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Preventing Poultice Problems: A Study of Ceramic Stain Reduction

1. Abstract:

Reducing stains from a ceramic can be a challenging task due to the wide variety of staining sources and the often complex composition of ceramic bodies and glazes/enamels. This three-part project was designed to learn more about the enamel decoration on a dish attributed to Spode, about the reduction of stains in ceramics, and finally the results were later applied in the successful reduction of staining on a particular dish.

The stain reduction research began with a study of the working properties of seven dry poultice materials: alpha cellulose pulp, alpha cellulose powder, Laponite® gel, and four Amberlite XAD® polymeric adsorbent resins. This project tested the poultice materials ability to reduce staining on a ceramic body when using only water as a solvent. The materials were tested on tiles stained with black tea, red wine and milk chocolate. Amberlite XAD® polymeric adsorbent resins were found to remove more stain particles than cellulose pulp, cellulose powder and Laponite® gel. Based on this study, Amberlite XAD 7HP® was used as a poultice material to reduce stains on the dish attributed to Spode.

In combination with poultice materials, bleaches are frequently used to reduce staining in ceramics. While hydrogen peroxide has traditionally been used for this purpose, the project tested instead the performance of carbamide peroxide, a stabilized form of hydrogen peroxide, on tiles stained with black tea, red wine, and milk chocolate. Carbamide peroxide, was found to successfully reduce staining on all of the tiles. Based on the results of this test, carbamide peroxide was used in a poultice system with cellulose pulp on the dish attributed to Spode, where it visually reduced staining.

The final portion of this project involved the study of the chemical composition of enamels on a dish attributed to Spode. The focus of the enamel study was on the green enamels as these were the only colors that seemed unstable and had suffered areas of loss. The green enamels were found by analysis with SEM-EDS to be applied as a single layer. Raman Spectroscopy identified the pigment Naples yellow in the green and brown enamels. Copper,

cobalt and nickel were identified with XRF as possible colorants in the green the enamels. Analysis did not indicate any factor that would cause the green enamels to be particularly fragile.

2.1 Introduction: A Study of Seven Poultice Materials

Stain reduction on a ceramic body is usually conducted through a poultice system that consists of a liquid reagent and a dry material. The dry material absorbs the liquid and holds it on the surface of the ceramic allowing time for the liquid to seep into the ceramic and interact with the stain. As the liquid evaporates, the stain is pulled into the dry material rather than being redeposited on the surface of the ceramic. A study was completed on the working properties of seven dry poultice materials: Laponite® gel, alpha cellulose in powder form, alpha cellulose in pieces, and four polymeric adsorbents. This study was conducted to determine whether polymeric adsorbents can effectively reduce staining in a ceramic and how their working properties compare to the other traditional materials. To effectively compare the ability of the dry poultice materials to reduce staining, only water was used as a solvent.

Laponite® is a synthetic inorganic colloid that has a tri-octahedral sheet structure similar to the natural clay hectorite (Lee, 1997). It is a white powder that forms a colorless thixotropic gel when combined with a solvent. In its gel form, Laponite® holds onto stain material through electrostatic forces. As the gel dries it cracks and shrinks, which can exert pressure onto the ceramic. Laponite® should therefore be removed before it is fully dry.

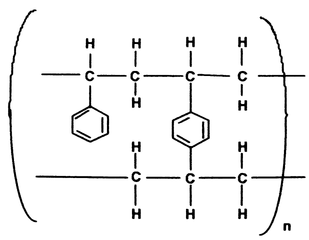
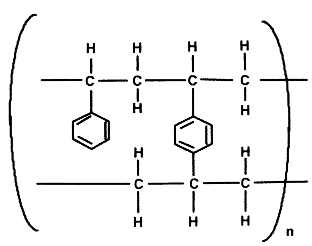
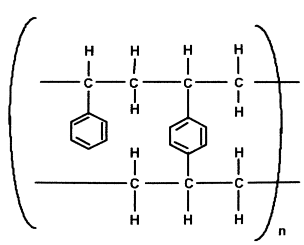
Alpha cellulose is an insoluble cellulose derived from plants. It is available in many grades based on the level of processing. It binds to stain materials through hydrogen bonding. Two grades of alpha cellulose were tested in this project. The first is a very fine alpha cellulose powder obtained from Sigma Aldrich. The second, Filter Flockenmasse, is an alpha cellulose pulp made from shredded filter papers. This product is no longer available, but the objects lab at Winterthur has a large quantity of it. Filter Flockenmasse is larger in size than the powder. It easily breaks into pieces and small clumps of fibers.

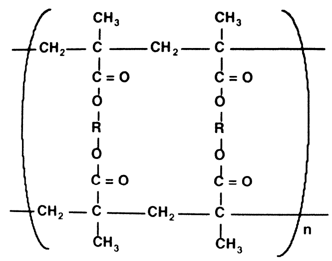
Amberlite XAD® polymeric adsorbents are manufactured by Rohm and Haas for the waste water treatment industry. These resins have also been used for chromatography and pharmaceutical processing. The resins are round, non–ionic inert polymers that have a macroporous structure. The large internal surface area, and chemical structure of the resin enable it to have adsorbent properties. The resins can be regenerated and are reusable (Rohm and Haas

2007). These resins are an ideal poultice material because they are inert, they can to be applied in various solvents, and can absorb a range of compounds.

Four Amberlite XAD® resins were tested as possible poultice materials to reduce stains from ceramics. Three of the resins, XAD 1600, XAD 1180, and XAD 16, are hydrophobic and the fourth, XAD 7HP is hydrophilic. XAP 7HP is capable of absorbing ketones, esters and aliphatic compounds from polar molecules (Rohm and Haas 2007). XAD 1180 can remove large molecules from polar or aqueous solutions (Rohm and Haas 2007). XAD 16 is marketed as being good for removing colored components and for removing aromatic hydrocarbons (Rohm and Haas 2007). XAD 1600 is used in chromatography to separate different organic components (Rohm and Haas 2007). More details on these resins in included in Table 1.

Table 1. Four Amberlite XAD resins. Structure images from Rohm and Hass website 2007

Amberlite XAD®	Structure	Structure	Surface area (m^2/g)	Average pore diameter (Å)	Mean diameter (μ)
XAD 1600	Cross linked aromatic polymer polystyrene (DVB)		800	150	400
XAD 1180	Cross linked aromatic polymer polystyrene (DVB)		500	400	530
XAD 16	Cross linked aromatic polymer polystyrene divinylbenzine (DVB) (may also be aliphatic)		800	150	700

XAD 7HP	Aliphatic cross linked polymer. aliphatic ester		500	450	560

The resins are packed and shipped in a small amount of water. Sodium chloride and sodium carbonate are added to the resins to prevent bacterial growth while the resins are in transit. It is recommended to rinse the resins with deionized water prior to use to remove the salts.

2.2 Using Carbamide Peroxide to Bleach Ceramics

Carbamide peroxide is an equal molar mixture of urea and hydrogen peroxide. Hydrogen peroxide and carbamide peroxide are oxidizing bleaches. When combined with urea, the hydrogen peroxide forms carbamide peroxide, which is a stabilized form of hydrogen peroxide. Carbamide peroxide is used in health and beauty products as a bleach and disinfectant. It is the main bleaching agent in teeth whitening products (Tam, 1999). The Food and Drug Administration approved concentrations up to three percent of hydrogen peroxide compounds, including carbamide peroxide, to be used in teeth whitening products that have the potential to be ingested. Most teeth whitening kits currently on the market contain 10% carbamide peroxide (Tam, 1999). Although these products are above the FDA recommendation there have been no reported problems from short term use, and the dental industry has accepted these products as a safe teeth whitening option (ADA, 2008). Concentrations of carbamide peroxide above 10% are professionally applied by a dentist. These higher concentration products whiten teeth within an hour while the lower concentration products require numerous applications over a span of time (Tam, 1999).

Hydrogen peroxide is very reactive, often reacting at and oxidizing only the surface of a substrate. Since it is more stable, carbamide peroxide is able to penetrate deeply into a substrate and theoretically should oxidize the substrate evenly. This characteristic is ideal in the teeth whitening industry to avoid creating a spotted substrate. This same principle of evenly whitening and reducing stains from a substrate can be applied to ceramic conservation where the ideal goal would be to whiten and reduce the stains of a substrate in an even and controlled manner. During the process, hydrogen peroxide breaks down into water and oxygen and urea breaks down into ammonia and carbon dioxide, all of which are volatile and leave behind no residue. As the system uses only water, the treatment can be accomplished without the need for fume extraction, although the proper precaution must be used when handling and using the solutions (refer to the appropriate MSDS).

2.3.1 Description of the Dish Attributed to Spode

The dish that was analyzed is part of a set of 30 pieces in the Winterthur Museum collection. The set does not contain a factory mark but is attributed to Spode, a ceramic company named for the founder Josiah Spode, based on design motifs. The dish is made from a white transparent clay body that is classified as bone china and is dated between 1830 and 1840 according to Winterthur's catalog records.

This square mold-made dish has a decorative rim with scalloped edges and a shell design in each corner, as shown in Figure 1. The rim in the lower right corner is extended forming a tab handle. The dish is elaborately decorated. A cobalt blue underglaze was applied to most of the interior edges of the dish, and also on portions of the rim. Then a clear glaze was applied to the entire surface of the dish, except for the foot rim, where the dish would have been in contact with the kiln shelf. The clear glaze acts as a foundation layer on which different colored enamels and gilding have been applied.

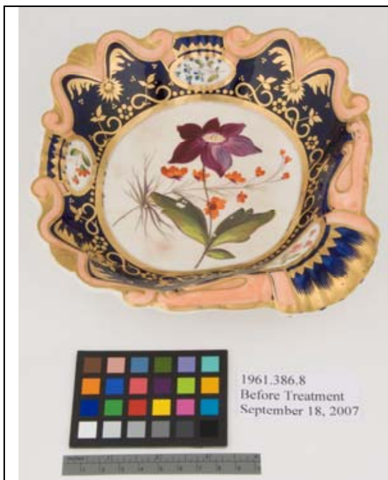


Figure 1. Image of the dish before treatment.

The dish is decorated on the interior by four reserves, each containing floral designs hand-painted in enamel. The reserves are set in cobalt blue underglaze. The largest of these reserves is in the center of the dish, where a purple flower attached to a stem is featured. Behind this flower is a sprig of thin brown and green foliage with small orange flowers, also attached to a stem. On the rim of the dish are three smaller reserves, all oval-shaped and containing a flower motif. The third reserve is larger than the other two and is located on the tab handle. The outline of each reserve is gilded. The scalloped rim of the dish has a low relief M-shaped scroll created with a peach-colored enamel.

In the center of each scroll is a gilded shell and at the bottom of the M is a gilded flower. Gilding was also utilized to create an S-curve, leaf and dot pattern over the blue underglaze band.

2.3.2 History of the Spode Ceramic Company

The Spode Ceramic Company was created by Josiah Spode in 1760 in Stoke-upon-Trent, England (Spode Limited 1975). Upon his death in 1797, the ceramic company was left in the hands of his son Josiah Spode II. (Wilkinson 2002). In 1800, Josiah Spode II introduced bone china to Spode Ceramic Company and in 1806 enamels were applied to bone china wares under the insight of Henry Daniel, who was hired in the new position of art director. Daniel held this position until 1822 (Wilkinson 2002). He introduced the enameling process to Spode and was not only the art director, but also a chemist creating different enamels (Whiter 1970). At one point Daniel had 192 people working for him, which created a legacy of highly trained artists employed at Spode (Wilkinson 2002).

Josiah Spode II died in 1827 and the company was acquired by Copeland and Garrett in 1833. The ceramic company continued under variations of the Copeland name until 1970 when it was changed to its present name, Spode Limited. This final name change was in honor of its founders (Spode Limited 1975).

2.3.4 Enamels used by the Spode Ceramic Company

Enamels consist of pigments that are ground into a powder with a flux, which is then combined with a binder into a paste that can be painted onto a ceramic (Buys, Oakley 2005). The ground particulates were historically made into a paste using animal glue and water or oil of turpentine as a binder. This paste was painted with a soft brush onto the ceramic and fired between 650 and 800°C. At Spode, the enamels and gold were fired at 790°C for 11 hours. (Spode Limited 1975). Enamels are often very fragile due to their low firing temperature and difficulty in adhering the colorants to the clear glaze. Enamels can be very soft and therefore are easily abraded.

Recipes for mixing enamel colors were highly guarded trade secrets. Cobalt is recorded in the director's book at the Spode factory to be used to make green and black enamels (Copeland 1980). In a three month period in 1808, the enamel factory of Spode imported 296 pounds of common cobalt and 253 pounds of the best quality cobalt from Sweden (Whiter 1970).

Cobalt is often contaminated with iron and nickel, which give the enamel a greenish hue (Kingery 1986). Potassium could be added to the cobalt blue to avoid forming green. The list of recipes containing cobalt in the Spode director's book includes one for making a blue stain that calls for "5 parts blue calx, 1 of flint, 2 of frit process 32, and 1 of enamel blue." (Copeland 1980, 164). There are instructions to grind the ingredients of this recipe into very fine particulates (Copeland 1980). Oxides of cobalt that contain tin and zinc were also used to make blue enamels. To make green enamel, there is an account in the director's book to combine antimony and litharge with the cobalt. Iron and manganese were combined with cobalt to make black (Copeland 1980). Spode was reported to have a green color called "Spode Green" which consisted of all the loose color powders collected by on the floor of the enamel studio in the factory and mixed together (Wilkinson 2002).

2.3.5 Previous Analysis of the Spode Dish

This dish is part of a set of dishes which are all stained to various degrees. It is a goal of the Winterthur Museum to display these dishes once each dish has been treated to reduce the staining. Two pieces of the set were treated in 2004 by Kate Cuffari, a WUDPAC Class of 2006 graduate. When she applied poultices to reduce the staining to the clay body, salts formed on the green enamel. In 2004 analysis using X-ray Fluorescence (XRF) and Fourier-transform infrared microspectroscopy (FTIR) was completed on the salts on the green enamel, the white underglaze, and the green enamel. Using XRF, the white underglaze was found to contain lead and calcium. Copper and lead were found in the green enamel and in the salts. FTIR results indicated that the salts were most likely metal soaps, but they could also be salts from a metallic acid. The presence of lead in the salts may have been due to an interaction with the poultice or it could have been from the composition of the glazes and enamels. There was therefore no direct correlation found between the composition of the green enamels and the salts that formed during poultice treatment, and the possible explanation for the salts was believed to be from a previous strain reduction treatment that used a chelating agent.

3.1 Experimental procedure of poultice material study

The handling and working properties of seven dry poultice materials: alpha cellulose pulp, alpha cellulose powder, Laponite® gel and four XAD resins XAD 1600, XAD 1180, XAD 16, XAD 7HP, were tested. These poultice materials were mixed with deionized water and applied as a poultice to ceramic tiles that were stained with food residues. This study was focused on reducing stain from the porous side of the glazed tiles in order to evaluate how the poultice materials interact with the stain without the glaze layer, which acts as a physical barrier. Overcoming the physical limitations of moving a stain through a glaze layer is a topic not addressed in this project and that should certainly be further studied.

White ceramic tiles were cut into small pieces and left to soak for forty-eight hours in Lipton black tea, Nestle's milk chocolate, or Wright Wine Works Chambourcin red wine. These three foods are commonly served in ceramics and have historically caused staining. The tiles were removed from their respective stain baths, rinsed with tap water and air-dried. The dry poultice materials were mixed with deionized water and applied to the stained tiles. The poultices were covered with plastic for 24 hours to avoid evaporation, allowing time for the water to penetrate into the tile. Afterwards the plastic was removed and the poultice material slowly air-dried. Once dried, the poultice materials were collected from the tile and saved in plastic bags so they could be compared at the conclusion of the study. This procedure was repeated twice on each tile.

Figure 2. Image of tiles in various stages of poulticing.

Colorimeter readings were taken with a Minolta CR-221 colorimetric C source with a 2^{o} detector window colorimeter in the L* a*b* color system on the same four locations on the unglazed side of the tile, before and after each poultice was applied. From these colorimeter readings, a ΔE value was calculated indicating color change through the equation $\Delta E = \sqrt{[(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]}$. A large ΔE value indicates a large color change, and therefore a significant stain reduction. A ΔE value above 1 indicates a color change that is visible to the human eye. The ΔE values were compared to determine the poultice materials that caused the most significant amount of stain reduction on the tiles.

Photomicrographs of the tiles were taken using a Nikon Eclipse 80i Binocular Microscope (4x, 10x, and 20x objectives X 10x) and a digital Eclipse DXM 1200f Nikon Camera in conjunction with the Automatic Camera Tamer (ACT-1) control software. Photomicrographs were taken of the same area on the porous surface of tiles before and after the poultices were applied to the tiles.

3.2 Carbamide Peroxide Experiment

An equal molar ratio of urea to hydrogen peroxide was combined to create carbamide peroxide. The carbamide peroxide was then diluted with water to make a 5% carbamide peroxide aqueous solution. This solution was added to the poultice material and applied to the tiles in the same manner as Part 1 when water alone was used as the solvent. This procedure again was repeated utilizing two tiles stained with the same foodstuff. Colorimeter readings were taken before and after the carbamide peroxide poultice was applied to the ceramic tiles.

3.3 Analysis of the Enamels on the Dish Attributed to Spode

Analytical methods that do not require destructive sampling to be sampled were utilized first on the Spode dish. These include X-ray fluorescence spectroscopy (XRF) and Raman spectroscopy. Upon completion of this analysis, SEM-EDS was conducted on very small samples of the light and dark green enamels. Samples were removed from the edges of area of loss as agreed on by the curator.

XRF analysis was conducted with the Röntec (Bruker) ArTAX µXRF with a molybdenum excitation source at 50kv, 600 microamp for 100 sec with a 100 µm spot size. The spectrometer is located within a lead lined room and the dish rested on a table directly below the x-ray tube, with approximately 2 mm between the tube and the object. The peaks of the spectrum, which indicate different elements, were labeled by the computer database using the ArtTAX Ctrl (RÖNTEC GmbH) version 3.5.0.20 software. As energy generated from the x-ray source can penetrate through the enamel and glaze layers and interact with the clay body, the analysis was also conducted comparatively on an area of clear glaze. The interference caused by the clear glaze can then be subtracted from the spectrum of the enamels.

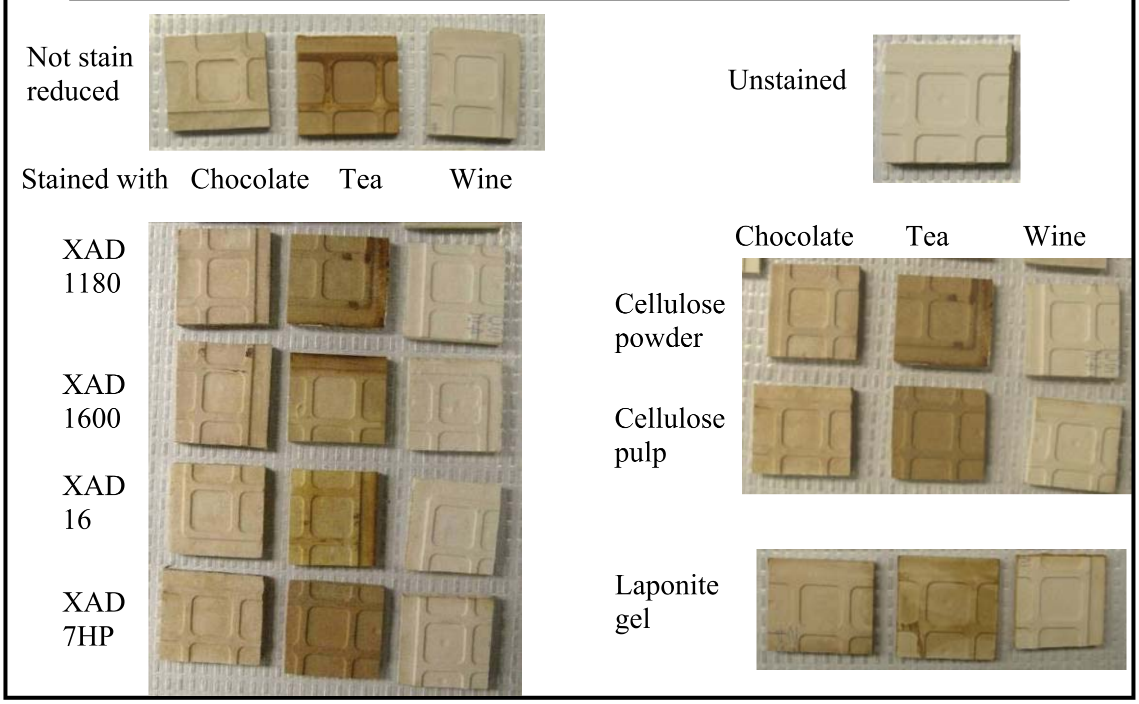
Raman spectroscopy was completed on a Renishaw InVia Raman Microscope. A 514nm argon laser (1800 lines/mm) was used for the green enamels. The spectral resolution of the system was 3 cm^{-1} with a 50x objective lens, exposure time 10 seconds for 10 scans at 10% or 50% laser power. The dish could fit inside the chamber of the instrument, however only the enamels on the bottom of the dish could be aligned under the microscope. The enamels on the side of the dish did not contain losses and could not be sampled, therefore only enamels on the bottom of the dish were analyzed. Renshaw Wire 2.0 Software was used to obtain the results and spectra. The spectra illustrate intensity (counts) versus wavenumber (Raman shift). These spectra were compared to databases within the computer to identify compounds and provide phase and polymorph information.

Scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) was performed using a Topcon ABT Scanning Electron Microscope equipped with an EDAX detector (Philips Electronic Instruments Co.) and an Ikegami Monitor. Samples of the dark green and light green enamel were taken and cast in Buehler Epoxicure® resin, wet sanded and polished with Buehler Metadi Supreme® water based rotating polish 6 micron polycrystalline and 3 micron diamond suspension. These cross sections were coated with carbon, while leaving the sample uncoated, and mounted on a carbon stub with double sided tape. Another sample of the dark green and light green enamel was removed from the Spode dish and placed directly on the carbon stub to study the top surface of the enamel. All samples were placed in the chamber of the SEM and a vacuum was drawn. The stage height was at 20mm and the angle was at 20° to generate accurate energy dispersive results. The samples were exposed to 20kV of energy allowing the electrons generated to penetrate between 1.5 and 2 microns into the dish. The energy generated during SEM does not penetrate as deeply as XRF which helped avoid interference of the clay body during analysis of the decorative materials. SEM-EDS created elemental mapping of each of the samples. The time of exposure needed to create these maps was fifteen minutes.

4.1 Results of Poultice Study

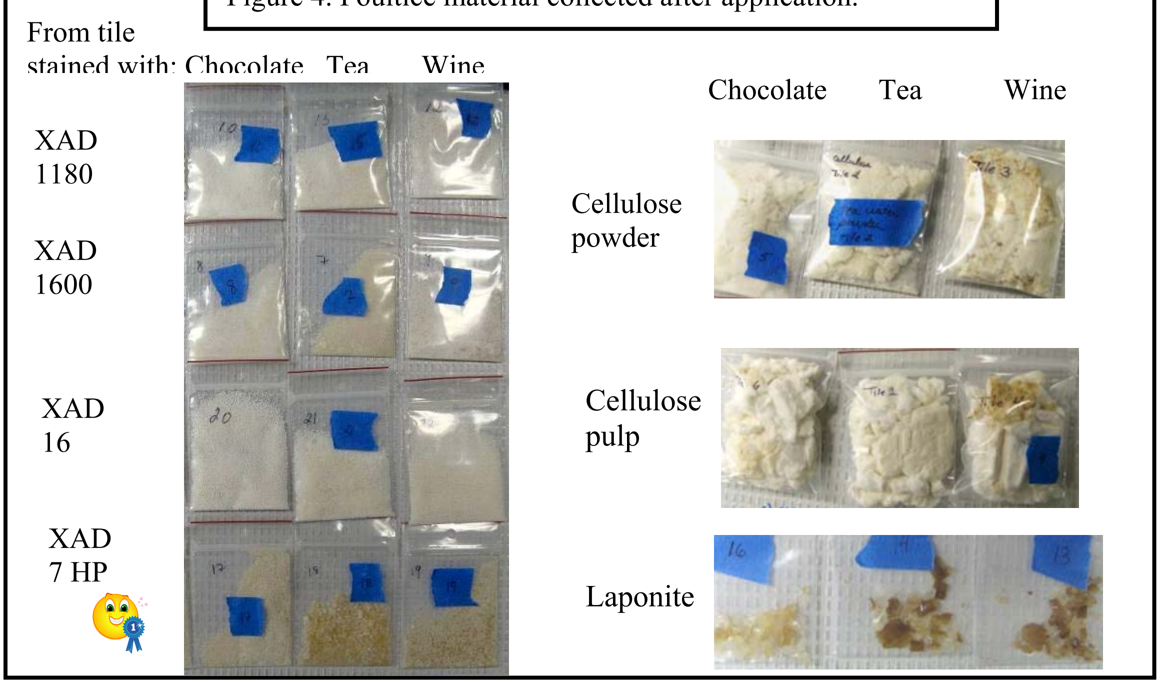
All of the tiles appeared to contain less stain material after the poultice in deionized water was applied, as is shown in the following pictures.

Figure 3. Tiles after one poultice in deionized water compared to an unstained tile and three tiles that were not poulticed.



The poultice material was collected from the tiles and the amount of discolored stain material collected on the tiles was visually compared as shown in the following pictures. The poultice material that contained the most discolored stain material is marked with a smiley face.

Figure 4. Poultice material collected after application.

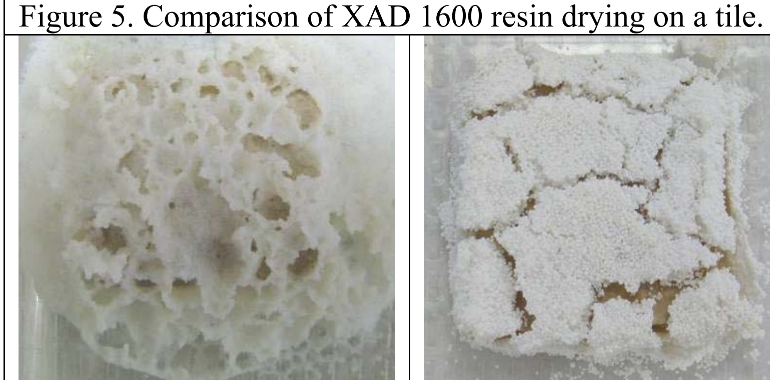


Colorimeter readings were taken on three locations on the porous side of each tile before and after each poultice was applied. The three ΔE values for each tile were averaged and these averages were compared. All of the poultices caused a ΔE greater than one, which indicates that a visible color shift occurred on each tile. The ΔE averages were between 2.6 for a tile stained with tea and exposed to a cellulose powder and deionized water poultice, and 12.41 for a tile stained with chocolate and exposed to Amberlite XAD®1180 and deionized water poultice. All of the Amberlite XAD® polymeric adsorbent resins generated a higher ΔE than either alpha cellulose powder, alpha cellulose pulp and Laponite® gel. The poultice material that generated the largest ΔE value was Amberlite XAD® 1180 followed by XAD 1600, XAD 7HP, XAD 16, Laponite® gel, alpha cellulose powder, and alpha cellulose pulp, which generated the smallest ΔE.

4.2 Results of Carbamide Peroxide Study

After application of carbamide peroxide in Laponite® gel, cellulose pulp and cellulose powder, the stain on all the titles was reduced so significantly that the tiles looked similar to an unstained tile. However when the carbamide peroxide solution was mixed with the Amberlite XAD® polymeric adsorbent resins and applied to the stained tiles the resin started to bubble. This bubbling action created pockets where the surface of the tile was not in direct contact with the resin. This resulted in an uneven degree of bleaching of the tile, and was considered to be unsatisfactory. Figure 5 shows a tile covered with a resin and carbamide peroxide with the voids created by the bubbling action, compared to a tile covered with resin and deionized water, both once the poultice is almost dry.

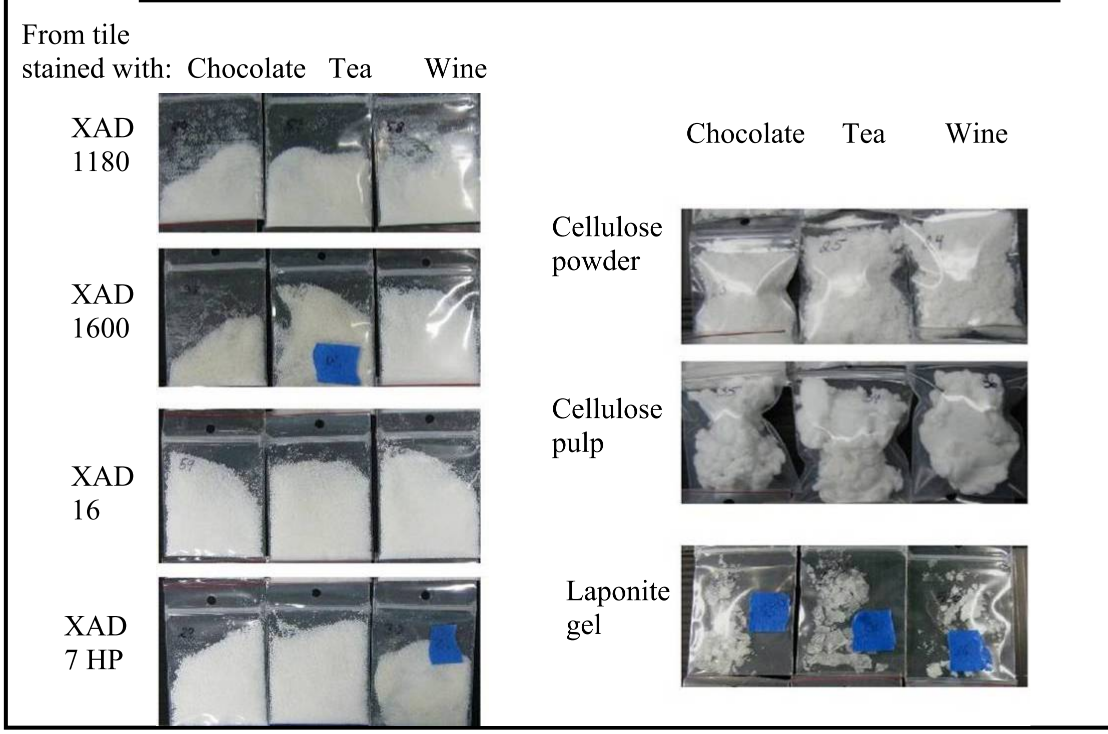
Figure 5. Comparison of XAD 1600 resin drying on a tile.



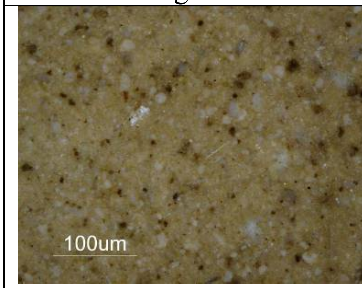
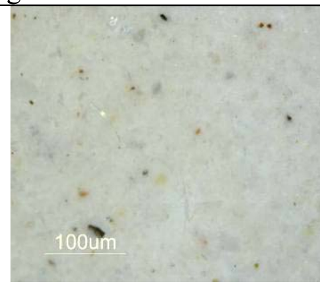
XAD 1600 and carbamide peroxide.	XAD 1600 and deionized water

To evaluate the color shift that occurred in the tiles due to application of carbamide peroxide, three colorimeter readings from the porous side of each tile were averaged. The averages for all tiles ranged between 5.67 on a tile stained with wine and bleached with carbamide peroxide and cellulose pulp to 43.39 on a tile stained with tea and bleached with carbamide peroxide and cellulose powder. When comparing the three tiles that were exposed to the same bleach and poultice material, it was found that all tiles stained with tea had the largest ΔE and the tiles stained with wine had the lowest ΔE values for all seven poultice materials. The resins had the widest range of ΔE for the three different food stains. For tiles bleached with carbamide peroxide and Amberlite XAD® 16 the ΔE average was 9.6 for the tile stained with wine and 33.29 for the tile stained with tea. Of all seven poultice materials, alpha cellulose powder had the most consistent and higher ΔE average for all three food stains. Figure 6 shows the poultice materials after they have been used to apply carbamide peroxide. The cellulose powder and cellulose pulp were white and the Laponite® gel was colorless as was expected. The resins, especially XAD 1180 and XAD 1600 contained discolored food stuff that was pulled out of the tile and not bleached.

Figure 6. Poultice material after application of carbamide peroxide.



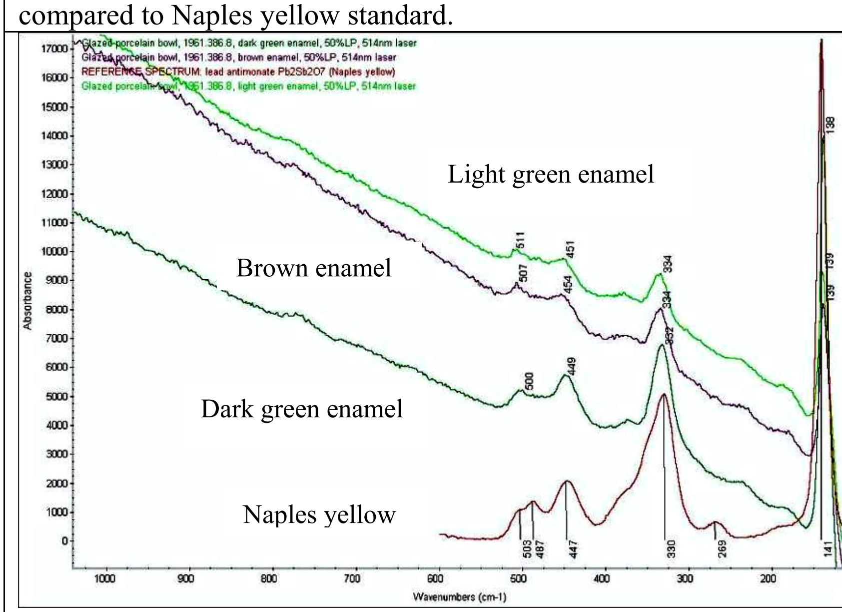
Photomicrographs were taken before and after six tiles were bleached with carbamide peroxide and Amberlite XAD® polymeric adsorbent. These images show that the amount of dark stain particles is visibly reduced and the tile surface was not etched or altered during the process.

Figure 7. Photomicrographs of a tile stained with tea. Images taken at 40x magnification	
	
Before bleaching	After application of carbamide peroxide and Amberlite XAD7HP®

4.3 Analysis of the Dish Attributed to Spode

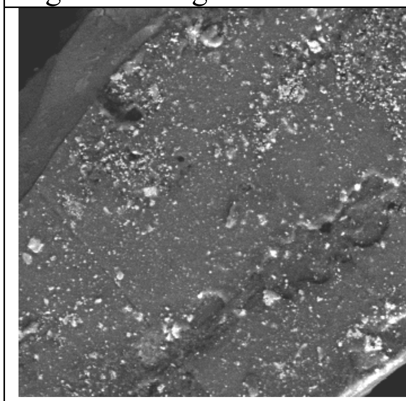
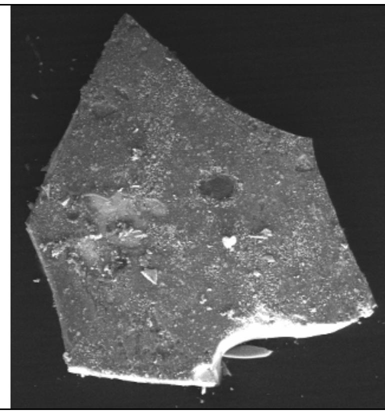
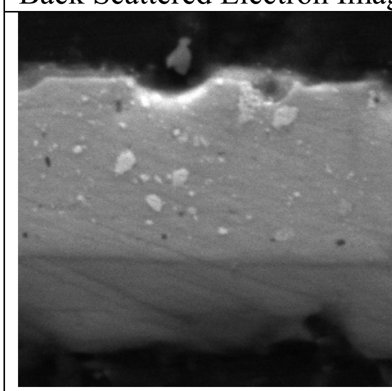
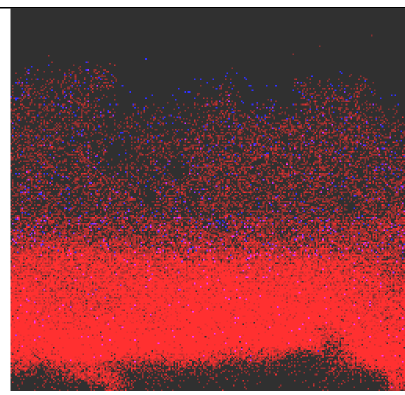
XRF was the first analytical method conducted on the enamels on the dish attributed to Spode. The enamels, clear glaze, and unglazed clay body were analyzed. The dark green enamel contained major x-ray lines for lead, copper, iron and cobalt. The light green enamel contained major x-ray lines for lead, copper and iron. Both colors contained minor x-ray lines for calcium, potassium and nickel. The dark green enamel also contained a minor x-ray line for manganese.

Figure 8. Dark green enamel, brown enamel and light green enamel compared to Naples yellow standard.



Lead antimonate ($Pb_2Sb_2O_7$, Naples yellow) was identified in the dark green, light green, and brown enamel. Figure 8 shows the dark green enamel, brown enamels and light green enamel compared to a lead antimonate, Naples yellow standard.

Only the light green and dark green enamels were analyzed with Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM) as these were the only two colors that contained losses and could be sampled. The top surface and cross sections of the two green colors were analyzed. The cross section revealed one layer that contained pigment and colorant particles on top of a lead based layer. Images of the top surface of the enamels show a wide range of particle sizes. Figure 9 contains the back scattered electron images and elemental mapping of the dark and light green samples.

Figure 9. Images from SEM analysis	
	
Sample 1. Image 1. Dark green enamel. 700x WD 26. 20kv Back Scattered Electron Image	Sample 4. Image 2. Light green enamel. 275x magnification, Back Scattered Electron Image
	 Colorant layer Lead based layer
Sample 6. Dark Green enamel. Cross section. 1100x magnification, Back Scattered Electron Image	Sample 6. Elemental mapping blue = copper red = silicon

5.1 Discussion of Poultice Study

All of the poultices applied to tiles stained with food residues were successful at reducing staining. Based on ΔE values and visible stain left on poultice materials, the Amberlite XAD® polymeric adsorbents removed more stain than the Laponite® gel, cellulose powder, and cellulose pulp respectively.

When the four resins were compared in terms of generating the largest ΔE on a tile and the amount of visible stain particles collected on the resin after the poultice was removed, it was found to be difficult to rank their performances. XAD 1180 which generated the largest Δ E had the least amount of visible stain material on the resin. XAD 7HP had the largest amount of visible stain on the resin but was ranked third for creating the largest ΔE. This difference may be due to the size and translucency of the polymers, which would effect how discolored they appeared. The following table compares the different poultice materials.

Table 2. Comparison of Poultice Materials

Poultice materials listed in order of creating the largest ΔE values to the smallest	Decreasing order based on visible stain materials on the poultice material
• XAD 1180 **Largest ΔE value** • XAD 1600 • XAD 7 HP • XAD 16 • Laponite® gel • Alpha cellulose powder • Alpha cellulose pulp **Smallest ΔE value**	• XAD 7 HP **Most stain material** • XAD 1600 • XAD 16 • XAD 1180 • Laponite® gel • Alpha cellulose powder • Alpha cellulose pulp **Least stain material**

XAD 7HP was the most discolored resin after application on the stained tiles. This resin was consistently darker than the other three resins for all three food stains. This darker color and slightly higher ΔE values indicate the resin removed the largest amount of colored stain material from the tiles. Based on these observations, this resin was selected to be used on the dish attributed to Spode.

XAD 7HP is a hydrophilic resin that absorbs polar compounds. Water was able to penetrate into the tiles dissolving and mobilizing parts of the stain compound and the polar components of the stain were absorbed into the XAD 7HP. The other three resins absorb non-polar material. As these three resins did not absorb as much colored material, it can be proposed that the colored portions of the stain are more polar in nature and have a greater affinity for a hydrophilic resin. Other factors such as size of the stain material and its ability to be dissolved in water may also impact the amount of stain removed by the resin.

The working properties of the seven dry poultice materials were also evaluated during this study. It was found that cellulose powder was the easiest to apply, but that the Amberlite XAD® resins were the easiest to remove. Due to their uniform round shape, the polymeric adsorbent resins had working properties similar to glass beads. With a small addition of water, the resins could be sculpted and applied to vertical surfaces. If too much water was added the resin flowed off the ceramic surface. It was found that these resins worked best when used slightly dry in the following method. The resin was applied first on the tile, then drops of deionized water were added with a micropipette until water was visible around the perimeter of the resin. This step involved trial and error as one extra drop of liquid could cause the resin to flow off the tile. Although these resins were difficult to apply, they were the easiest of all the poultice materials to remove since they could easily be brushed off the tile surface. This was unlike the cellulose powder and Laponite® gel that clung to the surface and were more difficult to remove, particularly from the porous surfaces of the tiles.

After reviewing the working properties, visible stain particles on the poultice materials and the ΔE values for the color change to the tiles, it was decided to use Amberlite XAD® 7HP resins to reduce the staining on the dish attributed to Spode.

5.2 Carbamide Peroxide Evaluation

Carbamide peroxide successfully and evenly bleached all three types of food stains on tiles when it was applied in cellulose pulp, cellulose powder and Laponite® gel. Due to the bubbling nature of the resins when combined with carbamide peroxide, tiles exposed to this combination were not bleached evenly. Beyond the uneven bleaching that can be created, this bubbling action could potentially cause physical stress and therefore it certainly would not be recommended for ceramics with delicate or sensitive surfaces. Still, though photomicrographs showed a decrease in dark stained particles after the bleach was applied in the resins and in our case, the unglazed clay body was not etched or altered during the process.

Carbamide peroxide and alpha cellulose pulp generated the highest ΔE values, indicating that this combination bleached the largest amount of stain particles. Alpha cellulose pulp and carbamide peroxide generated high ΔE values as did Laponite® gel and carbamide peroxide. Because the alpha cellulose pulp is easier to apply and to remove compared to alpha cellulose powder and Laponite® gel, it was decided to use carbamide peroxide and alpha cellulose pulp to reduce the stains on the dish attributed to Spode.

5.3 Discussion of Analysis of the Dish Attributed to Spode

Analysis with XRF revealed the enamels, clear glaze, and clay body to have a large lead content. The lead in the enamels may also be from the clear glaze, depending on the depth where the XRF instrument was able to record elemental information. The unglazed clay body has the least amount of lead and the greatest amount of calcium. The high amount of calcium is likely from the clay body as this dish may be a type of porcelain called bone china, whose formulation includes bone ash. Spode was in fact producing bone china at the same time period this dish was fabricated (Wilkinson, 2002). Bone china consists of 50% bone ash, 25% china clay, and 25% Cornish stone. Cornish stone, also called china stone, consists of feldspar rich granite that also contains quartz and mica. The presence of calcium in the enamels may be from a flux used to lower the melting point of the enamels. Potassium is also used as a flux and was found in both green enamel colors. The presence of potassium may be from the feldspar in the clay body as well.

Because copper was identified in both green enamels and all of the other enamel colors on this dish, it can not be determined if it is the main colorant of the green enamels. The dark green enamel contains cobalt, which was indicated in the director's book at the Spode factory as a colorant in many recipes for green enamel. Cobalt and manganese, which were both identified in the dark green enamel, were listed in the director's book as a way to produce black enamel. Due to the lack of cobalt in the light green color, it is not likely that cobalt was used to create a green enamel but added instead to obtain a darker green color. Nickel and iron are common impurities in cobalt ores and give the cobalt a greenish hue. Nickel was also identified in the light green enamel that did not have cobalt, and therefore it could not be determined if nickel was simply an impurity of the colorant. Based on the presences of iron in all parts of the Spode dish, it could not be determined if iron is an impurity or a colorant.

Lead antimonate ($Pb_2Sb_2O_7$), also known as Naples yellow, was identified in the spectra for dark green, light green and brown enamel colors with Raman spectroscopy. The Raman spectra for these three colors was almost identical to the spectrum for the lead antimonate reference. All four had peaks at approximately 500, 450, 331, and 140 cm-^{1}. There were two smaller peaks at 487 and 269 cm^{-1} that were in the reference spectra but not in the enamel colors. The absence of these smaller peaks may be due to slightly different sources of lead antimonate or different instrumental conditions among the analyses.

SEM-EDS analysis provided elemental and structural information about the dark and light green enamels. The cross sections of the enamels reveal a top granular layer that contains the majority of the colorants and a smooth lower silicon and lead-based layer. This lower layer may be part of the clear glaze on the dish. The single granular layer indicates that these enamels were applied in one layer. The colorant layer contains different sized particles, which may indicate that these enamels were made by a fritting process. There are historical recipes from the Spode Ceramic Company that use frit to make cobalt-based enamels (Copeland, 1980). Based on historical research and the image of the particles in the enamel, it appears as likely that these colors were created by fritting. More research would be required to confirm whether this process was in fact carried out.

SEM-EDS confirmed the majority of the elements in the composition of the enamels that were identified by XRF. SEM-EDS analysis confirmed the presence of silicon in both green enamels. Cobalt was not identified with SEM-EDS analysis, but was identified with XRF. Cobalt is a very strong colorant and only a few particles in the enamel mixture are needed to create a dark green color. The spot size for SEM-EDS analysis is so small it could have focused on an area that did not contain any cobalt pigments. Therefore additional cross sections and further analysis with SEM-EDS would be required to fully confirm the absence of cobalt in the dark green enamel. Tin and aluminum were identified with SEM-EDS in the top particulate layer, but not with XRF. These elements may be present in very small quantities and the SEM-EDS, which is more sensitive than the XRF, was able to detect them.

The elemental and compositional information generated from XRF, Raman, and SEM-EDS analysis did not show any elements that would have contributed to the formation of salts on the green enamels, as it occurred during previous treatment of a similar dish. Based on the results of this analysis and on the study of poultices and the potential that these salts were related to the application of a chelating agent in the poultice system, it was decided to first apply a poultice of Amberlite XAD 7HP® resin in deionized water, followed by an application of carbamide peroxide in cellulose pulp. And indeed no salts formed on the green enamel during the stain reduction treatment. This project certainly illustrates the benefit to considering a variety of poultice materials for the treatment of the same object, as the material most efficient at removing the staining material with water may be different from the poultice material that will be ideal when applying a bleach.

6. Treatment of the Dish Attributed to Spode.

After studying the composition of the fragile enamels on the dish attributed to Spode, a treatment procedure was conducted to reduce staining on the dish. This method first made use of Amberlite XAD 7HP® resin, the material that removed the most stain during the study of poultice materials. To begin treatment of the Spode dish, it was surface cleaned using a soft dry brush and cotton swabs lightly dampened with deionized water with care to not brush over the fragile enamels. Cyclododecane was applied to the green and brown enamels with a brush before each poultice application. The Amberlite XAD 7HP® resin was rinsed with deionized water, as per the instructions provided by the manufacturer, until the conductivity level of the resin matched that of deionized water. A poultice of Amberlite XAD® 7HP resin and deionized water was applied only to the undecorated areas of the dish. The application of XAD 7HP® resin was repeated twice. The XAD 7HP® resin reduced the staining significantly, but did not remove all discoloration in the clay body.

The staining in the clay body was further reduced using the second best poulticing system as determined during the study, that is with a 5% aqueous carbamide peroxide and cellulose pulp poultice. This poultice was applied only once to the back of the dish, while two applications of the poultice were necessary on the front of the dish. This makes sense as the bleach had a more limited access to the clay body on the front since the poultice was only applied around the enamels and decoration. A temporary issue arose however as powdery crystals developed on a few bands of gilded decoration adjacent to the locations where the poultice was applied as shown in Figure 10. These crystals were analyzed with FTIR and found to consist of sugars, which are breakdown products of the cellulose pulp. These crystals was easily removed with cotton swabs lightly dampened with deionized water, and did not reappear or affect these areas in any visible way.

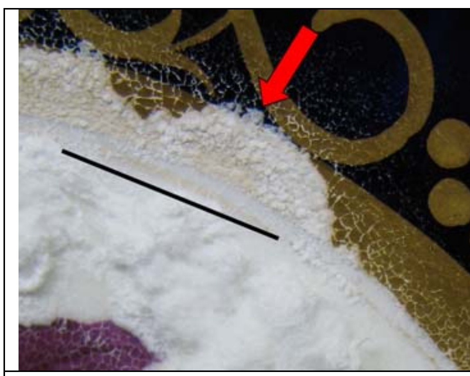


Figure 10. Detail photograph of the powdery residue that extended past the edge of the bleach application which is indicated with the black line.

After the stain was significantly reduced, the treatment of the dish continued with the consolidation of the areas of loss in the enamels with three applications of 2.5% Acryloid B-72 in acetone. Areas of losses in the green enamels were then inpainted with Golden Fluid Acrylics and coated with Acrysol WS-24 to approximate the gloss of the original enamels.

Figure 11. Photograph of the dish attributed to Spode after treatment

7. Conclusions and Further Research

The study on the working properties of seven materials that can be used in poultices to reduce stain on ceramics revealed their benefits and disadvantages. The polymeric adsorbents manufactured by Rohm and Hass removed more food stain particles from tiles, when compared to cellulose pulp, cellulose powder and Laponite® gel. Based on the results of this study Amberlite XAD 7HP® was applied in deionized water to the Spode dish and effectively reduced the staining on the dish. This procedure for reducing the staining on the dish can be safely carried out on the remaining dishes in the set.

Carbamide peroxide was found to effectively and evenly bleach food stains on ceramic tiles. However, combining this solution with the Amberlite XAD® polymeric adsorbents resulted in a bubbling action that could potentially cause physical harm to a delicate ceramic. When carbamide peroxide was applied in cellulose pulp, the bleach was effective at fully oxidizing the stain material, but also at breaking down components of the cellulose pulp into simple sugars. While the sugar crystals left behind did not harm the dish, the oxidized material extended past the line of application and had to be removed from the surface. Therefore, more work needs to be done to find the most effective poultice material to apply the carbamide peroxide solution.

Analysis of the enamels on the dish attributed to Spode indicated that the green enamels were applied in one application, creating one single colored layer. The green enamels have a lead silicate based composition that contains possibly copper, cobalt, iron, nickel, and tin as colorants.

Lead antimonate was identified in the green and brown enamels. Calcium, aluminum and potassium were identified in the enamels, but these elements may be from a flux that was added to lower the melting temperature of the enamels. While this elemental analysis provides insight into how the enamellist created the enamel colors, it does not indicate anything in the composition of the enamels that would promote the formation of salts, as was encountered with a related dish during a previous treatment.

In conclusion, the use of a poultice system to reduce a stain from a ceramic is an effective, but complex task that should continue to be studied. Questions related of particle size and physical entrapment of the stain in a glaze or clay body were not addressed in this project, but could become avenues for future research.

It is hoped that research into the use of Amberlite XAD® polymeric adsorbents for art conservation purposes will continue. As this project focused on using these resins in water and carbamide peroxide, their use in other solvents should be explored. Amberlite XAD® polymeric adsorbents are also reusable and this factor alone renders their use very cost-effective. They also offer the possibility to identify the staining material, after it has been extracted from the resin. According to the results of this study, Amberlite XAD® polymeric resins offer a great potential as a useful material in art conservation.

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