). The ability to identify an adhesive associated with a ceramic may facilitate the successful removal of a failing adhesive (*Koob 1998, Horie 1987*) and allow an assessment to be made of its performance. For instance with ageing, is strength lost, is the polymer still reversible with solvent, has the polymer yellowed considerably, is the polymer damaging any fragile components of the artefact? However treated artefacts often lack written records. Under these circumstances, simple methods that aid adhesive identification employ solvent solubility (*Horie 1987*), visual observation (*Koob 1998*), chemical spot tests (Koob 1998) and analytical techniques like infra-red (IR) spectroscopy (*Mills & White 1994*). Of particular use is a flowchart developed by *Derrick et al. (1999: 111)* for characterising synthetic polymers based on their (IR) absorption bands.

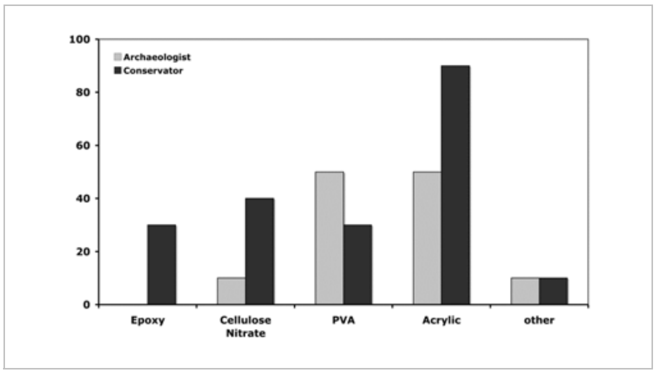


Fig. 1 Summary of adhesives used by questionnaire participants: 12 archaeologists and 11 conservators, to repair archaeological pottery

In order to identify issues associated with the use of adhesives on archaeological pottery, this investigation asked archaeologists and conservators what adhesives they use to repair archaeological pottery. This information was used to obtain relevant reference adhesive samples. An analysis methodology developed by *Nel (2007)*, based on visual observation, UV fluorescence, chemical spot tests and FTIR was tested on the known reference adhesive samples. These results were then used to identify adhesives removed from three Cypriot pottery vessels. Identification of these adhesives enabled an assessment to be made of their performance.

METHODOLOGY

Questionnaire

A questionnaire was distributed to Australian conservators and archaeologists, known to be associated with Cypriot archaeology or archaeological materials. One of the questions asked: ‘What adhesives have you used to consolidate / adhere / join archaeological ceramics? Please provide chemical composition and brand name (if known)’. The following options were provided: epoxy (eg. araldite), cellulose nitrate (CN) (eg. HMG, Duco cement, Durofix, UHU Hart), poly(vinyl acetate) (PVAc) (eg. UHU, Mowilith), acrylic (eg. Paraloid B72, Rhoplex AC33, Primal AC33) and other (eg. superglue).

Preparation of reference adhesives

Information provided by the questionnaire participants was used to procure a set of reference adhesive samples, which were cured on glass slides, removed using mechanical methods and stored for analysis purposes in labelled glass vials.

Chemical family	Brand name, manufacturer, batch number	Properties and use	Colour Ageing properties	Feller classification of polymer stability
Cellulose nitrate • synthetic derivative of cellulose • formulation mixed with plasticiser eg. dibutyl phthalate	• HMG – Heat and waterproof adhesive (blue tube), resin • Selleys – Tarzan's Grip (red & white), (product no. 38-276, batch 708A), resin • UHU (Sydney) – Hart (blue tube), resin	• Easy to use • Dries rapidly to form strong film • Reversible with acetone • Suitable for use in hot climates. • Tg ~ 50 °C	• Clear to light yellow. • Yellows, dries out, and becomes brittle with ageing.	• C • (6-20 years)
Poly (vinyl acetate) • synthetic derivative • based on single monomer unit	• Selleys – Aquadhere PVA wood glue (415211), emulsion • Mowilith (source unknown, possibly Hoechst), emulsion • UHU – all purpose (yellow), resin	• Sets quickly • Reversible with acetone • Softens when hot. • Tg ~ 20-30 °C	• Clear to slightly brown. • Yellows with ageing.	• A • (>100 years)
Acrylic • synthetic derivative • based on mix of acrylate and methacrylate monomer units	• HMG – B72 Restoration adhesive (purple tube), resin • HMG – B72 Restoration adhesive (purple & black tube), resin • Plextol B500 (source unknown, possibly Rohm), (PLE494), emulsion • Rohm & Haas – Paraloid B72, (sample no 2018262, batch no. 0070KB41), resin	• Not easy to use • Sets slowly • Reversible with acetone • Not suitable for use in hot climates. • Tg ~ 40 °C	• Clear. • Stable, resistant to ageing.	• A • (>100 years)
Poly urethane • Synthetic derivative • Based on reaction between isocyanate and alcohol groups	• Selleys – Tarzan's Grip (red & black) (1997 formulation change) (product no. 38-315, batch 811A), resin	• Cures to give a tough flexible surface • Unstable in light.	• Clear to yellow. • Yellows with ageing.	• Different stabilities.

Table 1 Summary of adhesive products investigated and their general properties (Buys & Oakley 1993, Horie 1987, Koob 1998, Sease 1994)

Removal of adhesive samples from archaeological pottery

Adhesive samples were removed from the pottery vessels by identifying any protruding adhesive bubbles at join lines, removing these with a scalpel blade and storing the sample in a labelled glass vial.

UV examination of adhesive samples

Adhesive samples were irradiated with a small dual UV lamp (Spectroline Model ENF-260c/FE, with long-wave UV 365 and short-wave UV 254 nm globes).

Chemical spot test analysis

Chemical spot test analysis is often the highest level of analysis available to a conservation laboratory. *Nel (2007)* found that of the chemical spot tests described by *Odegaard et al. (2000)* two are useful for analysing adhesive samples. The diphenylamine test for nitrate in cellulose nitrate (*Odegaard 2000: 164*); and iodine/iodide test for poly(vinyl acetate) (*Odegaard 2000: 166*) were used to identify CN and PVAc based adhesives. There is no chemical spot test available for identifying acrylics, however a negative response to the above tests would indicate that the adhesive may be an acrylic.

FTIR analysis

As recommended by *Nel et al. (2007)* each adhesive sample (reference adhesive / adhesive removed from pottery) (1 mg) was prepared as a KBr (50 mg) disc. FTIR spectra were collected using a Perkin Elmer FTIR Spectrometer – Spectrum 2000 using Spectrum software (v 5.3.1), in the range 4000 – 400 cm^{-1}, 32 scans, 8 cm^{-1} resolution, at 1 cm^{-1} intervals in absorbance mode. Data processing involved background subtraction, baseline subtraction and normalisation of the peak maximum to 1. Spectral libraries from the Infrared Users Group (IRUG, www.irug.org) and FTIR spectra obtained from the control adhesive samples were added to the reference database.

RESULTS

The questionnaire was distributed to 43 people (20 conservators, 22 archaeologists and one curator). The response was 53%, with 23 people, 11 conservators (indicated by dark grey columns) and 12 archaeologists (indicated by light grey columns) completing the questionnaire. It was found that adhesives most commonly used by participants to repair archaeological pottery are in order of popularity: acrylic, PVAc, CN and epoxy based adhesives (**Fig. 1**).

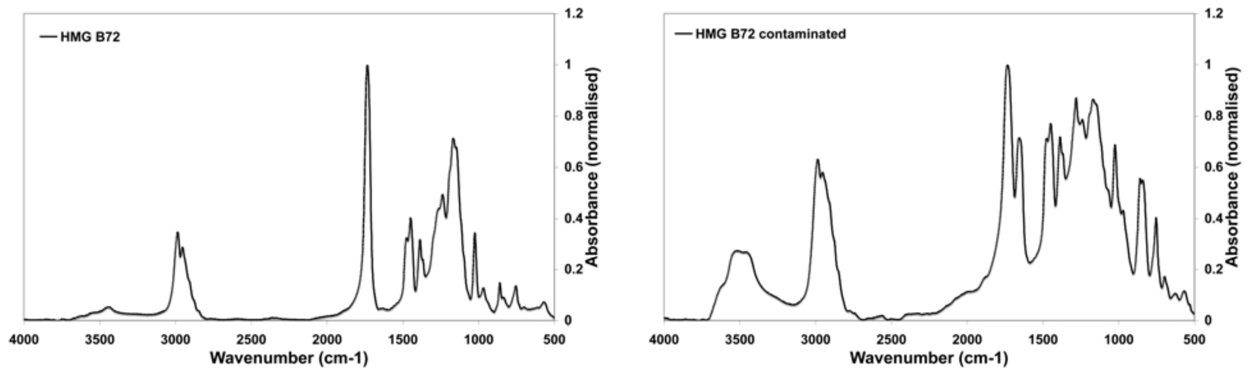


Fig. 2 FTIR spectra of HMG B72 restoration adhesive before (A) and after (B) formulation change in 1995

Specific products that were mentioned are: UHU, HMG, Tarzan's Grip, Paraloid B72 and Araldite.

Reference adhesive samples and their chemical groupings are summarised in **Table 1**:

Poly(vinyl acetate) (PVAc) based adhesives: Selleys Aquadhere PVA wood glue and UHU all purpose were commercially available. Mowilith (source unknown) was found at the Centre for Cultural Materials Conservation (CCMC) laboratories. Cellulose nitrate (CN) based adhesives: 'UHU-Hart' (blue tube) adhesive was provided by UHU (Sydney, Australia). 'HMG Product – Heat and waterproof adhesive' (H. Marcel Guest Ltd.) and an old tube of 'Tarzan's Grip' (red and white tube) were found at the CCMC laboratories. A new tube of 'Tarzan's Grip' (red and black tube) was commercially available. Acrylic based adhesives: Paraloid B72 (Rohm and Haas) was dissolved in acetone to a concentration of 50% (g/ml) according to the method described by *Koob (1986)*. 'HMG product B72 – Restoration Adhesive' (purple and black tube with white conical lid, H. Marcel Guest Ltd.), HMG B72 – Restoration Adhesive (purple tube with blue cylindrical lid, HMG Paints Limited) and Plextol B500 in an aqueous dispersion were found in the CCMC reference collection.

Consultation with the manufacturer (Selleys) determined that the formulation for Tarzan's Grip changed in 1997 from cellulose nitrate to polyurethane. Although not mentioned in the product's Material Safety Data Sheet (MSDS), a test for nitrate and FTIR analysis (**Fig. 2**) indicated the presence of cellulose nitrate in the HMG B72 restoration adhesive. Further instrumental analysis confirmed the presence of CN in the HMG B72 product (*Nel & Lau 2009*). Consultation with the manufacturer determined that the CN resin has been added to the HMG B72 product since 1995.

Three Cypriot pottery vessels, which were deemed too fragile for exhibition when assessed by a conservator in 2001, were investigated. In general mechanical methods were used to remove adhesive samples from the vessels (**Table 2**). A combination of visual appearance; UV fluorescence; solvent solubility; two chemical spot tests for nitrate and PVAc; and FTIR analysis were used to identify the adhesive samples removed from the pottery vessels (**Table 3**). This allows real-time assessment (as apposed to accelerated ageing studies) of performance and informs removal of the failing adhesive repairs.

Currently these vessels are stored and sometimes exhibited in the Ian Potter Museum of Art (IPMoA) at the University of Melbourne. The purpose built building meets International museum standards with the temperature controlled at 20°C and 50% relative humidity. However, in 2004/2005 the Collection was temporarily relocated to a climate-controlled store for about fifteen months, to upgrade the air conditioning system at the Potter building. Some items in the collection are still stored in the off-site climate-controlled store. IPMoA gradually took on the management of the collection in the late 1990s and the existing on-site store for the Classics Collection was built in 2001 as part of the new Classics Gallery space. Before the opening of the Museum building in 1998, the collection was stored in the Classics and Archaeology offices and rooms in the Old Arts building of the University, where environmental conditions were not controlled and therefore may be considered non-ideal. However the Old Arts building is a nineteenth century sandstone building, and therefore it is likely that good buffering was provided against adverse fluctuations in temperature and humidity. It is assumed that environmental factors (eg. elevated temperatures) in the earlier post-excavation years would have accelerated ageing of adhesives associated with the vessels.

Artefact A: This Cypriot Red Polished Ware Basin was excavated from a tomb at the Vounous site between 1937—1938. It is noted by the archaeologists that the tomb was disturbed by the action of water from spring showers, which is apparent on the now fragile and

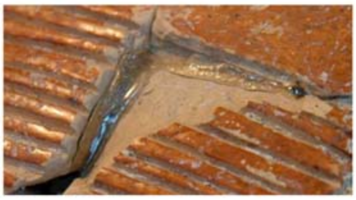
Artefact	Samples
 **A** – Red Polished Ware – Basin (handmade) J R B Stewart, Vounous (1937-1938), site A, tomb 118, no. 21, MU acc. no. 1987.0259.	 **A1**
 **B** – Red Polished Ware – Jug (handmade) J R B Stewart, Karmi Lapatsa (1962), Tomb 4, no. 7, MU acc. no. 1972.0121.	 **B1**  **B2**
 **C** – Bichrome Ware – Pedestal bowl (wheelmade) J R B Stewart, purchased possibly in Kition, MU acc. no. 1987.0179	 **C1**  **C2**

Table 2 Summary of Cypriot pottery artefacts investigated and adhesive samples removed

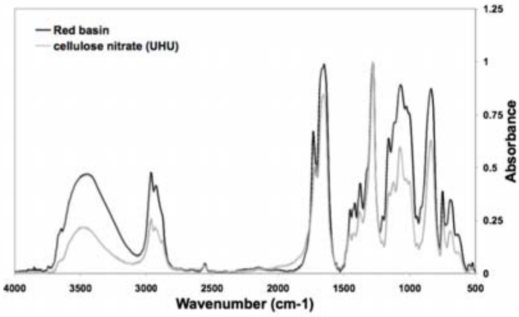
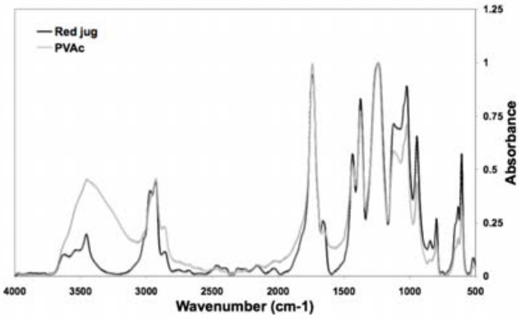
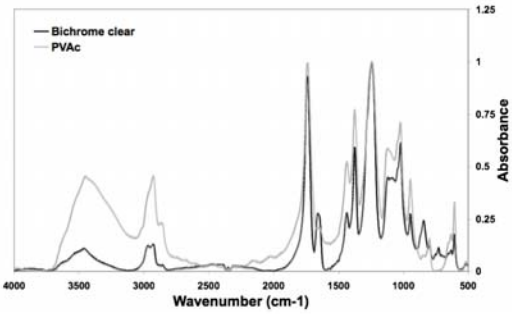
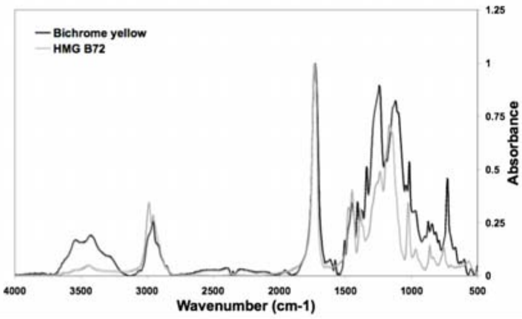
Sample	Observations	FTIR spectrum
A1  cellulose nitrate	Yellow Fluorescence – medium Nitrate test (+ve) PVAc test (-ve) FTIR correlation with UHU Hart is 0.95	
B1  PVAc + CN additive?	Clear Fluorescence – low Nitrate test (+ve) PVAc test (+ve) FTIR correlation with Aquadhere is 0.96	
B2  cellulose nitrate	Yellow Fluorescence – medium Nitrate test (+ve) PVAc test (-ve)	Not available.
C1  PVAc + CN additive	Clear Fluorescence – low Nitrate test (+ve) PVAc test (+ve) FTIR correlation with Aquadhere is 0.91	
C2  acrylic + additive	Yellow Fluorescence – high Nitrate test (-ve) PVAc test (-ve) FTIR correlation with Paraloid B72 is 0.64	

Table 3 Summary of analyses conducted on adhesive samples obtained from artefacts

damaged slip surface. It was acquired by the Australian Institute of Archaeology (AIA), and was later purchased by the University of Melbourne in 1987. Visual examination determined that there was one adhesive associated with the basin. Sample A1 was obtained from loose flakes lying in the interior of the basin. Sample A1's yellow appearance, medium level UV fluorescence, positive reaction to the nitrate test, characteristic IR peaks at 1655, 1280, 840 cm^{-1} and an IR spectral database match correlation of 0.949 with UHU Hart, indicate that this is a CN based adhesive.

Artefact B: This Cypriot Red Polished Ware Jug was excavated from a tomb at the Lapatsa site between 1960—1961. Unpublished excavation notes state that pots in the tomb chamber were badly shattered. Soon after the excavation the lead archaeologist died in 1962. In 1972, a friend and colleague of the deceased archaeologist delivered the artefact to the University of Melbourne. The jug had two different adhesives associated with it. The first adhesive, from which sample B1 was obtained, was visible as protruding bubbles in the front mid-section of the globular body and along the neck-body join. Sample B1's clear appearance, minimal UV fluorescence, positive reactions to nitrate and PVAc tests, characteristic IR peaks at 1740 and 1240 cm^{-1} and an IR spectral database match correlation of 0.96 with Aquadhere, suggest that this is a PVAc based adhesive, which may also contain a small amount of CN resin (as indicated by a small peak at 1655 cm^{-1}. The second adhesive had been neatly applied to most break edges and therefore was only visible at a small number of sections. Sample B2 was removed from one of these areas using an acetone dampened cotton wool swab. With sample B2, its yellow appearance, mild UV fluorescence, and positive reaction to the nitrate test, indicate that it is a CN based adhesive. It was not possible to safely remove a sufficient amount of sample for FTIR purposes.

Artefact C: It is believed that the Cypriot Bichrome Ware Pedastal Bowl was purchased by an archaeologist from a dealer before 1962. The artefact was featured in a 1988 exhibition at the University of Melbourne. As for artefact B, the pedestal bowl had two adhesives associated with it. The first adhesive was visible on most of the main body of the bowl. Sample C1 was removed from bubbles that protruded from the interior and exterior of a join line that runs along the front lower section of the bowl. Sample C1's clear appearance, minimal UV fluorescence, positive reactions to nitrate and PVAc tests, characteristic IR peaks at 1740 and 1240 cm^{-1} and an IR spectral database match correlation of 0.88 with Aquadhere, suggest that this is a PVAc based adhesive, which may also contain a small amount of CN resin (as indicated by peak at 1655 cm^{-1}). Sample C2 was removed from bubbles that protruded from a join line that runs along the front of the foot area of the bowl. Sample C2's negative reactions to the two spot tests, characteristic peak at 1740 cm^{-1} and a poor IR spectral database match correlation of 0.64 with Paraloid B72, suggest that this adhesive is an acrylic based adhesive. However this is at variance with the deep yellow appearance and high level of UV fluorescence (acrylics like Paraloid B72 tend not to yellow and are not normally UV fluorescent), which suggest the presence of an additive(s).

DISCUSSION

Adhesives that have been historically used to repair archaeological ceramics are shellac, animal glue, CN and PVAc (*Koob 1986, 1998*). Acetone reversible adhesives recommended by the conservation profession are CN, PVAc and the acrylic Paraloid B72 (*UKIC 1981, Sease 1994, Cronyn 1990*). Adhesives mentioned by the questionnaire participants reflect recommended conservation practice and indicate that they are generally aware of the appropriate materials to use for adhesion.

However it is of concern that participants were not aware that due to a formulation change in 1997, Tarzan's Grip is no longer appropriate for use. The old cellulose nitrate formulation is reversible with acetone. However, the current formulation is based on polyurethane, which is noted for its instability and becoming insoluble with age (*Horie 1987, Buys and Oakley 1993*) and therefore should no longer be recommended for use. Of further concern is the formulation change for HMG B72 that occurred in 1995, but does not appear to have been detected until recently (*Nel & Lau 2009*). Paraloid B72 is commonly used due to its thermoplastic properties, clear white appearance, good long-term ageing properties and solubility in acetone (*Horie 19878, Buys and Oakley 1993*). However the introduction of CN into the formulation reflects that there is an ongoing search to improve its working properties and to elevate its glass transition temperature (Tg) of ~40°C to reduce the risk of softening and slumping at high temperatures.

Identification of the adhesive samples removed from the artefacts, allowed an assessment to be made of their performance. The CN based adhesives associated with the two Red Polished Wares, clearly illustrate CN's stability issues. With the Red Polished Ware basin, advanced adhesive deterioration (visible as yellowing, brittleness, adhesive failure, slip surface damage) is clearly visible, where it was originally smeared along the interior break edge surface (**Table 4A**). It is argued that CN is reasonably stable inside break edges where exposure to light is minimal (*Shashoua et al. 1992*). Clearly this light sensitivity is a contraindication for smearing the adhesive along the pottery surface, where light induced degradation will damage the slip surface (especially if already fragile). With the Red Polished Ware jug, CN was carefully applied to the numerous broken edges (**Table 4B**). In this instance, adhesive failure occurred in the neck-to-body join area, possibly due to lack of strength and/or inappropriate handling of

Artefact	Issues
A  Adhesive deterioration visible as yellowing, brittleness, adhesive failure and slip surface damage of fragile fabric.	
B  Adhesive failure, due to lack of strength and/or handling.	
C  Adhesive pulling at fabric. Due to strength, technique of application, poor surface preparation and/or CN in adhesive formulation.	

Table 4 Adhesive issues associated with Cypriot pottery artefacts

the artefact. CN based adhesives are popular due to their ease of use, good working properties, rapid drying to form a strong film, solubility in acetone and high Tg of ~50°C, making it suitable for use in hot climates.

However, it yellows, dries out and becomes brittle with ageing (*Buys and Oakley 1993*, *Horie 1987*, *Sease 1994*). This means that a question mark hangs over its long-term stability especially when artifacts are exposed to undesirable storage conditions such as high temperatures and UV levels. These observations may also reflect the performance of an old cellulose nitrate based adhesive formulation that contains a plasticiser like camphor. This past formulation may be less stable than the modern CN adhesive formulation, which contains dibutyl phthalate. If used, artifacts should be handled with care (not be handled at appendages) and exposure to light should be minimized.

Poly(vinyl acetate)-based adhesives were identified on the Red Polished Ware jug and on the main body of the Bichrome Ware bowl. Users should be aware that because of the low Tg of ~20°C of PVAc adhesives, vessels are susceptible to dirt pick-up and cold flow (*Horie 1987*) and tend to soften in hot conditions (*Sease 1994*). As a result they are of limited use in the field, and perform best in a controlled environment. With the Red Polished Ware jug it is likely that PVAc was used to repair the neck to body join when the CN join failed. It also appears to have been used to insert a sherd that might have been found at a later date. With the Bichrome Ware bowl, the adhesive is pulling at the fabric (**Table 4C**). This may indicate that: the adhesive is too strong for the fabric; there is a problem with the technique of application; or poor surface preparation. Alternatively the presence of CN in the formulation may cause adhesive stability to become an issue.

CONCLUSIONS

Consultation with Australian conservators and archaeologists indicate that acetone reversible adhesives based on CN, PVAc and the acrylics are being used to repair archaeological pottery. Testing of control adhesive samples resulted in the detection of two formulation changes that illustrate the importance of monitoring adhesive products in order to identify issues that may require further investigation. Identification of adhesives associated with the Cypriot pottery vessels, allowed us to demonstrate how with ageing, CN starts to fail and pull at the fabric of fragile pottery. It is recommended that CN should be used with an awareness that it ages far more rapidly and with deleterious effects, than the PVAc and acrylic based adhesives and thus protective measures should be taken such as avoiding elevated temperatures and minimising light exposure.

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