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An Investigation into the Chemistry and Removal of Unrefined Shellac from Ceramic Substrates via Hydrolysis

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An Investigation into the Chemistry and Removal of Unrefined Shellac from Ceramic Substrates via Hydrolysis

A thesis submitted in partial satisfaction

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in Conservation of Archaeological and Ethnographic Materials

by

Cindy Lee Scott

2012

ABSTRACT OF THE THESIS

An Investigation into the Chemistry and Removal of Unrefined Shellac from Ceramic Substrates via Hydrolysis

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Cindy Lee Scott

Master of Arts in Conservation of Archaeological and Ethnographic Materials

University of California, Los Angeles, 2012

Professor Ioanna Kakoulli, Chair

For more than 200 years, shellac has been used in the repair and mending of ceramic materials. Over time, the shellac becomes brittle and the joins begin to fail, requiring retreatment. The removal of shellac from previous repairs presents a number of problems to conservators, as this resin is not easily soluble in solvents. To further complicate the removal process, recent research at the J. Paul Getty Museum has revealed that the use of fumed solvents for the removal of unrefined shellac causes the lac dye component of the resin to go into solution, absorb into the porous substrate of the ceramic fabric, and, through a complex chemical reaction, form an organometallic complex with metallic impurities in the ceramic, causing an irreversible purple-pink colored stain.

This study has sought new methods and materials for the removal of unrefined shellac, particularly from porous substrates. It explores the use of alkaline solutions, held within a gel support, as a method of hydrolyzing rather than solubilizing the resin, in order to prevent staining altogether. The results of experimentation have found that the use of sodium hydroxide (NaOH) in conjunction with ethanol, held in a rigid gel support composed of agar, effectively breaks down the resin molecules while preventing or minimizing staining from the lac dye component. Though more research remains to be done in order to refine the methods and materials, this study represents a starting point for a new direction in shellac removal techniques in conservation.

The thesis of Cindy Lee Scott is approved.

David A. Scott

Ellen Pearlstein

Marie Svoboda

Ioanna Kakoulli, Committee Chair

University of California, Los Angeles

2012

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Introduction

Brief Project History

In 2003, the J. Paul Getty Museum (JPGM) received a white-ground lekythos belonging to the Antikensammlung Museum in Berlin for conservation treatment. The vessel had initially been restored in the late 19th century using a variety of adhesives, including unrefined shellac[1]. When the vessel was fumed in a solvent saturated chamber of 1:1 ethanol and acetone for disassembly, the shellac unexpectedly turned pink. This pink color in turn caused a pink stain on the white-ground surface of the ceramic vessel. Testing by conservators and conservation scientists at both the JPGM and the Los Angeles County Museum of Art (LACMA) later revealed the pink coloration to be lac dye, which had formed an organometallic complex[2] with the ceramic substrate of the vessel, thus causing an irreversible pink discoloration of the surface (M. Svoboda, Tsatsouli, and Eng 2008; M. Svoboda 2007).

During the winter of 2010, a group of students from the UCLA/Getty Conservation Program undertook a research project[3] (Scott, Drolet, and Blaik 2010) to continue studying the chemical mechanism by which the lac dye was forming a complex within the ceramic substrate, in addition to experimenting with methods to remove or reduce the stain.

During the initial study conducted at the JPGM, Svoboda et al. (2008) discovered that the cause of the staining was due to lac dye, a chemical constituent of unrefined shellac

[1] Shellac is a natural polyester resin derived from the secretions of the lac insect. Unrefined shellac has not had the lac dye component removed from the resinous matrix (Schaeffer and Gardner 1938).
[2] An organometallic complex consists of a chemical compound containing bonds between carbon and metal. In this instance, the complex is formed through coordination bonds between metal and organic ligands through oxygen-based coordinating compounds (Crabtree 2005).
[3] The project conducted by the UCLA/Getty students will henceforth be referred to as the 'Lac Dye' study.

that was rendered soluble during the course of a solvent treatment. Based on their work, it seemed that the lac dye formed an organometallic complex with the calcium and potassium ions of the ceramic substrate by means of metal coordination chemical pathways (. It is not yet certain that these are the specific cations involved in the reaction, but analysis of different substrata containing different metallic impurities support this conclusion (**Table 1**) ().

Metallic Impurities: **White Grounds**	**Calcium (Ca^{2+})**	**Potassium (K^{+})**	**Titanium(Ti^{3+}/Ti^{4+})**	**Iron (Fe^{2+}/Fe^{3+})**
Lekythos	> 5%	1-5%	0.1 - 1%	0.1 - 1%
Batanas	> 5%	1-5%	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: Elemental composition of different white ground materials using XRF (M. Svoboda, Tsatsouli, and Eng 2008).

Based on the work of Svoboda et al. (2008), as well as Kongkachuichay et al. (2002) it seems that the metal cations in the white-ground discussed above and the carboxyl O-H functional groups of the laccaic acid (the main component of the lac dye) are responsible for the formation of the organometallic complex. Due to the introduction of the solvents and the changes in the molecular structure of the dye compound, a bathochromic shift occurs, which is a change in the absorption or reflectance of a molecule to a longer or shorter wavelength along the visible spectrum, which in turn, causes a pinkish-purple stain. It was also revealed that the development of this staining was not a unique occurrence 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 by using methods

ranging from poulticing[4] to solvent gels and even through heating (Bremner n.d.; Buys and Oakley 1996; Koob 1979; N. Williams 1993; Wouters 2007).

Through the course of the study by Scott et al. (2010), an approach was borrowed from textile dying processes involving the use of mordants[5] commonly used to render the highly water-soluble lac dye insoluble, an approach also explored by Svoboda et al. (2008) using Fuller's Earth. . The use of aluminum based mordants combined with different poultice supports were found to significantly reduce the lac dye stains from the white-ground on test tiles[6] stained with extracted lac dye, though the materials and methods have yet to be thoroughly vetted and cleared for conservation use. Ultimately, it was found that the aluminum sodium sulfate and aluminum sulfate performed best in the trials, especially in combination with a buffered solvent gel made of Carbopol[7], or with Pappina Neutra[8].

When testing was conducted on the replicated samples stained with unrefined shellac to reproduce the conservation issues of the original 'lekythos', a secondary problem was revealed; when the tiles were fumed in a solvent chamber of 1:1 ethanol and acetone, the shellac was not sufficiently removed from the test tiles, leaving a significant amount of shellac on the surface. Consequently, the experimental methods that had proven successful on test tiles stained with extracted lac dye were not effective in reducing the discoloration present on these tiles, as the treatment seemed unable to penetrate the residual shellac

[4] A poultice is used to draw out deep-seated contaminants or soiling from a porous substrate, most frequently through capillary action. Poulticing materials, usually clays or fibrous materials can also be used to control the localization of treatment and to carry solvents or other materials to aid in the dissolution of contaminants in the cleaning process (Woolfitt and Abrey 2000).
[5] A mordant is a chemical compound, usually a salt or a hydroxide of a trivalent metal such as aluminum, that forms a complex with the dye, rendering it insoluble and fixing to a substrate (Wipplinger 2004).
[6] A full description of the manufacturing and materials for the test-tiles can be found in Chapter 3.
[7] A polyacrylic acid.
[8] A wax emulsion.

(Scott 2010). Based upon the problems of staining and ineffective removal of the unrefined shellac during both the 'Lac Dye' study and the study conducted by the JPGM, it was determined that an alternative method for removing unrefined shellac from ceramic substrates required further research.

Shellac, either in its crude form or as a refined product, has been used extensively since the 1800s for the mending of archaeological ceramics from around the world, and continued in use well into the 1970s (Koob 1979; Buys and Oakley 1996). Invariably, it has become necessary to reverse these shellac repairs as they tend to become brittle with age and changes in temperature and relative humidity, which can cause the ceramic to become unstable or even to collapse or slump (Buys and Oakley 1996, 79), especially if exposed to relatively high ambient temperatures, as is often in the case in storage facilities in South America or the Mediterranean that do not have climate control.

Even when freshly applied, shellac is a deep orangey-brown color and is extremely difficult to remove (Koob 1979), particularly if both the shellac and the ceramic have been heated in its application (Buys and Oakley 1996, 79). In the past, pyridine was used as one of the few solvents in which aged shellac could be readily dissolved. Unfortunately, pyridine presents a number of health and safety issues, among which include a flash point of 20°C, a tendency for flash back explosions from vapors at temperatures above the flashpoint, and severe irritation of skin, pulmonary tract, and potential fatality if accidently ingested.

Other alternatives to pyridine for the removal of shellac have included nitromors, such as dichloromethane (Buys and Oakley 1996, 79-80), which is a proven carcinogen, and has been found to be "slow, messy and not recommended on glazed ceramics or glass"

(Koob 1979, 135)[9]. Beyond these treatments, it is generally possible only to swell the shellac, either with 50% by volume mixtures of ammonia and industrial methylated spirits (Koob 1979), or 50/50 mixtures of ethanol and acetone (M. Svoboda, Tsatsouli, and Eng 2008).

Pharmaceuticals research has shown that shellac cannot generally be dissolved at a pH lower than seven; in order for a treatment to be successful, then, it is critical that any treatment be kept in the alkaline range (≥ pH8) (Sontaya Limmatvapirat et al. 2004).

Aims and Scope of Current Research

The current study builds upon previous research conducted by Svoboda et al. (2008) and expands upon the experimental work carried out by Scott et al. (2010) and Scott (2010). While different methods and materials were tested and evaluated during the 'Lac Dye' study to reverse the staining, the additional treatment steps, the time required, and the interaction with the ceramic substrate during reversal, would favor the use of a method that would remove the crude shellac without allowing the lac dye to go into solution and chemically binding with the ceramic substrate.

As such, the focus of this thesis is to explore new methods and materials for the removal of unrefined shellac from ceramics, especially those with calcium and potassium cations in their substrates, while avoiding the migration of the lac dye component and the formation of the pinkish-purple stain. Because of the issues caused by the removal of unrefined shellac with solvents, this project explores alternative methods for removing or 'disintegrating' the shellac, in this case, primarily through the use of alkaline aqueous

[9] Koob (1979) does not elaborate the reasons for avoiding the usage of dichloromethane on glazed ceramics and glass.

solutions. It explores the usage of different gel mediums and alkali salts as effective methods for removing shellac by hydrolysis, rather than the more traditional methods of dissolution.

Finally, though it was not an initial goal of this study, a means to identify the presence of lac dye in shellac encountered in a previous repair was discovered. This spot test would allow for conservators to better tailor treatment methodologies for adhesive reversal to reduce incidences of undesirable outcomes.

Originally, the author had sought to investigate the usage of enzymes, at least from a theoretical standpoint. Time and expense, however, have precluded this aspect of the study and will be discussed in greater detail in 'Future Studies', below.

This study includes: (1) a literature review of past attempts by conservators to remove shellac and past use of alkali salts and different gel mediums cited in the conservation literature; (2) a thorough review of the raw materials, counting the physico-chemical properties of both shellac and lac dye, and the clay materials used in experimental trials; (3) an experimental part[10] with the methods and materials tested and evaluated not only for their effectiveness, but also for their potential adverse impacts on the ceramic substrate, both in the long and short term; (4) the results, discussions and further studies that investigate the experimentation undertaken in this study and seek to further our understanding of the interaction between shellac, lac dye and porous ceramic substrates.

[10] The experimental trials were conducted on test tiles as well as a series of fragments from an Attic red-figure vessel of Apulian origin, which was restored in the 1820s by an Italian conservator using a shellac mixture referred to as *colla*. These fragments have been provided courtesy of Antiquities Conservator, Marie Svoboda of the JPGM.

Chapter I: Literature Review

The risk of a stain caused by fuming unrefined shellac in a solvent saturated environment has been discussed by Koob as early as 1979, and later by N. Williams (1993) and D. Williams (2002). Only the work by Smith (1993) , however, appears to have identified the lac dye constituent of the unrefined shellac responsible for the staining, prior to the work by Svoboda et al. (2008; M. Svoboda 2007).

Previous published literature on the solubility of shellac on the other hand, has been widely covered and discussed by scientists and conservators alike (Burke 1984; Morrison and Boyd 1972; Stavroudis and Blank 1989; Stulik and Dorge 2004; Wolbers 2000). As stated, shellac resins are only soluble in a relatively narrow range of organic solvents, and in particular, they are limited to polar solvents containing –OH groups, which in addition to those listed previously, could also include ether-alcohols and their acetates (Phenix 2010). The work of Stavroudis and Blank (1989) would support such an assertion, mainly in their simplified explanation of solubility: “like dissolves like” (Stavroudis and Blank 1989, 1). However, an unavoidable conclusion was raised, based upon Stavroudis and Blank’s [20] explanations of polarity and ion exchange: the molecular similarities between shellac and the lac dye render it soluble in the same types of solvents, preventing a conservator from solubilizing only one of the two components. The earlier work of Burke (1984) further supports this theory.

The use of alkaline solutions for hydrolyzing shellac is not generally found in conservation literature, but rather, it can be found in the biological sciences, particularly in pharmaceuticals where its use as an enteric coating on pills and capsules requires that it dissolve at a specific pH. That said, alkali use has been suggested by Phenix (2010), as a

method of reducing the molecular weight (MW) of the shellac, and thus, increasing its solubility. Phenix would suggest the use of a weak organic base that can also act as a solvent, such as ethanolamine, or the use of alkaline ion exchange resins in order to limit the usage of water and reduce the risk of solubilizing the lac dye in the crude shellac.

Among the numerous references on the chemistry and composition of shellac are Schaeffer and Gardner (1938) who explore the constituent acids of shellac and Limmatvapirat et al. (2004) who focus on its physicochemical and mechanical properties as a polyester compound. Little to nothing however, has been published in the technical literature on the mechanism by which unrefined shellac cross-links as it ages, thus reducing or severely hindering its solubility. Insight into the differences in the molecular patterns of fresh and aged shellac by means of GC-MS, however, is detailed in an article by Colombini et al. (2003). The work of Limmatvapirat et al. (2004) explores the structure of shellac and the methods by which it is hydrolyzed in a 0.5M solution of NaOH. Colombini et al. (2003) focus on the spectral signature of aged shellac and explore the hydrolysis mechanism of a number of shellac constituents including Aleuritic acid and Shellolic acid, by means of a redox Cannizzaro-type disproportionation reaction; this type of reaction is a type of saponification reaction in which hydroxide anions react with a deprotonated aldehyde to form a carboxylic acid and an alcohol (Colombini, Bonaduce, and Gautier 2003).

The use of solvent gels in conservation is particularly well-known through the work of Wolbers (Wolbers 2000; Victoria and Albert Museum), using Carbopol, an acrylic acid polymer produced by BF Goodrich company (Stavroudis and Blank 1989, 6) as a gelling agent. Its use as a gelling agent has been widely accepted and propagated in the

conservation world, especially in paintings conservation, though it has taken its hold in the treatment of objects, chiefly for the disassembly and re-treatment of ceramics, stone and glass.

More recently, however, research by Cremonesi (2010) and other Italian conservators (Anzani et al. 2010) have continued to explore the use of rigid agar-based gels for use in the conservation of three-dimensional objects. Prior to their work, the use of a rigid gel had been largely the domain of paper conservation (Warda et al. 2007). The use of agar as a support for solvent systems has only just begun to be explored by conservators. Anzani et al. (2010) suggested its use as a gelling medium for chelating agents or surfactants, though such usage was not explored by them at the time of publication. Also in 2010, Gorel (2010) has explored the use of agar as a support for micro-emulsions in the cleaning of porous surfaces.

The conservation literature on enzymatic methods for the hydrolysis of adhesive repairs on three-dimensional objects has remained thin and under-researched. The use of enzymes in conservation up until now has resided very much in the realm of paper and paintings, and primarily for surface cleaning. Examples of the use of enzymes in the conservation of paintings can be found primarily in the works of Cremonesi (2010) and Makes (1979; 1988; 1996; 2006), as well as the research of Wolbers (1989; 2000), and in a number of other Italian studies (Valentini, Diamanti, and Pallesch 2010).

No studies have yet been found in the published literature on the use of enzymes in objects' conservation specifically for the removal of unrefined shellac through the enzymatic cleavage of the bonds of the composite molecules of the shellac itself. The research by Makes (2006) focuses on the use of enzymes for the hydrolysis of glues and

varnishes. For his research, he makes particular usage of enzymes that he has isolated himself from the Antarctic Krill (*Euphasia superba*), which he has identified as being proteases including carboxypeptidase A and B, chymotrypsin and trypsin-like enzymes. Given his success with these materials in conservation, it appears that there is potential in using similar processes to achieve the hydrolysis of shellac. Unfortunately, Makes does not refer in any of his published materials (1979; 1988; 2006) to his specific methods of manufacture, or to the issue of post-treatment clearance. Cremonesi (2010) alludes to the usage of enzymes within a rigid agar gel substrate for the cleaning of materials, though he is primarily interested in the consolidation of painted materials, rather than the removal of a natural resin adhesive, as is the goal of this project.

Chapter II: Chemical and Physical Properties of Shellac and Lac Dye

2.1 Shellac

Shellac has been used extensively from the 1800s onwards for the restoration of ceramic vessels, amongst its other uses in paintings and furniture. Many of the problems faced by conservators in dealing with the removal of this resin are directly related to its complex chemical composition. The complexity of the chemical structure is further increased by the tendency of the resinous compounds that form the chemical backbone of the shellac to further self-esterify and cross-link as it ages (Koob 1979; Buys and Oakley 1996).

Shellac is a natural resinous polymer, secreted by the lac insect (*laccifer lacca*) onto certain types of trees in China, India and Thailand (Sontaya Limmatvapirat et al. 2004). As a part of its life cycle, the female insect produces a resin that will encompass its body and larvae once they have hatched; the collection of these resin covered sticks is called stick lac (Kongkachuichay, Shhitangkoon, and Chinwongamorn 2002; Sontaya Limmatvapirat et al. 2004). When the stick lac is crushed, it is referred to as seed lac; both stick lac and seed lac are considered to be 'crude', or 'unrefined'.

The exact composition of unprocessed shellac consists of a number of polymeric waxes and resins in addition to the laccaic acid constituent of lac dye that gives to the resin its red color(M. Svoboda, Tsatsouli, and Eng 2008; M. Svoboda 2007; Kongkachuichay, Shhitangkoon, and Chinwongamorn 2002) and seems to vary to some degree depending the host tree (Mills and White 1994, 116). Moreover, the chemical composition of shellac is nearly constant with only small quantitative changes in the constituents based on the

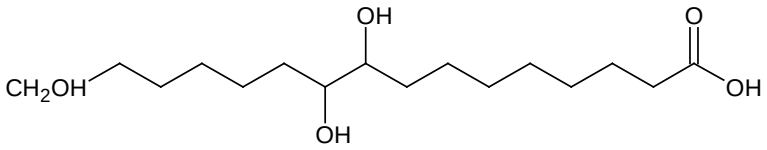
nature of the host trees on which the lac insects nest (Colombini, Bonaduce, and Gautier 2003).

Unrefined shellac in the form of the stick lac resin consists of 70-80% resins, 6-7% wax, 4-8% dye, and 15-25% of other materials such as debris and moisture (Mills and White 1994; Wang et al. 1999). Roughly, 70% of the resinous component of the shellac consists of a hard resin that is insoluble in ether and has a complex polyester composition (Colombini, Bonaduce, and Gautier 2003). The remaining 30% is a soft resin consisting of monoesters that are soluble in ether (**Figure 1)**.

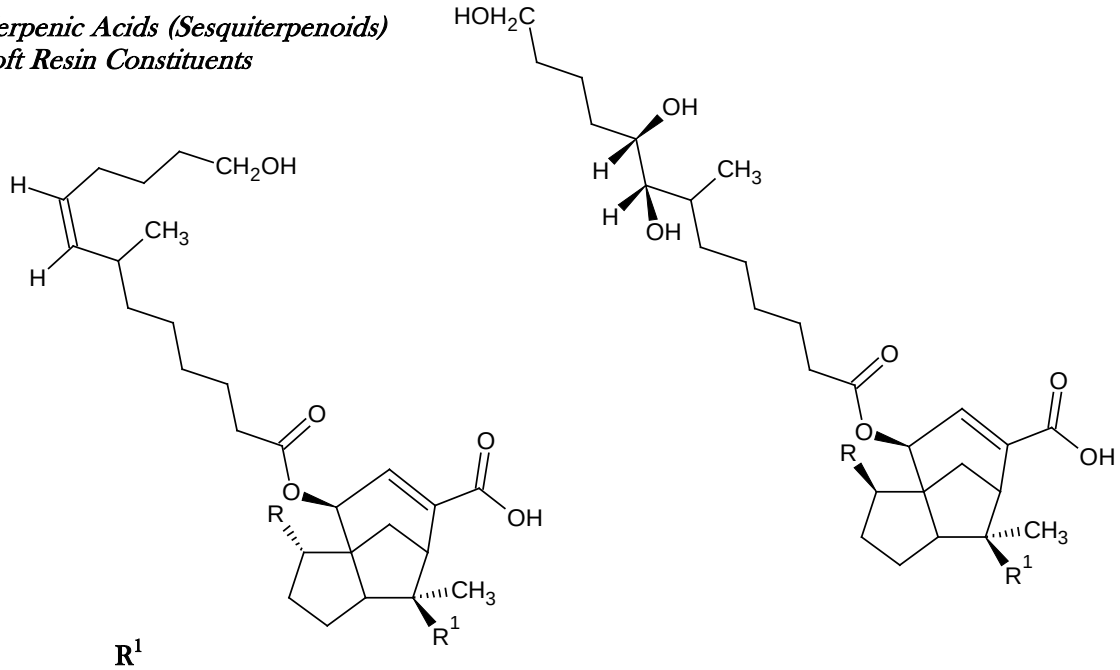
Early studies recognized that shellac was generally composed of low molecular weight oligomers "made up by the esterification of polyhydroxycarboxylic acids one with another" (Mills and White 1994, 117), which were isolated and identified through saponification (Mills and White 1994, 117).

The polyester composition is largely composed of terpenic acid parts with the two primary monomeric ester constituents being jalaric and laccijalaric acids, which is a dihydroxy monocarboxylic acid with an aldehyde group (Mills and White 1994, 117), aleuritic acid (9,10,16-trihydroxyhexadecanoic acid) and butolic acid (6-hydroxytetradecanoic acid) (Sontaya Limmatvapirat et al. 2004; Wang et al. 1999; Colombini, Bonaduce, and Gautier 2003) (**Figure 2**).

Aleuritic Acid

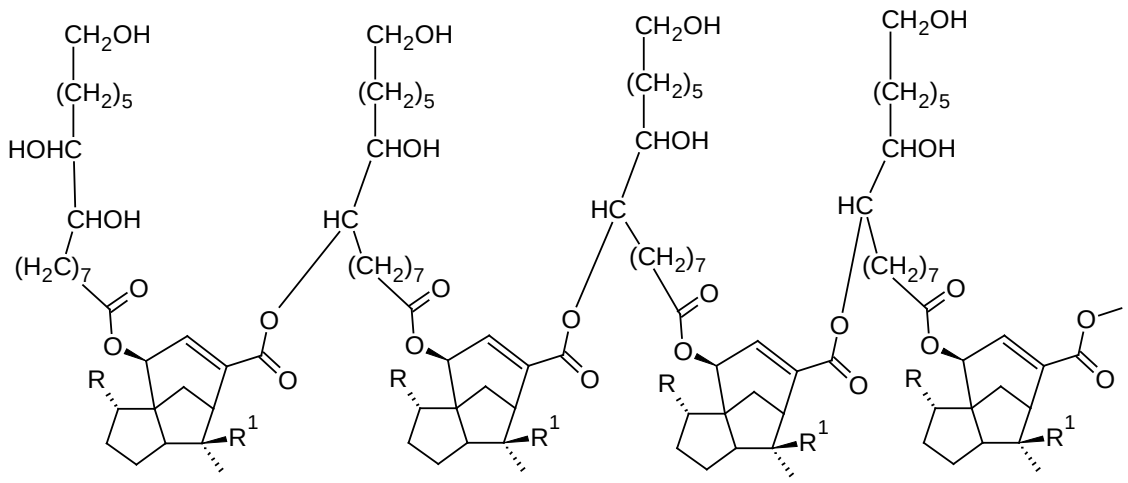


Terpenic Acids (Sesquiterpenoids)
Soft Resin Constituents



R	**R^1**	
COOH	CH_3	Laccishellolic Acid
CH_2OH	CH_3	Laccilaksholic Acid
CHO	CH_3	Laccijalaric Acid
COOH	CH_2OH	Shellolic Acid
CH_2OH	CH_2OH	Laksholic Acid
CHO	CH_2OH	Jalaric Acid

Figure 1: Monomeric soft resin constituents of shellac (Wang et al. 1999).



Jalaric Acid: R = CHO; R^1 = CH_2OH

Laccijalaric Acid: R = CHO; R^1 = CH_3

Figure 2: Suggested oligomeric polyester structure of the hard resin component of shellac (Wang et al. 1999).

The work of Wang et al. (Wang et al. 1999) found the relative ratios of terpenic acids, aleuritic acid and other fatty acids in Indian and Thai shellac samples to be 53:34:14 and 51:35:14, respectively (Wang et al. 1999), demonstrating only very minor changes in the relative make-up of shellac from different sources. The work conducted by Singh et al. (A.N. Singh et al. 1974) using gas-liquid-chromatography (GLC) isolated the methyl ester formates of the pure resin component of shellac, in order of its prevalence (in weight to area ratio) as Butolic acid, Aleuritic acid, Shellolic acid, Laksholic acid, Epi-shellolic acid, Epi-Laksholic acid, and Epi-laccishellolic acid (**Table 2**) (Nayak and B. Singh 2007).

Original Compound	Primary Products of Hydrolysis	Secondary Products of Hydrolysis
Jalaric Acid	Epishellolic & Shellolic Acids	Epilaksholic & Laksholic Acids
Laccijalaric Acid	Epilaccishellolic & Laccishellolic Acids	Epilaccilaksholic Acid

Table 2: Hydrolytic reaction products of shellac resin components (A.N. Singh et al. 1974).

Mills and White (Mills and White 1994), however, suspect that the presence of Shellolic, Laksholic, Epi-shellolic and Epi-Laksholic acids are all formed when Jalaric acid has been exposed to alkali materials for a prolonged period and are likely the reaction products of saponification (Mills and White 1994, 117).

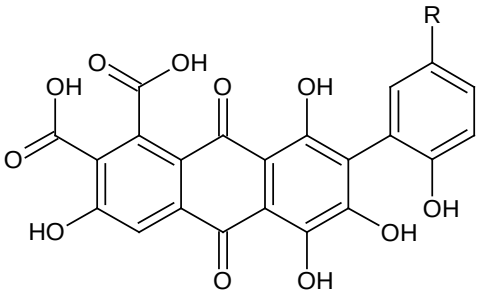
Indent? As shellac ages, it has been found that there is an increased variability in the primary constituents of the resin due to cross-linkage and enhanced polymerization, particularly in the hydroxyl aliphatic and sesquiterpenoid acids of the hard resin component, further increasing its insolubility (Colombini, Bonaduce, and Gautier 2003). As the aldehyde groups are easily oxidized to carboxylic acid groups, more free-hydroxyl groups become available for further esterification and thus, cross-linking (Mills and White 1994, 117). Fresh shellac is generally soluble in both ethanolic solutions and aqueous solutions of alkali salts, though the shellac seems to show greater stability when applied in solution of the latter (Sontaya Limmatvapirat et al. 2004). Pyrolisis (Py) assisted silylation-GC-MS patterns of aged shellac were very similar to those of fresh shellac particularly as concerns the butolic acids, while the aleuritic acid component showed an increase in the abundance of the aleuritic acid derivatives (Colombini, Bonaduce, and Gautier 2003).

2.2 Lac Dye

As it has been stated in the previous section, the acidic constituents of lac dye account for 1-8% of the composition of unrefined shellac. Lac dye is composed of three

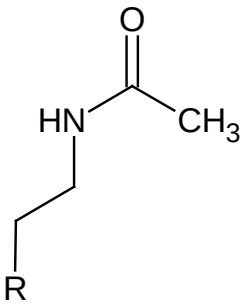
main constituents: laccaic acid, anthraquinone and erythrolaccin (**Figure 3**). According to Wouters (2007), laccaic acids are known to be soluble in relatively polar organic solvents, such as alcohols, while erythrolaccin is soluble in the former, but not the latter. Lac is a fugitive and highly light sensitive dye; without the addition of a polyvalent metal ion with which to form a coordinated organometallic complex, referred to as a 'mordant' (Baker 1958), the dye remains water-soluble and fails to bond with a given substrate.

The affinity of the lac dye with a specific metallic cation is directly related to the valency of the cation in question, as well as to the pH of the dye in solution. Trivalent and bivalent metal cations will tend to complex more easily and more strongly, for instance, than monovalent cations. Based upon the work of Svoboda et al. (2008) and Kongkachuichay et al. (2002), it appears that in the case of the white ground ceramics, it is the O-H functional groups of the laccaic acid that are forming an organometallic complex with the calcium and potassium cations naturally present as impurities in the ceramic body (**Figure 4**). When the lac dye comes into contact with the ceramic substrate, the previous studies (M. Svoboda, Tsatsouli, and Eng 2008; M. Svoboda 2007; Scott, Drolet, and Blaik 2010; Scott 2010) have shown that it is likely to form calcium salts and chelates to calcium ions through the phenolic hydroxyl groups, acting as a mordant (**Figure 5**) (Bremner 2007).

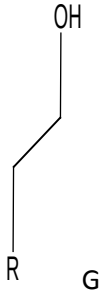


Laccaic Acid – Base Molecule

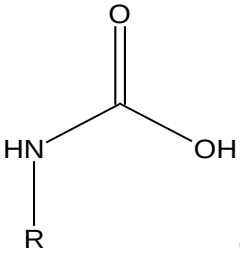
Functional Groups:



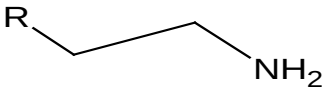
Group A



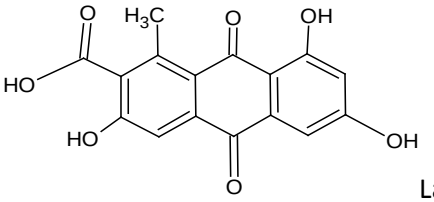
Group B



Group C



Group E



Laccaic Acid D

Figure 3: Molecular structure of Laccaic acid (A-E) (Cardon 2003).

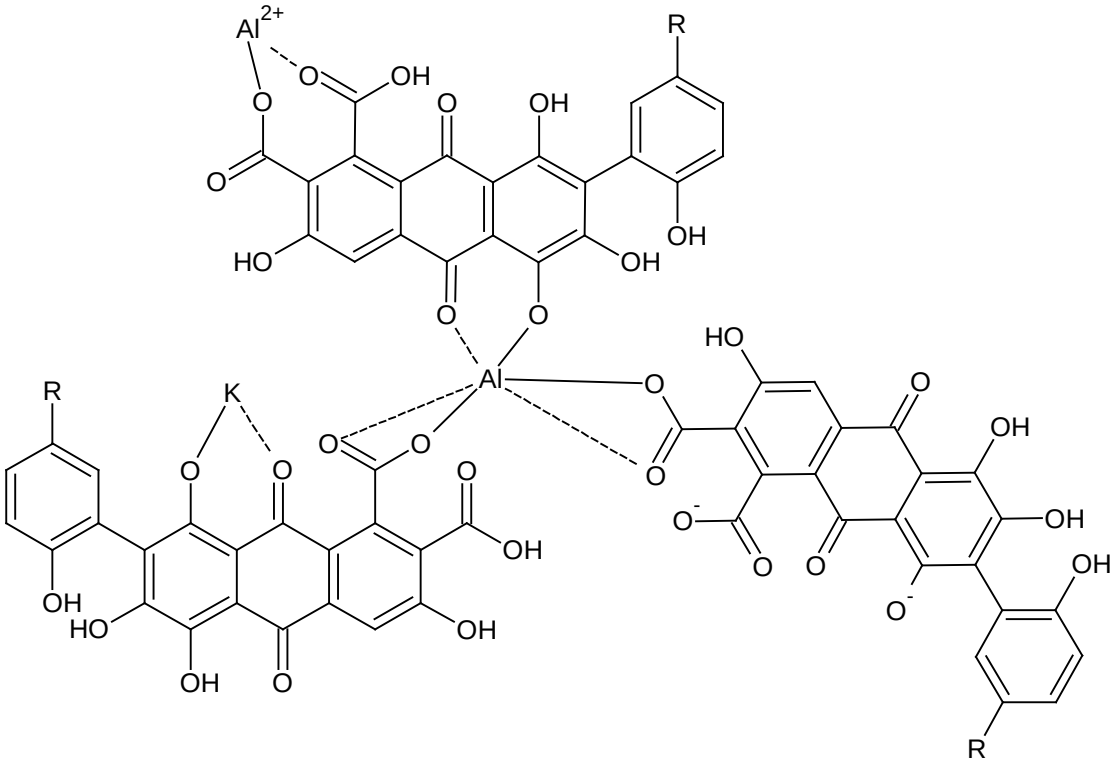
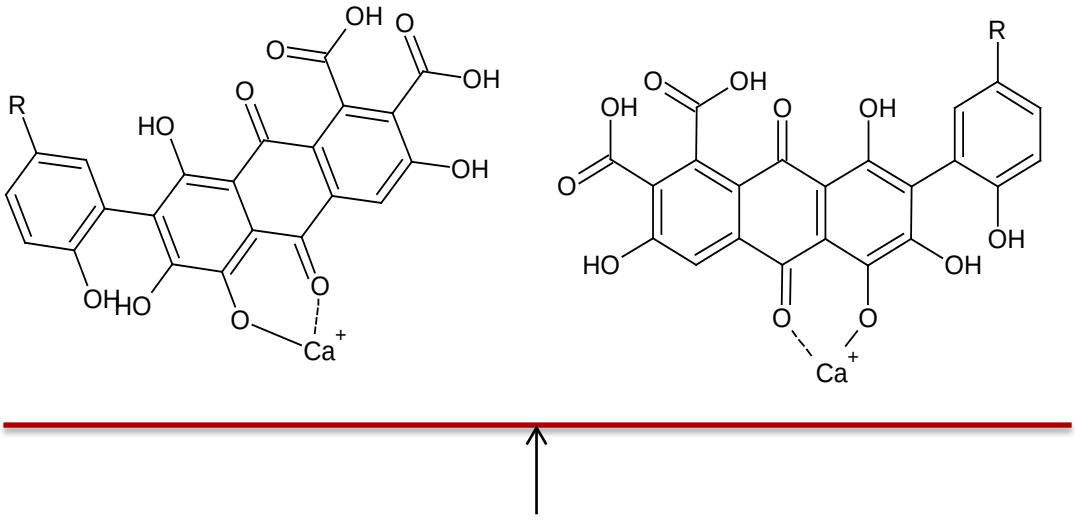


Figure 4: Proposed chemical structure of laccaic acid/metallic cation complexing (based on (Baker 1958)



Ceramic

Substrate

Figure 5: Proposed chemical structure of mordanted lac dye to the surface of the ceramic (highly schematic)

When the complex occurs, the dye undergoes a bathochromic shift, in this case causing the lac dye to change from a pinkish-red color, to a darker purple color (**Figure 6**). The reason that the dye undergoes a bathochromic shift appears to be related to the pH of the laccaic acid. Like its anthraquinone-type cousin alizarin, lac is a pH indicator dye; that is to say, as protons are donated or accepted by conjugated bonds of the molecule, there is an alteration of the chromophoric structure of the dye resulting in a change in the molecule's ability to absorb electromagnetic radiation (Tímár-Balázsy and Eastop 1998, 97).

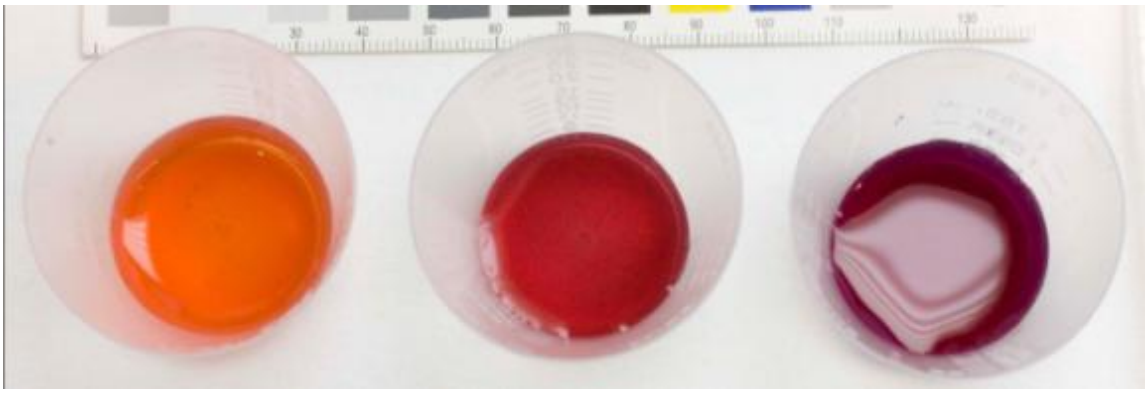


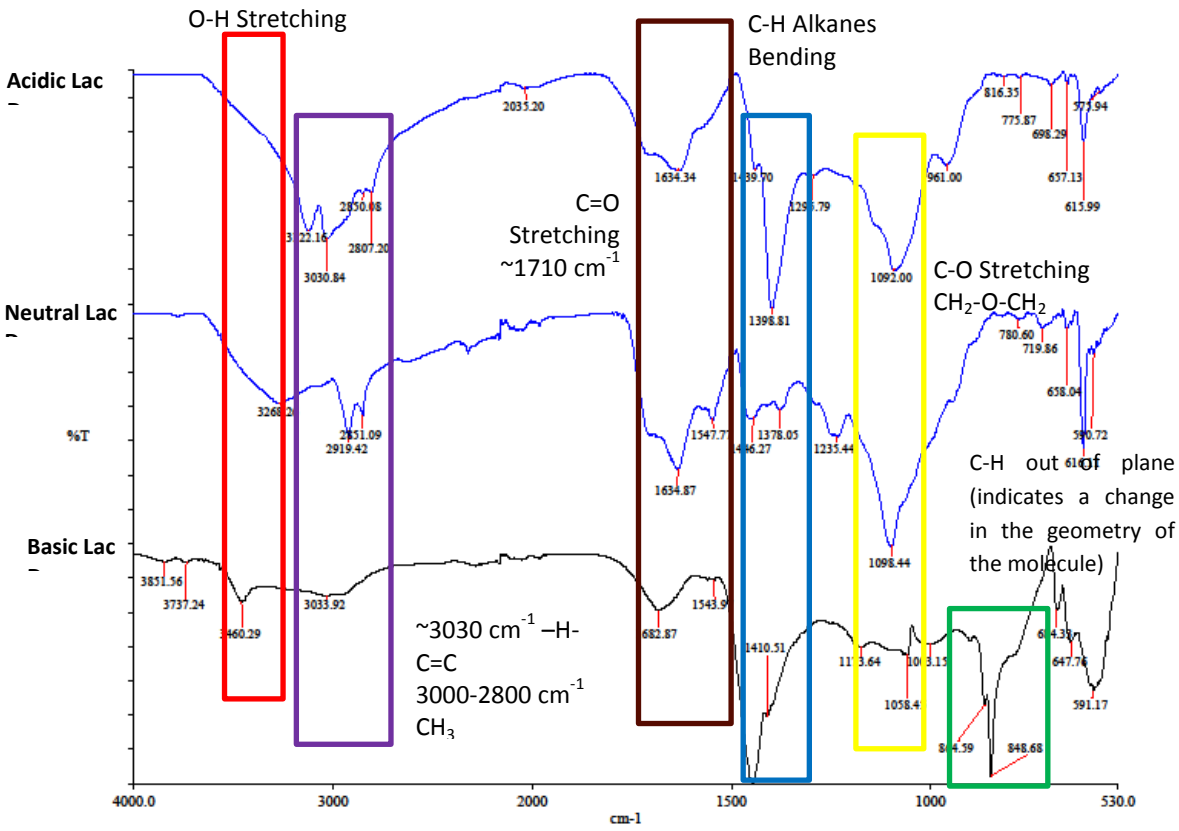
Figure 6: Lac dye extracted from seed lac in deionized water. From left to right, the dye was buffered to a pH of 2 by adding a few drops of 3M HCl, left neutral at a pH of around 7, and to a pH of 13.5 by adding a few drops of 5M NaOH.

Throughout experimentation, which will be discussed in greater detail below, samples of extracted lac dye were exposed to small[11] amounts of 3M hydrochloric acid (HCl) and 5M sodium hydroxide (NaOH). Using these solutions, it was found that although the dye initially turned purple in the presence of an alkali; it rapidly lost its color entirely, leaving a clear and colorless solution after a matter of a few days. According to Bremner

[11] The acidic and basic solutions were added to the dye using a pipette until the color change occurred – usually only two to three drops were required.

(2007), the changing pH of the lac dye can cause bathochromic shifts over a range of 2.5 to 11, and denatures the dye beyond these ranges. Therefore, the use of NaOH at a pH 13.5 would cause a breakdown of the dye at the molecular level via the same mechanism that the shellac is hydrolyzed. Fourier-transform infrared spectroscopy showed a change in the overall geometry of the lac dye molecule when exposed to high alkalinity that is likely related to the breakdown of the molecule in the presence of NaOH (**Spectrum 1**). Though the exact nature of the changes to the geometry of the lac dye molecule are not yet fully understood, they appear to affect the alkane structure of the molecule, predominantly, though a significant change to the C-O structures of the molecule have also been noted.

At the acidic end of the spectrum, there is a bathochromic shift towards the orange end of the visible spectrum, with FTIR showing changes to the alkane structures of the molecule, though to a far lesser extent than in the case of high alkalinity. Little change was noted with respect to C=O and C-O bands.



Spectrum 1: FTIR Spectra of Lac Dye at three different pHs. The pH of the lac dye was buffered to pH 2 using 3M HCl acid, and to pH 13.5 using 5M NaOH. All three samples were desiccated prior to testing. Areas in boxes indicate areas of changes that occur to the molecular structure of the polyesters and other components of the shellac as it ages.

Chapter III: Experimental Materials and Methodologies

This chapter explores the physical and chemical properties of the materials used in the experimentation process for this study. These materials include the clay substrates, poultice supports, alkaline solutions and the methods for the construction of test tiles.

The second component of this chapter looks to the experimental process itself. For the purposes of this study, it can be divided into three major trial types. The first set of trials were conducted on artificially aged test tiles made in the lab in order to establish workable and efficient methods for removing shellac without damaging the porous substrate. The second set of trials were conducted on fragments of an Apulian red-figure ceramic restored in the early 1820s to test only methods that were deemed successful and appropriate based upon results from the test tiles. The third and final set of trials addressed the question of the lac dye staining based upon observations of the dye behavior during the first rounds of testing. These last trials sought to better understand the effect of pH on the behavior of the dye with respect to its ability to form an organometallic complex. The results of these final experiments were assimilated to further our understanding of how and why the dye adheres to a porous substrate, allowing us to further refine our methods for preventing such staining while still successfully removing the shellac from which it comes.

For clarity, the trials have been numbered sequentially through all three experiments in order to avoid repeated numbers, and thus, avoiding confusion in the data and the results. In this way, the test tile trials are numbered 1-4, the object based trials are numbered 5-10, and the dye trials are numbered 11-13.

The experimental design used herein was based upon the findings of those studies discussed in the previous sections, particularly the works of Limmatvapirat et al. (Sontaya Limmatvapirat et al. 2004) and Colombini et al. (Colombini, Bonaduce, and Gautier 2003). In the first two trial sessions, the aim is to test the potential of using alkaline reagents, with and without the addition of solvents on ceramics, previously mended with crude shellac, to achieve the hydrolysis of the polyester resin component through solubilization and removal of the reaction products in a controlled fashion.

Due to space constraints, the detailed experimental notes can be found in **Appendix 7**. Only the most relevant data will be addressed directly here, with the methods and materials being summarized in tabular form below.

3.1 Materials

3.1.1 Seed Lac/Stick Lac/Button Lac

For this project, three types of unrefined shellac were used, all obtained from Kremer Pigments: stick lac[12], seed lac[13] and button lac[14]. In order to be used as an adhesive, these three types of unrefined shellac were prepared and applied in a total of eight different varieties. As such, the test tiles created were divided into eight equal groups and numbered according to their respective adhesive material and method (**Table 3**). For this part of the study, only tiles from groups 7 and 8 were used.

[12] Kremer Pigments 60430: Stick-Lac, unrefined Shellac
[13] Kremer Pigments 60490: Seed Lac, Crude Shellac
[14] Kremer Pigments 60500: Button Lac, Shellac, India

3.1.2 Clay Substrates

Test Tiles

The tiles (5 x 5 cm) used in the experimentation of this study were made using a terracotta body (5-7 mm thickness), which were then coated with layer (1 mm thickness) of batanas[15] clay. The tiles were fired in a Barnstead Thermolyne 1500 furnace, at 900 °C in about one hour and fifteen minutes, after which the tiles were left for thirty minutes at this temperature. These tiles were then broken using a mallet and mended using eight varieties of shellac, as described in the section above.

After application of the shellac, the tiles were aged in front of a window that allowed for the exposure of the tiles to ultraviolet energy by means of a lengthy exposure to sunlight. To amplify the effect, the tiles were placed on a board that was lined with aluminum foil; this was intended to both amplify the light exposure, as well as to increase the amount of heat produced by the direct sunlight. The tiles were left on the windowsill for six months.

Batanas

In order to test the various materials and treatments for this project, as in the 'Lac Dye' study, a series of test tiles were created; these tiles consist of a terra-cotta ground with a white ground slip. The white ground used in both of these studies is the same as that used in the study by Svoboda and the JPGM and similar to the original white slip found on Greek lekythoi (M. Svoboda, Tsatsouli, and Eng 2008) .

[15] Batanas is an aluminosilicate mineral with various metallic impurities from Greece, which is the closest match to the composition of Greek lekythoi slip with respects to its metallic cationic impurities.

This aluminosilicate mineral (clay), or 'batanas', was obtained from the Hellenic Clay Center (M. Svoboda, Tsatsouli, and Eng 2008). Chemically, batanas is a 1:1 kaolinite clay, which means that it is composed of one tetrahedral sheet bound to one octahedral sheet (Rice 1987). Generally speaking, kaolinite clays are relatively stable at low pH levels and are synthesized under equal concentrations of Al^{3+} and Si^{4+}. Since clays selectively adsorb ions, trivalent ions tend to be adsorbed more strongly than bivalent ions through isomorphic substitution[16]. Some of the most common cations include Ca^{2+}, Mg^{2+}, H^{+}, K^{+}, NH_4^{+}, and Na^{+} (Rice 1987) (**Table 3**).

Svoboda et al. (2008) conducted X-Ray fluorescence (XRF) analysis using a handheld X-ray Analyzer by Innov-X Systems using a tantalum source on a number of white grounds including pure kaolin tiles, the original Berlin lekythos, and the batanas. Both the Berlin lekythos and the batanas were found to have more than 5% of calcium and 1-5% of potassium, while the kaolin tile was found to have only 0.1-1% of calcium and an equal amount of potassium (**Table 1**).

[16] Isomorphic substitution is the process by which ions are selectively adsorbed by the clay to satisfy broken bonds on the edges of clay particles, or through the exchange of ions in the lattice structure or cleavage planes of the surfaces in the octahedral layer (Makes 2006).

Clay	Manufacturer/Distributor	Composition	
Leukos – White Clay Batanas (ΜΠΑΤΑΝΑΣ)	Hellenic Clay Center S.A. 55 G. Lyra Kifissia 14564 Greece	Chemical Analysis: SiO_2 61.23% Al_2O_3 17.90% Fe_2O_3 0.96% TiO_2 0.40% CaO 5.91% Mesh Size: <100 Colour: White Mineralogical Analysis: Kaolinite Quartz Feldspar $CaCO_3$ $MgCO_3$ Colored Oxides Other Oxides	MgO 0.73% K_2O 1.68% Na_2O 0.61% LOI 10.57% Shrinkage: 9% 38.20% 33.50% 15.10% 10.60% - 1.40% 0.70%
Terracotta Sculpt. Ceramic Blend	Laguna Clay Company City of Industry, CA 91746	Specific Gravity: 1.7-3.7 Mineralogical Analysis: Quartz 29% Talc 32%	

Table 3: Chemical composition of the clay materials based on product manufacturer information

The importance underlined by these differences is in the behavior of the lac dye. The stain formed on the batanas was insoluble and appeared firmly attached to the slip as was also with the case of the original lekythos. In contrast, the stain was readily removed from the kaolin substrate (M. Svoboda, Tsatsouli, and Eng 2008). Further analysis using X-ray diffraction (XRD) identified quartz in the batanas clay, while the kaolin tile was found to contain quartz and microcline, a potassium aluminum silicate (M. Svoboda, Tsatsouli, and Eng 2008). The surface pH of both fired clays were also assessed and found to be quite alkaline for the batanas (pH 11) and significantly closer to neutral (pH 8) for the kaolin (M. Svoboda, Tsatsouli, and Eng 2008). The surface alkalinity of the tiles will be discussed at greater length below.

For the Lac Dye project, FTIR spectra of the batanas clay, both fired and unfired, were taken using an FTIR-Perkin Elmer Spectrum One spectrometer equipped with an ATR-Crystal. Scans were taken between 4000.00 and 530.00 cm^{-1} at a resolution of 4.00 cm^{-1} and 128 scans. These parameters were used to increase the signal to noise ratio sufficiently to discern any small changes that could occur indicating either the formation of an organometallic complex during treatment, or other physicochemical changes on the ceramic substrates as a result of residual shellac or the treatment itself.

The important FTIR bands expected for an aluminosilicate clay are represented in **Table 4:**

Band (cm^{-1})	Assignments
3696.7	Al---O-H stretching
3622.5	Al---O-H (inter-octahedral)
3450.4	H-O-H stretching
1633.4	H-O-H stretching
1033.3	Si-O-Si, Si-O stretching
914.5	Al---O-H stretching
790.9	Si---O stretching; Si-O-Al stretching; (Al, Mg)---O-H. Si-O-(Mg, Al) stretching
693.4	Si-O stretching, Si-O-Al, stretching

Table 4: Important IR bands of clay and assignments [23].

Aluminosilicates embody the larger family of clays to which kaolinite and the batanas belong. The FTIR spectra obtained during the course of this study support the findings from the XRF and XRD in addition to giving a baseline from which to judge any changes from either the treatment, or the introduction of the lac dye. Bands at 3720.12 cm^{-1} and 3505.31 cm^{-1} correspond with the Al---O-H stretching bands (Nayak and B. Singh 2007), as do the very strong Si-O-Si stretching band at 1047.03 cm^{-1}; the medium intensity Si---O stretching and Si-O-Al stretching doublet band at 790.50 cm^{-1}; and the weaker peak at

689.49 cm^{-1}, which relates to the Si-O and Si-O-Al stretching bands (Nayak and B. Singh 2007).

In addition to the characteristic aluminosilicate bands, two C-H alkane stretching bands were assigned on the unstained batanas sample spectra at 2978.72 cm^{-1} and 2893.61 cm^{-1}. These bands have not yet been attributed to a specific compound, but seem to be due to organic impurities in the clay that are either inherent or external contaminants.

3.1.3 Support Materials

Based on preliminary results from previous work on the 'Lac Dye' project (Scott, Drolet, and Blaik 2010), the un-buffered Carbopol 934 gel and the Pappina wax emulsion were chosen as supports for the alkaline solutions. In this instance, the Pappina emulsion was left in its alkaline form without the addition of HCl as used by Kakoulli and Hodgins for neutralization (Kakoulli and Hodgins 1997). In addition to these two supports, agar was also added to the list for testing purposes in order to investigate the possibilities of a new rigid gel in cleaning, previously explored by Cremonesi (Paolo Cremonesi 2010). The use of support materials was pivotal to these trials as they played a crucial role in the application and performance of the treatment. Their use helped to: (1) improve the application and performance of the treatments by having more control over wetting; (2) control the depth of diffusion of the reagent; (3) regulate the rate of evaporation; (4) adjust and improve the contact with the surface; (5) control the time of action and (6) allow for localized controlled application as a part of a target delivery system.

Carbopol

Carbopol 934 is a commercially produced polymeric acrylic acid gelling agent (Stavroudis and Blank 1989, 6; Wolbers 1989) that has been used since the 1980s in conservation to thicken both aqueous and solvent solutions (**Figure 7**). The early work by Wolbers (Stavroudis 1990) found that by gelling organic solvent mixtures, the properties, in terms of handling, solubility, contact time, evaporation rate and control could be modified or enhanced.

In order to be used as a gelling agent, however, the acrylic acid groups in Carbopol must be compatible with the liquid, particularly with respect to polarity: the polarity of the final solvent solution must be in keeping with the polarity of the Carbopol itself, often requiring the addition of neutralizing agents, particularly for very polar organic solvents (Stavroudis 1990; Stavroudis and Blank 1989, 6). Additionally, if the Carbopol is not soluble within the solvent system, the Carbopol itself will "precipitate out of the solution as a sticky, white, stringy residue" (Stavroudis and Blank 1989, 7).

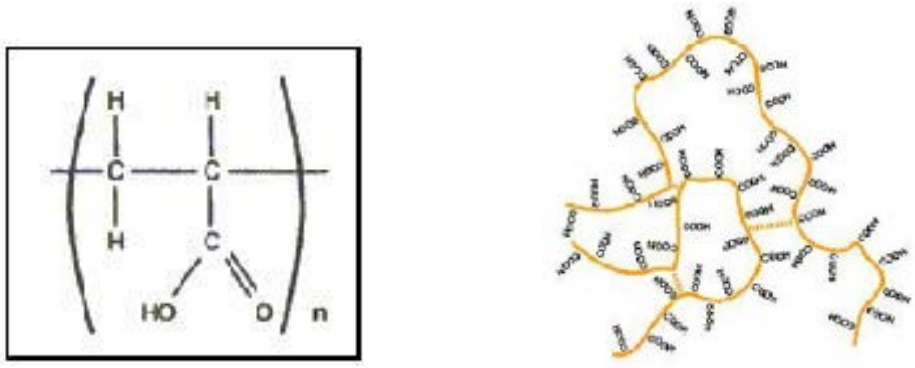


Figure 7: General structure of Carbopol polymer (right) and schematic drawing of a molecular segment of a cross-linked polyacrylic acid polymer (left) (Hosmani 2006).

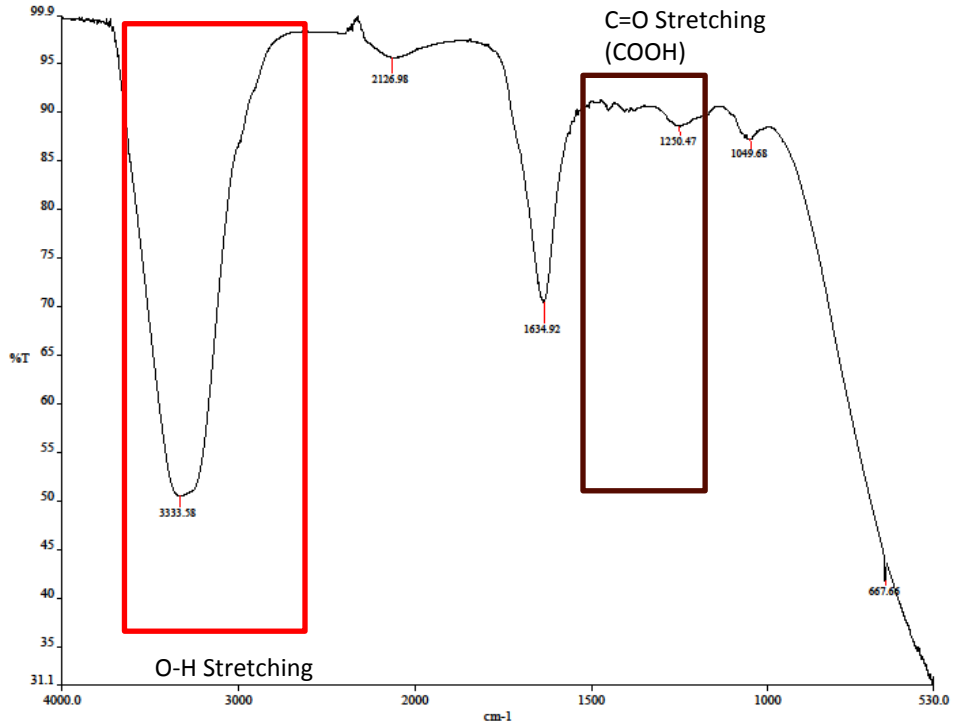
As a gelling agent, Carbopol was used in two distinct ways in this study. During trials conducted on fabricated test tiles, the Carbopol was used as a gel support for the

chosen alkali salt, in this case, sodium hydroxide (NaOH). In this case, the gel was prepared according to the instructions given by the distributor on the material's container[17]; a 6% w/v concentration of Carbopol in deionized water was gelled, after which a 2% w/v solution of NaOH was added in a drop-wise fashion until a pH of 13.5 was achieved.

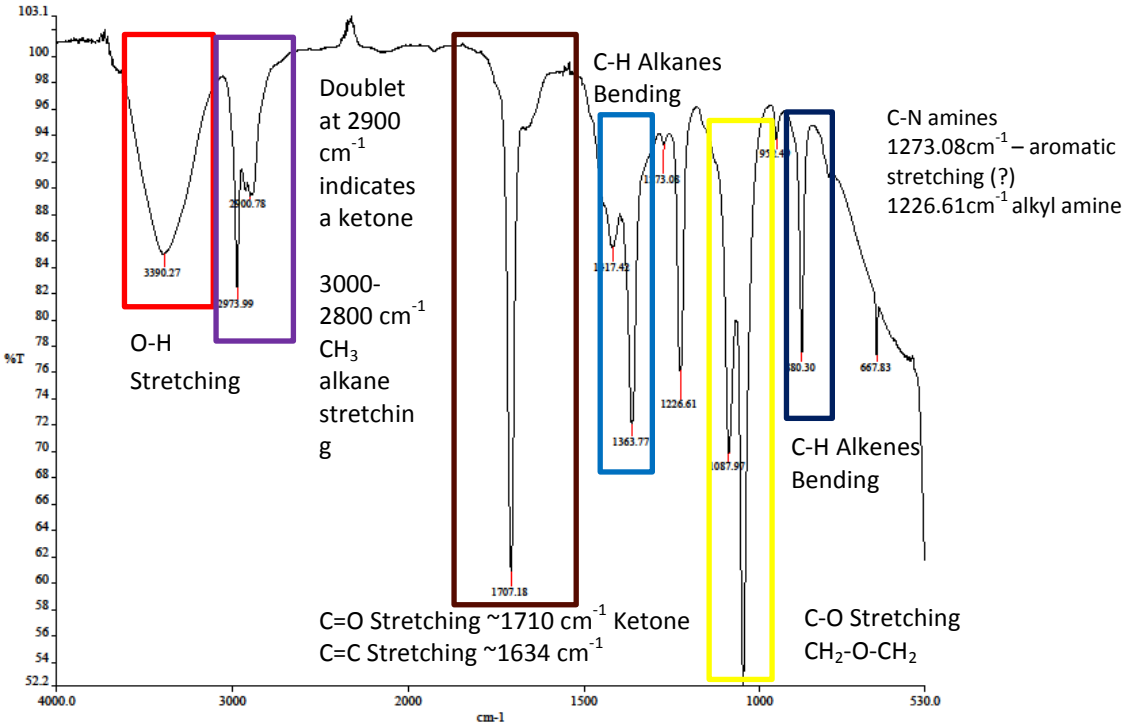
In addition to its use as a support for alkali salts, Carbopol was also employed as a solvent gel according to a recipe given by Richard Wolbers. This mixture involved a 1:1 (v) solvent solution of ethanol and acetone; Ethomeen C-25 (a tertiary amine ethoxylate) used as a surfactant and thickening and buffering agent; and a small amount of water. The exact formula and methods used in this study are included in **Appendix 2**.

The solvent gel formulation of Carbopol was used only on trials conducted on fragments of the Apulian vessels currently on loan to the JPGM in order to compare the efficacy of the methods in current use with those explored by this study. FTIR spectra for both Carbopol prepared only in deionized water (**Spectrum 2**) and Carbopol prepared as a solvent gel (**Spectrum 3**) were run to establish a baseline to assess clearance (total removal) after treatment.

[17] For the un-buffered Carbopol 934, the recipe was as follows: Carbopol 934 – 6g; Deionised water – 100mL.



Spectrum 2: FTIR spectrum of Carbopol 934 prepared as a 6% w/v mixture in deionized water. Significant o-H peaks and COOH peaks are clearly visible and expected of a polyacrylic acid in water (spectrum is neither baseline corrected nor smoothed).

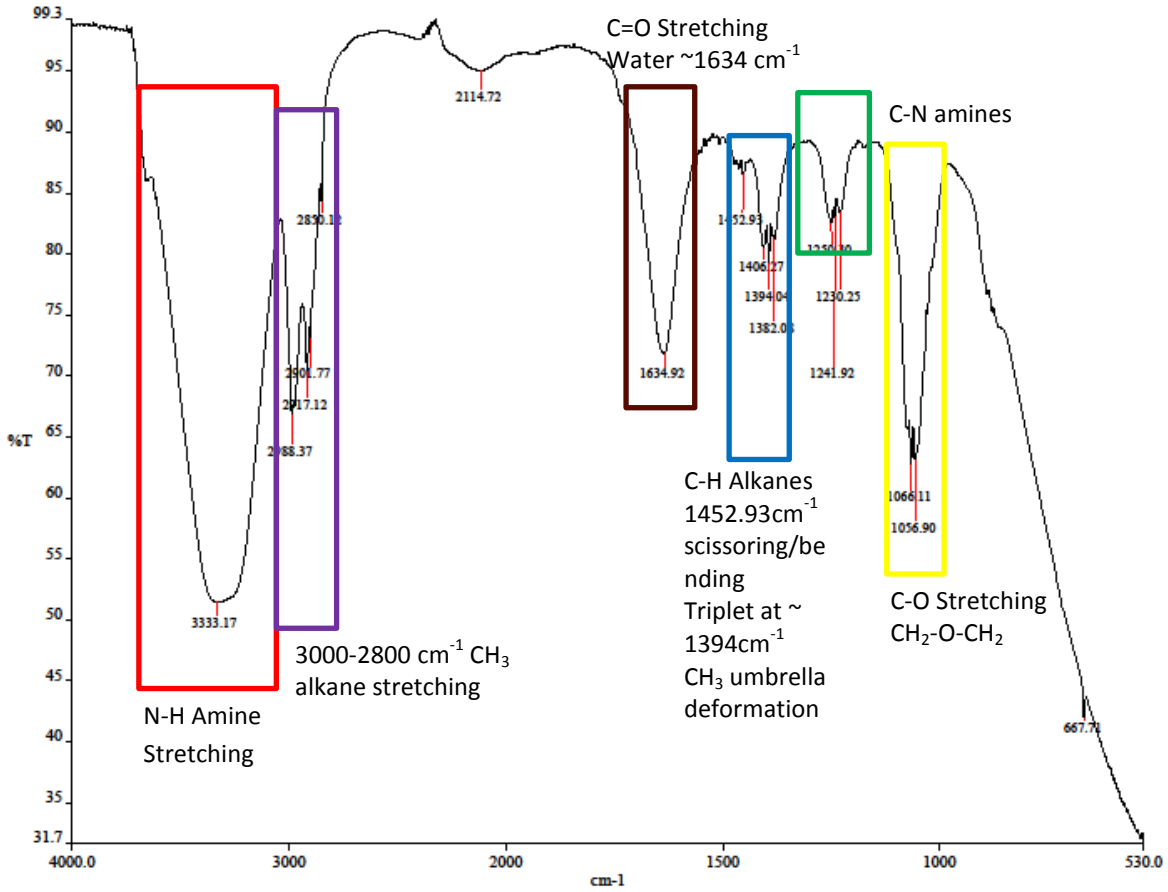


Spectrum 3: FTIR spectrum of Carbopol 940 prepared as a solvent gel using a 1:1 mixture of acetone and ethanol, deionized water and a surfactant, Ethomeen C-25.

Pappina Wax Emulsion

The Pappina wax emulsion is a complex mixture of ammonia solution, stearic acid, and bleached beeswax in deionized water[18]. The use of Pappina has been seen more frequently in the conservation of easel and canvas paintings but has also employed in wall paintings (Kakoulli and Hodgins 1997; Curteis 2002b)(Curteis 2002a). Unfortunately, little is published on this support, particularly in terms of its clearance and interaction with porous surfaces, and even less in English. In its application to porous substrates in this study, however, there have been problems with clearance of waxy residues, which are particularly harmful if they are buffered to the high pH necessary for the experiments explored in this study. The FTIR spectrum for the Pappina wax emulsion (**Spectrum 4**) was run to establish a baseline for clearance assessment after treatment.

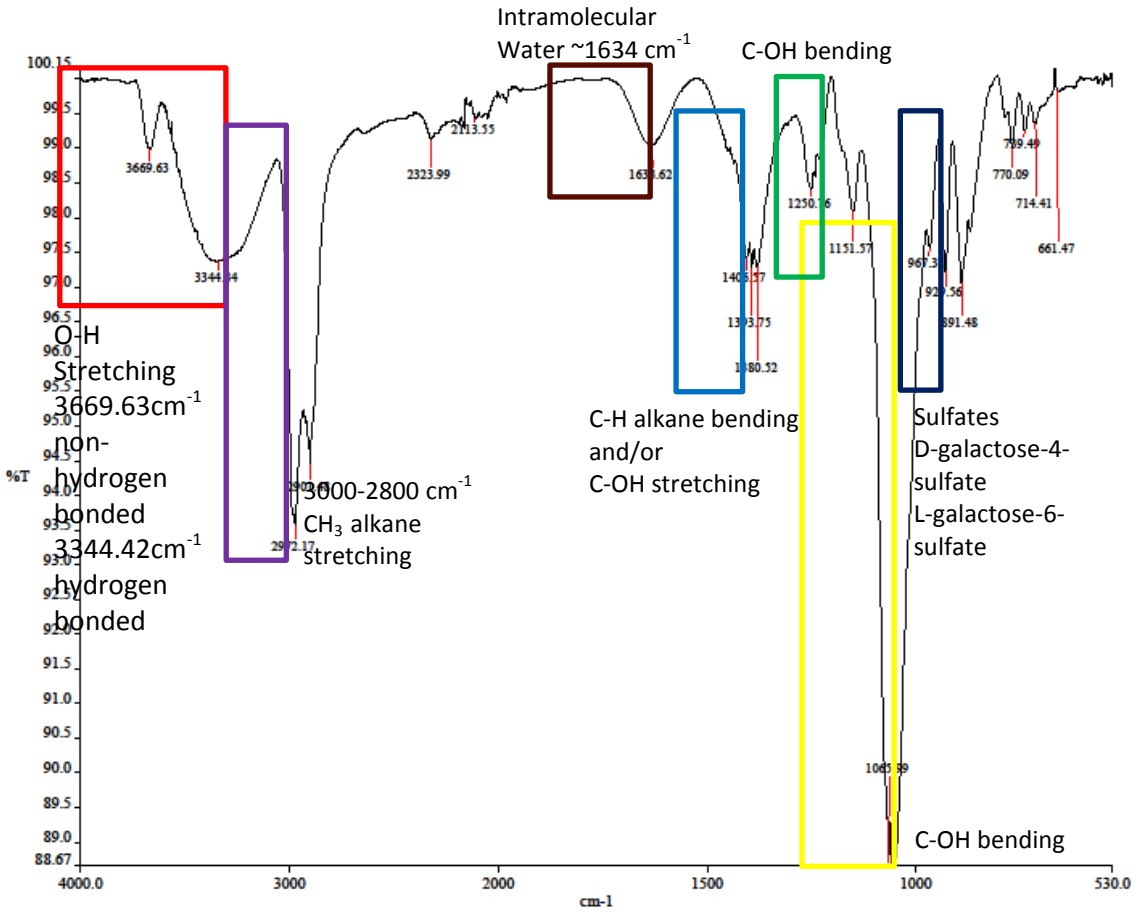
[18] The recipe used to prepare the Pappina Neutra is as follows (Kakoulli and Hodgins 1997): Stearic acid BDH 0.2 g; Ammonia solution 28%: 4 ml; Bleached beeswax 100 g; Deionised Water 150 ml.



Spectrum 4: FTIR of Pappina wax emulsion prepared using bleached beeswax, stearic acid and NH_3.

Agar/Agarose Rigid Gel

Agar, or agarose, is a rigid gel derived from the cell walls of a species of red algae of the *Gelidium* family (Davidson and Jaine 2006). It is primarily composed of the linear polysaccharides agarobiose and agaropectin consisting of D-galactose and 3,6-anhydro-L-glactopyranose (**Figure 8**)(Chaplin 2009). In addition to the main saccharide polymer chains, the gel also contains sulfate, pyruvate, and other methyl groups (Anzani et al. 2010, 42); their presence is visible on the FTIR conducted on dry powdered samples of the agar used for this study (**Spectrum 5**).



Spectrum 5: FTIR Spectrum for agarose powder used to mix the agar gel used in this study.

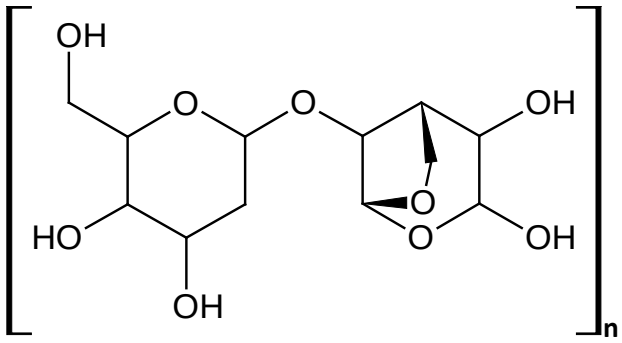


Figure 8: General structure of agarose polymer

Although agar is insoluble in cold water, it dissolves in boiling water and has a melting point of 85°C, which allows for the easy reheating and re-melting of the pre-

prepared gel in the microwave. The gelling of agar occurs after a separation process following cooling at approximately 35°C. Some 99.5% of the water used in the preparation of the agar remains in the solid media up to its melting point (Chaplin 2009; Anzani et al. 2010, 42). Though the gel can retain an enormous quantity of water, it can also subsequently release it through a phenomenon known as 'synerisis' (Anzani et al. 2010, 42).

The works of Cremonesi (Paolo Cremonesi 2010) and Anzani et al. (Anzani et al. 2010 (2010) explored the use of this rigid gel on three-dimensional works, since in the past it had typically been used on flat works in paintings and paper conservation; the rigid nature of the gel had typically prevented its use on other types of materials. Experiments in the application of the agar gel during its cooling phase as a semi-solid gel allowed for its application on a new category of materials.

Additionally, Anzani et al. (Anzani et al. 2010) have found that, unlike Carbopol gels (Wolbers 1989; Wolbers 2000), the agar does not tend to change the hygroscopicity of the porous substrate after treatment, and, in fact, shows no observable interaction with the treated surface including signs of erosion or residual polysaccharide materials (Anzani et al. 2010, 35). After the agar gel has cooled, the removal of the gel is simple and complete. Any residues, which show a fluorescent pale whitish color under UV light (λ_{exc}=365 nm), tend to separate naturally from the support after the water has evaporated completely from the sample; this tendency has been reported in previous studies (Cremonesi 2010; Anzani et al. 2010) and was observed during experimentation for this study.

Though all previous works in conservation using agar have used the gel mixed only in water and strictly as a carrier for water, its use in this study has shown distinct promise

as a support substrate for both solvents and alkaline materials. Furthermore, agar gel acts as a 'molecular sponge' in that it absorbs "from the support any materials dissolved by contact with the [gel]" (Anzani et al. 2010, 35). The regularly shaped cavities of the elastic colloid are of a sufficient size to allow for the absorption and diffusion of relatively large molecules (Anzani et al. 2010, 42). These qualities, in addition to its ease of removal favored the use of this gel medium over both the Carbopol and the Pappina wax emulsions for use in testing trials in this study.

For the test trials conducted in the course of this study, two different mixtures of agar were prepared. The first mixture, henceforth referred to as **Agar #1**, involved heating the powdered agar[19] in a 2 % (w/v) aqueous solution of sodium hydroxide (NaOH) in order to ensure a good distribution of the OH- ions throughout the gel. In order to gel the agar, it must be heated to near boiling temperature, after which, it is removed from the heat and allowed to cool. The heating process can be conducted on a hot plate or in a microwave. For this particular agar, a hot plate was chosen given the caustic nature of the solution. However, the heat required for gelling to occur caused a discoloration of the gel that had been buffered to a high pH prior to heating; this lead to staining of the tiles and will be discussed in greater detail below, but it necessitated a different approach for increasing the pH of the gel.

In the second variation, referred to as **Agar #2**, the gel was heated, again on a hot plate, using only the powdered agar and deionized water, in a 4 % w/v concentration. After removing the gel from the heat, a concentrated solution of the base (20 % w/v) was

[19] The ratio of powdered agar to aqueous solution was 4% (w/v) as suggested by the work of Cremonesi (Paolo Cremonesi 2010).

added drop-wise until the gel attained the desired alkalinity. This was found to mitigate the discoloration significantly while also allowing for the easy reheating of the gel in the microwave as needed for future applications.

Later trials, which introduced acetone and ethanol to the agar, in addition to the NaOH used a more concentrated agar, using 7% (w/v) in deionized water. This allowed for the addition of significant amounts of solvent without losing the gelling properties of the agar. As both of these solvents are highly flammable and have low flashpoints, they are added only to the gel after it has been heated, just prior to its application. Agar combined with solvents should not be reheated and can still be used as a rigid gel, though its efficacy is reduced through the loss of contact with the ceramic substrate.

3.1.4 Alkaline Solutions

Despite the inherent complexity and variation in the chemical structure of shellac (Schaeffer and Gardner 1938; Colombini, Bonaduce, and Gautier 2003), as mentioned above, the primary molecular backbone forming 70% of the resin, is a polyester. As discussed in the previous chapter, though shellac has shown a tendency to be resistant to solvent dissolution, it should be possible to hydrolyze the ester backbone by means of saponification, or de-esterification. Based on the work by Limmatvapirat et al. (Sontaya Limmatvapirat et al. 2004), sodium hydroxide (NaOH) was selected as one possible alkali for this study, though it is a very strong base. Due to its high alkalinity and the potential to form NaCl or other damaging salts when in contact with archaeological materials, used on its own and in an uncontrolled fashion, it is, in most respects, not an appropriate

conservation material and its use will require refinement in order to be used in such a form.

In order to explore the possibility of using a milder base, or one that is less likely to leave residues or cause damage to the ceramic substrate, particularly during a prolonged treatment time, a number of other alkaline materials were also tested; these included a 28% (v/v) solution of ammonium hydroxide with a ~pH12, saturated solutions of ammonium carbonate with a ~pH10, and calcium hydroxide, at a ~pH 12. The results of these experiments will be discussed below.

3.2 Trials Conducted on Test Tiles (1-4)

In preparing the test tiles for use in Trials 1 through 4, eight different shellac mixtures were used to mend the tiles after breaking (**Table 5**).

Tile Group #	Material and Preparation (100mL total)	Method of Application (brush)
1	Seed Lac (20% w/v in ethanol)	Mixture heated and applied hot
2	Button Lac (20% w/v in ethanol)	Mixture heated and applied hot
3	Stick Lac (20% w/v in ethanol)	Mixture heated and applied hot
4	Seed Lac (20% w/v in ethanol), Cellulose Pulp[20] (3.5g)	Mixture applied cold
5	Seed Lac (20% w/v in ethanol), Lead White[21] (10g)	Mixture applied cold
6	Seed Lac - aged 2 years (20% w/v in ethanol)	Mixture heated and applied hot
7	Seed Lac (20% w/v in ethanol)	Mixture applied cold
8	Seed Lac –aged 2 years (20% w/v in ethanol)	Mixture applied cold

Table 5: Materials and methods of application for shellac adhesives

Ultimately, the tiles prepared using mixtures 4 and 5 were not tested on for this study as they introduced too many new variables. Moreover, the tiles prepared using button and stick lac shellac were not tested either, as those mended using the seed lac mixtures were sufficient in number for the trials conducted here. There was no visible difference between

[20] Whatman – Fibrous Cellulose Powder CF11
[21] Kremer Pigments: Lead White

the observable behavior of tiles mended using either cold or hot shellac, though in their assembly, it was easier to mend the tiles with the heated shellac as it had more tack.

Tiles created for the 'Lac Dye' study in 2010 (Scott, Drolet, and Blaik 2010) were used in Trials 3 and 4. These tiles were prepared using a mixture of seed lac in ethanol (20% w/v); the shellac was applied to the surface of unbroken tiles using a dropper. These tiles had not been useful for the previous study because the application of shellac was too thick. They were, however, ideal here, as the surface-applied shellac allowed for adequate visual assessment of a treatment's efficacy.

The progression of experimental methods from one trial to the next was predicated upon the results from each previous trial. For example, the most successful solution from Trial 1 was incorporated into Trial 2, though the methodology or method of application would be modified or refined.

Experimental observations from Trials 1-4 have been summarized in **Table 6**. All images for the experiments carried out on test tiles can be found in **Appendix 3**.

Materials	Methods	Trial #	pH	Observations/Results
Sodium Hydroxide (2% w/v in deionized water)	Soaking – 24 hours	1	13.5	Joins separated after 12 hours Total hydrolysis of shellac after 24 hours
Ammonium Hydroxide (28% w/v)	Soaking – 48 hours	1	12	Joins separated after 36 hours Shellac residues remained after 48 hours
Ammonium Carbonate (20% w/v in deionized water)	Soaking – 48 hours	1	10	Shellac darkened in color Joins did not separate without mechanical action after 48 hours
Sodium Hydroxide in Pappina wax emulsion	Full application covered in plastic wrap – 72 hours	2	12.5	Shellac swelled after 7 hours – joins did not separate
	Localized application covered in plastic wrap using Japanese tissue paper (JTP) as an intermediary layer – 72 hours	2	12.5	Shellac swelled after 7 hours – joins did not separate
Sodium Hydroxide in Agar #1 **(When agar is heated in the presence of NaOH, the gel turns greenish-black)**	Full application – applied in semi-solid cooling phase – 48 hours	2	13.5	Shellac swelled after 25 minutes. Joins separated after 24 hours
	Localized application – applied in semi-solid cooling phase – 48 hours	2	13.5	Shellac swelled after 25 minutes. Joins separated after 24 hours
	Localized application – applied in semi-solid cooling phase using a JTP intermediary layer – 48 hours	2	13.5	Shellac swelled after 25 minutes. Joins separated after 24 hours.
	Localized application – applied as cool rigid gel – 48 hours	2	13.5	Shellac swelled after 30 minutes. Joins separated after 24 hours.
Sodium Hydroxide in Carbopol 934 (gel prepared 6% in deionized	Localized application covered in plastic wrap – 24 hours	2	13	Shellac swelled in 10 minutes Tile began disintegrated after 24 hours.

water)				
Sodium Hydroxide in Agar #2	Localized application – applied in semi-solid cooling phase – 48 hours	2	13.5	Shellac swelled in 10 minutes. Joins separated after 24 hours.
Calcium Hydroxide in Agar #2	Localized application – applied as a rigid gel (addition of $Ca(OH)_2$ immediately caused the gel to solidify) – 48 hours	2	13.5	Shellac swelled after 24 hours. Joins did not separate after 48 hours.
Sodium Hydroxide in Agar	Localized application using a JTP intermediary layer – applied in semi-solid cooling phase – 72 hours	3	12	Shellac swelled after 20 minutes. Joins did not separate
Sodium Hydroxide in Agar	Localized application using a JTP intermediary layer – applied in semi-solid cooling phase – 72 hours	3	10.5	Shellac swelled after 35 minutes. Joins did not separate
Sodium Hydroxide in Agar + 1:1 Ethanol and Acetone	Application to surface-applied shellac – treating only one half of the tile. Applied in semi-solid cooling phase – 24 hours	3	13.5	-Removal of most of the visible shellac though in areas with thicker amounts, removal was incomplete -Deep purple stain after treatment
Sodium Hydroxide in Agar + 1:1 Ethanol and Acetone	Application to surface-applied shellac – treating only one half of the tile. Applied in semi-solid cooling phase – 24 hours JTP intermediary layer used	4	13.5	-Removal of most of the visible shellac though in areas with thicker amounts, removal was incomplete -Deep purple stain after treatment (though stain appears lighter than in trial without JTP, owing perhaps to additional absorption of dye into the tissue paper).
Sodium Hydroxide in	Application to surface-applied shellac –	4	13.5	-Some removal of surface shellac, though poor

Agar + 1:1 Ethanol and Acetone	treating only one half of the tile. Applied as a cooled, rigid gel – 24 hours			surface contact is evident. -Purple staining after removal of shellac
Sodium Hydroxide in Agar + Acetone	Application to surface-applied shellac – treating only one half of the tile. Applied in semi-solid cooling phase – 24 hours	4	13.5	-Good reduction of visible shellac -Purple staining after removal of shellac
Sodium Hydroxide in Agar +Ethanol	Application to surface-applied shellac – treating only one half of the tile. Applied in semi-solid cooling phase – 24 hours	4	13.5	-Near complete removal of visible shellac -Light purple staining after removal of shellac
Agar + 1:1 Ethanol and Acetone	Application to surface-applied shellac – treating only one half of the tile. Applied in semi-solid cooling phase – 24 hours	4	7	-No observable changes after 24 hours. -No color change -Shellac remains intact.

Table 6: Summary of experimental methods, materials and observations for Trials 1-4.

3.3 Trials Conducted on Apulian Ceramic Fragments (5-10)

It was possible to test some of the more effective trials on shellac from a series of Apulian red-figure fragments[22]. These vessels had been restored in Italy in the early 19th century using a shellac mixture that the restorer referred to as 'colla'. Research conducted by the JPGM has determined the components of the 'colla' to include unrefined shellac, lead white, lead chromate, cinnabar, alunite and tephra (Svoboda 2011). The 'colla' was first created in 1820 and the vessels were restored prior to 1826, which allows for a very specific date for the shellac, making it an ideal sample on which to test.

[22] Ongoing collaborative project between Berlin and the JPGM.

After disassembly of the vessels, many the fragments still have extensive shellac residues on their break edges, allowing for some preliminary testing to be conducted. Though all of the solutions tested as a part of this study are highly alkaline, spot tests have shown that the Apulian clay is unaffected by such treatments in the short term. In an effort to mitigate any possible damage from the treatment, trials conducted on these vessels are kept to a minimum amount of time, with treatments being applied for only 1 to 2 hours, rather than the longer and more aggressive treatments used on the test tiles. Also, as the fragments are to be fully desalinated through prolonged submersion after treatment, there are little to no issues of salt formation from the treatments.

All images for the experiments carried out the Apulian fragments can be found in **Appendix 4**.

3.4 Lac Dye Trials (11-13)

As it was stated above, the goal of these three short trials was to better understand the behavior of the lac dye component as pertains to its capacity to form organometallic complexes with the ceramic substrate in correlation to its pH and the bathochromic shift it undergoes as it complexes and in response to changes in the pH.

It was noted in the course of experimentation to remove shellac via alkaline hydrolysis that the lac dye component shift in color from red to a deep and highly saturated purple. The increased visibility of the lac dye at high pH initially caused concern for an increase in discoloration to the ceramic substrate than the lac dye was already creating at a more neutral pH of 7. This became particularly problematic during trials using sodium hydroxide in agar gel, where a dark purple stain remained on the surface after the shellac

had been successfully hydrolyzed. Previous trials that involved immersion of test tiles in a solution of 2% (w/v) NaOH in deionized water showed no signs of staining, However, it was initially posited that at high pH, the lac dye remained water soluble and that, so long as the dye was not re-absorbed into the ceramic substrate, but rather stayed in solution, it would not stain the tile. As the initial trials using the agar gel tended to use only a single application, it appeared that the dye would be reabsorbed into the ceramic substrate once the gel had become fully saturated, indicating the need for frequent removal and reapplication of the gel poultice.

Unfortunately, though this theory seemed sound, once the dye, even at a high pH, had been absorbed into the ceramic substrate, it was equally difficult to remove as the neutral lac dye, and more so, did not respond to those treatments that were found to be successful in the 'Lac Dye' study for reversing the organometallic complex.

Experimental observations from Trials 11-13 have been summarized in **Table 7**. All images for the experiments carried out on test tiles can be found in **Appendix 5**.

Lac Dye	pH	Treatment	pH	Duration	Observations
Acidic (Trial 11) 	2	Water soak	6.7	24 hours	-When rubbed with a cotton swab in deionized water no changes in color noted on the tile. Some purplish pink on the swab, but it's particulate in nature and is likely a combination of uncomplexed lac dye and the ceramic fabric itself detaching from the surface of the tile from exposure to acidic lac dye. -When soaked in water for 24 hours there was no appreciable change in

					color.
Neutral (Trial 11) 	7	Water soak	6.7	24 hours	-When rubbed with a cotton swab in deionized water no changes in color noted on the tile. A significant amount of pink on the swab, but it's particulate in nature and is likely the ceramic fabric itself detaching from the surface of the tile the staining process. -When soaked in water for 24 hours there was no appreciable change in color or reduction in the staining.
Basic (Trial 11) 	13.5	Water soak	6.7	24 hours	-When rubbed with a cotton swab in deionized water no changes in color noted on the tile and no dye noted on the swab. -When soaked in water for 24 hours there was no appreciable change in color.
Acidic (Trial 12) 	2	2% w/v NaOH soak	13.5	24 hours	When rubbed with a cotton swab in 5M NaOH the dye on the surface of the tile darkened slightly (staining with acidic lac dye already created a fairly dark purple stain). A very small amount of dye was present on the swab After soaking in NaOH for 24 hours the surface of the tile had gone from purple to a dingy grey color.
Neutral (Trial 12)	7	2% w/v NaOH soak	13.5	24 hours	When rubbed with a cotton swab in 5M NaOH the dye on the surface of the tile darkened from pinkish-red to purple and the swab

					showed significant transference of the dye to the cotton. When soaked in 0.5M NaOH solution for 24 hour, the shellac in the joins hydrolysed and the tiles came apart. The treatment appears to have lessened the staining from the dye, but the tile has taken on a greyish color, even after 24 hours in deionized water to clear residual alkaline materials.
Basic (Trial 12) 	13.5	2% w/v NaOH soak	13.5	24 hours	When rubbed with a cotton swab in 5M NaOH the dye on the surface of the tile remained unchanged in color and there was a very small amount of dye transferred to the swab itself. When soaked in NaOH for 24 hours, the shellac in the joins hydrolysed and came apart. The treatment appears to have reduced the staining somewhat, though 24 hours after staining the tile showed very little evidence of the purple dye present before immersion.
Acidic (Trial 13) 	2	3M HCl soak	2	5 minutes	When rubbed with a cotton swab of 3M HCl the stain was instantly lightened to a very pale pinkish yellow. Because lac dye turns orange/yellow when its pH is lowered, the dye visible as transfer on the swab was very pale orange/yellow in color, but it was visible. Soaking in HCl caused an immediate reversal of the

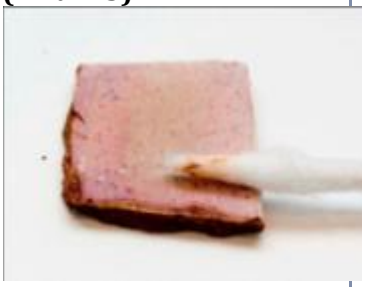
					stain and the tiles were removed and placed in water after only 5 minutes. After treatment and drying, the surface of the tile has a dingy and dark appearance.
Neutral (Trial 13) 	7	3M HCl soak	2	5 minutes	When rubbed with a cotton swab 3M HCl the stain was instantly reduced from the surface of the tile. Soaking in HCl caused an immediate reversal of the stain and the tiles were removed and placed in water after only 5 minutes. After treatment and drying, the surface of the tile has a dingy and dark appearance.
Basic (Trial 13) 	13.5	3M HCl soak	2	5 minutes	. When rubbed with a cotton swab of 3M HCl the stain was instantly lightened to a very pale pinkish yellow. Because lac dye turns orange/yellow when its pH is lowered, the dye visible as transfer on the swab was very pale orange/yellow in color, but it was visible. Soaking in HCl caused an immediate reversal of the stain and the tiles were removed and placed in water after only 5 minutes. After treatment and drying, the surface of the tile has a dingy and dark appearance.

Table 7: Methods, materials and observations of Trial 11-13

3.5 Assessment

In order to fully assess and evaluate the cleaning methods explored in the context of this study, criteria for judging the suitability of the methods and materials with respect to

the safety of the object being treated were created. Criteria for a successful treatment are as follows:

1. Surface contact of the treatment
2. Penetration and diffusion
3. Efficiency of the treatment
4. Physical effect on the treated surface
5. Chemical effect on the treated surface
6. Clearance

The evaluation of these criteria to evaluate not only the success of the treatment but also the degree of success (whether removal of the shellac was total, or partial) included a visual assessment at multiple scales from the macroscopic to the microscopic level under diffuse light and using ultraviolet-visible fluorescence photography. All imaging of test tiles was conducted using a Spex MiniCrimescope equipped with a tunable light source. The ideal excitation wavelength for the three materials listed above was found to be provided by the 300-400nm filter (λ_{exc}=365 nm). Visible fluorescence imaging of the Apulian fragments tested in Trials 5-10 was conducted using a handheld UV-lamp capable of emitting both long wave and short wave ultraviolet light, though only the long wave was used here; it was not possible to ascertain the exact wavelengths emitted by the lamp, but the long wave emissions can be estimated at around 365nm based on manufacturer's specifications for similar handheld lamps. All images were captured in the visible spectrum

using an unmodified Canon Rebel XSi DSLR equipped with a visible pass the PECA 916[23] visible pass filter.

Fourier-Transform Infrared Spectroscopy was also used both to characterize the raw materials employed in this study, as well as to detect chemical changes or residues to the treated surface after treatment. All spectra were acquired using an FTIR-Perkin Elmer Spectrum One spectrometer equipped with an ATR-Crystal. Though it was possible to acquire spectra either in absorbance or in transmission mode, all samples were run in transmission mode. Scans were taken between 4000.00 and 530.00 cm^{-1} at a resolution of 4.00 cm^{-1} and 128 scans.

[23] The Peca #916 Visible Pass Filter only allows light in the 400-700nm wavelength with some small leaks in the IR range. The spectrum for this filter can be found in **Appendix 6**.

Chapter IV: Results

This need to identify innovative and previously untested methods and materials for the removal of crude shellac from porous substrates emerged from the limitations of more traditional methods, as well as the additional challenges that arose from the findings of the lac dye staining projects conducted by both the JPGM (M. Svoboda, Tsatsouli, and Eng 2008; M. Svoboda 2007) and students of the UCLA/Getty Conservation Program (Scott, Drolet, and Blaik 2010; Scott 2010).

It was the goal of this study to find a method to remove shellac from a porous substrate without solubilizing its lac dye component, resulting in an organometallic staining complex requiring additional, and often aggressive, conservation treatment in order to be cleared.

A theoretical solution to the stated problem comes in the form of a rigid gel, an alkali salt and a solvent material, the combination of which was shown to hydrolyze crude shellac without solubilizing the lac dye and allowing its diffusion and consequential complexing with the ceramic surface

4.1 Visual Assessment

The visual assessment of the efficacy of any given trial was based upon the following criteria: (1) the ability of the treatment to remove visible traces of shellac; (2) the amount of visible residue left of either the shellac, lac dye, or treatment materials after treatment; (3) the presence of physical change to the surface of the sample after treatment. Any changes in the surface texture, color, or cohesion after treatment are considered to be evidence of physical damage. Finally, the practicality of using the techniques explored in this study on ancient artifacts need also be considered.

4.1.1 Macroscopic Evaluation

Macroscopic evaluation of the efficacy of a treatment was conducted by establishing the following: (1) Did the treatment adequately remove or reduce the shellac?; (2) Did the treatment leave lac dye staining that could not be removed by immersing the tile in water?; (3) Were there any visible residues left on the surface of the tile from treatment materials?; (4) How easy was it to remove/clear the treatment?; (5) Were there any readily visible changes to the surface of the tile after treatment?; (6) Did the treatment show evidence of good contact with the area being treated?; (7) How long did the treatment require to effectively remove the shellac?; and (8) How easy was it to control the localization of the treatment?

None of the materials and methods tested on the fabricated tiles from Trials 1 through 4 provided completely satisfactory answers to all of these questions. In Trial 1, the most effective method proved to be the immersion of the tile in 2% (w/v) NaOH solution for 24 hours. Thus, it satisfied criteria 1 through 7, but the method of immersion did not allow for localized or controlled application of the treatment.

In Trial 2 the most efficacious treatments were those using a combination of sodium hydroxide and agar gel applied in its semi-solid cooling phase. When applied as a rigid gel, surface contact was generally poorer than when it was applied as a soft gel and removed after cooling. Treatments using Carbopol or Pappina were either extremely difficult to remove, leaving large deposits, or were extremely detrimental to the structure of the tile, causing it to disintegrate. As in Trial 1, NaOH was the most successful base used for the hydrolysis of the shellac. With respect to criteria 3 and 5, there did not appear to be any discolorations or residues from treatment with NaOH and agar gel, though the amount of

shellac used to mend these tiles was minimal and later trials showed that in cases of more heavy shellac deposits, the risk of staining and inadequate removal is significant.

In Trial 3 it was noted that a thick application of shellac posed an exponentially increased risk for staining residues, as evidenced on the tiles that had shellac applied to their surface, rather than those that had shellac in their joins. It also found that for every point on the pH scale that the treatment dropped, the treatment time required also increased exponentially. At a pH of 13.5, shellac hydrolysis was noted after only a few minutes, while at a pH of 12 and 10.5, very little hydrolysis had taken place after several days of treatment.

As in Trial 3, Trial 4 found that if the initial amount of crude shellac present is significant, extreme care must be taken to avoid migration of the lac dye into the substrate, even with solvents present. Despite the increased risk of solubilizing the lac dye and driving it further into the ceramic substrate, the presence of solvents in the gels did not show an increase in staining when compared with the results of Trial 3, which were conducted without the use in solvent. In fact, there was a reduction in discoloration when solvents were included, as long as the gel was changed with sufficient frequency; this allowed for the for solubilized lac dye to migrate into the gel, rather than into the ceramic.

In Trials 5 through 10, the most efficacious treatment was in keeping with the results of the first four test trials. A combination of NaOH, ethanol and agar gel, applied in its semi-solid state and removed shortly after cooling and gelling was complete, which ensured that the lac dye was not given the opportunity to migrate back into the ceramic substrate. Because these tests were conducted under severe time constraints, it was not possible to follow a treatment through to completion, and so, the most successful of these

trials, Trial 10, satisfied all the criteria save for the first, in that some shellac still remained visible on the fragment edge.

While collecting samples from the test tiles post-treatment for FTIR spectroscopic analysis, differences in the surface were noted with respect to the coherence and density of the surface after treatment; e.g. on the tiles in 3M HCl, scraping of the surface easily removed particles as it was considerably softened in comparison to the tile that was not exposed to an acidic environment. The surface of the tiles soaked in 2% (w/v) NaOH, however, had a harder and denser crust that was more difficult to collect a sample from. On the tiles treated using an acidic lac dye, the surface had also considerably softened, allowing for easy sample removal. This would seem to indicate a greater susceptibility of the batanas-coated surface to acid rather than alkaline materials, which showed a hardness and coherence equal or greater to untreated tiles.

Areas treated with the NaOH, ethanol and agar combo that had stained through improper clearance or post-treatment cleaning were extremely hard, almost as though there was a solid skin over the surface of the ceramic making it very difficult to collect a scraped sample, even using a fresh scalpel blade. This degree of surface hardness was not presented on untreated and unstained controls.

4.1.2 Microscopic Evaluation

Microscopic evaluation of materials after treatment was conducted only on the manufactured test tiles and not on the Apulian fragments due to time constraints. While at most optical microscopy was used as a confirmatory technique to support visual observations, it proved a useful and complementary method of assessment to observations

made at the macroscopic level with naked eye; particularly in the identification of crystals, possibly salts, post-treatment, and for the evaluation of minute changes to surface topography caused by exposing the ceramic substrate to high levels of alkalinity for extended periods of time. The issue of salts will be discussed at greater length in the next chapter, but it was possible to observe the presence of a crystalline substance that tested positive for chlorides[24], particularly on those tiles that were soaked in the NaOH solution (Trial 1).

With respect to changes in the ceramic's topography, it was found that for Trials 1 and 2, there were no observable changes to the substrate, while in Trials 3 and 4, particularly on tiles with a surface application of shellac, that insufficient clearance of the shellac or lac dye components, which are readily visible to the naked eye, prevented a conclusive assessment regarding any physical changes to the surface of the tiles.

4.1.3 Ultraviolet-induced Visible Fluorescence Photography

Ultraviolet-induced visible fluorescence was used to evaluate the efficacy of a treatment, as well as a means of assessing any residues remaining after treatment. This was possible because of the distinct fluorescence of shellac, lac dye and agar, wherein shellac fluoresces a distinct orange color, lac dye fluoresces in a more muted purple tone, and agar fluoresces a pale milky white (**Figure 9**).

[24] The exact procedure for chloride testing is discussed in section 5.4: Salts. Though these crystals were readily visible under a binocular microscope, they were not readily apparent in photographs and as such, the images have not been included here.

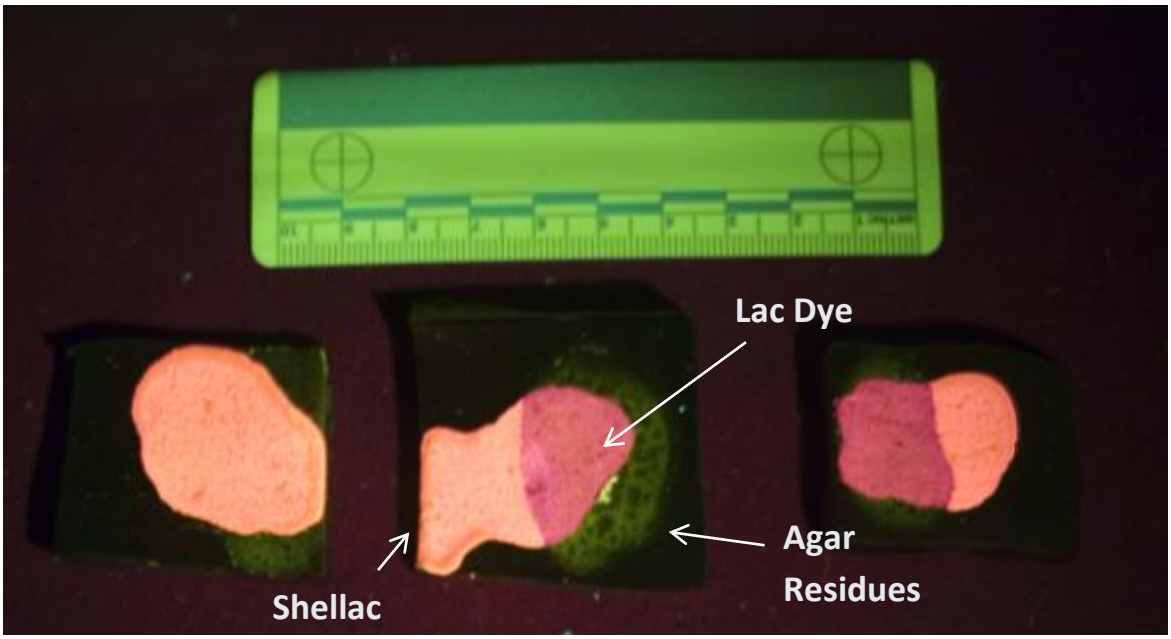


Figure 9: UV-induced visible fluorescence photograph (λ_{exc} = 300-400 nm) showing the distinct fluorescence of the lac dye, shellac and residual agar after treatment.

Ultraviolet-visible induced fluorescence was therefore used successfully to gauge the efficacy of a given treatment to remove or reduce shellac by comparing before and after images; the less orange visible after treatment, the more effective. In this way, it was found that immersion of shellac in a 2% (w/v) solution of NaOH for 24 hours (Trial 1) was the most effective at completely removing shellac without leaving post-treatment residues, as both the lac dye and the hydrolyzed shellac stayed in solution. Unfortunately, immersion treatment in such a highly alkaline environment is inappropriate for any conservation treatment as it can be aggressive and uncontrollable. With respect to more localized treatments, the combination of 5M NaOH in a mixture of agar gel and ethanol was found to have the greatest degree of shellac removal, especially after repeated applications.

In Trial 3, agar gel residues were found on the surfaces of treated tiles that had not received any additional treatment after the alkaline gel was removed for clearance. Tiles

that were soaked in deionized water for 24 hours after treatment did not show signs of residual agar. Because it is not always practical or possible to immerse ceramic fragments after treatment, a cotton swab soaked in deionized water was rolled across the surface of a treated fragment edge after treatment; no agar residues were visible under Ultraviolet-induced visible fluorescence after a few passes.

Ultraviolet-induced visible fluorescence photography of the tiles from Trial 3 as well as those from Trials 11-13 demonstrated that fluorescence could detect residual lac dye. On the white batanas-coated surface of the test tiles this was largely unnecessary as any lac dye residues were readily visible to the naked eye; when conducting tests on the red-bodied fragments of the Apulian fragments, however, this technique proved useful in distinguishing the presence of the pink dye on a similarly colored fabric after treatment. Initial trials, which tended to use fewer applications and the gels were left on for longer periods of time, showed that lac dye did tend to migrate back into the surface of the ceramic fabric. A change in application methods, as discussed in previous sections, seems to have alleviated this problem and residues appear to be reduced in ultraviolet-induced visible fluorescence.

4.2 Fourier-Transform Infrared Spectroscopy (FTIR)

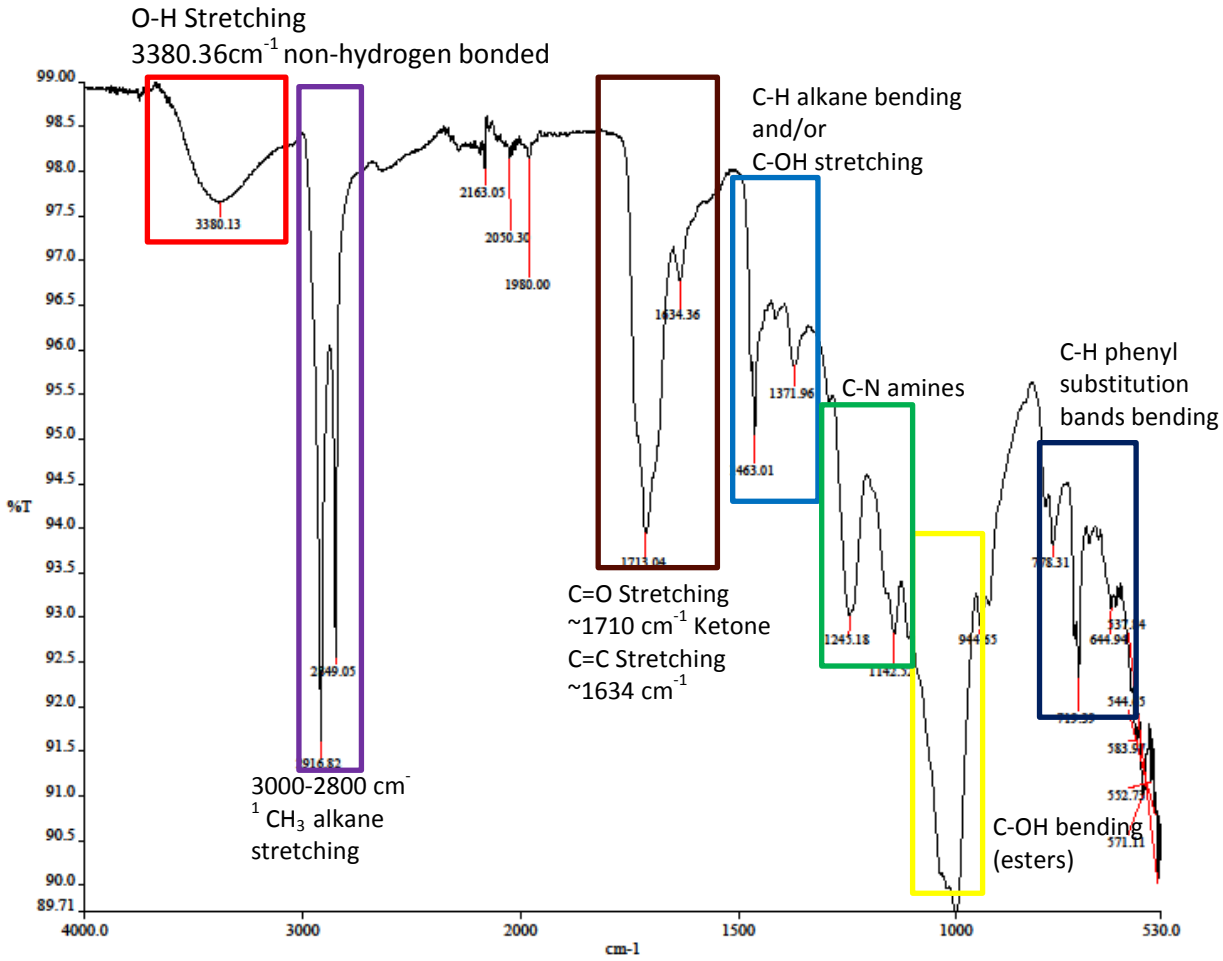
Fourier Transform Infrared Spectroscopy (FTIR) served a number of functions throughout this study: it was used for the initial characterization of many of the raw materials; it was used: (1) to better understand the chemical changes incurred by lac dye when exposed to acidic or alkaline conditions and (2) to ascertain whether any significant chemical changes took place as a result of the treatments undertaken herein, be it in the

form of residues or alteration of the substrate. FTIR spectroscopy was also used to help address the question of end products from the hydrolysis reaction.

Given the interpretative nature of FTIR spectroscopy, it must be understood that the results presented herein are in no way definitive. The data yielded by the FTIR spectra, in conjunction with other methods discussed above, are a useful gauge of the efficacy of a treatment based on analysis of the post-treatment spectra in comparison with those of the raw materials.

4.2.1 Materials Characterization

FTIR was performed on samples of shellac used during the testing phase of this project. Spectra were obtained from the crushed stick, seed and button lac, as well as the prepared crude shellac mixtures in ethanol. The spectra show, along with the significant laccaic acid peaks, additional bands from the waxes, resins and sugars associated with the production of the different types of shellac tested; these have not yet been fully identified (**Spectrum 6**).



Spectrum 6: FTIR spectrum of seed lac, crushed to a fine powder to ensure good contact.

Further interpretative FTIR work for the purposes of identifying shellac has not been pursued, as it is so easily identified non-invasively using UV(λ_{exc}=365 nm)-induced visible fluorescence imaging. With that being said, FTIR analysis conducted during this study identified peaks at c.1712 cm^{-1}, c.1633 cm^{-1}, c.1245 cm^{-1}, c. 945 cm^{-1}, c. 719 cm^{-1} and c. 649 cm^{-1}, in addition to the laccaic acid peaks, as being indicative of the presence of crude shellac or crude seed lac[25].

[25] These peaks have been identified on spectra run by the author on crude seed lac, crude shellac (80% w/v in ethanol) and on spectra of seedlac from the IRUG 2000 Database (INR00117 Seedlac, AF Suter, #4858, PMA, tran), and unrefined shellac (INR00069 Shellac, garnet, unrefined, AF Suter, BM, tran).

As a part of the investigation into molecular changes occurring in the shellac as it ages, FTIR[26] was run on four samples of prepared crude shellac. The first three samples were prepared in the lab using the same methodology though at different times. All three samples were made by mixing seed lac with ethanol at a concentration of 20% (w/v). Sample 1 was mixed one week prior to testing. Sample 2 was mixed one year ago as a part of the lac dye project that was conducted during the winter and spring of 2010 (Scott, Drolet, and Blaik 2010; Scott 2010). Sample 3 was mixed by Marie Svoboda in her lab during their own study in 2008 (M. Svoboda, Tsatsouli, and Eng 2008; M. Svoboda 2007) and donated to me for the purposes of experimentation during both the 'Lac Dye' study and this one.

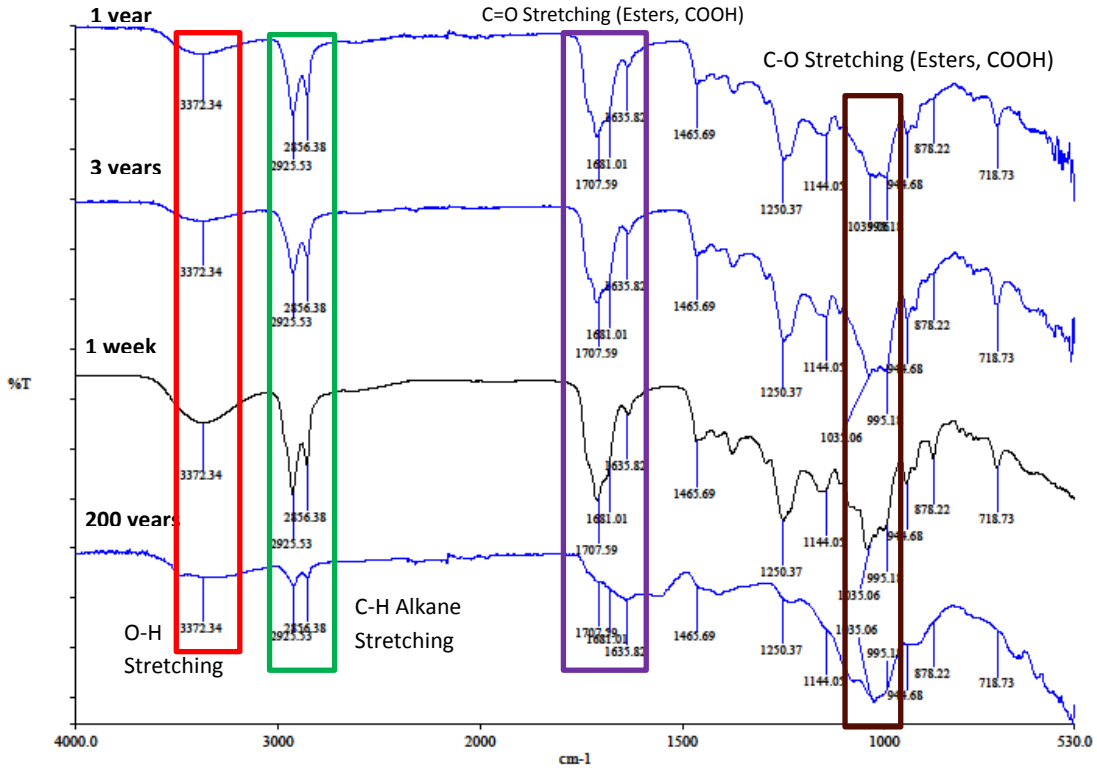
The final sample tested was collected from a series of Apulian red-figure ceramics currently on loan to the JPGM. Based upon the historical research conducted by conservators at the JPGM, it is likely that these vases were restored around 1820 by Italian restorer, Rafaelle Gargiulo, using his own patented 'colla', of which the largest constituent was shellac (Marie Svoboda 2011, 1). Care was taken when collecting samples for testing here to remove only from areas that appeared to be relatively pure shellac, though it must be noted that there are a certain number of unknown additives likely to be in the sample.

FTIR results show few changes in the spectra of the first three samples, particularly between Samples 2 and 3 whose spectra were nearly identical with exception of some minor changes in the number and intensity of peaks around 1150 cm^{-1}. The differences between Sample 1 and 2 are somewhat more significant, though still slight. Again, the

[26] FTIR was conducted on an FTIR-Perkin Elmer Spectrum One spectrometer equipped with an ATR-Crystal. Scans were taken between 4000.00 and 530.00 cm^{-1} at a resolution of 4.00 cm^{-1} and 64 scans.

doublet peaks at around 1150 cm^{-1} show some changes in the %transmission, while the triplet peaks around 1022 cm^{-1} also show changes in %transmission. The most significant change occurs around 879.50 cm^{-1}, where the peak attributed to C-H aromatic bending has either been severely attenuated or is being masked by other peaks in this area (**Spectrum 7)**.

The most significant changes, unsurprisingly, were found in the spectrum for Sample 4. In this sample, the C=O carbonyl stretching ubiquitous to shellac spectra at 1711.75 cm^{-1} is completely absent. Additionally, the C-H alkane bending peaks typically found between 1463 and 1444 cm^{-1} are also absent, as are the C-O ester bending peaks around the 1248 cm^{-1} range. Finally, there is a broadening and shift to the C-O ester and carboxylic acid stretching between 1100 and 1000 cm^{-1} (**Spectrum 7**).



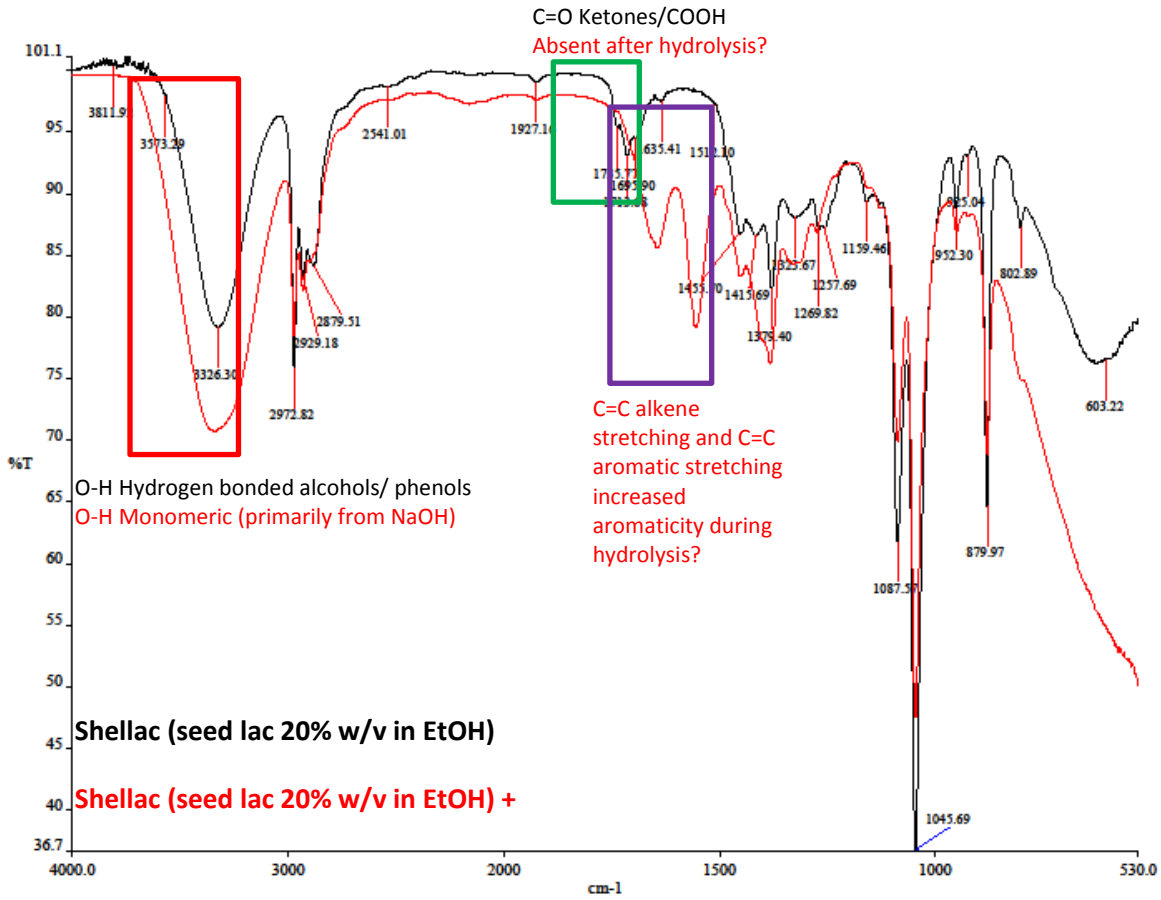
Spectrum 7: FTIR Spectra of Shellac ages 1 week, 1 year, 3 years and 200 years (natural ageing). Areas in boxes indicate areas of changes that occur to the molecular structure of the polyesters and other components of the shellac as it ages.

Preliminary analysis appears to indicate that during the first year of ageing, the most significant changes that occur in the resin occur in regions with C-O bonds, particularly those relating to carboxylic acids and esters, as well as in the region of C-H aromatic bonding. With respect to the drastic changes seen in the spectrum for Sample 4, we again see changes in those areas pertaining to esters and carboxylic acids. It is known that shellac cross-links as it ages, which would likely change the overall molecular configuration of its polyester backbone, but unfortunately, little research has been done to explore the exact nature of these molecular changes and it is beyond the scope of this study to fully explore this aspect.

FTIR was also conducted on two samples of shellac; while both samples were prepared by solubilizing seed lac in ethanol at a concentration of 20% (w/v), the second sample had a few drops of 5M NaOH added in order to begin hydrolysis. In order to give the reaction sufficient time to occur, both samples were allowed to sit in a dark, cool location for five days prior to testing. Results from the spectra indicate changes in the hydrolyzed sample to be most prevalent in the 1700-1350 cm^{-1} range, indicating significant changes to the carbon-oxygen carbonyl bonds, and the carbon-carbon alkene and aromatic bonds. In particular, there is a loss of the C=O stretching ketone peak at 1713.68 cm^{-1}, and a gain or increase of intensity of the C=C alkene and aromatic stretching peaks at around 1645 and 1455 cm^{-1}. It is also possible to see a reduction in absorbance of the C-O stretching ester peaks at 1087.57 and 1045.69 cm^{-1}, which is in keeping with the de-

esterification reaction theorized above, though the continued presence of the peaks, albeit reduced, shows that de-esterification is not complete. Further, the spectra do not show any absorption band shifts from the introduction of sodium salts, indicating that any post-treatment spectral shifts cannot be attributed to the introduction of sodium (**Spectrum 8**).

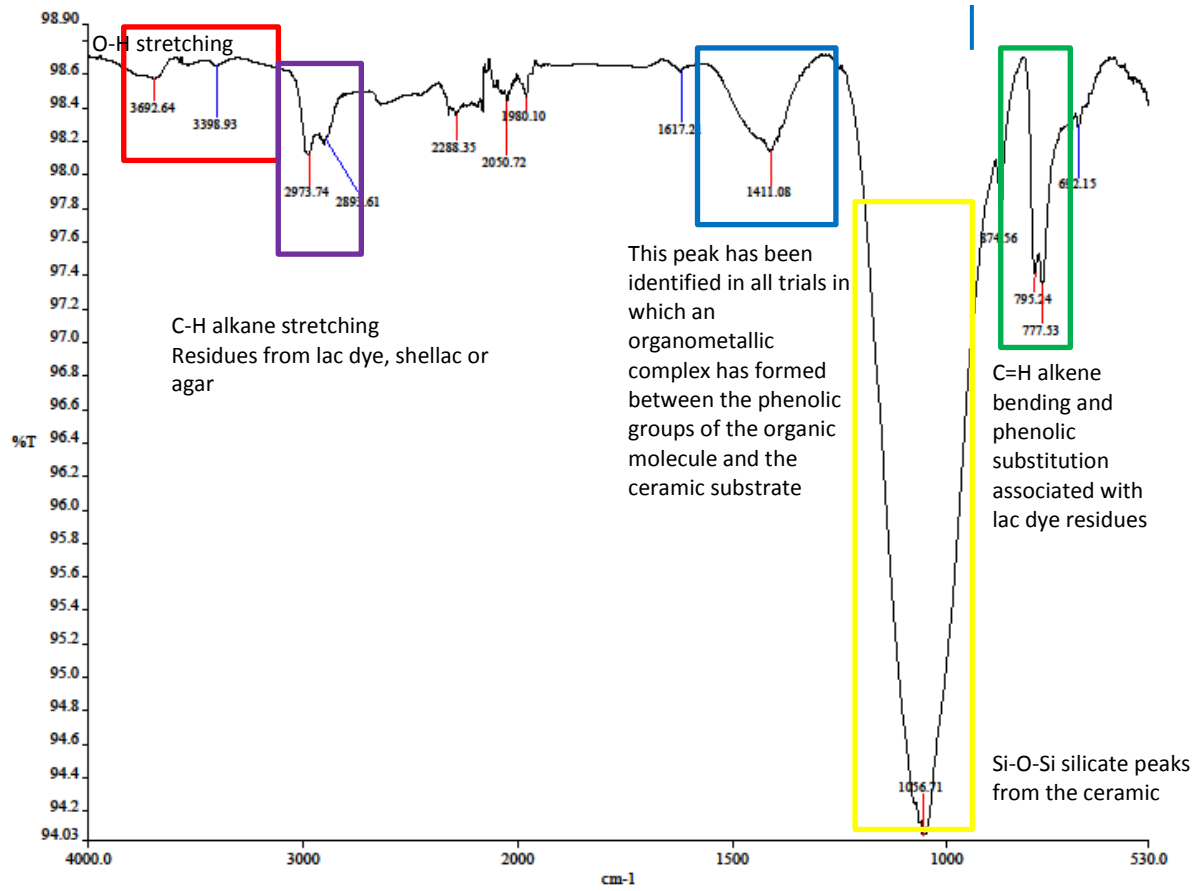
Additionally, FTIR conducted on lac dye samples that were buffered to different pH values has helped to clarify some of the structural changes occurring in the molecule in reaction to protonation and deprotonation of its functional groups. In particular, when the pH of the lac dye is raised significantly, there are some noteworthy changes to the molecular structure of the dye. It would seem then, that rather than suggesting that the dye cannot complex with the ceramic substrate when it is highly alkaline, rather, the dye is being hydrolyzed to a degree to which it can no longer act as a dye.



Spectrum 8: FTIR Spectra for Shellac (Seed lac 20% w/v in ethanol) and Shellac treated with 5M NaOH. Differences highlighted in boxes shows changes to the functional groups representing carboxyl groups, aromaticity, and hydrogen bonding of O-H groups through the Canizzarro hydrolysis reaction.

4.2.2 Post-treatment Analysis

Generally speaking, there do appear to be post-treatment residues, though it is difficult to distinguish what they are; this is further hampered by the fact that a full visual clearance of either the shellac, the lac dye or the treatment materials was never fully achieved. As such, residual peaks, particularly the C-H alkane stretching peaks around 2981 and 2890 cm^{-1} can be attributed to either residual shellac, residual lac dye, or to residual agar gel (**Spectrum 9**).



Spectrum 9: FTIR spectrum of a test tile from Trial 4 after treatment. Treatment used the ethanol/NaOH in a semi-solid agar gel without the use of an intermediary layer. The tile was immersed in deionized water for 48 hours after treatment to clear residues. Note the lack of C=O stretching peaks between 1700-1630cm^{-1} indicating the reduction of carboxyl groups from both the shellac and the lac dye.

A broad post-treatment peak centered at 1411.79 cm^{-1} can be more definitely attributed to the organometallic complex formed between the lac dye and the ceramic substrate, based on work conducted during the 'Lac Dye' study (Scott 2010). This seems to negate the theory that lac dye at a high pH will not complex with the ceramic substrate, though further studies are still required to fully understand the mechanisms involved here.

The splitting of the single Si-O-Si silicate peak around 1033 cm^{-1} (**Table 4**) into a triplet more characteristic of C-O ester stretching can also be attributed to both residual shellac and lac dye, as can the doublet at 793 and 780 cm^{-1} (**Spectrum 9).**

Chapter V: Discussion

5.1 Solubility, Hydrolysis and Saponification of Shellac

Either fresh or aged, shellac does not dissolve in a solution at a pH of below seven; as the pH increases in solution, the acid-salt equilibrium shifts to the formation of an increasingly water soluble compound by means of increasing alkaline hydrolysis of the polymeric chains (Sontaya Limmatvapirat et al. 2004). As it has been stated above, the list of solvents in which shellac can be completely dissolved is a short one, particularly when dealing with aged shellac. Koob's work (1979: 134) claims that pyridine is the only solvent that has proven effective in completely removing "raw, refined, and bleached samples" of shellac from ceramic substrates. While exposure to a saturated atmosphere of pyridine vapor typically only softened shellac; full and prolonged immersion was found to completely solubilize the resin at room temperature. Post-treatment, Koob claims that the pyridine will completely volatilize out, "leaving no staining or harmful residue needing further treatment… [as well as] no discoloration of pigments or damage" (Koob 1979, 134). More work would be required to fully assess the degree to which pyridine persists in ceramic bodies.

Other solvents, including ethanol, acetone, industrial methylated spirits (IMS), and dichloromethane have tended to show only partial efficacy in softening the shellac, allowing for mechanical removal, particularly in the form of cleaning gels (M. Svoboda 2007; Wolbers 1989; Wolbers 2000). As was the case in the 'Lac Dye' study, however, the risk of staining from the lac dye constituent of unrefined shellac has proven to be highly problematic (M. Svoboda, Tsatsouli, and Eng 2008).

The work of Limmatvapirat et al. (Sontaya Limmatvapirat et al. 2004) has found that the pH at which the polymeric shellac can be dissolved is controlled by the pK_a[27] and the number of carboxyl groups present; as the hydrolysis of the polyester chains in shellac occurs, the number of free carboxyl groups are increased (Sontaya Limmatvapirat et al. 2004). During their experiments, Limmatvapirat et al. (Sontaya Limmatvapirat et al. 2004) noted different rates of hydrolysis of the shellac, which they attributed to the different ester bonds involved in the reactions (the linked aleuritic acid and terpenic acid groups, and the monomeric terpenic acids and aleuritic acids) by means of different bond strength or steric hindrance (Sontaya Limmatvapirat et al. 2004).

Typically, shellac is subjected to alkaline saponification in order to hydrolyze it for study using GLC or gas chromatography mass spectrometry (GC-MS). Because of steric hindrance in the structure of the polymeric ester chains, the sesquiterpenoid compounds do not undergo an Aldol condensation, but rather undergo a Cannizzaro-type disproportionation (Colombini, Bonaduce, and Gautier 2003) (**Figure 10**).

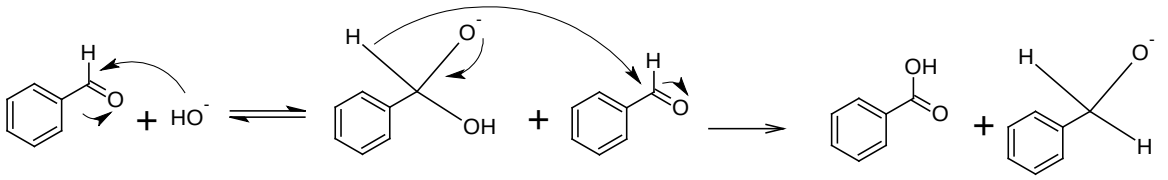


Figure 10: Cannizzaro-type disproportionation mechanism (Anon. 2007).

Based on the literature, the saponification of fresh shellac using KOH(aq) 1M at 25◦C took a minimum of five hours to a maximum of ten days, at which all the sesquiterpenoid

[27] The pK_a is the acid dissociation constant, which is a quantitative measure of the strength of an acid in solution based on the equilibrium constant in acid-base reactions with respect to the molecules ability to accept or to donate protons (Miessler 1991).

compounds had been disproportionated (Colombini, Bonaduce, and Gautier 2003). Some of the common alkaline salts used for the hydrolysis of shellac resin include KOH (aq) [9], NaOH (aq) (Sontaya Limmatvapirat et al. 2004) and tetramethylammonium hydroxide ($(CH_3)_4NOH$, TMAH) (Wang et al. 1999).

In their study, Limmatvapirat et al. (Sontaya Limmatvapirat et al. 2004) noted that a higher rate of hydrolysis seemed to occur during the initial period, after which hydrolysis of the shellac occurred at a much reduced rate. They believed that this was occurring because of the inherent complexity and variety of ester bonds that compose the resin that would have inherently different hydrolysis rates, different bond strengths, and show varying degrees of steric hindrance (Sontaya Limmatvapirat et al. 2004). A similar decrease in reaction rate was also noted during experimental trials conducted during this study; while the first applications required frequent changing, as the reaction proceeded, the amount of time between applications increased. The rate of change initially occurred roughly every five minutes for the first two or three applications, after which the rate tended to increase by a factor of two.

The resulting compounds from a full hydrolysis of shellac using the Cannizzaro-type disproportionation are listed in **Table 2**. The Aleuritic and Butolic acid compounds of the polyester chains result in the formation of short chain fatty acids (Colombini, Bonaduce, and Gautier 2003). The alkaline hydrolysis products of shellac showed the complete separation of the Aleuritic acids from the Terpenic acids and a separation of several Terpenic acid components from the main polyester backbone (Wang et al. 1999) (**Figure 11**).

During analysis of old paint samples using Py assisted by silylation-GC-MS, Colombini et al. (Colombini, Bonaduce, and Gautier 2003) found that there was the unexpected presence of Shellolic, Epishellolic, Laccishellolic and Epilaccishellolic acids together with the Jalaric and Laccijalaric acids, and the absence of Epilaksholic, Laksholic and Epilaccilaksholic acids, the alcohols that are typically produced during a Cannizzaro reaction, showing that this reaction did not occur. They theorized that the Shellolic, Epishellolic, Laccishellolic and Epilaccishellolic acids were present naturally in the shellac and through prolonged ageing, their concentrations increased and "back worded the Cannizzaro equilibrium reaction in the saponification step" (Colombini, Bonaduce, and Gautier 2003, 362). They also found that the present of certain organic compounds that can, and have, been added to the shellac can hamper the hydrolysis during the saponification step (Colombini, Bonaduce, and Gautier 2003).

Jalaric Acid: R = CHO; $R^1 = CH_2OH$

Laccijalaric Acid: R = CHO; $R^1 = CH_3$

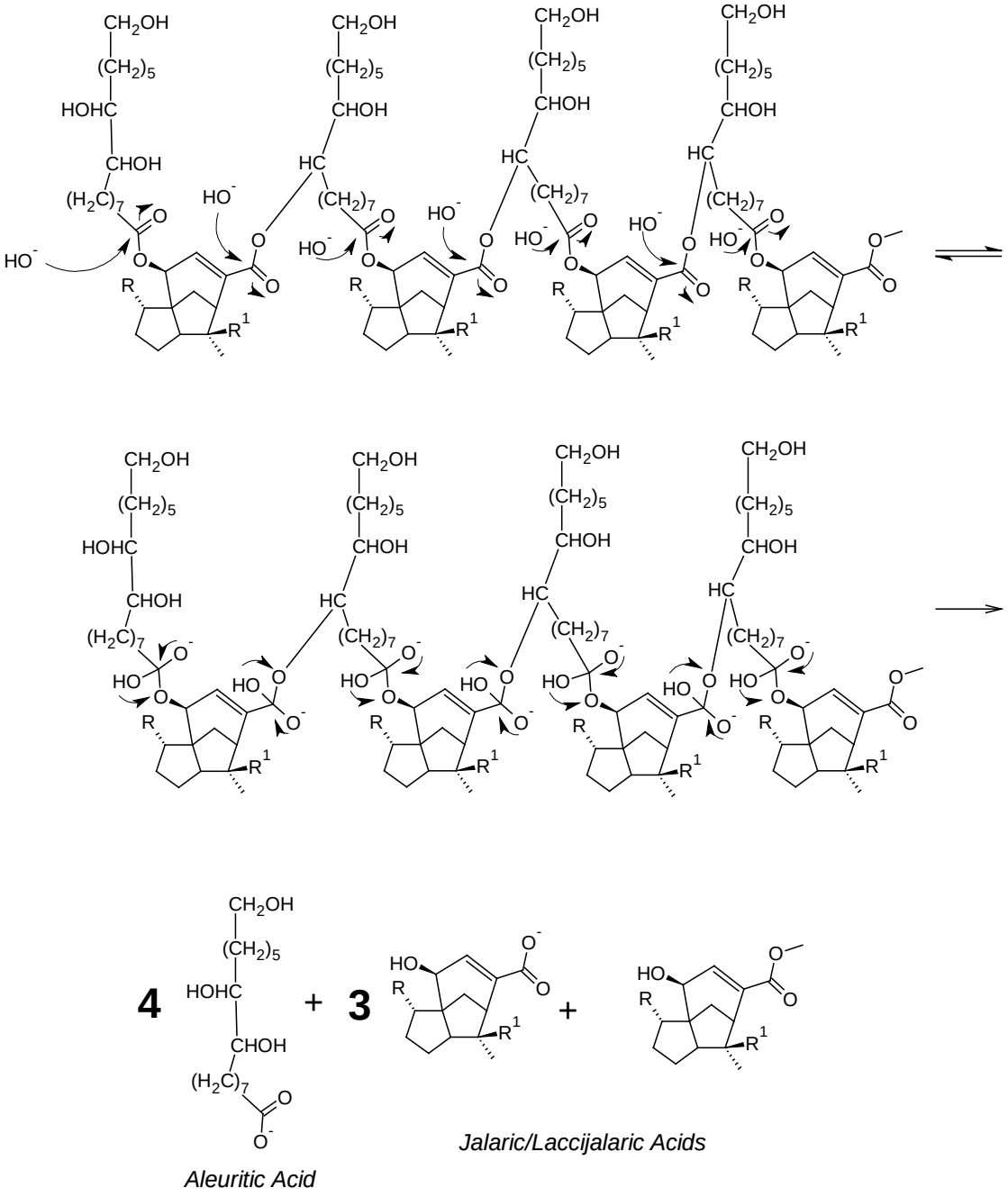


Figure 11: Proposed Cannizzaro-type disproportionation mechanism for the hard resin polymer components of shellac.

5.2 Experimental

The results of Trial 1 demonstrated the efficacy of a sodium hydroxide solution for the hydrolysis of the shellac in its entirety after a period of 24 hours in a 2% (w/v) aqueous solution. Upon placing the tiles in the various alkaline solutions, however, caused the shellac to turn a very dark purple in color, likely caused by the drastic change in pH; the higher the pH, the more quickly and dramatically the shellac turned purple. Although the lac dye component of the shellac turned a dark purple color, this color does not appear to have stained the tile; any apparent staining was water soluble and the color came out into solution when the tile was soaked in deionized water post-treatment in order to clear any residual NaOH.

While NaOH proved to be efficacious for the hydrolysis and dissolution of the shellac, the ammonia hydroxide and ammonium carbonate solutions did not yield the same results. The ammonia hydroxide did show some surface swelling after several days of treatment, but the tile did not come apart without mechanical action. In the case of the tiles treated in ammonium carbonate, there was a surface darkening of the shellac, though it was not as intensely purple in color as the other two treatments.

Based upon the results of Trial 1, NaOH was the base chosen for the majority of the support tests for this trial. The results of Trial 2 demonstrated the greatest efficacy of agar as a poultice support, over both the Pappina and the Carbopol, both of which were significantly more difficult to remove. The ability of the agar gel to act as a molecular sponge, absorbing the hydrolyzed reaction products as the reaction progressed, also favored this material as a support for the alkaline solution. The difficulty in removing the Carbopol as a solvent gel was also seen during Trials 7 and 8.

The agar also acted to minimize the diffusion of the NaOH, while allowing it to penetrate into the join and thus soften the shellac in that area; the wetting ability of the Pappina was significantly less than that of the agar, while the mixture of Carbopol and NaOH seemed to cause the partial disintegration of the tile after only 24 hours of treatment. For this reason, Carbopol was eliminated, though the exact reason for the disintegration of the tile is not fully understood at this time.

In order to better understand the reasons for the greater success of NaOH over its counterparts in Trial 1, a mixture of agar and calcium hydroxide were tested in order to determine whether an equally strong hydroxide base would be as effective as the sodium hydroxide, where the ammonia compounds were not. It was found that in mixing the Ca $(OH)_2$ into the agar during its cooling period, it caused the agar to become a very rigid gel very quickly. This reduced the efficacy of the treatment since the more rigid gel prevented the same level of contact with the surface of the tile as applying the agar in its semi-gelled state. Furthermore, the $Ca(OH)_2$ treatment in a rigid gel still did not perform as well as the NaOH when it too was applied as a rigid gel; there was some color change of the shellac on the surface of the tile, but the tile did not separate even after several days of treatment.

The results of Trial 3 concur very much with the results of Trials 1 and 2 in that, at a higher pH, the rate of hydrolysis was greatly increased, despite the same reagent being used in every instant. Of the three variations at a pH of 10, 12 and 13.5, both tests at a pH of 12 and 14 showed some efficacy in swelling the shellac, if not outright separating the mend. By far, the most effective treatment occurred with the agar and NaOH at a pH of 13.5; a color change and softening of the shellac was noted almost immediately after application on both the tile onto which the shellac had been added with a dropper to the

surface, and on the tile that had been mended with shellac. The amount of shellac that was added drop-wise onto the tile caused a particularly concerning amount of purple discoloration, which in this case, may not be entirely reversible due to the degree of saturation. Subsequent trials showed that more frequent changing of the agar gel, as soon as it becomes saturated with dye, is necessary to prevent the dye from diffusing down into the surface of the ceramic matrix, rather than up into the gel poultice.

Although the agar and NaOH buffered to a pH of 12 did cause the shellac on the mended tile to swell eventually, the shellac on the surface-coated tile remained unaffected even after three days of treatment; neither softening nor color-change were noted. In the case of the buffered treatment at a pH of 10-10.5, no changes were noted on either the mended or the surface-coated tile. The shellac remained unchanged in color and did not show signs of hydrolysis, even after three days of treatment.

The results of Trial 4 by large and far concur with the results from previous trials, though the added efficacy of the JTP intermediary was not replicated here. An initial theory had thought that the combination of solvents in a pre-gelled agar would prove to be most effective, with the surprising result being that the use of ethanol only was most effective. Further research needs to be conducted regarding this result, but some preliminary research on the chemical properties of ethanol has revealed that in acid-base chemistry, the neutral ethanol molecule can be easily converted to its conjugate base by means of a reaction with an alkali metal, in this case, with the sodium of the NaOH (Morrison and Boyd 1972):

$2\ CH_3CH_2OH + 2\ Na \rightarrow 2\ CH_3CH_2ONa + H_2$ *(Chemical Reaction)*

Initially, it was thought that the efficacy of the ethanol was based on its polarity and solvency, but based on this new research, it is possible that it lies rather more in its ability to react with the dissociated sodium from the alkaline solution, further enhancing the hydrolysis of the hard resins of the shellac.

The trials conducted on the 200 year old shellac from the Apulian vessels showed results in keeping with those from the test tiles, though as expected, the kinetics of the reactions were much slower. Given the auto-catalytic polymerization that shellac undergoes as it ages, it is not at all surprising that the reaction would take more time due to higher steric hindrance and the increased number of bonds requiring hydrolysis in order to break down the polyester backbone of the resin. Furthermore, the particular mixture used in the 1820s, which did not just include shellac, but also a mixture of other pigments and materials, are likely to also play a role in the efficacy of the treatment. Overall, however, there has been good success with the treatments, though further work to evaluate the potential long term post-treatment damage from the highly caustic treatment still need to be properly evaluated before the treatment should be undertaken on other objects, particularly low-fired ceramics, highly porous substrates, polychrome vessels, or other alkaline sensitive tempers and clays.

It was noted in Trial 9 that when applying the agar gel over a large surface, it is necessary to reheat the gel several times, each time losing some water through evaporation. In order to compensate for the loss of water, deionized water was added with every reheating until the agar looked to have regained the desired consistency.

Unfortunately, this resulted in a loss of precision by the final applications, and a severe reduction in the concentration of the agar in the gel with repeated heating.

The implications of the lac dye tests conducted in Trials 11-13, in conjunction with the observed behavior of the lac dye during previous trials has been discussed in other sections. Testing using a prepared tile and three samples of lac dye at different pH revealed that the stain was darkest using the acidic dye and no stain occurred on the tile using the alkaline dye. This supports the theory that the formation of the organometallic complex cannot occur in an alkaline environment and requires at least a slightly acidic environment (< pH 6.7).

5.3 Clearance

One of the most significant requirements for assessing the efficacy of a proposed cleaning treatment revolves around the issue of clearance. If a treatment leaves residues that are potentially damaging to the ceramic substrate (e.g. by creating harmful by-products; changes in the hydrophilic/hydrophobic properties of the ceramic etc.), or requires significant and/or aggressive subsequent treatment to clear, it cannot be considered as wholly effective. Ideally, a given cleaning treatment will not leave residues of any type; in reality, this is seldom the case. If the cleaning materials used are water soluble or volatile, then clearance can and should be relatively straight forward. In some instances, however, it is not advantageous to expose a treated object to repeated applications of water, either through immersion or through poulticing or swabbing (Wolbers 2000, 158). For the purposes of this study, however, the water solubility of residual materials is the ideal scenario, as the materials are generally insensitive to aqueous solutions.

The experimental section of this study explored a number of methods for reducing and removing shellac from porous substrates, some of which present greater clearance issues than others. As it has been discussed previously, both Carbopol and Pappina presented issues of clearance, particularly on the porous substrates tested herein. Though Wolbers (Wolbers 2000) and Stavroudis and Blank (Stavroudis and Blank 1989) have explored the issues of clearing polyacrylic acid based solvent gels, particularly by adjusting its solubility through the addition of surfactants, experimental trials during the course of both this study and the 'Lac Dye' study (Scott, Drolet, and Blaik 2010; Scott 2010) have shown clearance, even at the macroscopic level to be extremely difficult and seldom achieved.

FTIR was conducted on a sample of the prepared Carbopol gel in order to establish a baseline to determine the degree of clearance in comparison with spectra collected from samples treated with a Carbopol mixture, even when a visual determination of clearance was achieved. Some of the more distinctive peaks that can be attributed to Carbopol residues, based on the mixture used in this study, include the unlikely presence of O-H alcohol bands around 3390.27 cm^{-1} and ketone bands around 2900.78 cm^{-1} from the solvents, and the much more likely amine residues from the Ethomeen, which appear at 1226.61 cm^{-1}, as well as the C=O carboxylic acid band at 1707.18 cm^{-1}, and C-O carboxylic acid bands at 1087.97 cm^{-1}, and 1045.69 cm^{-1}. Though the latter of the COOH bands would arguably be masked by the Si-O band from the batanas in this region, it is possible that residues from these carboxylic groups could potentially cause shifts or splits of the Si-O band.

Significant research in the clearance of wax emulsions from porous surfaces has been found to be lacking and limited to the work by Kakoulli and Hodgins (Kakoulli and Hodgins 1997). In this study, experimental results for its removal were much in keeping with the results of the Carbopol trials. In the case of post-treatment FTIR analysis of the Pappina, it was difficult to distinguish between residual C-H alkane bands at around 2988 cm^{-1} and 2917 cm^{-1} from those present in the lac dye. The distinct peaks seen in a triplet at 1394.04 cm^{-1}, as well as in two other triplets centered at 1241.92 cm^{-1}, attributed to a C-N amine band, and at 1066.11 cm^{-1}, were unfortunately obscured by the silicate bands of the clay and therefore the presence of Pappina residues could not be confirmed (**Spectrum 4**).

The results of the agar gel trials, however, show a cleaning system that, in theory, leaves only water soluble residues. As discussed above, the reaction products of the Cannizzaro disproportionation reaction of shellac consist of water soluble monomers, dimers and free carboxylic acids (Buys and Oakley 1996; Colombini, Bonaduce, and Gautier 2003; Mills and White 1994). The agar itself is also water soluble, and as such, any remaining residues can be removed by immersion, if possible, or by cotton swab in deionized water, when immersion is not possible. Additionally, when comparing it to its Carbopol counterpart, which has a 'stickiness' to it that binds it loosely to a given substrate, the agar gel is held to its given substrate by gravity alone. As the agar cools, it becomes a rigid but flexible gel that is easily removed as a single piece.

Post-treatment FTIR analysis of tiles treated using agar gel does not tend to show peaks that can be definitely and distinctly identified since, as an organic substance, it shares many of the same peaks as shellac and lac dye residues, particularly in the 2690-2850 cm^{-1} alkane stretching range and the 1260-1000 cm^{-1} C-O range representing the

presence of alcohols, ethers, carboxylic acids or esters. When comparing the post-treatment FTIR spectrum of a tile treated with agar, ethanol and NaOH with the spectrum of agar alone, there is a notable absence of a C=O stretching peak at 1633cm^{-1} and sulfate peaks at 967.32cm^{-1}, 929.56cm^{-1} and 870.50cm^{-1}. The absence of these peaks on the post-treatment spectrum, despite the overlaps with the original shellac and lac dye peaks would suggest that, at the very least, these elements of the agar were adequately cleared from the surface of the tile (**Spectrum 9**).

As it was discussed in the previous chapter, however, ultraviolet-induced visible fluorescence at an excitation wavelength (λ_{exc}=365 nm) can adequately reveal the presence of agar residues in the case of inadequate clearance, while differentiating them from lac dye and shellac residues, as each is characterized by a distinctive fluorescence.

5.4 Salts

The deleterious effects of water soluble salts in porous materials is well known and well established in the conservation literature (Buys and Oakley 1996; Johnson 1998; Cronyn 1990; Sease 1992). The use of NaOH as the alkaline agent in these trials raises some concerns for the potential of salt formation, particularly on pieces that are being retreated – especially if those pieces had been treated in HCl, as was and still is standard in many parts of the world, and in particular in parts of the Mediterranean. In such instances, if adequate clearance of Cl- ions or Na+ cations is not achieved, the possibility of forming sodium chloride crystals is not only possible, but highly likely, and highly detrimental to the integrity of the ceramic substrate as sodium chloride is a highly hygroscopic salt prone to deliquescence in high relative humidity and recrystallization as the humidity drops

(Buys and Oakley 1996, 23). If left untreated or unmitigated, the damage from the recrystallization cycles of sodium chloride can lead to spalling, significant loss of surface material and even to the complete disintegration of the vessel due to the pressure exerted by the crystals (Johnson 1998, 1).

Microscopic analysis of some of the test tiles treated in this trial has shown signs of salt crystallization. Micro-chemical spot tests[28] using 0.2M silver nitrate ($AgNO_3$) and 5M nitric acid (HNO_3) have confirmed the presence of chlorides in these crystals. As these tiles were prepared in the lab, it is known that they were never deliberately exposed to chloride ions, and as such, the source of such ions remains unknown.

The crystals are particularly evident on tiles from Trial 1, in which the tiles were soaked in a solution of 0.5M NaOH, and were not at all in evidence on tiles from Trials 3 and 4, owing possibly to the increased presence of hydroxide ions that allow the treatment reaction to proceed using less sodium hydroxide than when the ethanol is not present. Though all the test tiles were similarly immersed in deionized water for several days after treatment, it would seem that a longer desalination period would have been required for tiles that were immersed in solution and fully saturated.

Greater research will need to be done to find a better source of hydroxide anions that will not leave cation residues that will form salts in archaeological or pretreated materials. Tiles tested using ammonia and ammonium carbonate did not show evidence of salt crystals under microscopic examination, though the tiles had been soaked in solution.

[28] The spot test used follows the methodology published by Odegaard et al. (Odegaard, Carroll, and Zimmt 2005, 108).

Unfortunately, as it was discussed above, neither of these bases was particularly efficient of hydrolyzing the shellac and so another alternative should still be sought.

5.5 Timed Trials (Lac Dye Identification Test)

The creation of a chemical spot test to identify the presence of lac dye in shellac was inadvertently discovered during this study. Prior to the treatment, a drop of an alkaline solution can be applied to a micro-sample of shellac; the production of a bright pink stain would confirm the presence of lac. This discovery can guide the conservator to the best treatment option.

Timed assays were conducted under the microscope using two sets of samples. In the first instance, fresh samples of seed lac were crushed into smaller particles and placed on glass slides to which a single drop of 5M NaOH solution was applied. In the second experiment, samples of shellac were collected from the untreated fragment edges of the Apulian vessel by M. Svoboda, to which the same 5M NaOH solution was also applied. Five samples of the fresh seed lac, and ten samples of the aged shellac were run in this way, taking note of the amount of time required for a color change to occur. In new samples, this color change is rapid, dramatic and easily observed, turning the seed lac from an amber color to a bright fuchsia or purple. Such is not the case with the aged samples, where the color change requires significantly more time and is much more subtle, often requiring a control sample or a before treatment image with which to compare the results, as the sample will frequently become only a very pale pink color not very different from the sample prior to contact with alkaline materials. This problem can be mitigated by having a larger sample size, though this might not always be possible.

The assay times are summarized in **Table 8** but on average, fresh seed lac will react and turn pinkish-purple in approximately 3 seconds, while the aged shellac generally required upwards of 5 to 10 minutes, with some samples not reacting until 30 minutes had elapsed. It was noted that all the samples had produced a color change after 30 minutes, and that after approximately 40 minutes, the color change begins to dissipate as the dye denatures from the high alkalinity (**Table 9**).

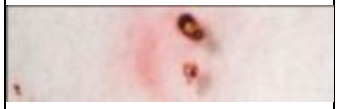
Time:	Apulian Sample (~ 200 years)	Time:	Seed Lac (new)
0 minutes		0 minutes	
5 minutes		50 seconds	
10 minutes		114 seconds	
30 minutes		10 minutes	

Table 8: Timed Assay for seed lac showing the sample starting to turn pink at around 50 seconds, turning purple at 114 seconds, and diffusing into solution after 10 minutes.

Times Assay for 200 year old shellac from Apulian vases shows a much slower and more subtle color change. Samples should be read after 30 minutes to ensure that the reaction has had time to proceed, but not later than 40 minutes, as the lac dye will begin to break down in the alkaline environment and lose its color completely, leading to a false negative. For this sample, the color change is the most evident at 10 minutes, with hydrolysis of the shellac sample occurring at 30 minutes.

Sample 1	2:41 minutes	
Sample 2	1:48 minutes	
Sample 3	1:45 minutes	
Sample 4	3:06 minutes	
Sample 5	1:35 minutes	
Sample 6	2.20 minutes	
Sample 7	1:32 minutes	
Sample 8	3:28 minutes	
Sample 9	2:58 minutes	
Shellac BT		
Micrograph taken 30 minutes after exposure to 5M NaOH. Final image shows color of shellac before treatment.		

Table 9: Nine additional samples of the Apulian shellac were tested in order to ascertain an average time until the color change occurred. The time indicated in the table above refers to the first observed presence of pink or purple in the sample after introducing the NaOH onto the sample. The average time until the first observable color change is 2 minutes and 12 seconds.

On very old samples of shellac, the color change is very subtle, but can be more easily discerned after allowing the sample to react for 30 minutes, as pictured in the table. After 40 minutes, the sample begins to hydrolyze and denature, and ultimately the color change can be missed, as discussed above in **Table 8**.

As such, when using this method testing, it is helpful to either have a control sample or a before treatment photograph as a reference, and it is critical to read the test between 30 and 40 minutes after the addition of the NaOH to ensure that the reaction has had sufficient time to react, but that the color change was not missed by allowing the dye to denature, thus avoiding a false negative. As with most micro-chemical spot tests, there is a danger of receiving a false positive. Reproducibility of the results excluded this possibility, unless the sample has been contaminated; if the sample turns pink or purple, there will be lac dye present and additional care should be taken in the treatment of the object to avoid migration of the dye.

5.6 Agar as an Alternative Gel to Carbopol

In spite of many of the aforementioned issues raised by the materials and methods used throughout this study, one of the single most notable findings has been in the use of agar as a new medium for the creation of solvent and alkaline gels as an alternative to Carbopol. In comparison with its Carbopol and Pappina counterparts, agar is a relatively simple polysaccharide molecule that is readily soluble in hot water and resistant to both high alkalinity and high acidity, making it a favorable, safe and non-toxic eco-material for use in conservation treatment (Gorel 2010; Chaplin 2009; Craigie and Wen 1984).

Many of agar's physical and chemical properties, as discussed in previous chapters, make it an ideal product in this application, and shows significant promise as a material for other uses in conservation. As with any material that one uses for conservation treatment, additional research into the aging, potential residues and interaction with different

substrates is required before it can and should be used on other types of materials, but the properties seen within the scope of this study have shown it to be a promising material.

Also, it is possible to control the amount of solution that is released by the agar and dispersed into the substrate by adjusting its concentration. Diffusion studies were carried out by Anzani et al. (Anzani et al. 2010, 48) on agar gels prepared using only water found that after a period of twenty minutes, a 4% (w/v) agar gel will diffuse up to 2mm into a given porous substrate, while a 2% (w/v) gel will diffuse to a depth of 4mm under the same conditions. In comparison, the researchers also applied a cotton poultice soaked in water and found that the water had diffused to a depth of 5-6mm after only 3 minutes (**Figure 12**). This study found a concentration of around 3 to 4% to be ideal, but for highly sensitive materials, a higher concentration, up to 8% can be easily mixed.

In addition to controlling diffusion and localization by means of concentration, the application method can also be used; agar can be applied as either the fully cooled rigid gel, or in its semi-solid warm phase. When applied in its semi-solid phase, it allows for good contact on three dimensional objects, as well as on vertical surfaces. As a rigid gel, it can easily be sliced and carved into a needed conformation, allowing for a great deal of control of the extent of a treated area. In its semi-solid phase, the gel tends to allow for greater diffusion, while in its rigid phase, roughly the same diffusion rates were observed as found in the study by Anzani et al. (Anzani et al. 2010, 49) .

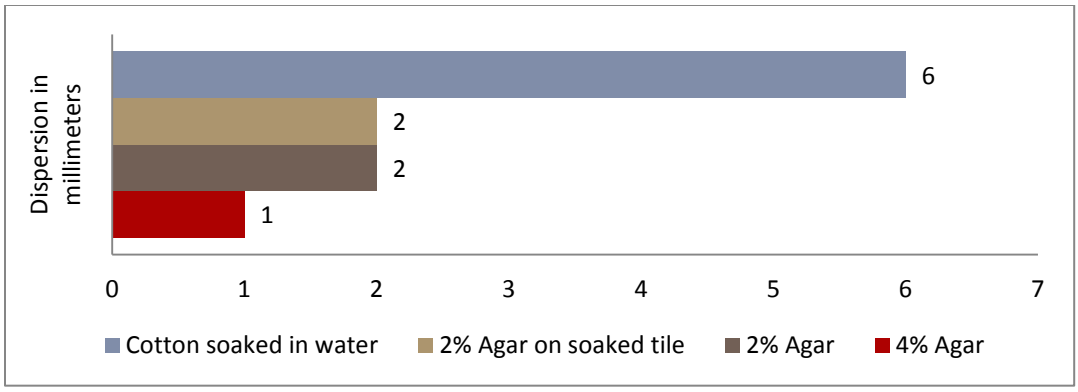


Figure 12: Dispersion of water into a gypsum substrate using different concentrations of agar gel and a cotton poultice. Depth of penetration was calculated after 3 minutes. Supports included cotton soaked in water, 2% (w/v) agar in deionized water applied to a sample that had been immersed in water for 72 hours, 2% (w/v) agar in deionized water, and 4% (w/v) in deionized water. These results show a greater ability to control dispersion of water from a poultice support in agar than in cotton. The degree of dispersion can be controlled by increasing or decreasing the concentration of agar in the gel solution (from Anzani et al. 2010, pp. 48-49).

The drying time of the agar can be easily influenced by the thickness of its application. Even at applications as thin as 2mm, the surface of the gel in contact with the treated substrate will stay moist for more than a day without being covered. Covering the gel can extend the drying period over several days, though it should be noted that in warm and humid environments, extended application can lead to mold growth and should be avoided. In its application for this study, however, frequent changes of the gel favored a more efficient treatment, and as such, drying out was not an issue.

One drawback of this gel, as is often the case with biological materials, is the limited shelf life of the agar gel after mixing. As a powder, the agar can last for years; once the gel has been made, however, it generally lasts about a week or two, if refrigerated. Also, if using the gel as a carrier for flammable solvents, it is not possible to keep the agar solvent gel premixed as one does with Carbopol, unless it will only be used as a rigid gel and not reheated. If reheating is necessary, the solvents should be added only after heating, just

prior to application. Once a gelling temperature was reached, the agar was removed from the heat source, and the concentrated NaOH was added drop-wise into the cooling agar to reach a pH of 13.5.

The production of neutral agar also allowed re-workability by heating in the microwave as many times as necessary, which brought the gel back to its semi-solid state, allowing for easier application and better contact[29].

Finally, as discussed in Chapter 3, it is agar's ability to act as a molecular sponge that can serve as its most useful property in conservation practice. It is this quality that truly sets it apart from either Carbopol or Pappina; the agar can act simultaneously as a poulticing material as well as a solvent gel, thus not only solubilizing the materials it is in contact with, but drawing them away from the surface and holding those materials within its gel matrix (**Figure 13**).

[29] If the NaOH is already introduced to the gel, reheating appears to cause an unacceptable color change (to dark green); NaOH should always be added after the heating process is complete and during the cooling and gelling process to prevent this color change.

Figure 13: Agar poultices after removal from shellac coated edges (from Trial 10) showing the lac dye and other small particulate matter from the fragment edge having been drawn into the gel matrix (lending the gel a pinkish color).

Chapter VI: Conclusions and Future Studies

The results and observations that have emerged from this study represent an important beginning and new direction for the study of shellac removal from not only porous substrates, but any cultural material. This work represents the culmination of more than eighteen months of research and experimentation of a number of ceramic substrates ranging in age from modern to ancient and testing both traditional and new conservation materials and techniques in an effort to find a solution to a problem that has continued to plague objects and paintings conservators alike.

By the study and chemistry of shellac in other fields, particularly in pharmaceuticals, this project has sought to present conservators with a new way of thinking about its removal. When faced with this natural resin, it has typically been our wont to 'dissolve' the unwanted adhesive, and as such, we have traditionally sought out a range of solvents running the gamut from relatively benign to highly toxic and extremely dangerous to both the object and the user. By abandoning the principles of solubility entirely, I have sought to explore the removal of shellac by means of molecular hydrolysis using aqueous alkaline materials, in which the polyester backbone of the resin itself is not simply swelled or sent into solution, but saponified and broken down into water soluble monomers, dimers and free carboxylic acids.

The necessity for a treatment that does not rely on the dissolution of shellac, particularly unrefined shellac, has been highlighted by a number of previous studies including an early paper by Stephen Koob in 1979 (Koob 1979), and more recently highlighted by the works of Svoboda et al. of the JPGM in 2008 (M. Svoboda, Tsatsouli, and Eng 2008), as it can easily lead to a pinkish-purple stain that has chemically bonded to the

metallic cations of the substrate. Although an experimental treatment was found for the removal of these stains (Scott, Drolet, and Blaik 2010; Scott 2010), the ability to remove unrefined shellac from a similar substrate without the risk of staining, and thus additional treatment steps, is highly advantageous. Further, it was found in the course of this study, in conjunction with results from the 'Lac Dye' study (Scott 2010) that a singular treatment for reversing shellac and staining in one step is impossible, as the former necessitates a high pH, and the latter requires a low one.

In addition to exploring the use of alkaline materials, this study also investigated both traditional and novel materials as carriers for both solvents and aqueous solutions. For example besides Carbopol, agar gel and the Pappina wax emulsion were also tested, ultimately finding the agar gel to perform with the greatest efficiency for the purposes of this study.

Ultimately, the results of this study have presented materials and methods for the hydrolysis of crude shellac on porous substrates that are efficient in laboratory testing with the most efficient treatment consisting of a mixture of 1:1 ethanol and agar gel (4% w/v in deionized water) buffered to a pH of 13.5 by adding a few drops of 5M NaOH. At this level of alkalinity, and with frequent poultice changes to mitigate migration of the lac dye and other reaction products from the hydrolyzed shellac, the reaction occurred very quickly and a significant reduction of even thick layers of shellac could be removed in under an hour.

The long term effects, residues and potential retreatment problems of such an aggressive level of alkalinity, however, need greater exploration before this treatment would be recommended for standard use in a conservation laboratory. Materials should

always be tested for resistance to alkalinity prior to any such treatment. Furthermore, as the agar is a water-based gel system it cannot be used on a water-soluble substrate or water-sensitive paint layers.

Though the treatments investigated in this study do have limitations, a number of valuable pathways for future investigations have been brought to the forefront. In particular, research should focus on finding a more suitable base, one that can help to hydrolyze the shellac at a lower pH that can be used on a wider variety of substrates. The use of ethanolamines, for example, or ether-alcohols and their acetates is one avenue that certainly bears further examination. As results from the trials conducted on test tiles seem to indicate that the success of a base for hydrolyzing shellac is not based on its pH, but rather on its dissociation value. The dissociation value is a base's capacity to release OH- ions into solution, as well as its ability to react with carboxylic acids; this appears to be the determining factor for the rate and degree of hydrolysis. This is likely because of the required number of OH- ions required to free the carboxyl groups, as discussed in the work of Limmatvapirat et al. (2004).

Another avenue of research that remains to be fully explored is that of enzymatic hydrolysis for crude shellac, either as a method for the direct hydrolysis of the shellac constituents, or to explore the use of enzymatic catalysts used in conjunction with an alkaline solution, allowing the Cannizzaro-type redox reaction to occur at a lower pH and for a significantly shorter duration, thus reducing the potential for alkaline-induced damage caused by a vigorous, albeit effective, treatment at a high pH over a number of days.

Of the enzymes that Wolbers describes as having use in conservation practice, it is the lipases, and their ability to hydrolyze fatty acid ester and carbohydrases, and their ability to hydrolyze carbohydrates into short polysaccharide units, that are the most likely to yield results of any sort within the confine of this study, based on the structure of the shellac molecular components (Wolbers 1989). Wolbers (1989) also looks at the differences between chymotrypsin and trypsin, two proteases with serine/histidine mechanisms at their active sites, but while the former catalyzes the hydrolysis of peptide bonds in aromatic amino acids, the latter catalyzes the hydrolysis of peptide bonds adjacent to basic amino acid. This has great import for future studies in this field, as the basic molecular structure of the components of shellac would hydrolyze more readily in chymotrypsin, rather than the trypsin. Unfortunately, there does not appear to be any direct usage of enzymes in the degradation, hydrolysis or other treatment of shellac itself, and so, the efficacy of these types of enzymes is left in question.

Hence, this study presents a beginning, rather than an end to this avenue of investigation. Many of the theories explored herein can be adapted and modified for greater efficiency or less extreme conditions, making them practicable for future conservation treatment of objects previously restored using crude shellac.

Appendix 1: MSDS Sheets and Materials

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
Poulticing Materials
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
Agar: Fluka Analytical: 05040-100G

Alkali Materials

Ammonium Carbonate: Fisher Scientific: A657-500
Ammonium Hydroxide Solution (28%) (NH3): Alfa Aesar, CAS 1336-21-6, Stock# L13168
Sodium Hydroxide: Fisher Scientific Pellets: S78605 500G
Calcium Carbonate: Fisher Scientific CAS 1305-62-0 Cat C-97

Acids

Hydrochloric Acid (HCl): Sigma-Aldrich, 37% A.C.S. Reagent 258-148-100ML

Solvents

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

Appendix 2: Conservation Methods

Pappina Emulsion (Kakoulli and Hodgins 1997, 41)

Stearic Acid BDH	0.2g
Ammonia solution 28%	4mL
Bleached beeswax	100g
Deionized water	150 mL

Mix the ammonia and stearic acid to form ammonium stearate (emulsifying agent between wax and water).

Mix water with wax in a large beaker and heat on a double boiler just below 100◦C. When the wax melts, blend the mixture. Add the ammonium stearate solution and stir. The mixture can be rapidly cooled by plunging the beaker into a cold water bath. Continuous stirring of the mixture during the whole process is crucial.

Carbopol 934 Gel (from instructions on the container)

Carbopol 934 powder	6g
Deionized water	94mL

Add the water to the Carbopol powder and mix aggressively until a gel is formed.

Carbopol 934 Solvent Gel (modified from WAAC Newsletter)

Acetone	50mL
Ethanol	50mL
Ethomeen C25	10mL
Carbopol 934	2g
Deionized Water	10mL

Agar Gel (4% w/v) (from Anzani et al. 2010, pp. 43)

Agar powder	8g
Deionized water	192mL

Add agar powder to cold deionized water and stir well.

Mixture can be heated using a double boiler on a hot plate, stirring regularly until the mixture thickens and gels.

Alternatively, the mixture can be heated in the microwave on medium power for 2 to 3 minutes (depending on amount made), stirring occasionally. Mixture is ready when it comes to a boil. Be sure to watch the mixture carefully in the microwave as it tends to bubble dramatically and can boil over – should this happen, stop heating – the gel will be sufficiently hot.

The gel should be kept in the refrigerator when not being used in a tightly sealed jar (one that can be heated). The gel can be reheated when necessary for application. The more often the gel is reheated, however, the greater the loss of water. Water should be added with every re-heating to compensate. This will, of course, create a solution of unknown concentration – though a workable consistency similar to toothpaste is a good guideline.

Agar Solvent Gel

Agar powder	16g
Deionized water	192mL
Ethanol	half of amount being used
NaOH	added dropwise until desired pH is achieved

Add agar powder to cold deionized water and stir well.

DO NOT add the solvent or alkali to the agar gel prior to heating. In the case of the solvent, the risk of fire or explosion is too great, in the case of the alkali material, for unknown reasons, the heating of the gel with alkali added to it causes it to darken in color to a greenish-black, which leaves dark residues on light colored surfaces. These materials should be added to the warm gel just prior to use.

Mixture can be heated using a double boiler on a hot plate, stirring regularly until the mixture thickens and gels.

Alternatively, the mixture can be heated in the microwave on medium power for 2 to 3 minutes (depending on amount made), stirring occasionally. Mixture is ready when it comes to a boil. Be sure to watch the mixture carefully in the microwave as it tends to bubble dramatically and can boil over – should this happen, stop heating – the gel will be sufficiently hot.

The gel should be kept in the refrigerator when not being used in a tightly sealed jar (one that can be heated). The gel can be reheated when necessary for application. The more often the gel is reheated, however, the greater the loss of water. Water should be added with every re-heating to compensate. This will, of course, create a solution of unknown concentration – though a workable consistency similar to toothpaste is a good guideline.

When ready to use, reheat the agar gel as described above. Mix the amount needed at a ratio of 1:1 of agar gel and ethanol so as to have an overall concentration of 4% agar (w/v). Add the sodium hydroxide one drop at a time, until the desired pH is achieved. The more NaOH used, the faster the reaction will be, though the risk to the object being treated also increases exponentially.

Appendix 3: Test Tile Trials (Trials 1-4)

The test tiles created for the initial experiments in this study were made using a terracotta body, slipped on the surface with a white clay called 'batanas'. The tiles are roughly 5 cm by 5 cm in size and roughly 7mm in thickness, with the batanas coating representing an average thickness of less than 1mm. The tiles were fired in a Barnstead Thermolyne 1500 furnace at a temperature of 900°C for approximately one hour and fifteen minutes, and were allowed to cool for thirty minutes in the oven.

After fabrication, some tiles had crude shellac added to the surface with a dropper, while other tiles were broken using a mallet and mended, again using a solution of crude shellac. The shellac used was prepared from seed lac in ethanol at a concentration of 20% w/v. Though eight different mixtures of shellac, including varieties that were bulked using lead white and cellulose powder, only the tiles that were mended with seed lac in ethanol were used in order to minimize variables.

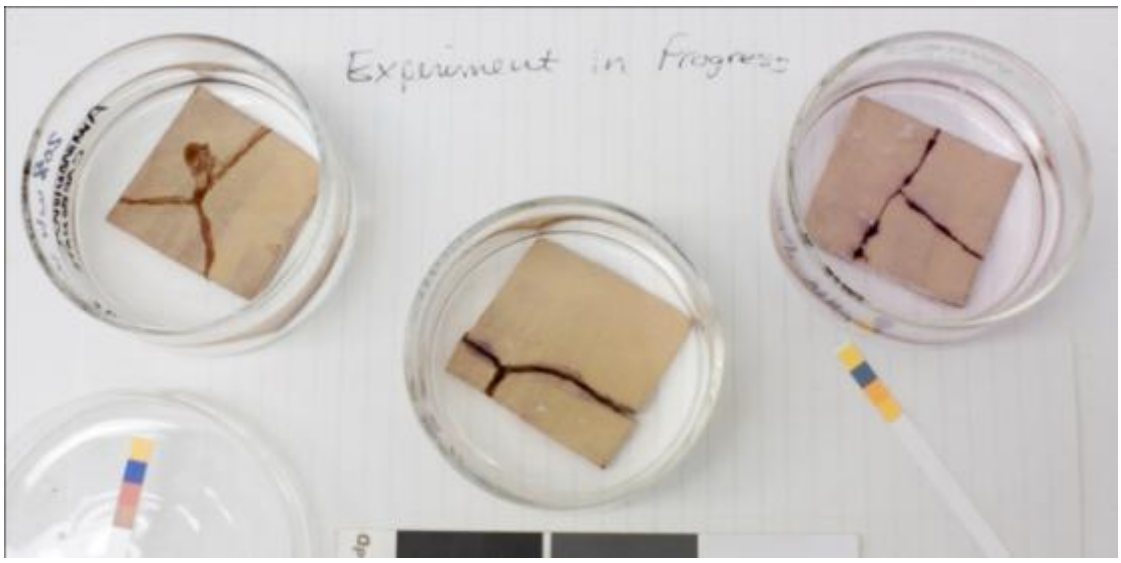
The test tiles were then left to age on a window sill that allowed for the exposure of the tiles to ultraviolet light and changes in temperature for a period of 6 to 9 months.

Trial 1

Date: November 16th, 2010

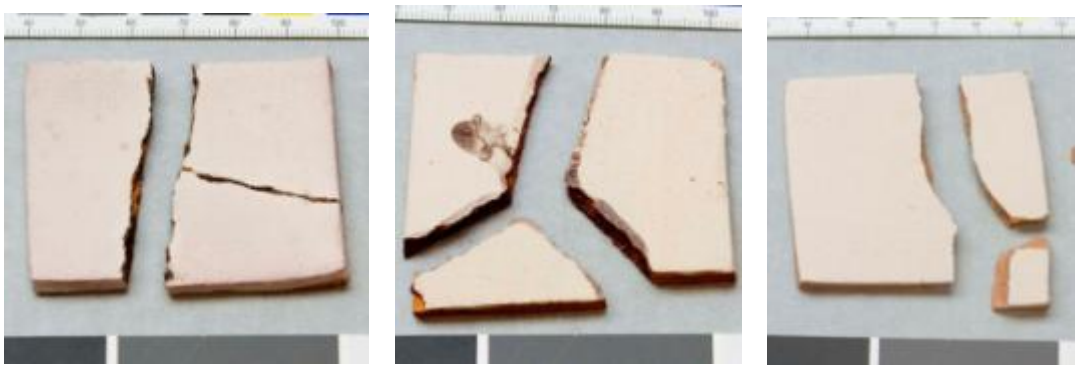
Ammonia Hydroxide 28% Ammonium Carbonate 20% in deI water NaOH 2% in deI water

Before Treatment Photograph of tiles to be soaked in 3 different alkaline solutions as indicated.



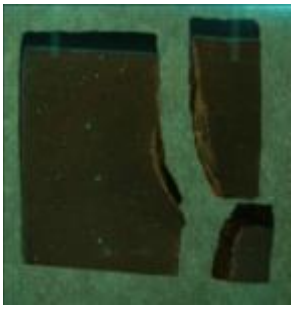
Ammonium Carbonate 20% NaOH 2% in deI NH3 28%

During Treatment Photograph of tiles being soaked in 3 alkaline solutions, as indicated.
Time elapsed = 12 hours



Ammonium Hydroxide tile AT Ammonium Carbonate tile AT Sodium Hydroxide tile AT

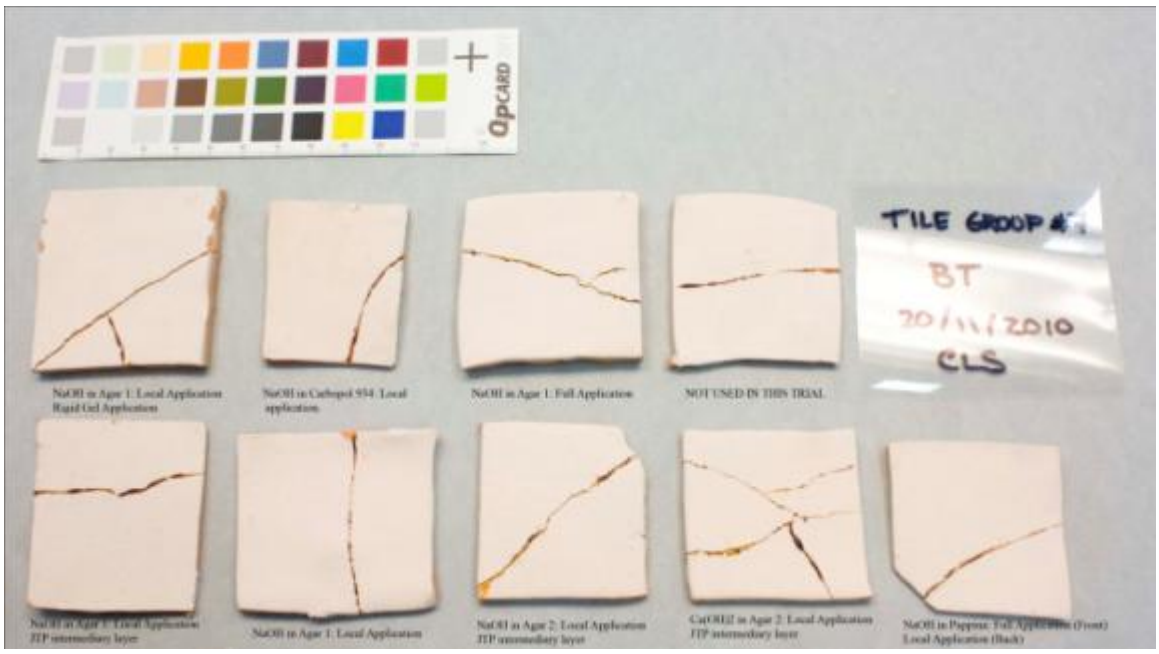
After Treatment Photographs of tiles after soaking in alkaline solutions for 3 days and soaking in deionized water for desalination/clearance of alkaline residues for 2 days.



After treatment Ultraviolet induced fluorescence image. A tuneable forensic light source was used at an excitation wavelength of 300-400nm. The image was captured using an unmodified Canon Rebel XSi DSLR fitted with a Peca 916 visible pass filter. In order to increase contrast, an additional yellow filter to cut near ultraviolet wavelengths below 480nm.
Faint traces of fluorescence can be discerned along the edge that could be attributed to very minimal shellac residues and some salt residues from treatment.

Trial 2

Date: November 18th, 2010



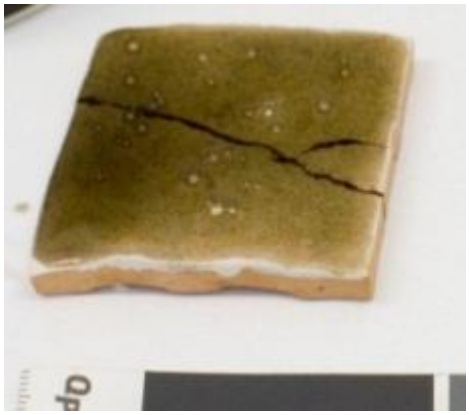
Before Treatment Photograph of tiles to be used for support material testing.

NaOH in Agar # 1

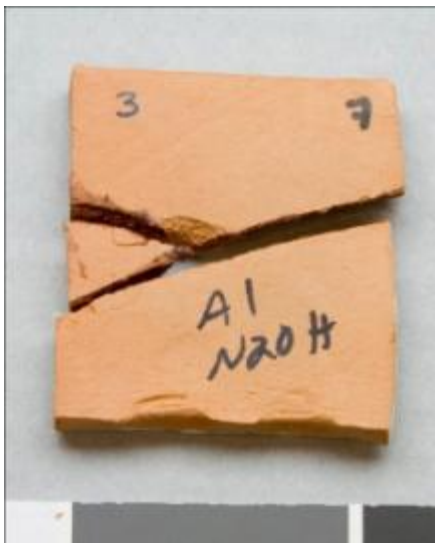
Sodium Hydroxide in Agar #1: Localized application, applied as cool rigid gel.

After treatment: top and bottom views (left to right)
Total duration of treatment = 48 hours

Sodium Hydroxide in Agar #1: Full surface application, applied in semi-solid cooling phase.

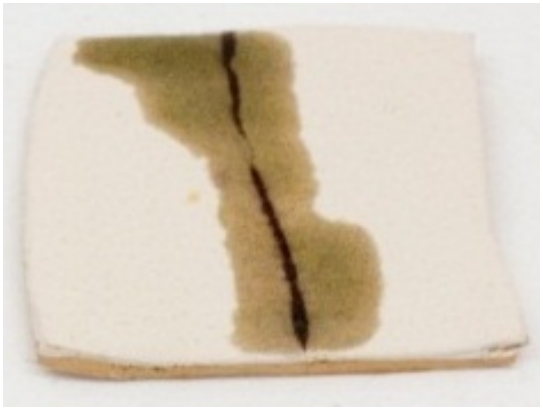


During treatment: top view (showing greenish color of agar when heated with NaOH)



After treatment: top and bottom views (left to right)
Total duration of treatment = 48 hours

Sodium Hydroxide in Agar #1: Localized application, applied in semi-solid cooling phase.



During treatment: top view (showing greenish color of agar when heated with NaOH)

After treatment: top and bottom views (left to right)
Total duration of treatment = 48 hours

Sodium Hydroxide in Agar #1: Localized application, applied in semi-solid cooling phase using a JTP intermediary layer.

After treatment: top and bottom views (left to right)
Total duration of treatment = 48 hours

NaOH in Agar # 2

Sodium Hydroxide in Agar #2: Localized application, applied in semi-solid cooling phase using a JTP intermediary layer.

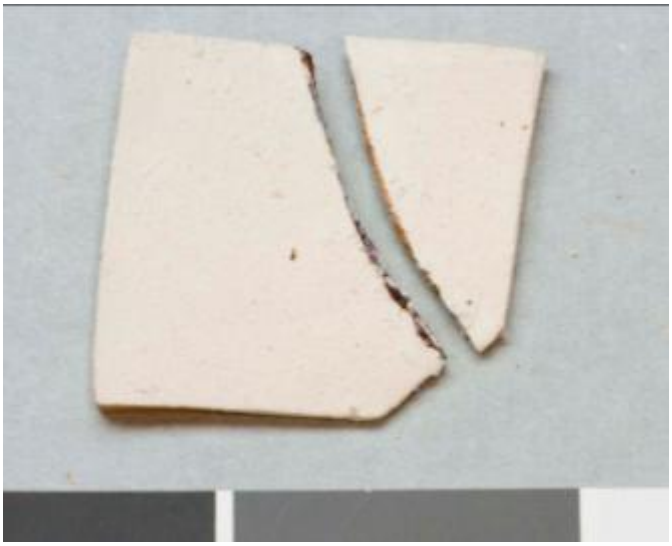
After treatment: top and bottom views (left to right)
Total duration of treatment = 48 hours

NaOH in Carbopol 934 (prepared in deionized water, 6% w/v).

After treatment: top view
Total duration of treatment = 24 hours

NaOH in Pappina Wax Emulsion

Sodium Hydroxide in Pappina Wax Emulsion: Full application, applied with a spatula using a JTP intermediary layer



After treatment: top view
Total duration of treatment = 72 hours

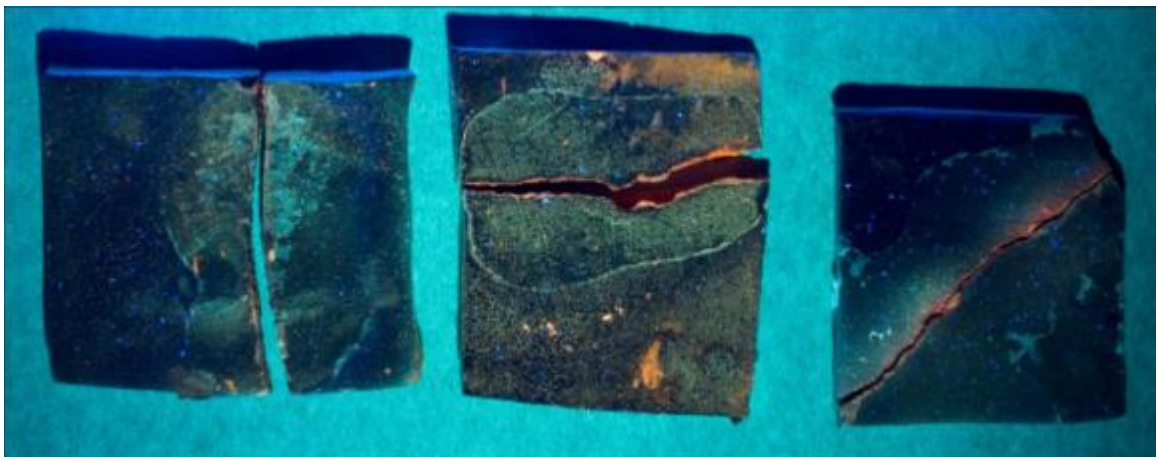
Sodium Hydroxide in Pappina Wax Emulsion: Localized application, applied with a spatula using a JTP intermediary layer (on bottom of same tile used to test full application of Pappina)

After treatment: bottom view
Total duration of treatment = 72 hours

$Ca(OH)_2$ in Agar #2

Calcium Hydroxide in Agar 2: Full surface application, applied as a rigid gel using a JTP intermediary layer

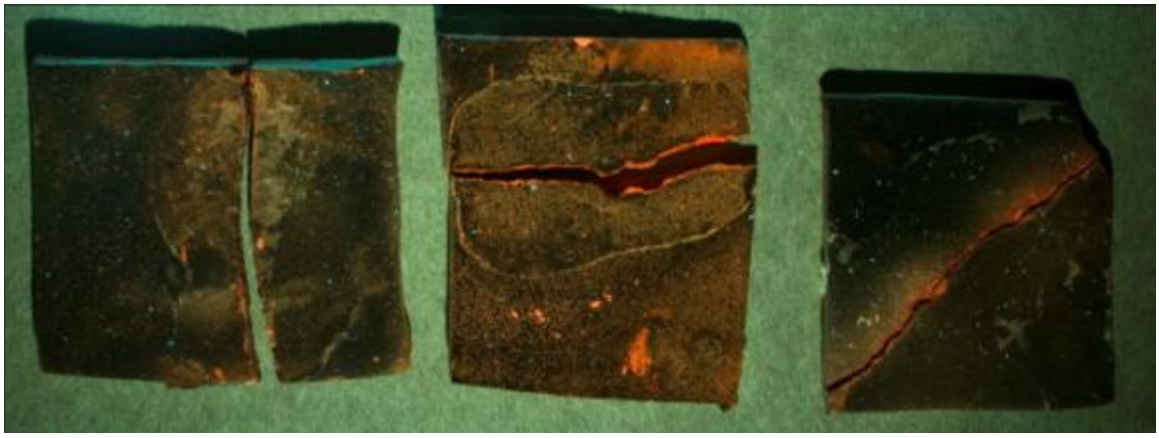
After treatment: top and bottom views (left to right)
Total duration of treatment = 48 hours



All tiles were treated with a combination of agar gel and NaOH, with the centre tile having used a JTP intermediary layer.

After treatment Ultraviolet induced fluorescence image. A tuneable forensic light source was used at an excitation wavelength of 300-400nm. The image was captured using an unmodified Canon Rebel XSi DSLR fitted with a Peca 916 visible pass filter.

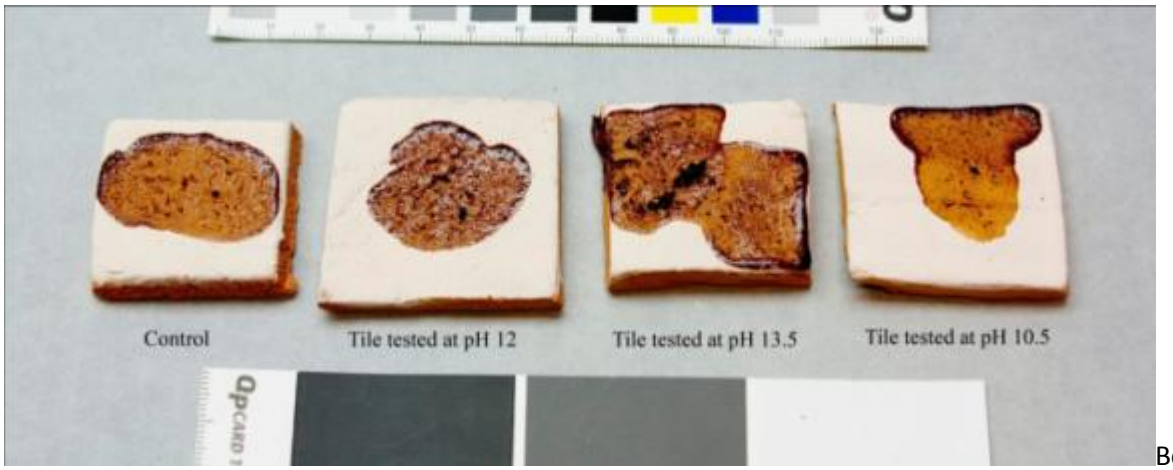
Faint traces of fluorescence can be discerned along the edge that could be attributed to very minimal shellac residues and some salt residues from treatment. Additionally, pale whitish colored residues and tide lines can be attributed to agar residues. It is also possible to see that some of the shellac has migrated, particularly in the centre tile.



Same image and parameters as above, though in this instance, an additional yellow filter to cut near ultraviolet wavelengths below 480nm to increase contrast.

Trial 3

Date: December 12th, 2010



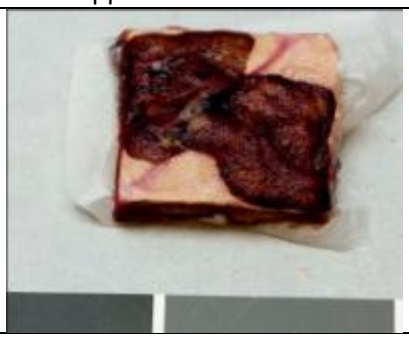
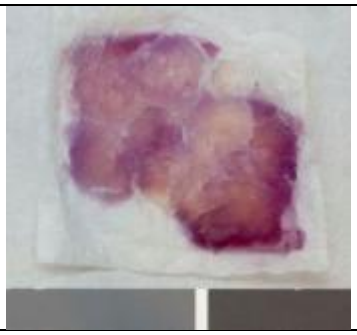
Before Treatment: Tiles to be tested during Trial 3 for surface deposition of shellac

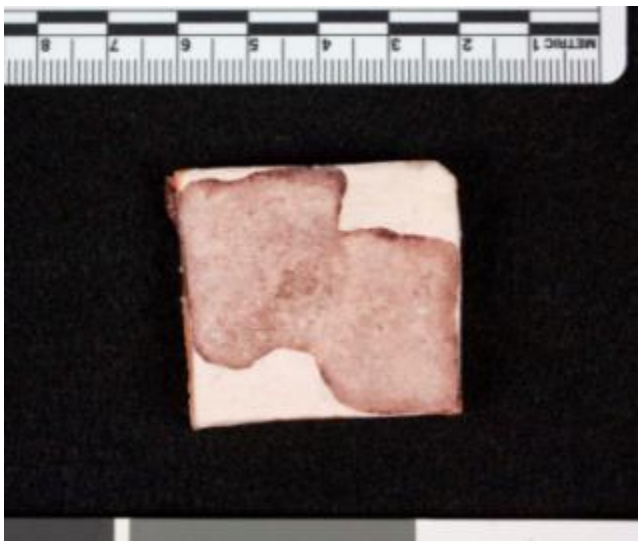
NaOH in Agar applied as warm soft gel at pH 13.5

		
pH `13.5: 0 minutes	pH 13.5: 5 minutes	pH 13.5: After Treatment

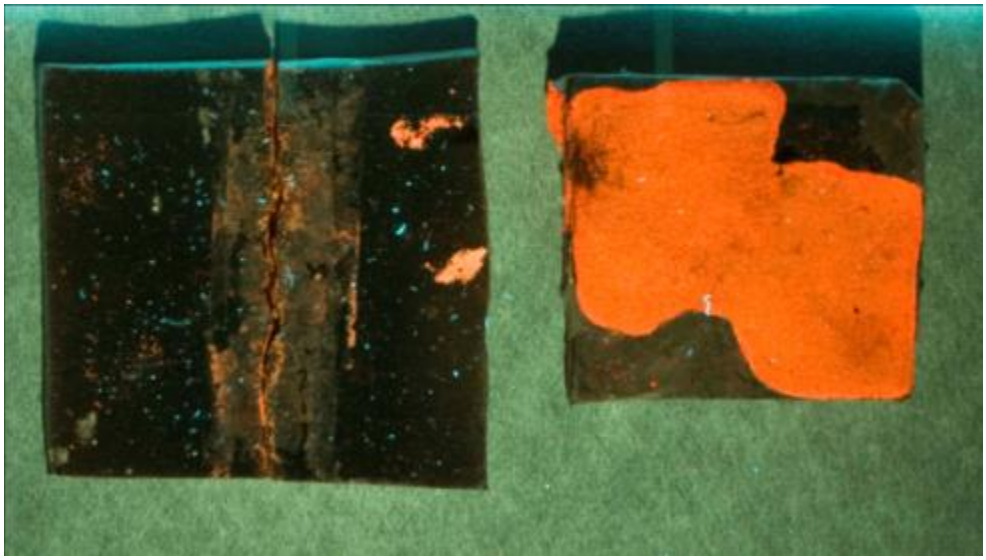
During and after treatment: top views

Total duration of treatment = 72 hours Applications = 5

		
pH 13.5: 0 minutes	pH 13.5: 5 minutes	Agar gel after removal (5 mins)



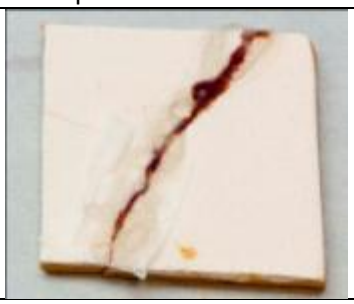
After treatment: top view
Total duration of treatment = 72 hours Applications = 4



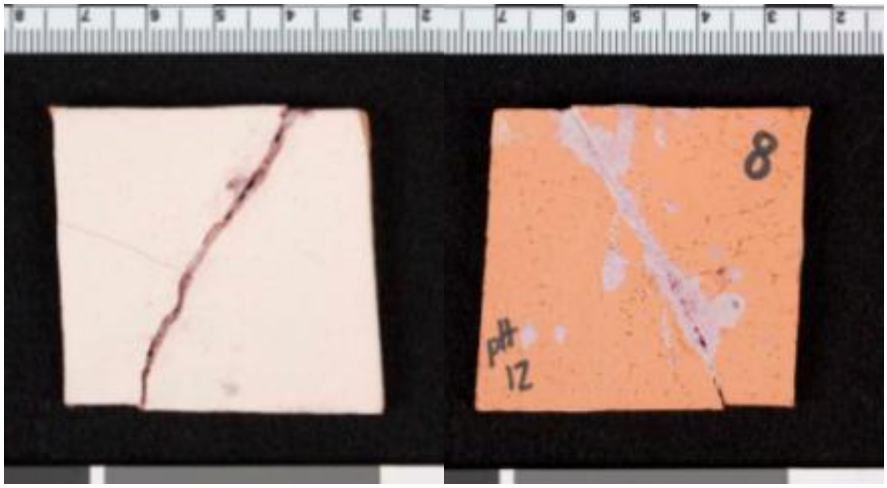
After treatment Ultraviolet induced fluorescence image. A tuneable forensic light source was used at an excitation wavelength of 300-400nm. The image was captured using an unmodified Canon Rebel XSi DSLR fitted with a Peca 916 visible pass filter. An additional yellow filter to cut near ultraviolet wavelengths below 480nm was used to increase contrast.

Faint traces of fluorescence can be discerned along the edge that could be attributed to very minimal shellac residues and some salt residues from treatment. Additionally, pale whitish colored residues and tide lines can be attributed to agar residues. It is also possible to see that some of the shellac has migrated beyond the original mend on the left side tile.

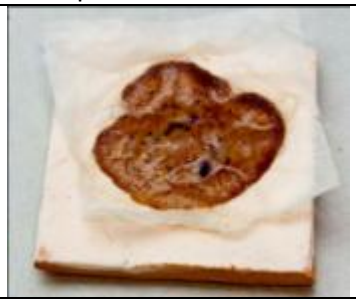
NaOH in Agar applied as warm soft gel at pH 12

		
pH 12: 0 minutes	pH 12: 5 minutes	pH 12: 10 minutes
		
pH 12: 15 minutes	pH 12: 20 minutes	pH 12: 25 minutes

During treatment: top views

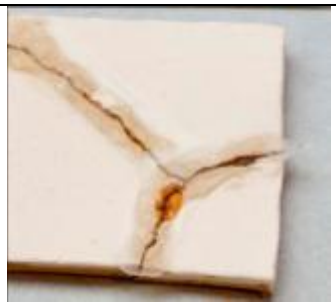
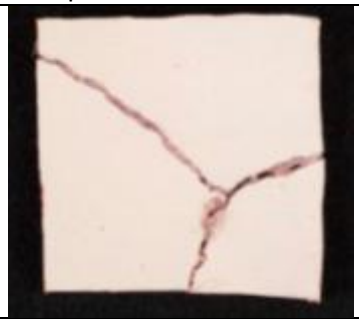
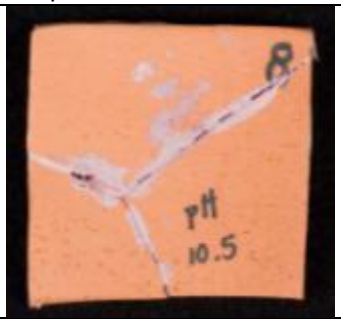


After treatment: top and bottom views (left to right)
Total duration of treatment = 72 hours Applications = 4

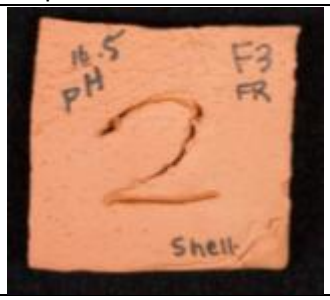
		
pH 12: 0 minutes	pH 12: 5 minutes	pH 12: 10 minutes
		
pH 12: 15 minutes	pH 12: 20 minutes	pH 12: 25 minutes

After treatment: top view
Total duration of treatment = 72 hours Applications = 4

NaOH in Agar applied as warm soft gel at pH 10.5

		
pH 10.5: 0 minutes	pH 10.5: 5 minutes	pH 10.5: 10 minutes
		
pH 10.5: 20 minutes	pH 10.5: After Treatment (top)	pH 10.5: After Treatment (bottom)

During and after treatment
Total duration of treatment = 72 hours Applications = 4

		
pH 10.5: 0 minutes	pH 10.5: 5 minutes	pH 10.5: 10 minutes
		
pH 10.5: 15 minutes	pH 10.5: After Treatment (Top)	pH 10.5: After Treatment (Bottom)

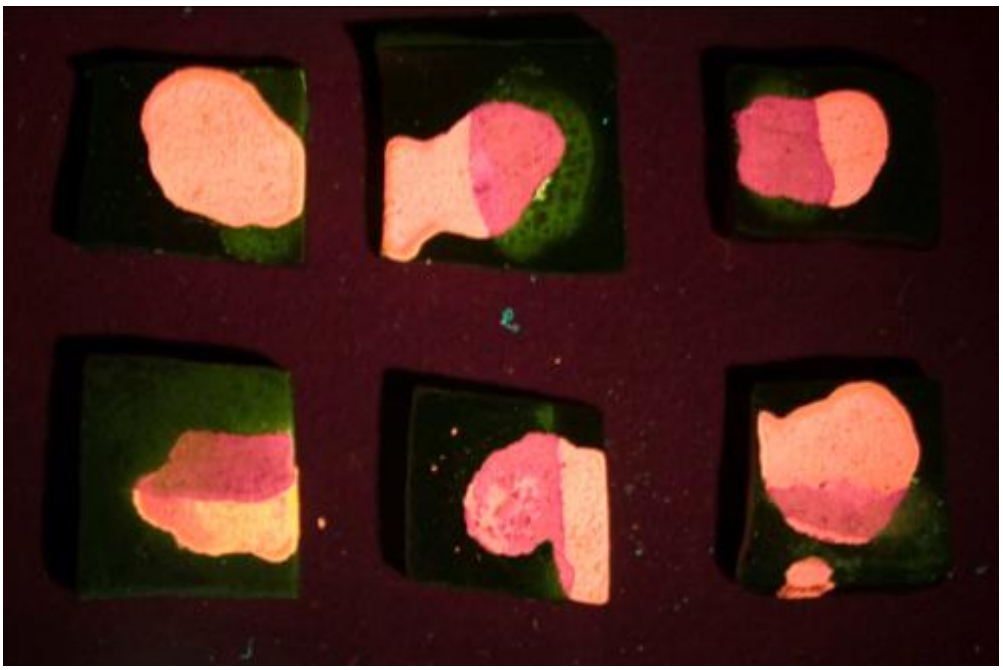
During and after treatment
Total duration of treatment = 72 hours Applications = 4

Trial 4

Date: February 7th, 2011

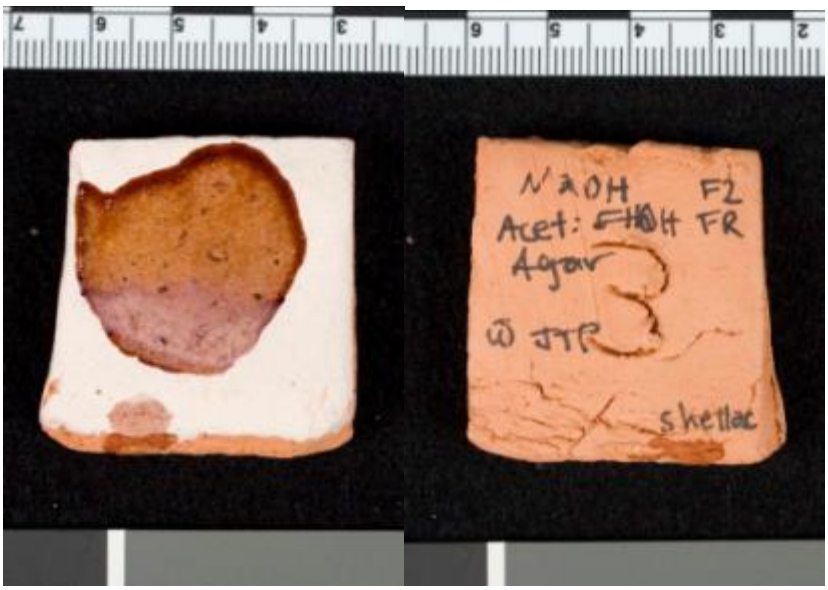
Trial 4 tiles before treatment – photograph taken in diffuse light

Trial 4 tiles after treatments – photograph taken in diffuse light



Trial 4 tiles after treatments in UV-Visible Fluorescence (excited at 300-400nm, captured at 400-700nm)
Orange = Shellac Pink = Lac Dye White = Agar Residues

1:1 Ethanol and acetone in agar and NaOH – applied as a warm soft gel at pH 13.5 w/o intermediary layer (Top and Bottom views)



1:1 Ethanol and acetone in agar and NaOH – applied as a warm soft gel at pH 13.5 using a JTP intermediary layer (Top and Bottom View)

1:1 Ethanol and acetone in agar and NaOH – applied as cooled rigid gel w/o intermediary layer at pH 13.5 w/o an intermediary layer (Top and Bottom View)

1:1 Ethanol and acetone in agar – applied as a warm soft gel at pH 7.5 w/o an intermediary layer (Top and Bottom View)

Acetone in agar and NaOH – applied as a warm soft gel at pH 13.5 w/o an intermediary layer (Top and Bottom View)

Ethanol in agar and NaOH – applied as a warm soft gel at pH 13.5 w/o an intermediary layer (Top and Bottom View)

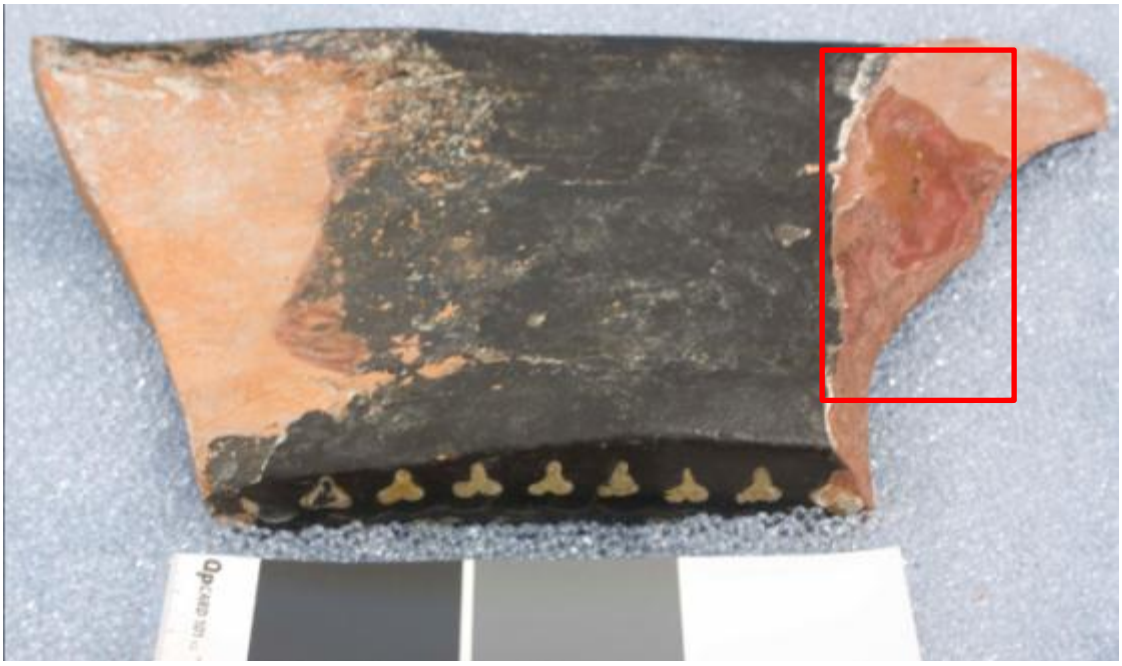
Appendix 4: Apulian Ceramic Trials (Trials 5-10)

The ceramic fragments on which the techniques of this study were tested on were graciously provided by Marie Svoboda, Antiquities Conservator with the J. Paul Getty Museum, in Malibu CA. The fragments come from a series of Apulian vases, on loan to the JPGM from the Antikensammlung Museum in Berlin for their conservation. It is believed that these fragments were initially conserved sometime between 1820 and 1826 by Rafaelle Gargiulo for Frantz Koller. In addition to a number of organic and inorganic bulking agents, a significant component of the adhesive used on these vessels is known to be unrefined shellac (Milanese 2010), making these fragments ideal for the testing of materials that showed success in reversing shellac on the test tiles (Trials 1-4).

Prior to testing, spot tests were conducted to ascertain whether the ceramic body could sustain prolonged exposure to high pH. As the end products of the hydrolysis are water soluble, clearance will be accomplished during the desalination process that the JPGM had previously decided to undertake.

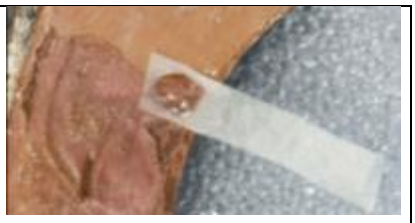
Trial 5

Date: January 14th, 2011



Fragment BT showing residual shellac, already showing pinkish discolouration from lac dye.

Detail of area to be treated (shown in red box in above image). The treatment used employed NaOH in warm soft gelled agar with a Japanese tissue paper intermediary layer. pH = 10.5

 0 minutes	 5 minutes	 10 minutes
 15 minutes	 20 minutes	 25 minutes
 30 minutes (left dot is 0 minutes)	 35 minutes (left dot- 5 minutes)	 40 minutes (left dot–10minutes)

Detail of spots tested during treatment.

Preliminary Results: No observable changes after 40 minutes of treatment.

Trial 6

Date: January 20th, 2011

Spot 1: NaOH + EtOH + Agar; Spot 2: NaOH + Acetone + Agar; Spot 3: Carbopol Solvent Gel

Sample 1 Tile before treatment

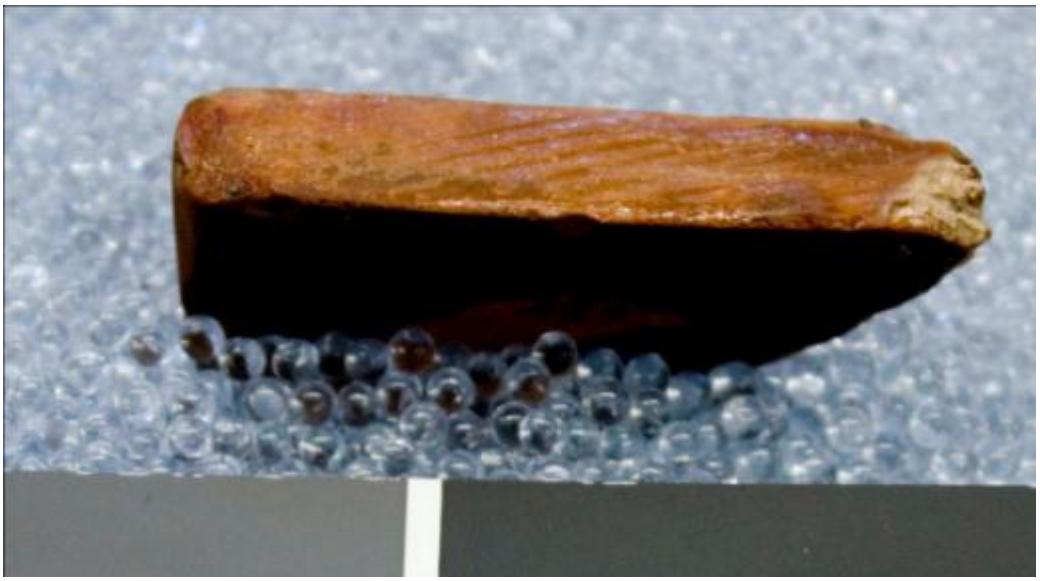
Sample 1 Tile During Treatment: After 10 minutes of treatment

Sample 1 Tile During Treatment: After 40 minutes of treatment

Sample 1 Tile after treatment

Trial 7

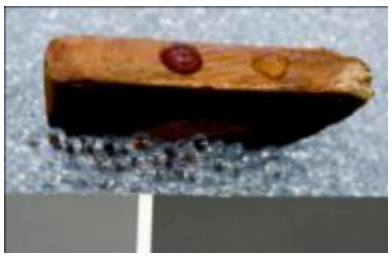
Date: February 14, 2011



Ceramic edge before treatment

Sample 2 Tile after treatment

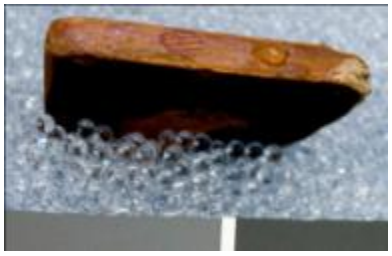
Spot 1: Carbopol Solvent Gel (acetone, ethanol, Ethomeen C25, Carbopol 934); pH = 9
Spot 2: NaOH + EtOH+ agar (applied warm as soft gel); pH = 13.5
Spot 3: Agar in deionized water (applied warm as soft gel); pH = 7



Application 1 – 0 minutes
Spots 2 and 3

Application 1 – 5 minutes
Spots 2 and 3

Application 1 – Spots 1 and 3 (5/10 minutes)
Application of agar in H20 to Spot 2 to clear



AT of Application 1 to Spots 1 and 2
15 minutes for Spot 3

Application 2 to Spot 2
5 minutes after application

Application 3 to Spot 2
10 minutes after application

Trial 8

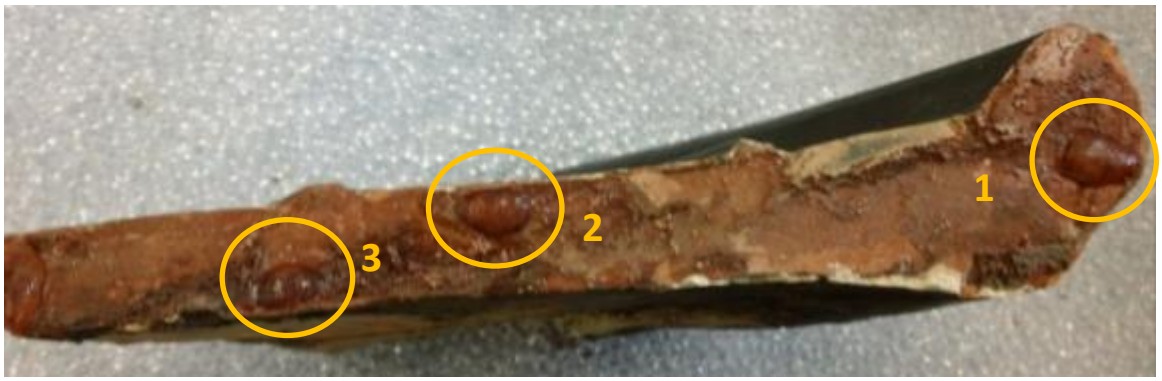
Date: March 14, 2011

Rim fragment from Apulian red-figure ceramic used for testing. Before Treatment

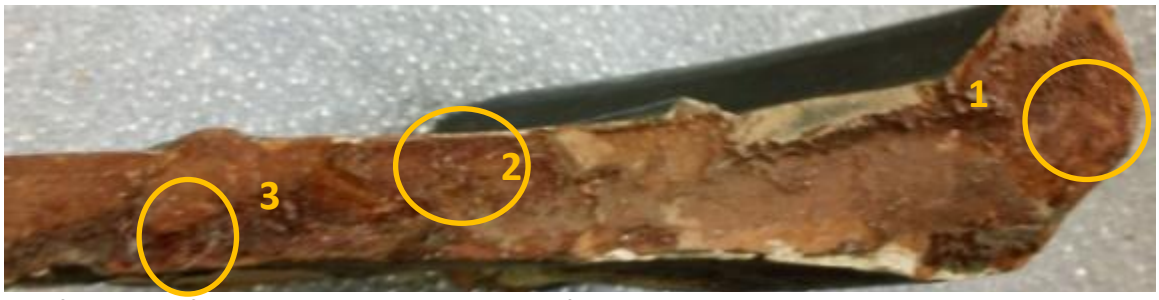
Rim fragment during treatment (1 minute after application).
Spot 1: NaOH + EtOH + agar applied as warm gel; pH = 12.5
Spot 2: NaOH + EtOH + agar, applied as warm gel; pH = 13.5
Spot 3: Carbopol solvent gel (ethanol, acetone, Ethomeen C25); pH = 9

Rim fragment during treatment. Second application: 1 minute after application. Total time elapsed = 22 minutes

Rim fragment during treatment – after removal of third application. Total time elapsed = 40 minutes



Rim fragment during treatment. Fourth application: 1 minute after application. Total time elapsed = 70 minutes.

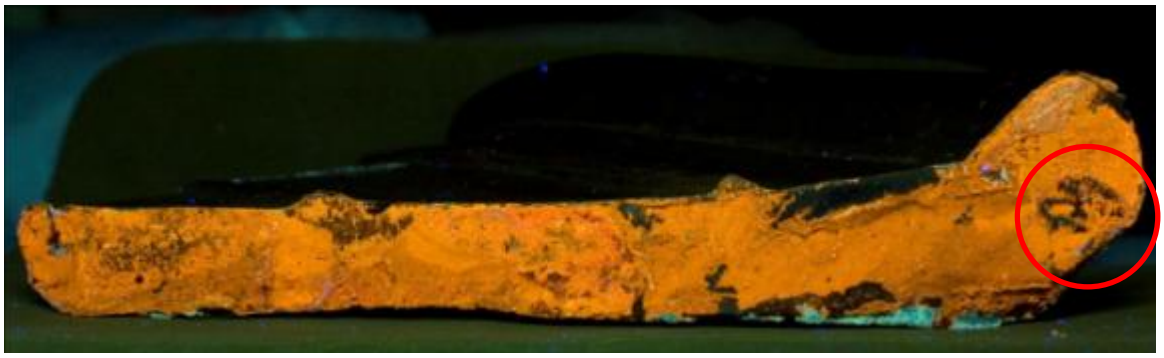


Rim fragment after treatment. Total number of applications = 4. Total time elapsed = 1 hour 37 minutes.

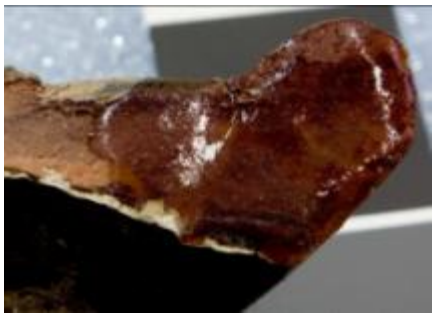
Trial 9

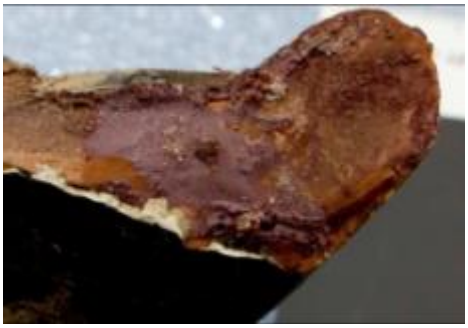
Date: April 28 and May 5, 2011

Rim fragment from Trial 8 to be used for Trial 9. BT



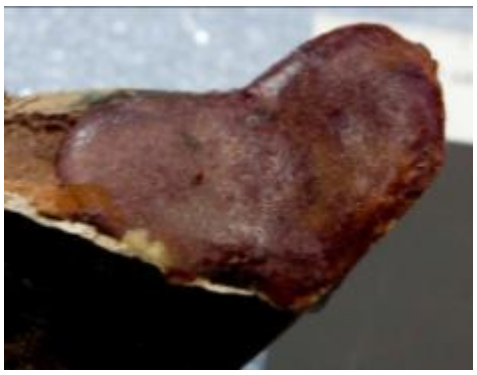
Rim fragment used in Trial 9 BT using Long wave Ultraviolet-visible fluorescence. Orange indicates the presence of shellac. It is possible to see areas of shellac removal from Trial 8 (indicated above).





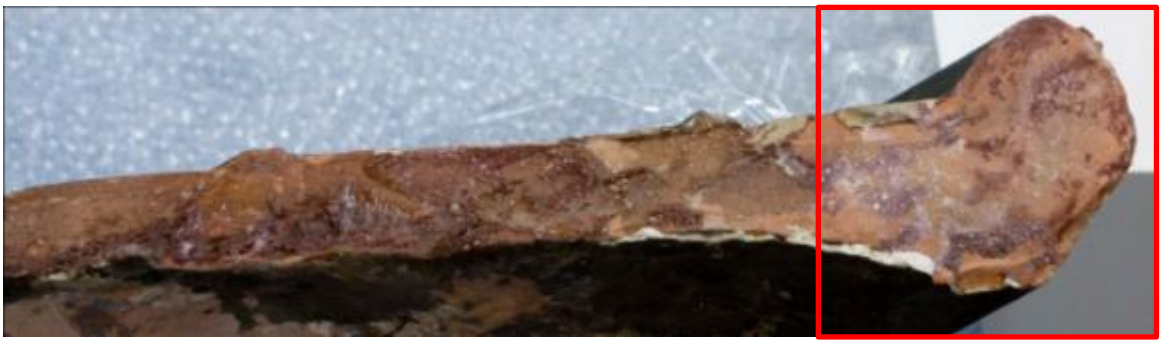
During treatment: First poultice application (left) and after removal of first poultice (right)
Time elapsed = 20 minutes

Treatment: NaOH, ethanol and agar, applied as warm soft gel. pH = 13.5



Application 3
Total time elapsed: 50 minutes

Application 4



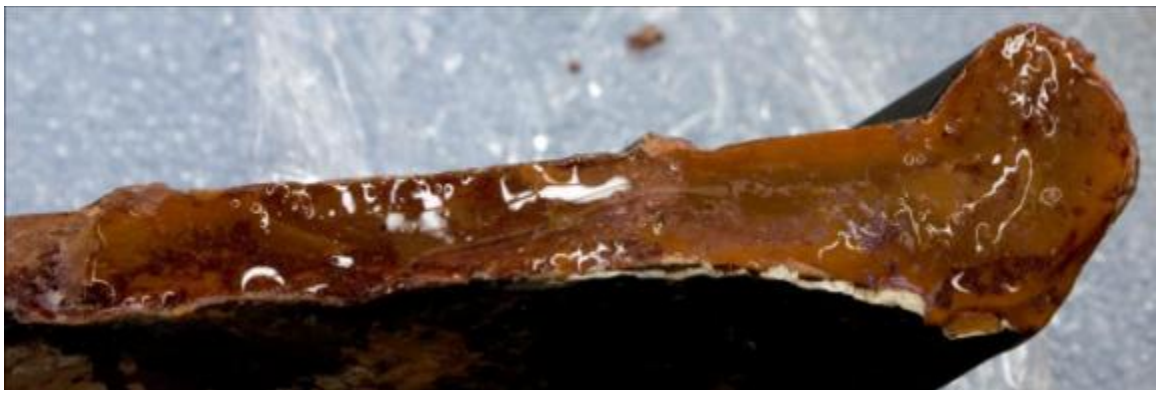
Rim fragment 1 week after first round of treatments (Applications 1-4). White encrustations likely to be residues from previous week's treatment (no clearance measures were taken).

Application 5 (0 minutes after application)

Extension of agar to cover more surface of the fragment edge. Application 6.
Time elapsed = 10 minutes

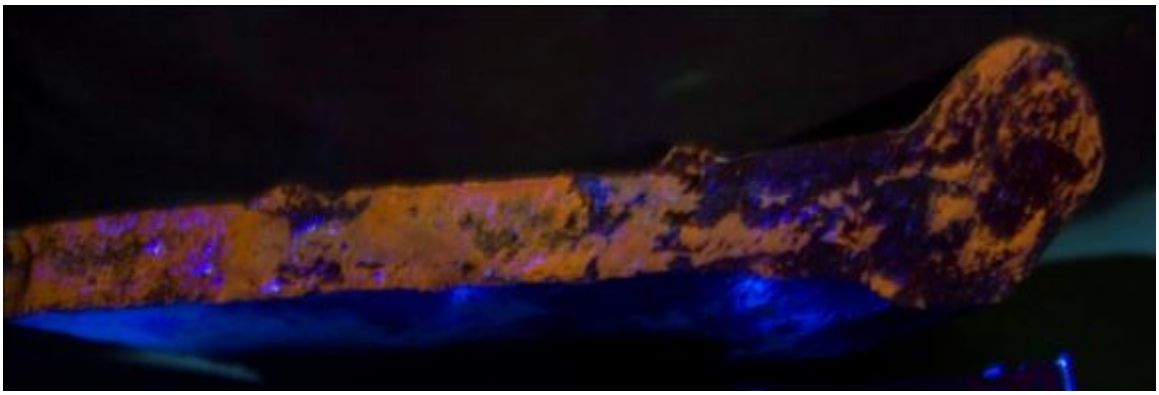
Application 6 Time elapsed = 23 minutes

Application 7 Time elapsed = 13 minutes



Application of agar in deionized water (7% w/v) after NaOH and ethanol treatment in order to improve clearance of residual alkali materials and to lower the surface pH; Agar pH = 7, Surface pH = 12.

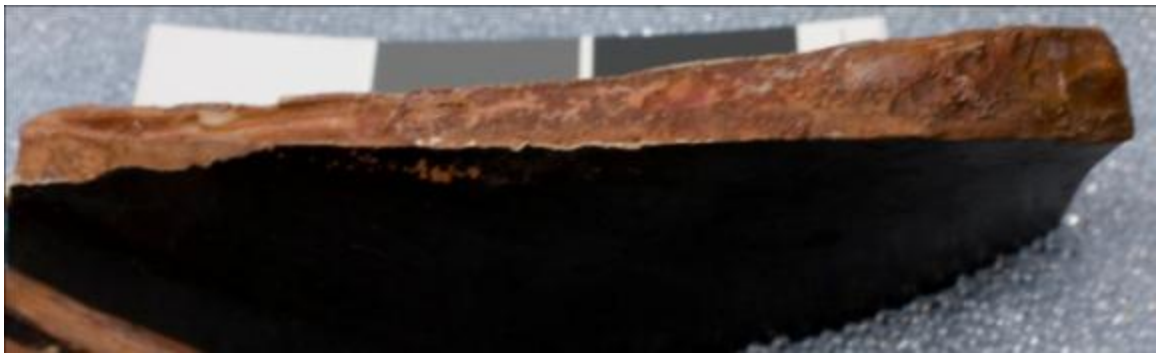
Rim fragment after treatment.



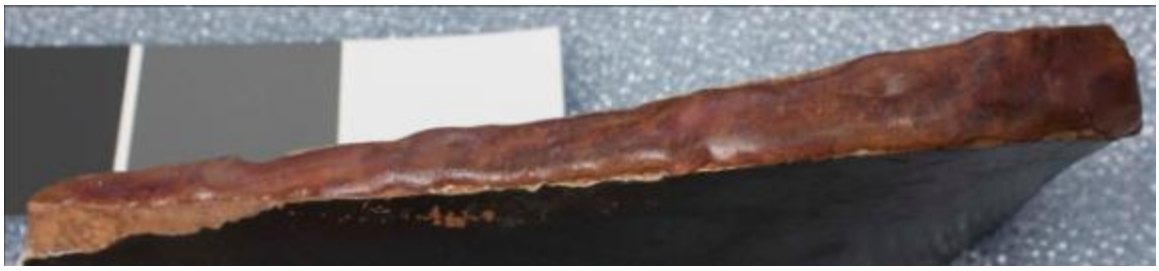
UV-Visible fluorescence photograph of rim fragment after treatment. Long-wave ultraviolet light was used to excite the shellac (in orange). The image was captured using an unmodified DSLR with a visible-pass filter (400-700nm with some leaks in the IR range).

Trial 10

Date: May 5 and May 12, 2011



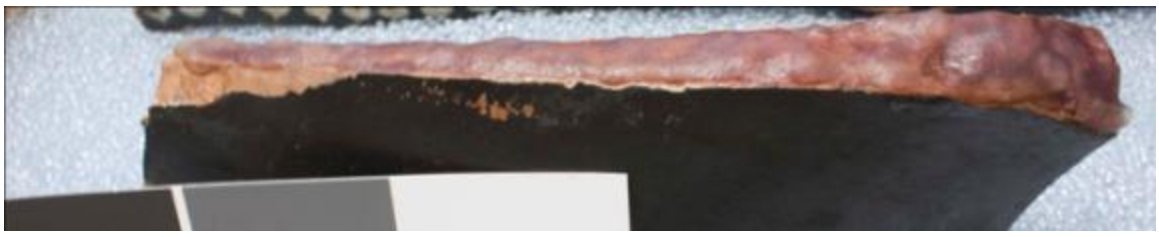
Apulian vessel fragment used for Trial 10 – BT



Treatment application 1: pH = 13.5 Time Elapsed = 5 minutes

Treatment: NaOH, ethanol and agar, applied as warm soft gel.

During treatment after removal of second application Time Elapsed = 40 minutes



During treatment application 3; pH = 13.5 Time Elapsed = 5 minutes

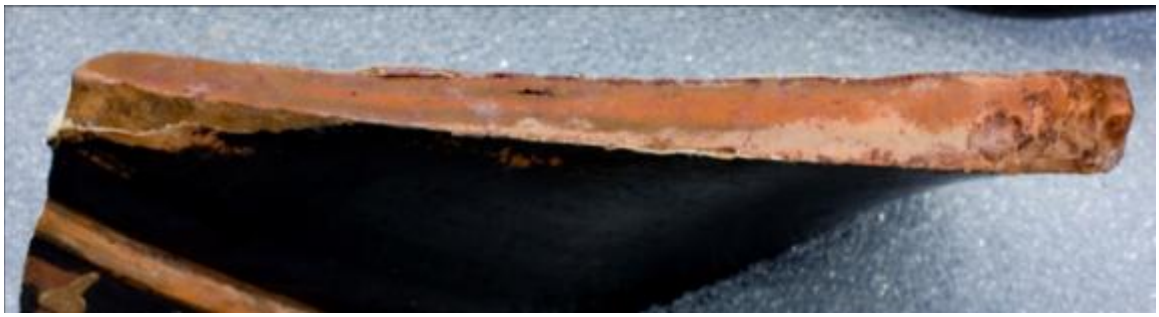
During Treatment after removal of third application. Total time elapsed = 1 hour 40 minutes

Applications 1 and 2 after removal from surface of fragment. Pink color is from absorption of dye and shellac into the gel matrix.

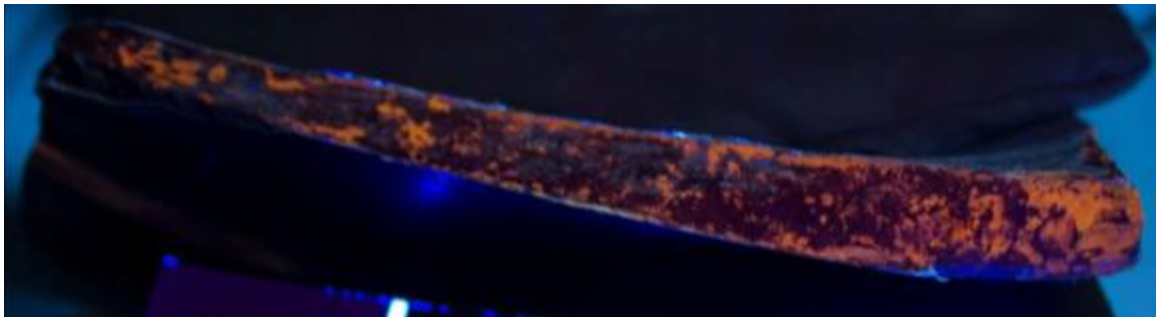
During treatment application 5; pH = 13.5 Time Elapsed = 2 minutes

Application of agar in deionized water for clearance post-treatment.

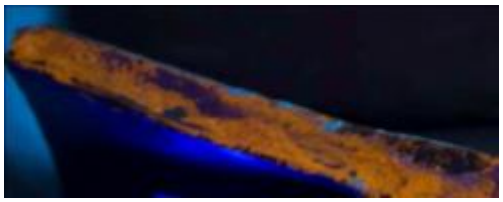
Total number of alkaline applications = 6
Total number of agar clearance applications = 2
Total Time of Treatment = 2 hours 40 minutes



After treatment



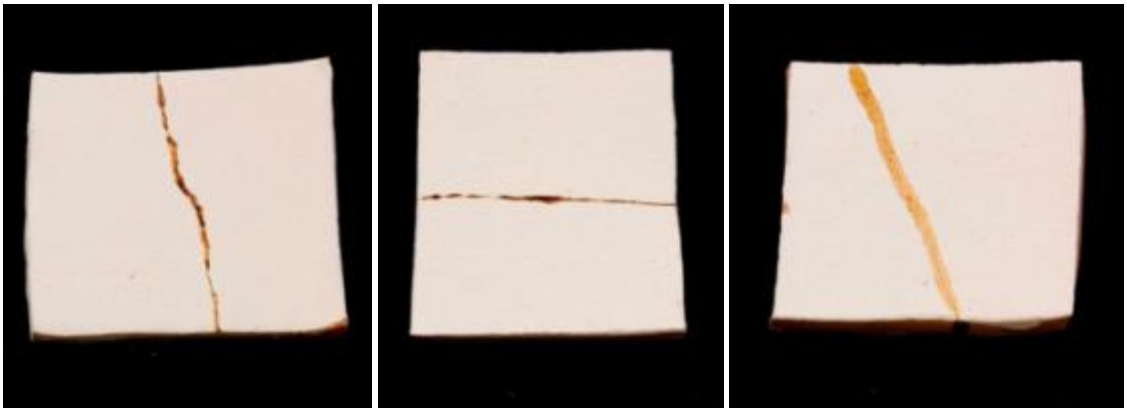
UV-Visible fluorescence photograph of fragment after treatment. Long-wave ultraviolet light was used to excite the shellac (in orange). The image was captured using an unmodified DSLR with a visible-pass filter (400-700nm with some leaks in the IR range).



UV-Visible fluorescence photograph of an untreated section of the same fragment as above. Long-wave ultraviolet light was used to excite the shellac (in orange). The image was captured using an unmodified DSLR with a visible-pass filter (400-700nm with some leaks in the IR range).

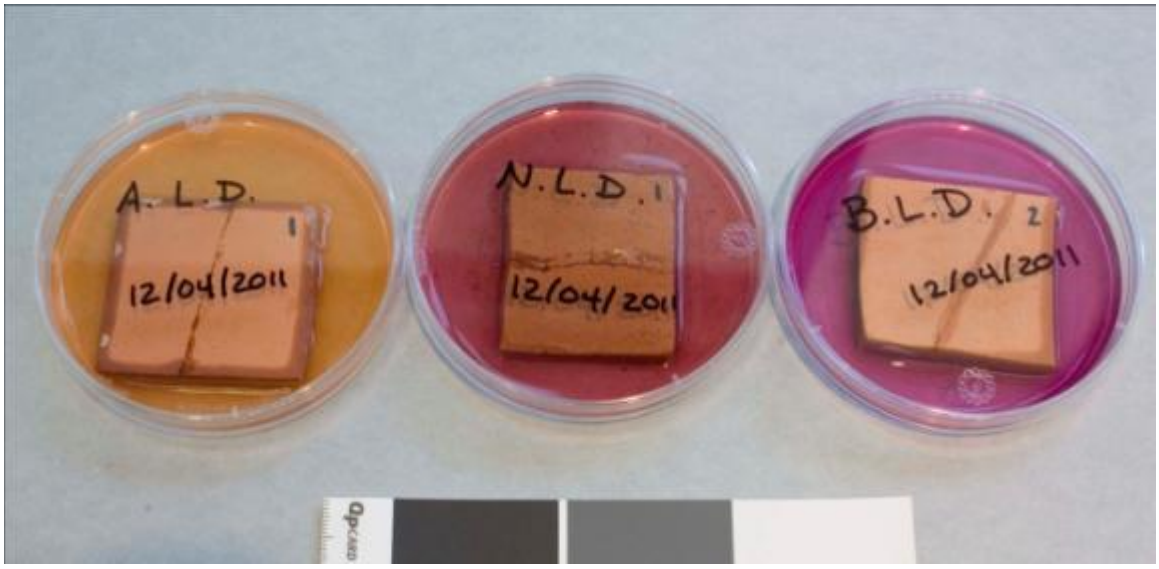
Appendix 5: Lac Dye Trials (Trials 11-13)

Trial 11

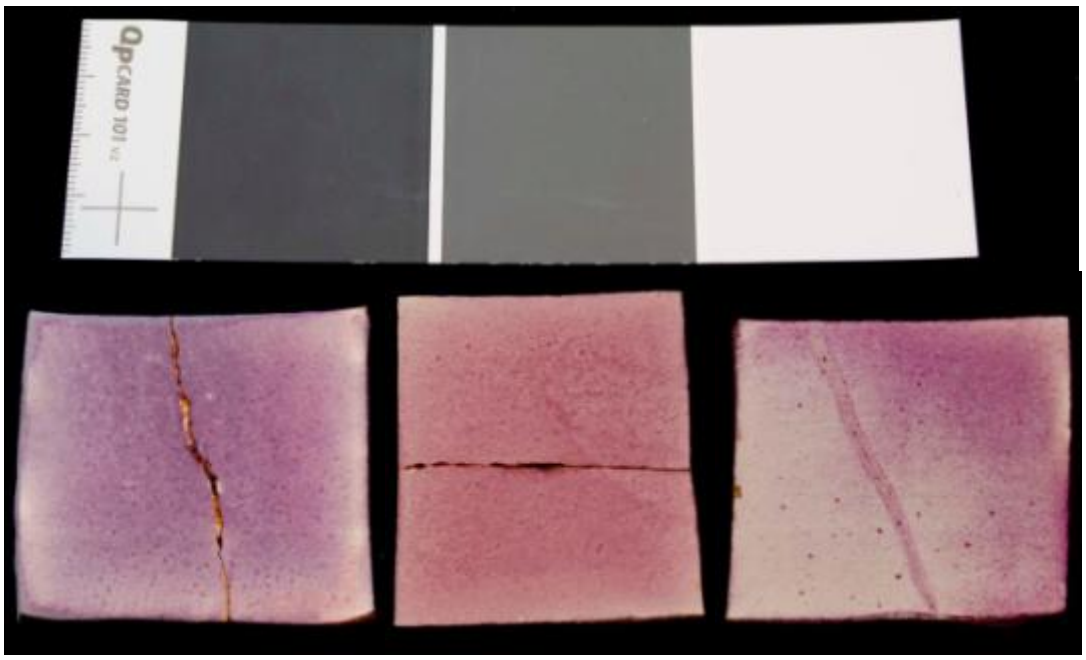


Acidic Lac Dye | Neutral Lac Dye | Basic Lac Dye

Ties to be stained with lac dye prior to staining.

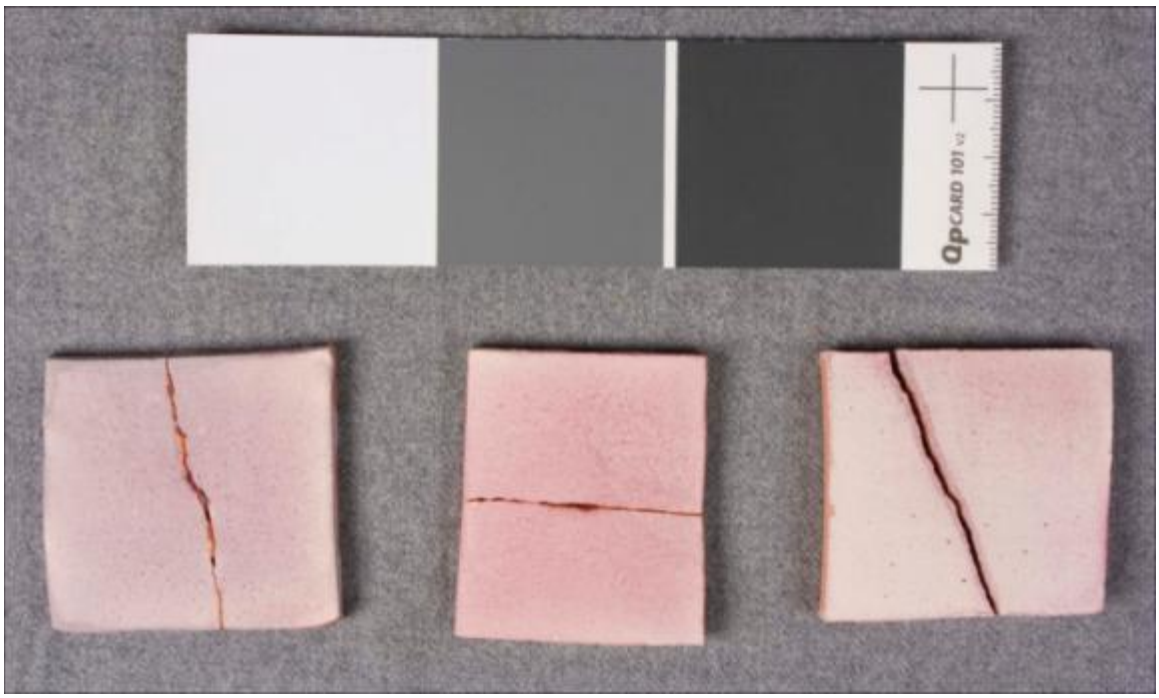


Tiles being stained, face down in (left to right) acidic, neutral and basic lac dyes.
Soaking time = 1 hour



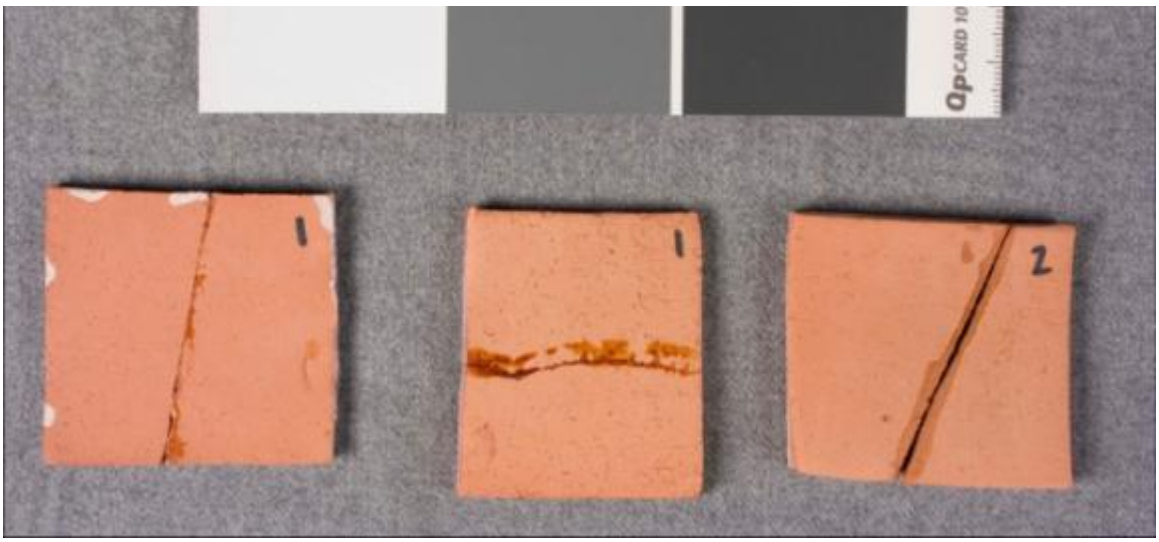
Acidic Lac Dye Neutral Lac Dye Basic Lac Dye

Tiles 5 minutes after removal from dye baths.



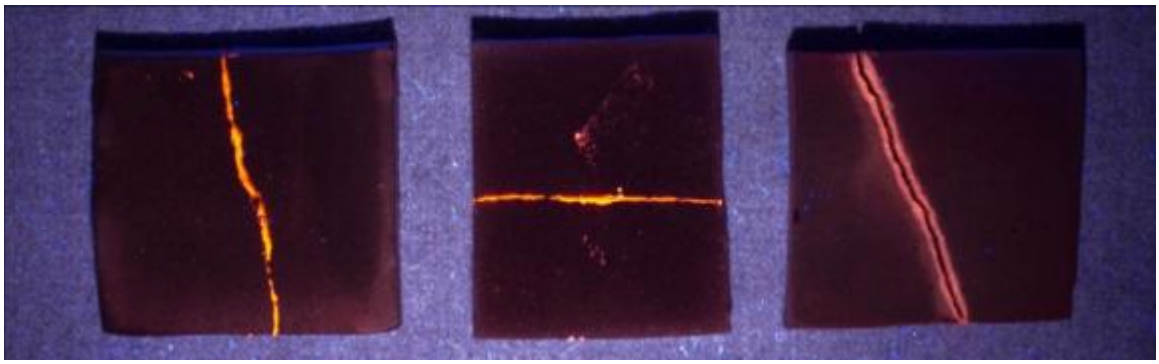
Acidic Lac Dye Neutral Lac Dye Basic Lac Dye

Tiles after drying for 3 days, top view - BT.



Acidic Lac Dye Neutral Lac Dye Basic Lac Dye

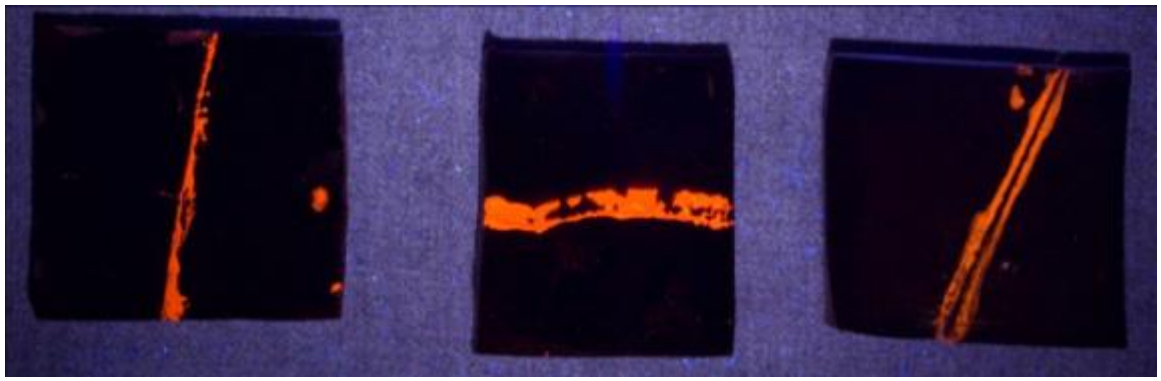
Tiles after drying for 3 days, bottom view – BT



Acidic Lac Dye Neutral Lac Dye Basic Lac Dye

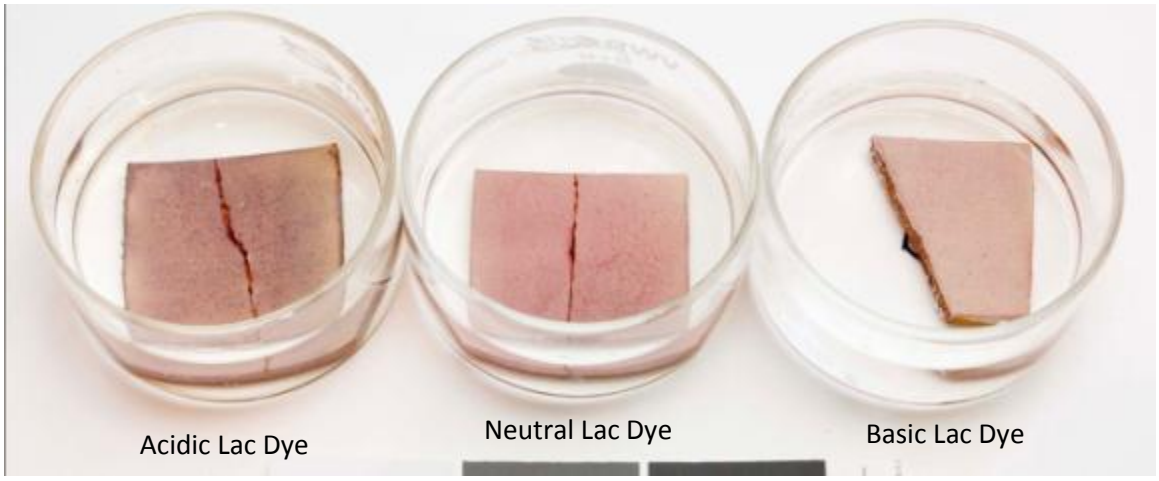
Tiles after staining and drying, top view – BT.

UV-Visible induced fluorescence (300-400nm excitation source, captured using visible pass filter)

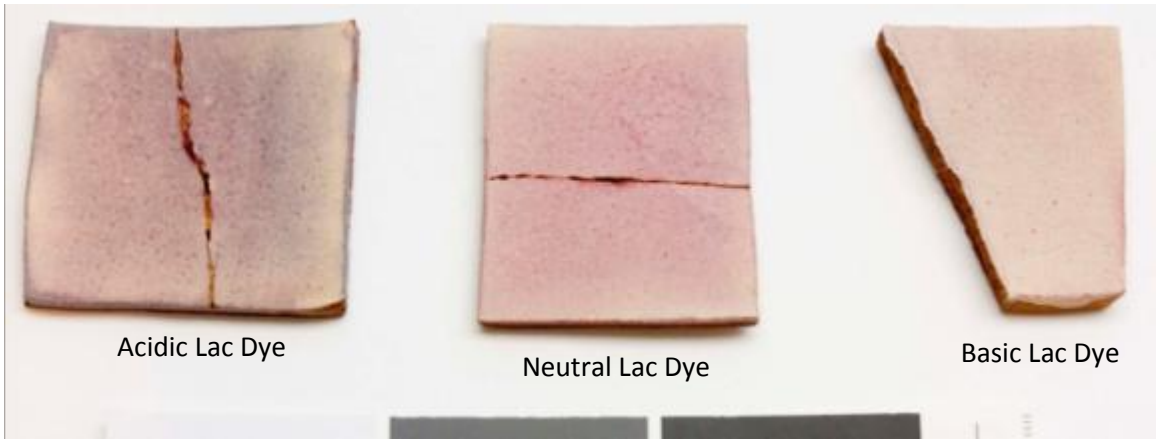


Acidic Lac Dye Neutral Lac Dye Basic Lac Dye

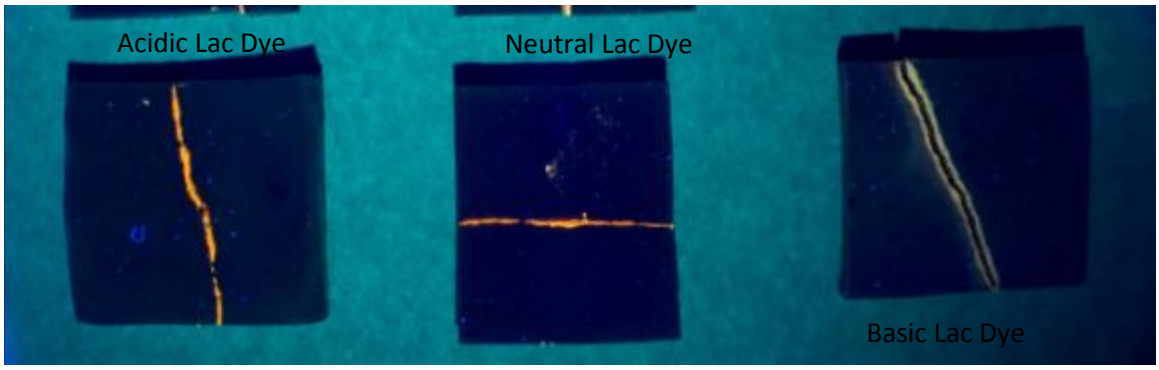
UV-Visible induced fluorescence (300-400nm excitation source, captured using visible pass filter)



Tiles being soaked in deionized water – time elapsed is 12 hours.

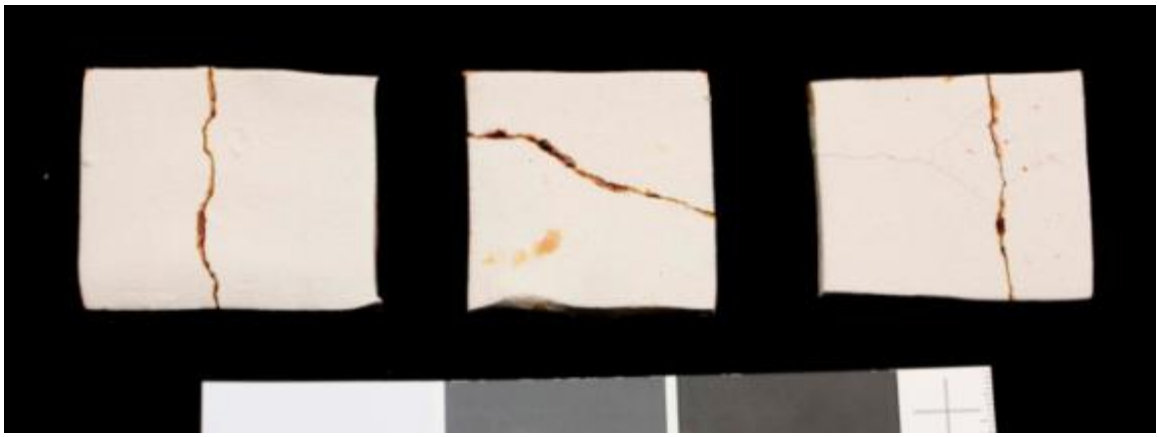


Tiles after soaking in deionized water for 24hrs. Tiles are still damp.



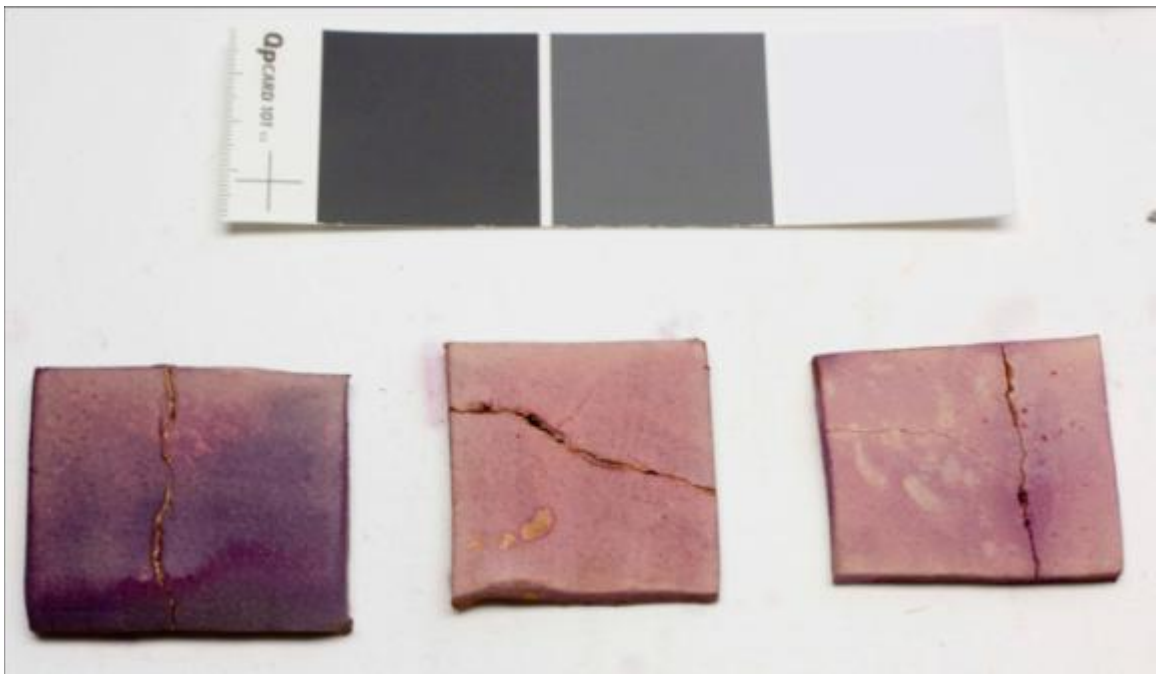
After treatment photograph using UV-visible induced fluorescence. The excitation source was a tuneable Forensic light using a 300-400nm excitation wavelength. Image was captured on an unmodified Canon Rebel XSi DSLR equipped with a Peca 916 visible pass filter. The faintly purple hue visible correlates to residual lac dye, while the orange correlates with shellac residues.

Trial 12 – Alkaline Soak



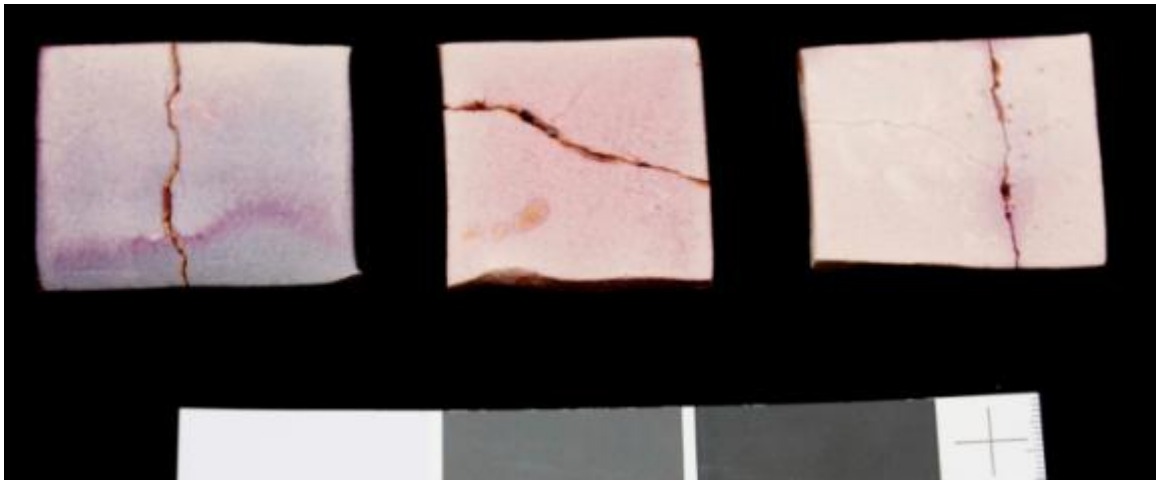
Acidic Lac Dye Neutral Lac Dye Basic Lac Dye
Ties to be stained with lac dye prior to staining.

Tiles being stained, face down in (left to right) acidic, neutral and basic lac dyes. Soaking time = 1 hour



Acidic Lac Dye Neutral Lac Dye Basic Lac Dye

Tiles 5 minutes after removal from dye baths.



Acidic Lac Dye Neutral Lac Dye Basic Lac Dye

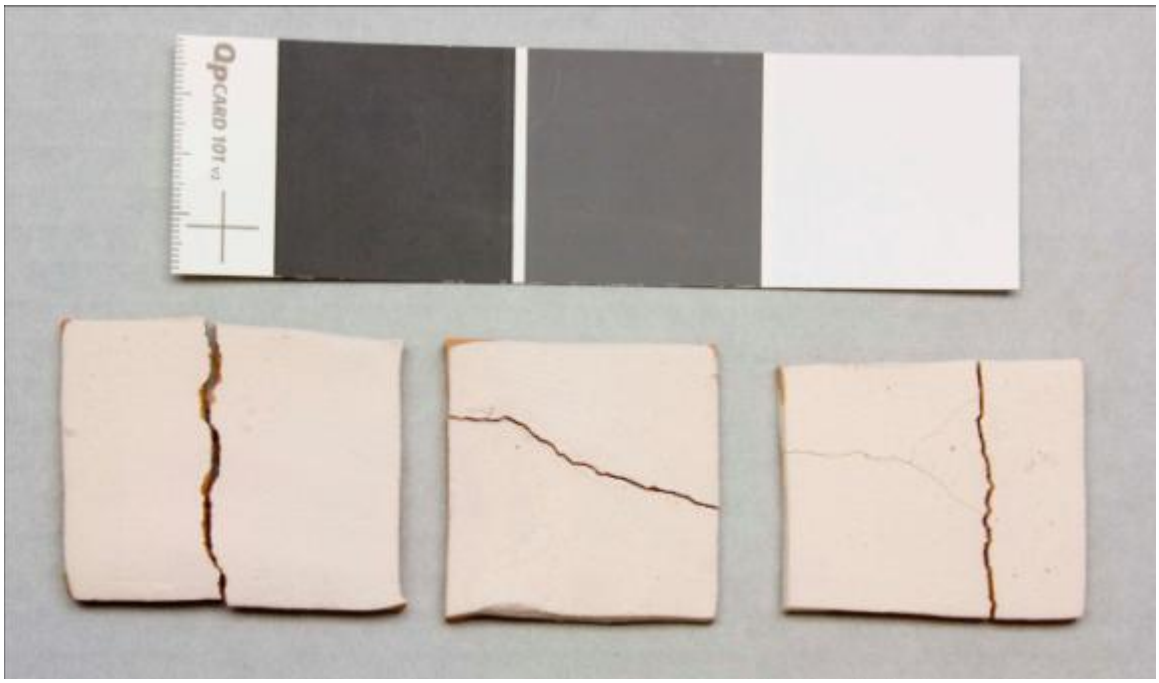
Tiles after drying for 3 days, top view - BT.

Acidic Lac Dye Neutral Lac Dye Basic Lac Dye

Tiles being soaked in NaOH (0 minutes)

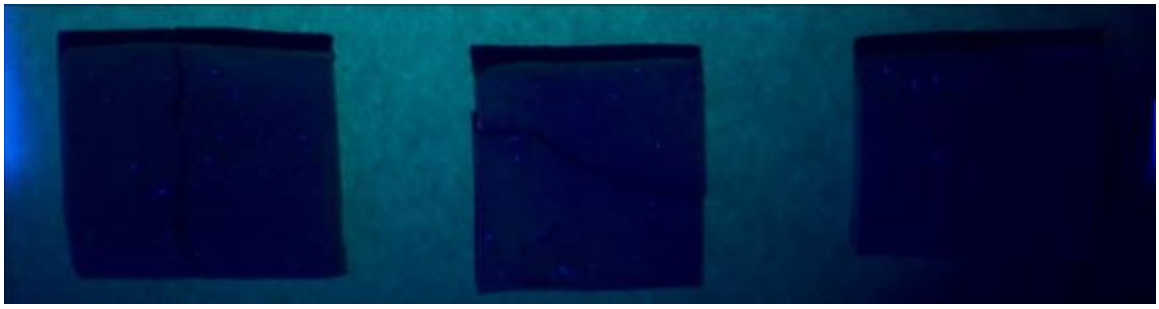
Acidic Lac Dye Neutral Lac Dye Basic Lac Dye

Tiles being soaked in NaOH – time elapsed is 25 minutes



Acidic Lac Dye Neutral Lac Dye Basic Lac Dye

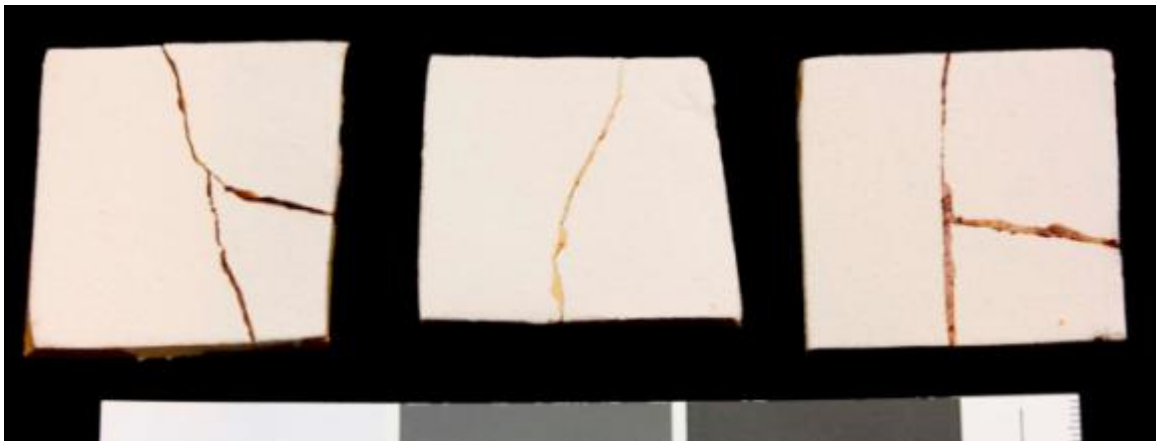
After treatment in 2% w/v NaOH and clearance in deionized water (tiles photographed 2 weeks after treatment carried out).



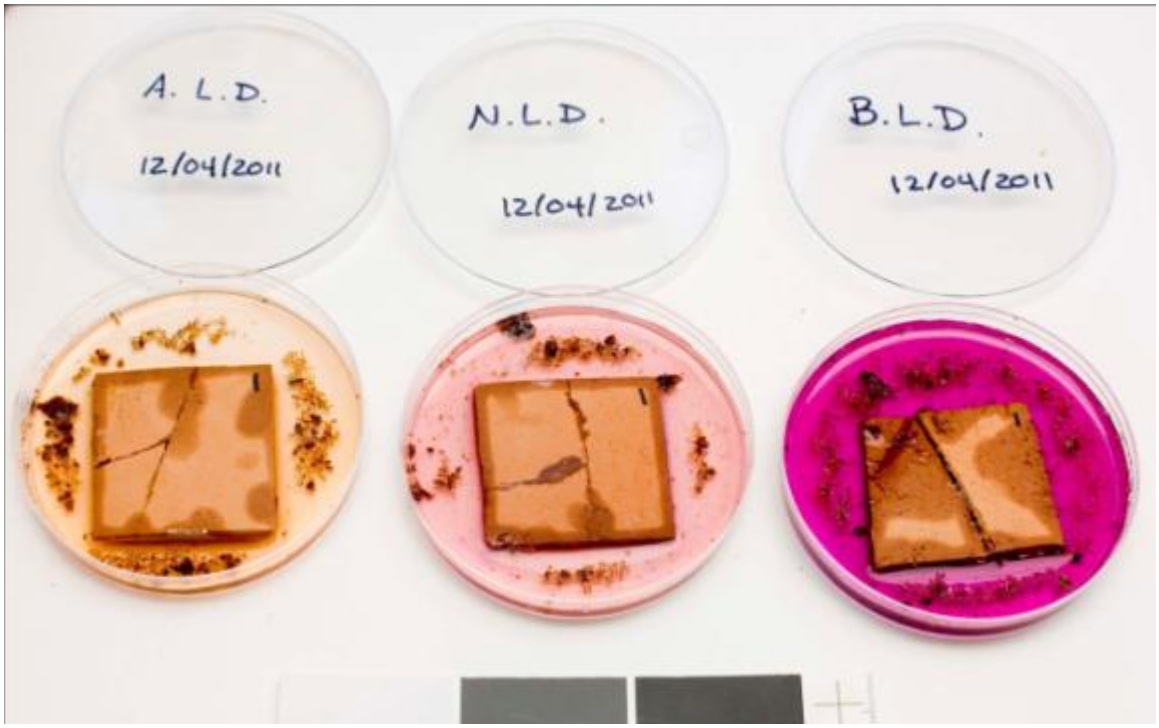
Acidic Lac Dye Neutral Lac Dye Basic Lac Dye

After treatment photograph using UV-visible induced fluorescence. The excitation source was a tuneable Forensic light using a 300-400nm excitation wavelength. Image was captured on an unmodified Canon Rebel XSi DSLR equipped with a Peca 916 visible pass filter. The faintly purple hue visible correlates to residual lac dye that is not visible in diffuse light. Additionally, the treatment in NaOH has completely removed all traces of shellac, which, if present, would fluoresce bright orange in the regions of the joins.

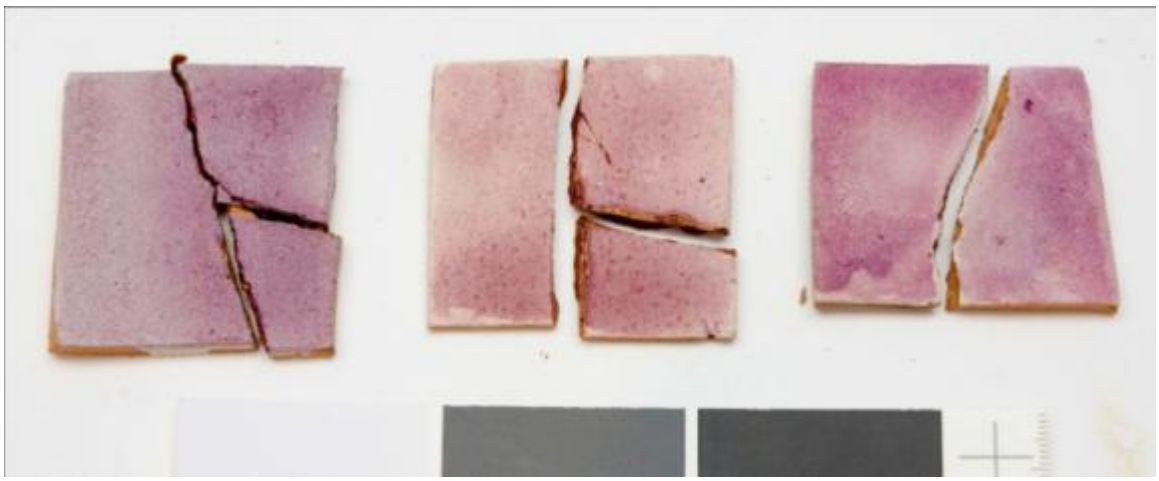
Trial 13: Acid Soak



Acidic Lac Dye Basic Lac Dye Neutral Lac Dye
Ties to be stained with lac dye prior to staining.

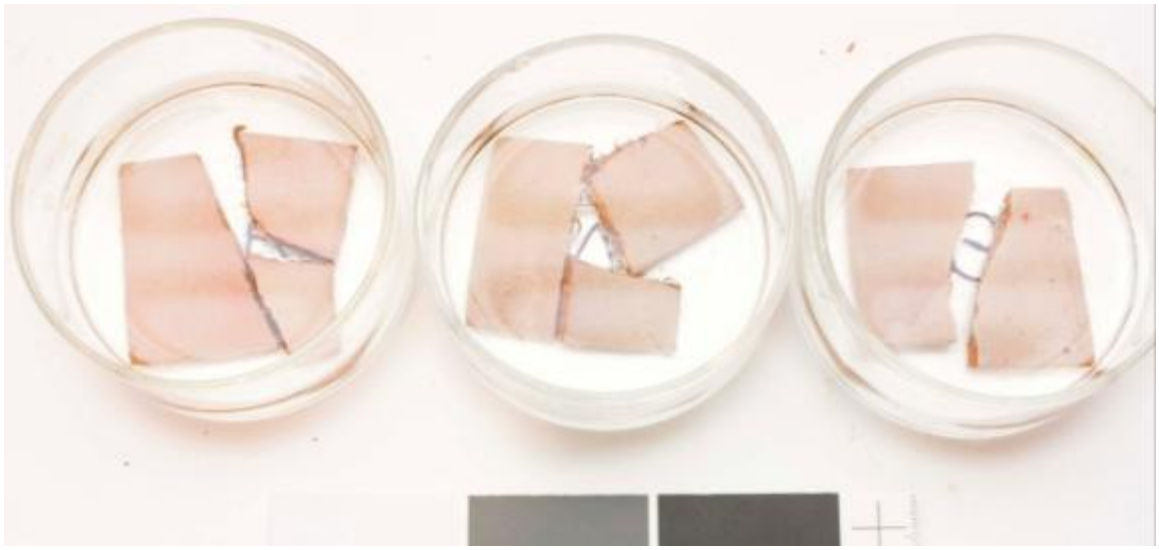


Tiles being stained, face down in (left to right) acidic, neutral and basic lac dyes. Soaking time = 1 hour



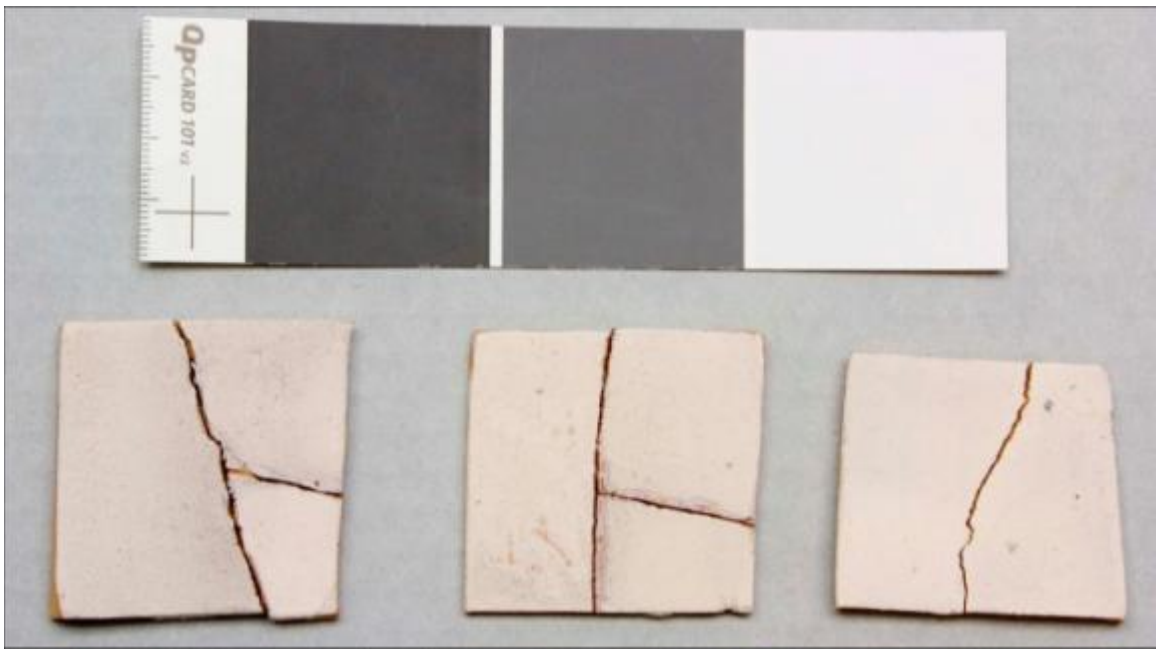
Acidic Lac Dye Neutral Lac Dye Basic Lac Dye

Tiles after staining – after 24 hours of drying, before treatment



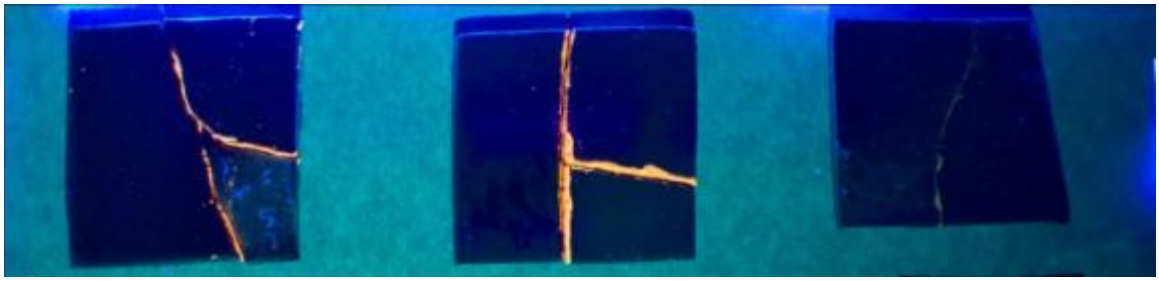
Acidic Lac Dye Neutral Lac Dye Basic Lac Dye

Tiles being soaked in dilute HCl (60 seconds)



Acidic Lac Dye Neutral Lac Dye Basic Lac Dye

After treatment in dilute HCl and clearance in deionized water (tiles photographed 2 weeks after treatment carried out).

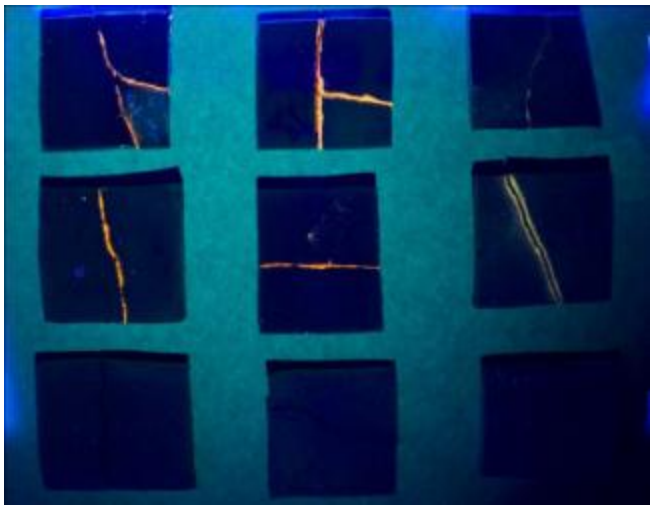


Acidic Lac Dye Neutral Lac Dye Basic Lac Dye

After treatment photograph using UV-visible induced fluorescence. The excitation source was a tuneable Forensic light using a 300-400nm excitation wavelength. Image was captured on an unmodified Canon Rebel XSi DSLR equipped with a Peca 916 visible pass filter. The faintly purple hue visible correlates to residual lac dye that is not visible in diffuse light, while the bright orange correlates with residual shellac. There is less shellac visible on the tile stained with basic lac dye because the staining process, being highly alkaline, started the hydrolysis reaction.

Trials 11-13 – Comparative Results

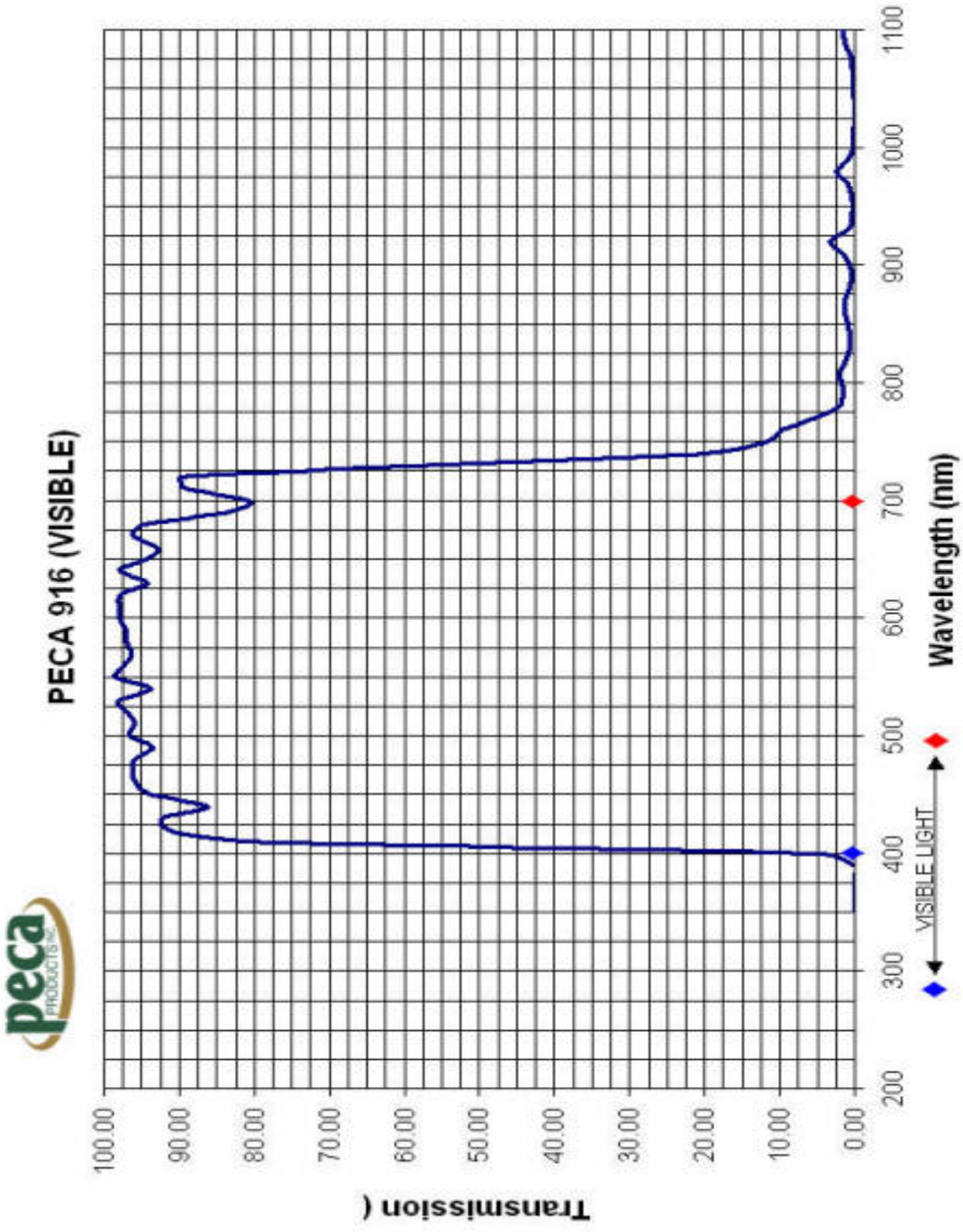
After treatment photograph in diffuse light of all tiles tested during Trials 11-13. As several weeks had elapsed since the tiles had been stained and treated, a significant amount of fading was noted (likely from exposure to light). In the future, tiles should be kept in a dark location when not being treated in order to minimize this variable.



Left to Right: Acidic Lac Dye; Neutral Lac Dye; Basic Lac Dye
Top to Bottom: HCl Treatment; Water Treatment; NaOH Treatment

After treatment photograph using UV-visible induced fluorescence. The excitation source was a tuneable Forensic light using a 300-400nm excitation wavelength. Image was captured on an unmodified Canon Rebel XSi DSLR equipped with a Peca 916 visible pass filter. The faintly purple hue visible correlates to residual lac dye that is not visible in diffuse light.

Appendix 6: Filter Spectrum Curve



Appendix 7: Experimental Methodology

Trial 1

The first experiment sought to assess the most effective reagent. Three alkaline reagents were chosen: a 2% (w/v) solution of NaOH, a 20% saturated solution (w/v) of ammonium carbonate), and a 28% solution (v/v) of ammonia hydroxide. In the first experiment, three tiles were selected from group 1 of the test tiles created, and emerged in the above solutions for 24 hours.

Based on the results from the table above, it was found that the NaOH solution was the most efficacious at hydrolyzing the shellac in the least amount of time. It is not certain at this time whether these results are based on the respective pH of the solutions, or if the results are more directly related to the pKb of each base.

Base	pH	Observations	Results
Sodium Hydroxide (2%)	14	Some bubbling	tile separated after 12 hours Total removal of dissolution of shellac after 24 hours
Ammonium Hydroxide (28%)	12	Intense effervescence. Shellac turned purple	tile separated after 36 hours. Residues remain
Ammonium Carbonate (20%)	10	Smallest bubbles. Shellac darkened.	tile does not separate

Tests and observations from Trial 1.

Trial 2

After the successful saponification of the shellac using a 2% (w/v) solution of aqueous NaOH, a second experiment was designed to treat the shellac in a more localized manner, as the extremely caustic nature and high pH of the NaOH makes it an aggressive treatment that may not be applicable in most conservation practices, particularly on sensitive substrates with alkaline sensitive pigments or tempers.

Based on the preliminary results from Trial 1, one tile was tested using a mixture of calcium hydroxide rather than sodium hydroxide in order to assess whether another strong base with a lower pH (12) would be equally effective.

For these experiments, like in the Lac Dye project (Scott, Drolet, and Blaik 2010), a number of poultice materials were used as supports. These supports were buffered to a pH of 14 when possible, or to a pH of 12 or 13 when the amount of sodium hydroxide introduced into the system began to cause the de-cohesion of the support material; this was particularly the case for the agar, which is at its most desirable consistency at a concentration of 4% (w/v) deionized water. In order to raise the pH of the support, a concentrated aqueous solution of NaOH (20% w/v) was added drop-wise until the desired pH was achieved. Some tiles used an all-over application, while others used only a localized application, in order to evaluate diffusion and effectiveness. Also, some trials used a barrier of Japanese Tissue paper, while others were applied directly to the surface of the tile. The tiles used in Trial 2 were those from group 7.

For this trial, the poultice was left in place for 24 hours in a single application, covered in cling wrap and placed in a polyethylene bag. After 24 hours, the tiles were assessed for swelling of the shellac; separation of the mends; and any possible discoloration from the lac dye component, or from the treatment itself. The maximum number of contact hours for this treatment trial was 72. Generally, if the shellac had not swelled after 72 hours of treatment, it was decided that the treatment was not feasible.

As in Trial 1, it was found that NaOH solutions produced the greatest results in hydrolyzing the shellac in the least amount of time. It was also found that the combination of NaOH and the agar showed the greatest results.

Treatment	pH	Application	Cover	Barrier	Time to Swell	Duration	# of Apps
NaOH in Pappina	12.5	full	Cling wrap	No	7 hours No sep	3 days	2
NaOH in Pappina	12.5	localized	Cling wrap	JTP	7 hours No sep	3 days	3
NaOH in Agar #1*	13.5	Full Semi-solid	No	No	25 mins 24 hrs sep	2 days	1
NaOH in Agar #1*	13.5	Local Semi-solid	No	No	25 mins 24 hrs sep	2 days	1
NaOH in Agar # 1*	13.5	Local Semi-solid	No	JTP	25 mins 24 hrs sep	2 days	1
NaOH in Agar #1*	13.5	Rigid gel	No	No	30 mins 24 hrs sep	2 days	1
NaOH in Carbopol 934	13	Local	Cling wrap	No	10 mins Tile disint.	1 day	1
NaOH in Agar #2*	13.5	Local Pre-gel	Cling wrap PE bag	JTP	10 mins 24 hours	2 days	1
$Ca(OH)_2$ in Agar #2*	13.5	Full Rigid gel	Cling wrap PE bag	JTP	24 hours No sep	2 days	1

Treatments tested during the course of Trial 2.

Trial 3

The third round of experiments sought to further test the effectiveness of the NaOH and Agar#2 combination at different pH values in order to determine the lowest possible pH at which saponification of the shellac can occur. For this trial, tiles from group 8 were used (see Table 5), as well as tiles from the 'Lac Dye' study onto which aged shellac had been added using a 3mL plaster dropper directly onto the surface [3]. Both sets of tiles were used to assess (1) the ability of the treatment to hydrolyze a large amount of shellac

on the surface of a tile and (2) the ability of the treatment to hydrolyze the shellac locally, within the mend itself.

A Japanese Tissue Paper (JTP) has been used as an intervention layer (between the surface of the tile and the poultice/reagent) in this set of trials based on the results from Trial 2. The inclusion of such an interfacial layer not only improved one's ability to remove the gel after treatment, it also assisted at drawing the hydrolyzed shellac and solubilized lac dye away from the tile, thus making the treatment more effective and easier to control. To further improve the surface contact of the treatment the alkaline agar was applied in a semi-gelled form. During the trials, the gel was removed and replaced with a fresh one when it began to dry and shrink, or when it looked to have absorbed a significant amount of the hydrolyzed shellac (denoted by its turning deep purple in color).

For this trial, the tiles were photo-documented immediately after the application of the gel to the surface, and then at five minute intervals until the shellac could be seen to visibly swell on the surface. The treatment itself was done in multiple applications, as needed, and the tiles were covered with carboxymethyl cellulose, cling wrap and placed into a polyethylene bag when allowed to sit for longer than 12 hours. The total duration of all tiles for Trial 3 was 72 hours.

The agar itself, named Agar #3, was prepared in the same way as Agar #2, discussed in the materials and methods section. The NaOH was added drop-wise to created solutions as close to pH 10, 12 and 14 as possible for all respective applications.

The results of these trials showed that the lower the pH of the agar and NaOH treatment, the longer the treatment needed to be applied in order to see a reaction. At a pH of 10.5, the reaction did not begin to occur even after 72 hours and multiple applications. It

appears that there needs to be a sufficient amount of hydroxide anions present in the agar in order for the reaction to occur; when the agar is buffered only to a pH of 10.5, there is very little NaOH actually present in the gel, and as such, the contact between the shellac and the OH- ions is severely hindered and the hydrolysis slowed.

Treatment	pH	Application	Barrier	Time to Colour Change	Time to Swell	Duration	Applications
NaOH in Agar#3 – Mended	14	Local	JTP	5 mins	5 mins	72 hours	5
NaOH in Agar #3 – Surface	14	Full	JTP	5 mins	5mins	72 hours	4
NaOH in Agar #3 – Mended	12	Local	JTP	10 mins	20 mins	72 hours	4
NaOH in Agar #3 – Surface	12	Full	JTP	n/a	n/a	72 hours	4
NaOH in Agar#3 – Mended	10.5	Local	JTP	35 mins	35 mins (minimum)	72 hours	4
NaOH in Agar#3 – Surface	10.5	Full	JTP	n/a	n/a	72 hours	4

Methods and materials of Trial 3.

Trial 4

The fourth round of experiments sought to test the enhanced effectiveness of the NaOH and agar combination when mixed with an additional solvent. The two solvents tested here included ethanol and acetone, used together and individually; these solvents were chosen because of their traditional use in conservation achieving successfully the dissolution of shellac, albeit limited, when used in a solvent cleaning gel, despite the risk of staining (Koob 1979).

For this trial, tiles from the 'Lac Dye' study onto which aged shellac had applied to the surface using a 3mL plastic dropper. This set of tiles was used to assess the degree of hydrolysis and to ascertain the risk of lac dye staining, which would be amply evident on the type of surface provided by these tiles. Also, depending on the success of the treatment on these tiles with excessive amount of shellac on their surface, subsequent trials could be conducted to establish the efficacy of a given treatment within a mend.

The agar used in this trial was of a much higher concentration than in previous trials in order to conserve the gelling concentration required after the addition of the solvents following heating. In this case, a gel was made in the microwave at a concentration of 8% (w/v) in deionized water, adding the flammable solvents only after the gel had begun to cool thus keeping the risk of reaction to a minimum. After application of the gel, the tiles were wrapped in plastic cling wrap and placed into polyethylene bags for 24 hours.

In keeping with the previous trials, an intermediate intervention layer of Japanese tissue paper (JTP) was used on one of the tiles to compare its effect on the treatment. For all tiles, save for one, the alkaline agar was applied in a warm, semi-gelled form in order to improve the contact with the surface. One sample was tested as a control using the cooled rigid gel only without the use of alkali materials. Furthermore, one other tile was tested using only the agar gel with the solvents, in order to properly assess the benefits of adding the NaOH solution. In all other instances, the NaOH was added to the mixture until a pH of 13.5 was established.

For this trial, the tiles were photo-documented before and after the treatment both under visible and ultraviolet (λ_{exc} = 365 nm) light in order to assess the degree of shellac removal.

The gel was applied only to one half of the shellac on the tile, to better gauge the degree of clearance.

The results from these trials showed that the use of ethanol in conjunction with the agar and NaOH gel, applied in its pre-gelled state without a JTP intermediate layer was the most effective at removing the shellac, though a purple stain was left on the surface of all tiles.

Treatment	Solvent	pH	Duration	Apps	Observations
Pre-gelled Agar w/o JTP	1:1 EtOH and Acetone	13.5	24 hrs	1	Removal of most of the visible shellac, though in areas with thicker amounts removal was incomplete. Deep purple stain remains after treatment.
Pre-gelled Agar w JTP	1:1 EtOH and Acetone	13.5	24 hrs	1	Removal of much of the visible shellac, with little difference in efficacy from the trial without JTP. The stain, however, appears to be somewhat lighter, owing to the greater absorption into the JTP during treatment (?)
Rigid gel Agar w/o JTP	1:1 EtOH and Acetone	13.5	24 hrs	1	Some removal of surface shellac, though poor surface contact from the use of the rigid gel is evident. Purple staining after removal of shellac.
Pre-gelled Agar w/o JTP no NaOH	1:1 EtOH and Acetone	7	24 hrs	1	No change after 24 hours. No color change, no presence of dye and the shellac appears intact.
Pre-gelled Agar w/o JTP	Acetone	13.5	24 hrs	1	Successful removal of visible shellac, though dark purple stain remains
Pre-gelled Agar w/o JTP	Ethanol	13.5	24 hrs	1	Complete removal of visible shellac, lightest of the stains after treatment.

Treatments undertaken in Trial 4

Trial 5

The solutions tested for this trial are based off of the results from Trial 3. For this trial, two spots were tested on the shellac coated break edge of one of the Attic vessels; this area had been exposed to solvents for the initial disassembly, but has not been retreated since (Marie Svoboda 2011) . After conducting the spot tests described above to verify for corrosion resistance of the fabric, the materials tested included the 4% (w/v) agar, prepared in deionized water, and different amounts of concentrated NaOH in deionized water (20% w/v). The first spot tested used the agar gel in its warm, pre-gelled state, buffered to a pH of 10. The second spot tested used the same agar gel, but this time,

buffered to a pH of 13.5. Both spots used a Komo Kashmir Japanese tissue paper as an intermediate layer in order to ease removal of the materials in excess and to encourage diffusion of the dye and resins away from the ceramic matrix.

Unlike the test tiles, which tend to react quickly, particularly at a high pH, after 2 hours of treatment, there had been no noticeable effect. UV-induced visible fluorescence photography revealing the characteristic orange color of shellac confirmed that it had not been successfully removed.

Spot #	Treatment	pH	Duration	# of Apps	Observations
1	Agar 4% w/v NaOH 20% w/v	10	2 hrs	4	Some slight softening of the shellac. No noticeable removal in either visible or UV-Vis fluorescence.
2	Agar 4% w/v NaOH 20% w/v	13.5	2 hrs	3	Removal and softening of the visible shellac. Deep purple staining around the perimeter of the treated spot which was removed in subsequent applications.

Treatments undertaken in Trial 5

Trial 6

Based on the lack of success from Trial 5, it was thought that the Japanese tissue paper was reducing the surface contact between the agar and the aged shellac, thus preventing hydrolysis from occurring. A second trial was then undertaken, on the same fragment edge using the same parameters, though without the use of the JTP intervention layer. Also during this trial, a third spot was tested using a Carbopol solvent gel, as it was a mixture that Svoboda had had success with in the past for removing shellac. This solvent gel was buffered to a pH of 9.

The results from this trial showed that the lower pH agar/NaOH combination had caused the shellac to soften slightly, while the higher pH agar/NaOH combination caused

the shellac to turn purple (as on the test tiles, confirming the presence of lac dye in the shellac), and softened the shellac sufficiently to allow for it to be mechanically removed with a scalpel. This treatment, however, caused some concern initially, in that the edges of the spot showed the migration of the dye into the surrounding untreated areas. Further applications of the gel, however, picked up the dye, and no stains remained.

The spot tested with the Carbopol solvent gel showed some softening of the shellac and no evidence of staining, but the treatment required prolonged contact with the surface, as opposed to the agar treatments, which tended to show evidence of a chemical reaction very rapidly. Also, in comparison to the agar, which cools and becomes rigid, allowing for easy removal, the clearing of the Carbopol gel was a more difficult and laborious process.

Spot #	Treatment	pH	Applications	Duration	Observations
1	NaOH + EtOH + Agar	13.5	5	2 hours	Gel turned purple rapidly. After repeated applications there was a noticeable softening of the shellac. Under UV light, there was a reduced amount of shellac present.
2	NaOH + Acetone + Agar	13.5	5	2 hours	No visible reaction. Under UV light the shellac is still present. No softening of removal. No color change.
3	Carbopol Solvent Gel	9.5	2	1 hour	No noticeable reaction in visible or UV light.

Methods and observations of Trial 6.

Trial 7

Three methods were tested during Trial 7: the first spot tested was treated using the Carbopol solvent gel applied and removed using a cotton swab. The second spot used the alkaline/solvent treatment consisting of a 1:1 mixture of agar gel and ethanol buffered to a pH of 13.5 with sodium hydroxide. The gel was applied in its semi-solid cooling phase and changed frequently, around every 15 minutes or so as it became saturated with the purple

lac dye. This was done in order to mitigate the tendency of the lac dye to absorb into the ceramic body by favoring diffusion into the gel. It was noted in trials where a tile was soaked in solution that the dye did not absorb into the ceramic but rather, stayed in solution. Additionally, it was observed that in trials that made use of a more frequent changing of the gel, that staining was less noticeable or not present.

The final spot tested, used only agar in deionized water at a concentration of 4% (w/v) and a pH of 7, also applied in its semi-solid cooling phase. Agar was tested on its own to evaluate, the degree to which the gel support contributed to the efficacy of the treatment.

Preliminary results of these trials showed that, for the same duration of application, the Carbopol solvent gel did not affect the shellac in any discernable manner. There was equally no change observed in the area treated with the agar alone. In the area treated with the NaOH/EtOH mixture in agar, however, there was a rapid color change to purple as the dye component became exposed to an alkaline environment and significant softening and removal of the shellac resin itself. Ultraviolet-visible fluorescence imaging after treatment supported the visual findings and demonstrated a significant reduction in the signature orange colored fluorescence of the shellac in the area treated with the alkaline mixture.

Spot #	Treatment	pH	Applications	Duration	Observations
1	Carbopol Solvent Gel	9.5	1	15 minutes	neither color change nor noticeable softening of shellac.
2	NaOH + EtOH + Agar	13.5	2	20 minutes	Initially left purple stains but frequent changes of the gel did not result in noticeable stains after test was complete. Noticeable removal of resin in visible and UV light.

3	Agar in del water	7	2	30 minutes	no noticeable changes.

Methods and observations of Trial 7

Trial 8

As in Trials 4 and 5, the objective of this trial was to find the lowest possible pH at which the hydrolysis reaction would occur, this time with the addition of the ethanol, without extending the treatment time over a course of days. This trial was conducted along the break edge of a single fragment and tested areas that had shellac residues of varying thicknesses; spots 1 and 2 had roughly equal thicknesses of shellac that were thin in relation to Spot 3.[30]

All spots were tested using the 8% (w/v) agar gel in deionized water, applied while warm and in its soft gel phase. A 1:1 mixture of agar and ethanol were mixed, reducing the overall concentration of the agar gel to 4%, in keeping with all other trials. The solvent and agar were then buffered using 20% (w/v) NaOH in deionized water to a pH of 12.5 for Spot 1, and a pH of 13.5 for all other spots.

It was found that the higher the pH, the faster the reaction and associated color change. As the poultice is changed and more shellac is removed, the reaction occurs more slowly and the poultice needs less frequent changes. There is softening of the shellac at a lower pH, which allows for the mechanical removal of the shellac after treatment. This might be a viable option, as the lower pH allows causes a less drastic color change, and therefore, presents less risk of staining.

[30] It is not possible to objectively measure the thickness of the shellac; instead, they will be described in relation to each other as thicker or thinner.

If a color change was already noted in the shellac prior to the alkaline treatment, possibly due to exposure to high RH at some point in the object's history causing the lac dye to go into solution, then the color change was more rapid and more intense and required more frequent changes of the poultice.

When the gel is applied after it has been freshly heated, there is a faster reaction. It can be theorized that heat likely speeds of the reaction, which is not truly surprising. It should be noted, however, that with the use of flammable solvents, the use of the gel at high temperatures in excess of 70◦C is not recommended and can pose of potential hazard.

Spot #	Treatment	pH	Applications	Duration	Observations
1	NaOH:EtOH:Agar	12.5	5	25 mins	Reaction occurred very slowly.
2	NaOH:EtOH:Agar	13.5	5	25 mins	Color change and softening of shellac occurred rapidly, requiring a change of the gel within the first 5 minutes.
3	NaOH:EtOH:Agar	13.5	5	25 mins	Shellac was significantly thicker in this area. The reaction was somewhat slower and less intense than spot # 2. There was less of a pink color in the shellac prior to treatment in this area.

Methods, materials and observations of Trial 8.

Trial 9

Trial 9 was conducted on the same rim fragment as the tests from Trial 8, though in this instance, the goal of this trial was to expand the surface area undergoing treatment; this was done in order to evaluate the efficacy of effective treatments from small test spots over a larger surface area as well as to evaluate the working properties of the agar gel over a larger surface area.

As in previous trials, the agar was applied in its semi-solid cooling phase, at an approximate temperature of 45 to 50◦C. After application, the gel rapidly cooled to below its gelation temperature of 38◦C, especially over a large surface area. As in previous trials, it was found that the warmer the gel, the more quickly the reaction occurred and particles were more readily absorbed into the gel matrix prior to gelation. Thus, when working over a larger area, it is necessary to find a way to keep the prepared agar warm until application is complete.

Initially, a section of particularly heavy surface deposition was treated with the mixture of agar gel, NaOH and ethanol measuring approximately 5cm in length toward the rim edge of the fragment. As the gel turned pinkish-purple, indicating that lac dye had been

absorbed into its matrix, it would be removed and a new poultice would be applied. During the two hours of treatment time, the gel poultice was changed seven times; as the color change was weaker with each successive application, the length of time the gel was left in place was increased accordingly.

In many areas the surface deposits were too heavy to be readily absorbed into the gel matrix, though they had been significantly softened. In such instances, these deposits would be removed using a scalpel blade and bamboo skewer, taking care just to lift the softened material and expose new surface deposits beneath them to the alkaline treatment. At no point was the surface scraped to remove unsoftened surface deposits; only those deposits that could be removed easily without pressure or much effort were removed in order to better evaluate the efficacy of the gel as a molecular sieve as much as possible.

Because of time constraints, it was necessary to conduct this trial over a period of two days with five applications being completed on the first day, and two more on the second. The sixth and seventh applications increased the amount of surface area being treated by another 5cm, effectively treating approximately half the length of the fragment edge. As such, the area between 5 and 10cm from the rim edge only received two applications, and the degree of shellac removed reflects the reduced number of applications and exposure time. After seven applications, a final application of agar gel in deionized water was applied to help clear the alkaline materials from the surface of the ceramic. Though there was an appreciable reduction in the surface pH after this final application, from pH 13 to pH 11, it was decided to soak the fragment in deionized water post treatment to more effectively clear the residues from testing as well as to desalinate

the fragment[31]. Despite any color changed to the shellac and other surface depositions, the ceramic edges revealed after treatment showed no signs of discoloration or color change.

Spot #	Treatment	pH	Applications	Duration	Observations
1	NaOH: EtOH: Agar	13.5	7	2 hours	Very quick color change occurred with first few applications. Color change occurred more slowly with subsequent applications. Softening of shellac allowed for mechanical removal between applications, furthering the efficacy of the treatment. Multiple applications required for full reduction of the shellac
2	NaOH: EtOH: Agar	13.5	2	45 minutes	Observations are the same as above. The fewer number of applications and reduced treatment time show less shellac removal overall.
1-2	Agar in del water	7	1	30 minutes	No changes – agar was applied to try and clear materials from the treatments.

Methods, materials and observations of Trial 9

Trial 10

Trial 10 was conducted on a fragment that had not been treated or tested on in any previous trial. The fragment edge was coated in a fairly thick (less than 1mm) and uniform coating of shellac and other residues from previous conservation treatments that remain unidentified. The color of this surface coating was faintly purplish in color, indicating the presence of lac dye that had partially migrated out of the shellac.

As in Trial 9, the goal of treatment here was to test the NaOH/ethanol in agar mixture on a complete fragment edge, rather than in small test spots, and to test the reproducibility of the results seen in Trial 9, while also attempting to fine tune the

[31] The decision to desalinate the fragment by immersion was one taken by the conservators of the JPGM and was conducted on all fragments of the Apulian vases, irrespective of any experiments I had conducted on the fragments.

application process of the gel in its pre-gelled state. In total, eight applications were conducted, two of which were agar and deionized water in order to reduce the surface pH after treatment and to clear residual alkaline salts.

As in Trial 9, the chemical reaction resulting in the color change of the shellac and agar gel slowed with subsequent applications. It was noted that if the softened surface coating was reduced between applications, any lifted residues would be readily absorbed into the gel matrix upon subsequent gel applications.

Though some shellac residues remained after six alkaline gel treatment applications, the reduction was significant, as confirmed by UV-visible fluorescence imagery. It is likely that additional applications would be sufficient to remove any remaining shellac residues.

Application #	Treatment	pH	Duration	Observations
1	NaOH: EtOH: Agar	13.5	20 mins	Very quick color change (within five minutes). Some softening of the surface shellac
2	NaOH: EtOH: Agar	13.5	30 mins	Color change occurring within 10 minutes of application. Significant softening of the shellac
3	NaOH: EtOH: Agar	13.5	50 mins	Color change occurring less quickly, after 20 minutes or so. After removal of poultice, shellac was softened sufficiently to allow easy removal by mechanical means (i.e. scalpel)
4	NaOH: EtOH: Agar	13.5	50 mins	Significant absorption of particulate matter on the surface from previous mechanical cleaning into the matrix of the gel.
5	Agar in deI water	7	30 mins	Applied to help lower the surface pH and clear some of the alkali materials. The initial surface pH was measured at 11, after a single application of neutral agar; the surface pH was reduced to 9. The initial pH of the agar poultice was 7; after removal it was measured at 10. There is good transfer of alkali materials to the neutral gel after treatment.
6	NaOH: EtOH: Agar	13.5	30 mins	Reaction and color change occurring much more slowly. Significantly less shellac is being removed with each application, though what remains does soften, allowing for mechanical removal.

7	NaOH: EtOH: Agar	13.5	30 mins	Color change and softening is barely perceptible. Treatments stopped after this poultice.
8	Agar in deI water	7	30 mins	As in application 5, this application sought to help clear the alkali materials from the treatment. There were no visible changes, but the surface pH was lowered from 11 to 8.5 after 30 minutes.

Methods, materials and observations of Trial 10

Trials 11-13

Testing was conducted to better understand the influence of pH both on the dye itself, as well as on techniques for its removal. For these trials, tiles were stained with lac dye extracted from seed lac in deionized water. The dye was then buffered to a low, neutral and high pH in order to evaluate its behavior in its acidic, neutral and basic states. In order to raise the pH of the dye, 5M NaOH was added drop wise until the dye became uniformly purple; in order to lower the pH, 3M HCl was added drop wise until the dye became uniformly yellow. Approximately 3mL of dye was applied with a dropper to the surface of the tiles and allowed to dry for 24 hours before testing.

The trials were conducted in two ways. In the first instance, a cotton swab was soaked in either deionized water, 5M NaOH or 3M HCl and rubbed five times each over the surface of the stained tiles, recording any reduction in staining, color changes, transfer of dye to the swab or loss of surface materials.

In the second instance, the tiles were placed in 80mL of either deionized water, 0.5M NaOH or 0.3M HCl, and with the exception of tiles soaked in the dilute acid, were left to soak in solution for 24 hours. Tiles in HCl reacted so quickly to treatment that it was only necessary to leave them in solution for 5 minutes before total reduction of the stain. After

treatment, all tiles were soaked for 24 hours in 100mL of deionized water for a minimum of 24 hours to clear residues from treatment.

When the pH of lac dye is modified, there is an associated bathochromic shift, as discussed in Chapter 2.2. At low pH, the dye acquires an orange color, while at a high pH, it is deep purple. When mordanted with the surface of the ceramic tile as occurs during the staining process, however, there is an inverse correlation between the apparent saturation of the original dye and the intensity of the stain on the ceramic surface. That is to say, the light colored acidic lac dye left a darker and more intense purple stain on the surface of the tile than the basic lac dye. Also, after drying the tiles for 24 hours following staining, it was noted that the tiles stained using basic lac dye had lost most of their color and left only the lightest of faintly purple stains on the surface.

Trial 11 sought to explore the effects of treating the stained tiles with water only, while Trial 12 looked at the use of NaOH at a pH of 13.5 as a method for reducing the stain, and Trial 13 used HCl at a pH of 2. The results were as expected based upon previous testing during the 'Lac Dye' project; in order to complex, the dye requires an acidic environment. Conversely, in order to reverse or break the complex, an acidic environment is again required. As such, the more intense stain caused by acidic lac dye and the rapid discoloration of the stain using an acid, as seen in these trials, supports the experiments of the previous trial.

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