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The Characterisation and Removal of Lac Dye Staining on White Ground Ceramics

This project began with the conservation of a polychrome white-ground lekythos on loan to the Department of Antiquities Conservation of the J. Paul Getty Museum by the Antikensammlung Museum in Berlin in 2006 (**Figure 1**). This piece had been previously restored in the late 19th century with unrefined, or crude, shellac as an adhesive to "glue" the fragments together. During the current conservation at the JPGM, in an attempt to remove the shellac and to re-establish the integrity of the object, the vessel was fumed in a solvent rich environment of a 1:1 mixture of acetone and ethanol. Although the shellac was swelled and the vessel was disassembled, the fuming seemed to have caused a pinkish purple stain to migrate onto the surface in the areas where the shellac was present (**Figure 2**). The causes, characterization and methods for the removal of this staining has since been the subject of a study undertaken by both the J. Paul Getty Museum (JPGM) and conservation scientists at the Los Angeles County Museum of Art (LACMA) (Svoboda 2008; Svoboda, Tsatsouli, and Eng 2008). During the course of this study, it was found that the development of this staining was not unique and that there were other instances of such discoloration on a variety of ceramic types as a result of attempts by different conservators to remove unrefined shellac using methods ranging from poulticing to solvent gels. Unfortunately, a satisfactory method for reducing the stain has not yet been found, though some success was found using Fuller's Earth; this method only served to reduce the stain, rather than remove it altogether (Svoboda, Tsatsouli, and Eng 2008).

The white-ground on the Berlin lekythos has been identified as an aluminosilicate clay with various metallic impurities. Through XRF testing performed on a variety of white-ground ceramic substrates by the previous study ((Svoboda, Tsatsouli, and Eng 2008), it was found that a white, clay-rich soil from Greece, called Batanas, was the most similar to the original white-ground of the lekythos chemically and in terms of behavior towards the staining (**Table 1**).

Metallic Impurities	**Calcium (Ca2+)**	**Potassium (K+)**	**Titanium (Ti3+/Ti4+)**	**Iron (Fe2+/Fe3+)**
Lekythos	> 5%	1-5%	0.1 - 1%	0.1 - 1%
Batanas	> 5%	1-5%	0.1 - 1%	0.1 - 1%
Ward's Hardware	1-5%	0.1 - 1%	0.1 - 1%	0.1 - 1%
Ultra White	> 5%	0.1 - 1%	0.1 - 1%	0.1 - 1%
White Star	> 5%	0.1 - 1%	0.1 - 1%	0.1 - 1%
Kaolin	0.1 - 1%	1 - 5%	< 0.1%	1 - 5%
Glass Frit	Not detectable	0.1 - 1%	Not detectable	< 0.1%

Table 1: White grounds tested by Svoboda et al. (Svoboda, Tsatsouli, and Eng 2008, 1)

Batanas has been used in Greece since antiquity as a slip for the decoration of ceramics. These tests also revealed that the impurities of particular interest for the complexing of the lac dye are a combination of the calcium and potassium cations. Tests on glass frits and kaolin, to which the staining did not adhere in any way revealed, in the instance of the glass frits, that the stain was not being held physically or mechanically within the porous substrates, and for the kaolin, that the staining is directly related to the metal cations that are present as impurities within the ceramic ground, particularly the calcium. Tests on other white-grounds, such as the Ultra White and White Star, which did not show the same behaviour towards the stain as the Batanas, though it had similar calcium values, show that the differential potassium values are also playing a role. As such, though the organometallic complex between the stain and the white-ground substrate is still not fully understood, a relationship to both the calcium and the potassium cations is clearly revealed here.

Unrefined shellac is composed of 1 to 8% lac dye, in addition to its wax and resin constituents. Previous studies indicate that the occurrence of the discolouration is directly related to the lac dye constituent of the shellac, and not necessarily to the shellac itself, since staining does not occur on objects that have been treated with refined shellac from which the lac dye has been removed or reduced (Svoboda 2008; Svoboda, Tsatsouli, and Eng 2008). The lac dye itself is composed of three main constituents: laccaic acid (**Figure 3**), anthraquinone and erythrolaccin (Cardon 2003; Kongkachuichay, Shitangkoon, and Chinwongamorn 2002).

Lac dye, like many natural red dyes, is a fugitive dye; that is, without the addition of a polyvalent metal ion, called a 'mordant', with which to form coordinating complexes (Baker, 1958) the dye remains water-soluble and fails to bond with a given substrate. It is the ability of the dyes to complex with mordants that makes them useful in the textile dyeing industry. The affinity of specific dyes with specific mordants is directly related to the valency of the mordant itself and the pH of the solution. Thus, trivalent and bivalent cations will tend to complex more easily and more strongly than monovalent cations. Based on the work of Svoboda *et al.*(2008), as well as Kongkachuichay (2002) and Baker (1958) it seems that the metal cations in the white-ground discussed above and the O-H functional groups of the laccaic acid are forming an organometallic complex which causes a bathochromic shift and hence the purple stain (**Figure 4**). A bathochromic shift is a change in the absorption, reflectance, transmittance or emission of a molecule to a longer wavelength along a spectrum; in this case, it is the bathochromic shift that causes the discolouration to appear as pinkish-purple in colour (Baker 1958).

Initial tests, as well as traditional textile dying techniques indicated that the complex formed between the lac dye and the ceramic substrate could be reversed in an acidic environment . Since the use of strong acids could be harmful on ceramic substrates, a different approach has been investigated in search of a method that can remove the stain in a neutral or alkaline environment (Svoboda 2008).

The goal of the current study is to continue the work started by Svoboda *et al*. (2008), in finding an appropriate method for the removal of the lac dye discolouration and to further our understanding of the chemical characterization and mechanism that has caused the stain in order that it might be avoided altogether. The intractability of the staining, as well as the difficulties of its removal using conventional materials and methods have motivated a slightly different approach than that used in the previous study. Here, we have chosen to approach this problem using dye chemistry processes in order to reduce the stain through re-solubilisation and re-complexing to a new mordant material supported within a poultice.

Initially, eight metallic compounds commonly used as mordanting materials in textiles were selected. Of these, four were tested based on their working properties, and our ability to buffer them to an acceptable pH (close to neutral). These four mordants included aluminium acetate, aluminium hydroxide hydrate, aluminium sulphate and aluminium sodium sulphate. At the end of the first testing trial, aluminium acetate was removed from testing, as it did not harbour favourable results. There were additional concerns for the introduction of acetate salts into the ceramic body, as they have a higher rate of deliquescence than the sulphates (Charola 2000), and thus could be potentially more destructive if adequate clearance were not achieved.

To overcome the strong affinity between the lac dye and ceramic body, the goal in using these materials was to find a substance for which the lac dye could have a greater chemical affinity. The metal cations that are most likely to be complexing with the lac dye in the white-ground appear to be calcium and are bivalent, with the monovalent potassium cations playing some subsidiary role in the complex that is not yet fully understood. If it were possible to de-complex the lac dye and re-solubilise it, it might be possible for it to re-complex with the trivalent aluminium cations within the mordanting material itself.

In addition to the mordant materials chosen for this study, five poulticing materials were selected to act as supports These included: attapulgite, sepiolite, Carbopol 934, Carbopol 940 and Pappina Neutra.[1] The poulticing materials were used not only as supports for the mordants and solvents, but also to control the depth of penetration of the treatment, since it was important to keep the action on the surface to avoid diffusion of the discoloration into the ceramic body. The attapulgite was selected because it was the most effective material in the previous study and we wished to see if we could increase its success with the addition of a mordanting material (Svoboda, Tsatsouli, and Eng 2008). Sepiolite was selected to see if clay of a slightly different composition could achieve similar or improved results. After the first trials, attapulgite was removed from test as it yielded similar results to the sepiolite tests, and in instances where there was a difference, the sepiolite tended to perform better.

The Carbopol gels and Pappina Neutra were selected in an effort to determine if non-clay poultices could also be effective. Carbopol is a commercially produced polyacrylic acid, which is used as a gelling agent to create solvent gels for use in conservation cleaning. In this study Carbopol grades 934 and 940[2] were used (Henry 1990). The un-buffered Carbopol 934 was prepared according to the manufacturer's directions using a 6% solution in deionised water. The buffered Carbopol 940 was prepared according to a different recipe that made use of a higher solvent ratio and a surfactant in order to raise the pH[3]; Ethomeen C-25, (polyoxyethylene(15)cocoamine) was used as the buffering agent and surfactant here (Curteis, 1991). The difference in Carbopol grades reflects a difference in viscosity and was based on their availability in the lab; in this study, any difference in results should be attributed to a difference in preparation rather than the grades. Pappina Neutra is a wax emulsion that is made by combining ammonia solution with stearic acid, and combining the mixture with melted beeswax in deionized water (Kakoulli and Hodgins 1997).[4]

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[1] Pappina Neutra when first made is slightly alkaline, and is generally neutralized with a strong acid, although this was deemed unnecessary in this study.

[2] Carbopol 940 was used instead of the 934 because it is more viscous and therefore, requires less Carbopol in the mixture, and so exposed the tile to fewer chemicals.

[3] For the buffered Carbopol 940, the recipe was as follows: Carbopol 940 - 1.5g; Ethomeen C-25 – 8g; Acetone 137.5mL; Ethanol 137.5mL; deionised water 10mL.

[4] The recipe used to prepare the Pappina Neutra is as follows (after Kakoulli and Hodgins 1997): Stearic acid BDH 0.2 g; Ammonia solution 28%: 4 ml; Bleached beeswax 100 g; Deionised Water 150 ml

In order to properly characterize our materials and their efficacy, test tiles were made using a terracotta body coated with the batanas. The tiles themselves are roughly 5cm by 5cm in size, and roughly 7 mm in thickness. The batanas coating is generally less than 1mm in thickness. Three types of control tiles were created: unstained, lac dye stained but untreated, and shellac stained but untreated. The remaining tiles were stained with either extracted lac dye, or using unrefined shellac and a solvent-rich environment in order to replicate the formation of the stain from the lekythos study. Also, four tiles were treated using only the mordants without the poulticing support and four tiles have been treated using only the poultice supports. The testing of the mordants and poultices on their own served as a control, to help us to recognize whether it is just the mordant, just the poultice support or the particular combination of the two that is reducing the stain; conversely, it also helped us to assess the causative factor of any deterioration caused by a particular treatment.

An analysis of a treatment's efficacy was based on the following criteria: ability to remove or reduce the stain; the workability of the materials; the ability to clear the materials from the surface after treatment; and the degree of damage caused by the materials used to remove the staining. An ideal treatment for reducing the stain will adequately reduce the visibility of the stain, be easily workable with ceramic substrates of varying degrees of fragility, be cleared without damage to the substrate or residues that may cause future complications, and will not cause physical or chemical changes to the substrate, inasmuch as this is possible.

Four trials have been carried out thus far, the first two were conducted on tiles stained with the extracted lac dye, the third on tiles stained with shellac[5] that was subsequently removed by fuming in a 1:1 solution of acetone and ethanol, and the fourth having been conducted with the use of a barrier of Japanese tissue paper in order to improve clearance and removal of the poultices.

The analysis and evaluation of the first trials were predominantly visual in nature (Figures 5-7). Stain reduction was measured by visual comparison of before and after treatment photographs. It is important to note that while a visual assessment provided a good visualization of surface damage at the macroscopic level and with the use of low powered binocular

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[5] The tiles were stained with a 80% w/v mixture of seed lac and ethanol, which was then droppered onto the surface of the tiles. After drying, the tiles were aged for a week in an oven at 70°C and then placed in a solvent chamber. As the shellac was softened, it was removed mechanically to reveal the stain.

microscopy (Figures 8-9), further studies will be required using more vigorous analytical techniques including UV-VIS-NIR spectroscopy, FTIR spectroscopy and SEM.

In general, it was found that many of the mordants and the un-buffered Carbopol were highly acidic, ranging in pH from 2 to 4.5. As this treatment is intended for use on a ceramic substrate that is often polychrome, the use of low pH materials for the removal of the stain is not feasible in practical application. Generally, however, the support materials tended to be neutral to alkaline in pH and as a result, tended to buffer out the mordants, leading to less acidic mordant-support combinations. After the first trials, it was decided to remove the un-buffered Carbopol 934, in addition to the attapulgite and the aluminum acetate, since it was highly acidic and tended to cause moderate to severe damage to the surface of the testing tiles, ranging from discolourations to surface loss upon removal.

The ease of removal for each of the mordant-support systems was equally critical in choosing which methods would be viable for further testing. In many instances, the mordant-support system became very hard and concretized upon drying and the efforts to remove and fully clear the systems caused physical damage or did not fully clear the tile surfaces, leaving either large accretions, or a haze over the surfaces of the affected tiles. One of the main concerns for materials throughout this study has been the issue of clearance. The addition of a surfactant (Ethomeen) to the Carbopol mixture enables an improved wetting ability by the gel, and deeper penetration of the material into the body of the ceramic, but this can contribute to problems in removal of the material after the treatment. Both Carbopol and Ethomeen can potentially leave residues, and when dry can be extremely difficult to remove. Additionally, the Carbopol itself can potentially complex with bivalent and trivalent ions, such as calcium and magnesium, both of which are found in the ceramic bodies tested in this study. This complexing renders the Carbopol insoluble in water and is an important consideration in the use of this material (Curteis, 1991).

While many questions remain unanswered in efforts to characterize the cause and exact nature of the lac dye staining, much progress has been made in attempts to develop possible treatments for the removal of the stain. The aluminium sodium sulphate and aluminium sulphate performed best in the trials, especially in combination with buffered Carbopol 940 and Pappina Neutra. Further research is necessary, however, in order to thoroughly vet each of the effective material combinations, and to find better methods for removal of the shellac itself.

Future trials will make use of UV-VIS-NIR spectroscopy in order to better understand the degree of reduction, and the nature of the bathochromic shift . FTIR spectroscopy data has been used in order to validate the issues of clearance, and to detect the chemical signature of the lac dye-white-ground complex. The workability of a material was judged through experimentation and usage and will generally be a comparative and relative value based on the materials being tested. Finally, the integrity of the surface will be analyzed using before and after microphotography with the use of VPSEM and 3D surface reconstruction software to further analyze changes to the surface topography induced by the application of the poultices and mordants in this project.

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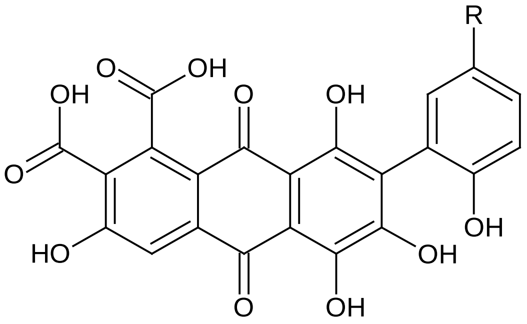
Figures

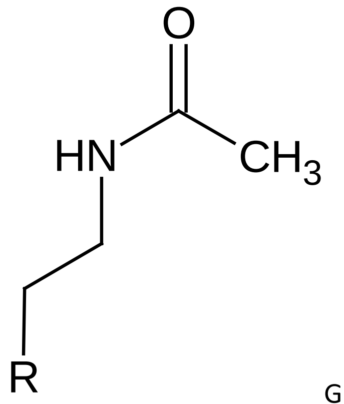
Figure 1: White-ground lekythos from Antikensammlung museum in Berlin (courtesy of M.Svoboda)

Figure 2: Stain after removal of unrefined shellac in solvent chamber (courtesy of M. Svoboda)

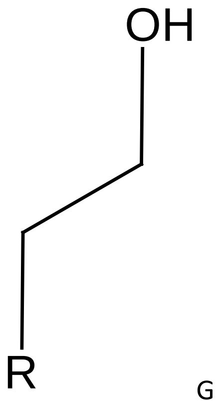


Laccaic Acid – Base Molecule

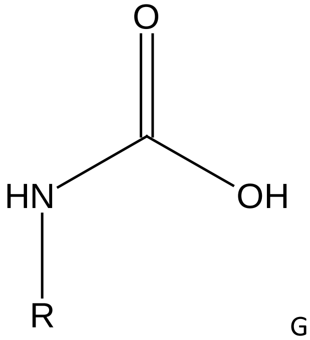
Functional Groups:



Group A



Group B



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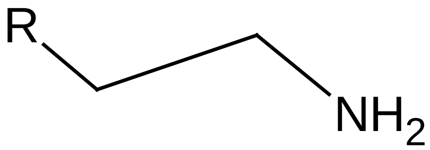
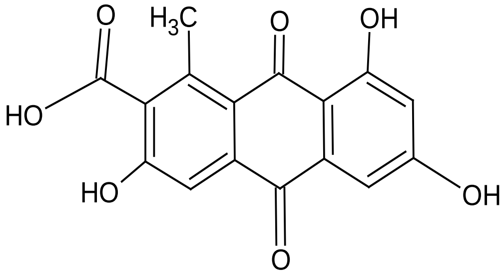


Group E



Laccaic Acid D

Figure 3: Molecular Models of Laccaic Acids A-E (Cardon 2003)

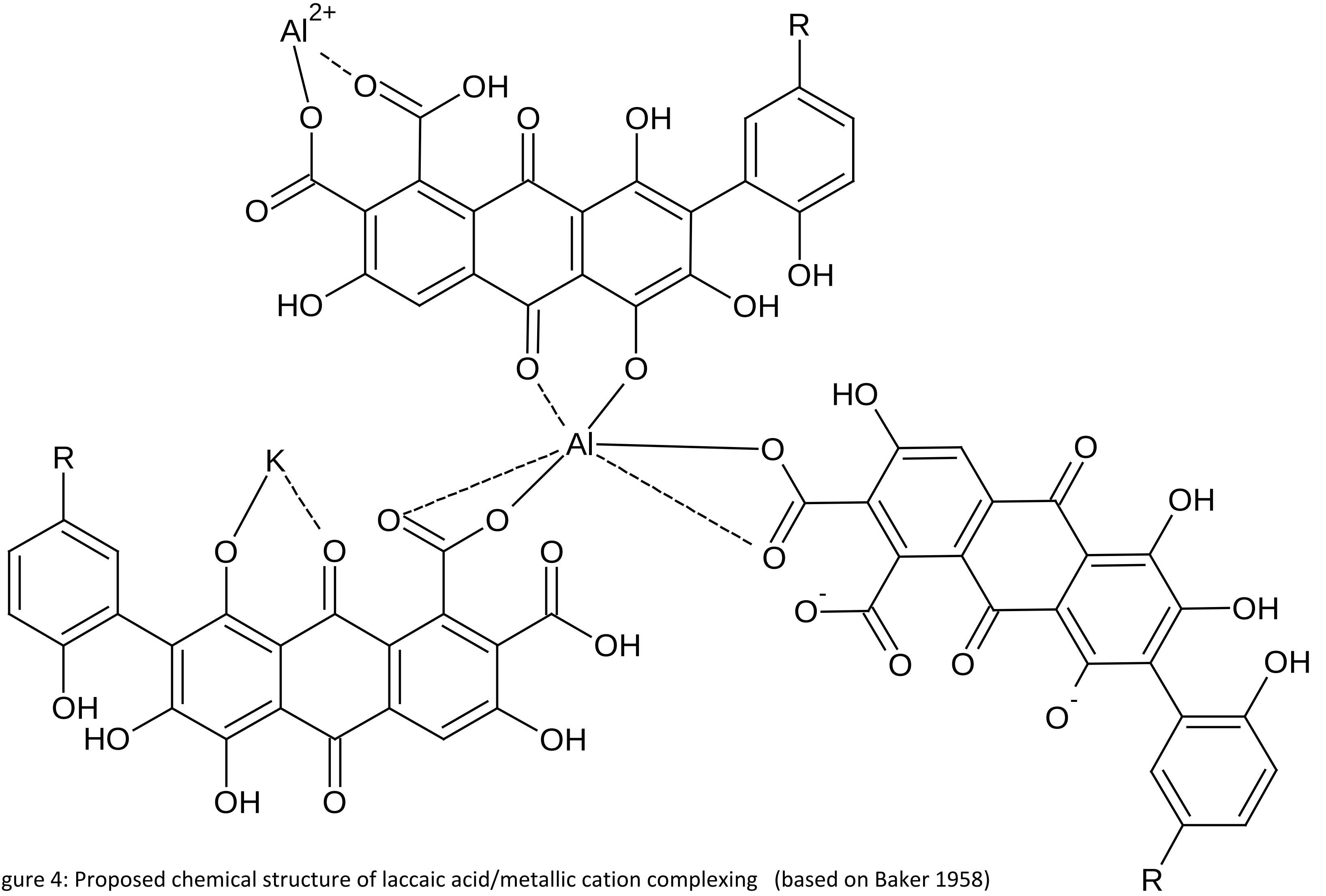


Figure 4: Proposed chemical structure of laccaic acid/metallic cation complexing (based on Baker 1958)

Figure 5 - Trial 2: Before and After Treatment of Tiles with Extracted Lac Dye

Mordant: Aluminium Hydroxide Hydrate

Poultice Material:	Sepiolite	Carbopol 934	Carbopol 940	Pappina Neutra
Before Treatment				
After Treatment				

Mordant: Aluminium Sulphate

Poultice Material:	Sepiolite	Carbopol 934	Carbopol 940	Pappina Neutra
Before Treatment				
After Treatment				

Mordant: Aluminium Sodium Sulphate

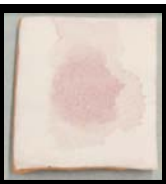
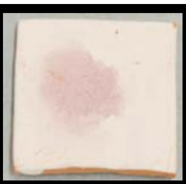
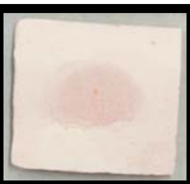
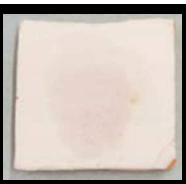
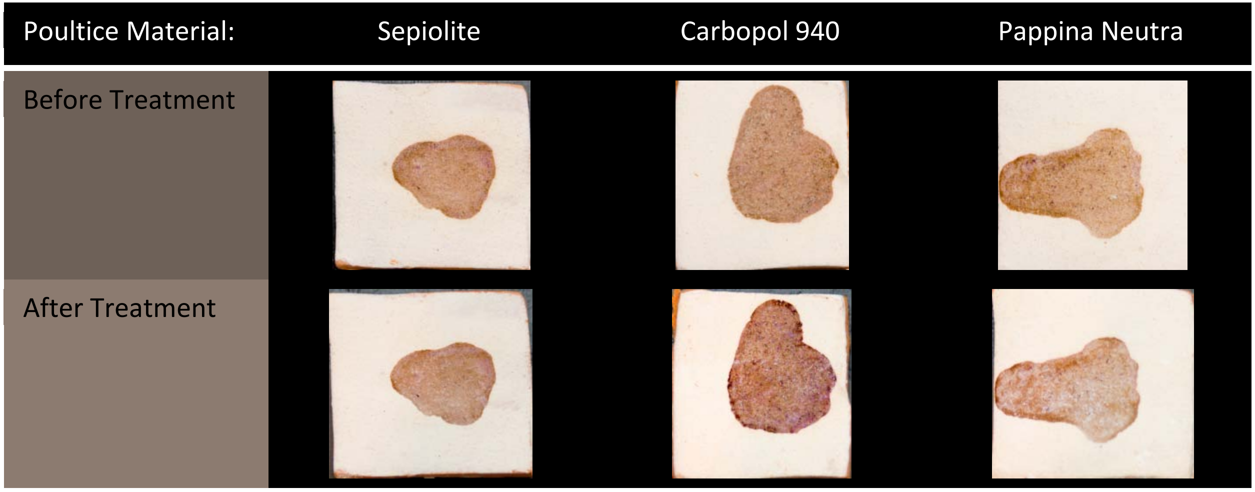
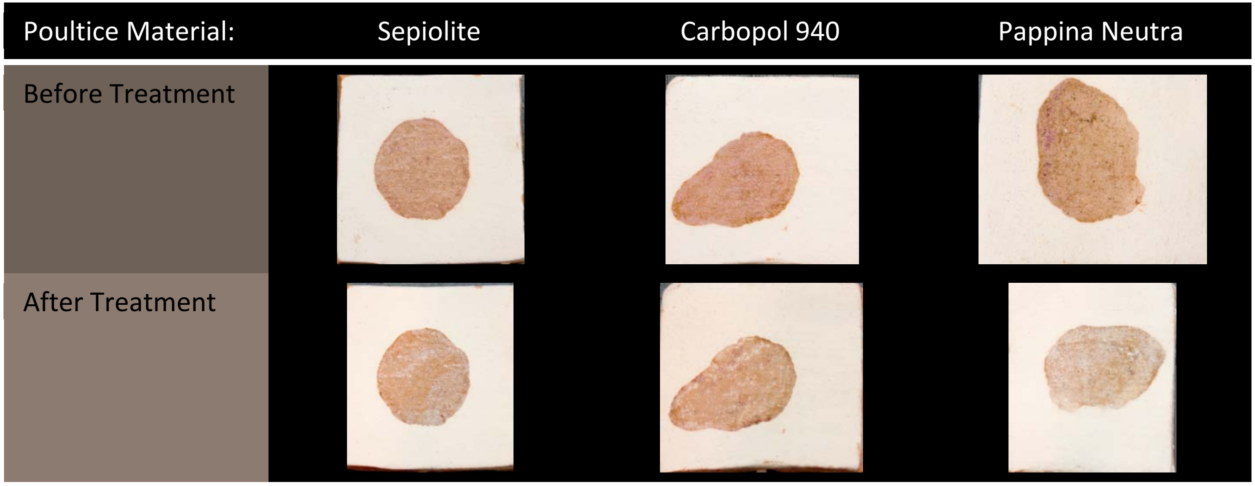
Poultice Material:	Sepiolite	Carbopol 934	Carbopol 940	Pappina Neutra
Before Treatment				
After Treatment				

Figure 6 - Trial 3: Before and After Treatment of Shellac Treated Tiles

Mordant: Aluminium Hydroxide Hydrate



Mordant: Aluminium Sulphate



Mordant: Aluminium Sodium Sulphate

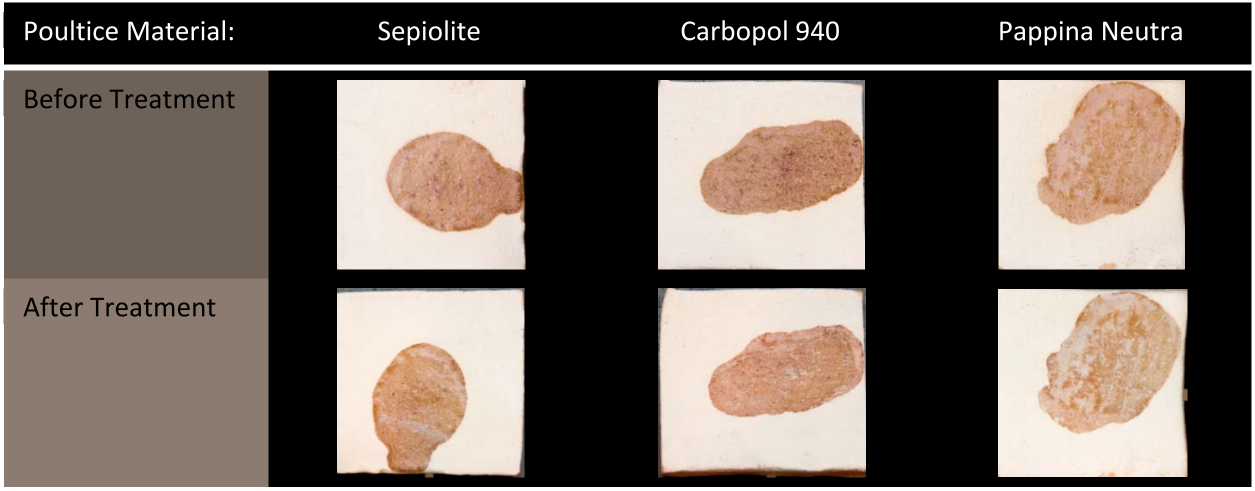
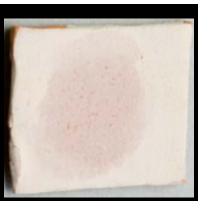


Figure 7: Trial 4: Before and After Treatment of Tiles using Yukuy-shi Thin tissue paper as a barrier

Mordant: Aluminium Hydroxide Hydrate

Poultice Material:	Sepiolite	Carbopol 940	Pappina Neutra
Before Treatment			
After Treatment			

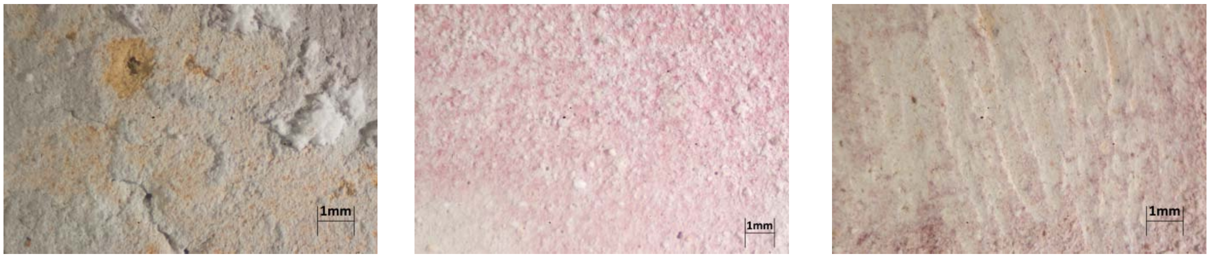
Mordant: Aluminium Sulphate

Poultice Material:	Sepiolite	Carbopol 940	Pappina Neutra
Before Treatment			
After Treatment			

Mordant: Aluminium Sodium Sulphate

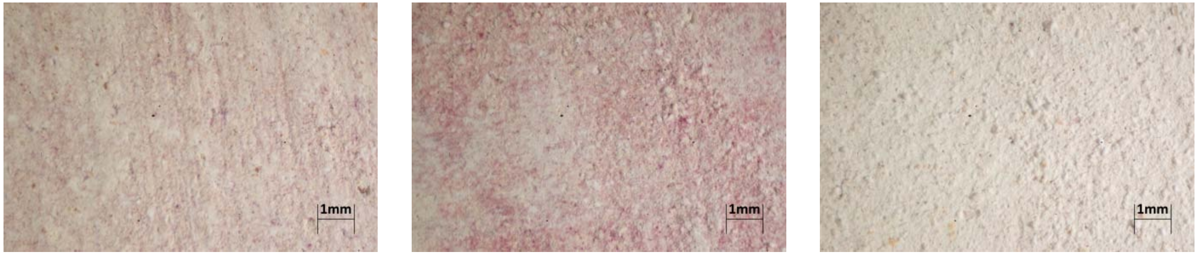
Poultice Material:	Sepiolite	Carbopol 940	Pappina Neutra
Before Treatment			
After Treatment			

Stained Untreated Tile Aluminum Acetate + ATT Aluminum Acetate + SEP



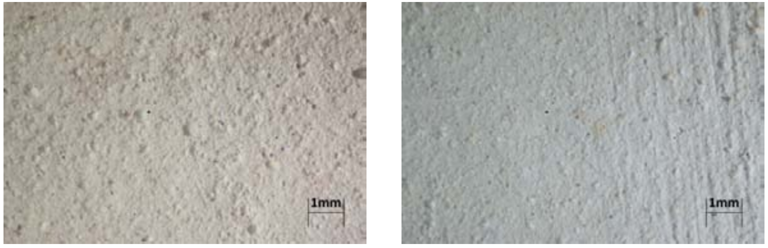
Aluminum Acetate + CARB Aluminum Acetate + PN Aluminum Hydroxide Hydrate + ATT

Aluminum Hydroxide Hydrate + SEP Aluminum Hydroxide Hydrate + CARB Aluminum Hydroxide Hydrate + PN



Aluminum Sulphate + ATT Aluminum Sulphate + SEP Aluminum Sulphate + CARB

Aluminum Sulphate + PN Aluminum Sodium Sulphate + ATT Aluminum Sodium Sulphate + SEP



Aluminum Sodium Sulphate + CARB Aluminum Sodium Sulphate + PN

Figure 8: Photomicrographs – Trial 1

Stained Untreated Tile Aluminium Hydroxide Hydrate + PN Aluminium Sulphate + CARB 936

Aluminium Sulphate + CARB 940 Aluminium Sulphate + PN Aluminium Sodium Sulphate + CARB
936

Aluminium Sodium Sulphate + CARB 940 Aluminium Sodium Sulphate + PN

List of Abbreviations:
ATT = Attapulgite; SEP = Sepiolite; CARB = Carbopol 936 (unbuffered); PN = Pappina Neutra
CARB 936 = Carbopol 936 (unbuffered); CARB 940 = Carbopol 940 (buffered) PN = Papina Neutra

Figure 9: Photomicrographs – Trial 2

Conservation Materials: Technical information and suppliers on materials used in testing

Clays

Batanas: Hellenic Clay Center S.A.55 G. Lyra Kifissia 14564 Greece
Terracotta: Laguna Clay Company; 14400 Lomitas Avenue, City of Industry, CA 91746

Lac Materials

Seed lac: Kremer Pigments (36020) – Seed Lac, Crude Shellac
Kremer lac dye: Kremer Pigments (60490) – Lac Dye, C.I. Natural Red 25

Poulticing Materials

Sepiolite: Conservation Resources (SR2S)
Attapulgite: Kremer Pigments (58903) – Attapulgite (Fullers Earth)
Carbopol Resin 934/940: Conservation Support Systems (CL-24935-0100)
Ethomeen C-25: Talas (TCD024001) – Ethoxylated (15) cocoalkyl amine
Ammonium Hydroxide 28%: Alfa Aesar (L13168) – CAS NO. 1336-21-6
Bleached Beeswax

Mordants

Aluminium Hydroxide Hydrate: Aldrich Chemistry (A1577-500G) – CAS NO. 1330-44-5
Aluminium Sodium Sulphate: Fisher Scientific (S75025) – CAS NO. 10102-71-3
Aluminium Sulphate: Sigma Aldrich (A0843-250G) – CAS NO. 17927-65-0
Aluminium Acetate: Alfa Aesar (A11620) – CAS NO. 142-03-0
Aluminium Ammonium Sulphate: Fisher Scientific (S79888) – CAS NO. 7784-26-1
Aluminium Potassium Sulphate: MCB Reagents (AX0715-1)
Iron II Sulphate: Fisher Scientific (I146-500) – CAS NO. 7782-63-0
Iron III Sulphate: Fisher Scientific (S93242) – CAS NO. 10028-22-5

Solvents

Acetone: VWR International (BDH1101-4LP) – CAS NO. 67-64-1
Ethanol: J.T. Baker (9401-06) – CAS NO. 64-17-5