Investigation of Pink Staining on

Introduction

During the 2008 conservation of four marble sculptures in the antiquities collection at the J. Paul Getty Museum (JPGM), localized bright pink discoloration in association with a brownish, slightly rubbery adhesive was observed on join surfaces. (Figure 1) All four objects had been treated sometime in the 1970s with unknown materials, including undocumented adhesives.

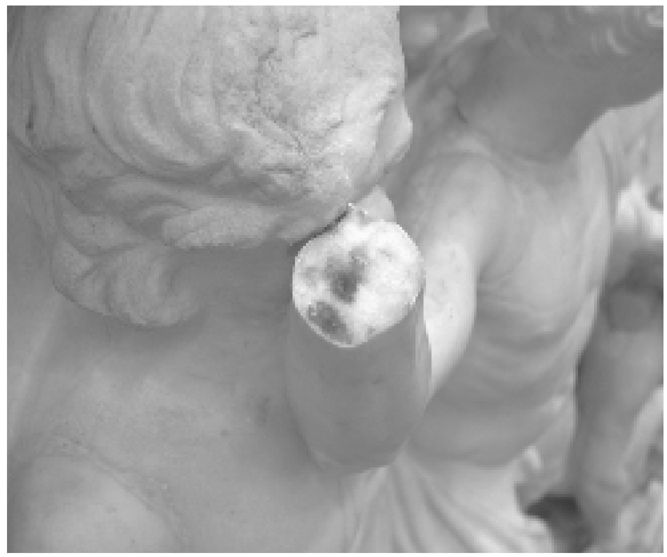

Figure 1. Pink staining on the join surface of JPGM 78.AA.61.

While retreating the sculptures in 2008, JPGM conservators encountered pink discoloration already present on join surfaces and observed its active formation. Upon the introduction of deionized water and polar organic solvents, the pink material became very mobile, and in some cases bled to the exterior surface of the stone and newly applied fill material.

In 2009, samples of the brownish adhesive with pink staining were removed in order to understand the nature of the discoloration, how to prevent its formation, and how best to remove the stain. Following characterization of the adhesive, experimental trials were conducted to determine if the pink stain could be replicated, thereby helping to reveal the mechanism by which it forms.

Research and Results

Samples of pink stained adhesive from the four sculptures were investigated with polarized light microscopy (PLM), Fourier transform infrared spectroscopy (FT-IR), and scanning electron microscopy- energy dispersive spectroscopy (SEM-EDS) in order to characterize the adhesive and to better understand the composition of the pink color. FT-IR spectra were acquired for pink and brown portions of stained adhesive samples, and the pink-colored material's spectrum was isolated by subtracting that of the brown. Extractions were made with water and ethanol.

In attempts to characterize the adhesive, results were compared to the FT-IR spectra of four epoxy resins obtained from a sample board created in 1988 as part of an adhesive study initiated by former GCI senior scientist Cecily Grzywacz and assistant antiquities conservator Susan Lansing Maish. (Figure 2)

The 1988 sample board included the following epoxy resins: UHU plus quickset, Devcon 5 minute, Devcon 30 minute, and Araldite 506 (unknown hardener). A more recent sample of Araldite AY 103 epoxy resin was also compared to the unknown samples.

FT-IR confirmed that the adhesive associated with the pink discoloration is an epoxy and that the same epoxy was used on several of the marble sculptures. The analyses showed a very good match between the samples and UHU plus quickset and Devcon 5 minute epoxies from the 1988 GCI reference board, suggesting the use of a rapidly setting epoxy.

An ethanol extraction did not appear to effect the discoloration, while the water extraction revealed that it is partially soluble in water, consistent with conservators' experiences when attempting to remove the staining.

SEM-EDS was used to investigate the presence of metal elements in the pink-stained areas. The elemental analysis of the pink material revealed the presence of chlorine, sulfur, calcium, carbon, and oxygen on the adhesive and marble. No metals were observed, indicating that the discoloration is organic.

The similarity between FT-IR spectra of the sampled adhesive and the UHU plus quickset epoxy from the 1988 reference board prompted further investigation of UHU plus quickset epoxy. A representative of the company confirmed that the product was launched in the early 1970s, which is consistent with the treatment dates of the marble objects in this study. It was also reported that the formulation has only been changed "in very small parts" since 1988, when the reference sample board used to aid identification of the adhesive was created. Detailed information on the nature of such changes was not provided.

New tubes of UHU plus quickset epoxy were purchased (Shell-lap Supplies, Australia). The FT-IR spectra of the newly purchased epoxy matched those of the GCI reference board and two adhesive samples from the objects, with very minor differences assumed to be due to age related changes.

After tentative identification of the adhesive associated with the pink discoloration as UHU plus quickset epoxy (via comparison to the GCI reference sample as well as to a sample of recently purchased UHU plus quickset epoxy), trials with the recently purchased UHU were initiated in order to see if the pink staining could be replicated.

The experimental trials sought to correlate the pink staining with the presence of other conservation materials and/or with environmental conditions. In order to examine the effects of binder: hardener ratio and foreign materials (cyanoacrylate, cellulose nitrate, Paraloid B-72, 3M double-sided tape, and copper flakes), UHU plus quickset epoxy was applied to four marble boards in varying binder: hardener ratios, and correct binder: hardener mixtures were applied to the marble surface in contact with the materials listed above.

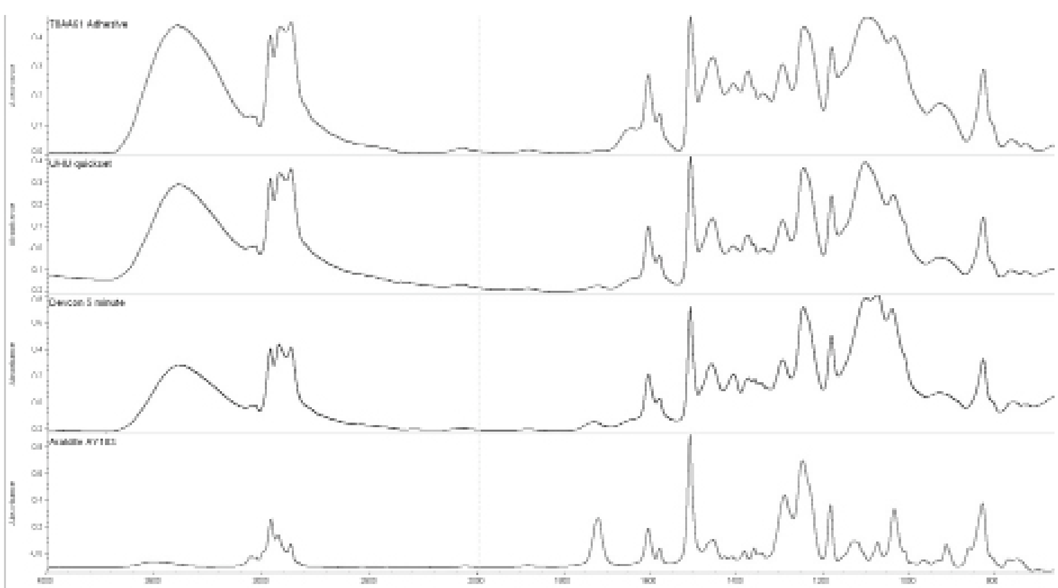

Figure 2. FT-IR spectra of:

pink-stained adhesive from JPGM marble sculpture 78.AA.61

UHU plus quickset epoxy (applied 1988)

Devcon 5 minute epoxy (applied 1988)

and Araldite AY 103 epoxy (applied 2009).

To investigate the possible effects of moisture, solvent vapor, and direct wetting, boards were subjected to elevated relative humidity (approximately 100%) during setting, exposure to acetone fumes during setting, and direct wetting during setting.

One control board was stored in a cool, dark location with minimal relative humidity fluctuation, and another board was later heated at 60ºC at low humidity for one month to accelerate deterioration of the adhesive.

During the course of experimental trials, it was discovered that a slab of marble once used as display furniture at the Getty Villa exhibited pink discoloration in association with a brown rubbery adhesive used to attach hardware. FT-IR spectra of the adhesive found on the furniture slab strongly resembled those of the adhesive sampled from the four statues and the UHU plus quickset epoxy from the 1988 reference board. The date of application of the adhesive to the furniture slab is unknown, but could be roughly contemporaneous with the original treatment of the four statues.

The slab of marble was subdivided and used to carry out additional investigation of the effects of high relative humidity, direct wetting, and high pH on both newly applied and naturally aged adhesive on a marble surface. (Figure 3)

Pink staining developed in two locations on the experimental marble pieces over a period of four months. In both instances, pink discoloration appeared on the marble surface adjacent to new UHU plus quickset that had been cured at elevated relative humidity. On the board which had been prepared at near 100% relative humidity, a faint pink halo appeared around the application of 1:3 binder: hardener (v: v) UHU plus quickset, the excess hardener formulation. No other pink staining appeared on any of the marble boards.

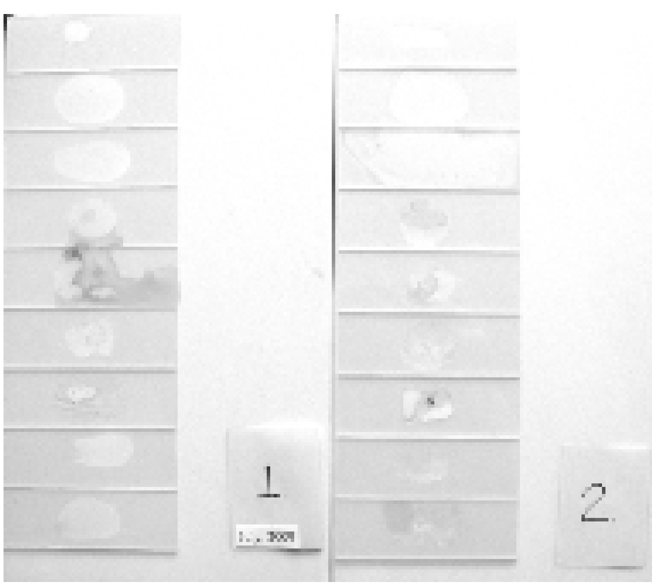

Figure 3. Experimental marble boards 1 (control) and 2 (cured at elevated relative humidity) four months after the application of UHU plus quickset epoxy. Faint pink discoloration formed on board 2, slide 3, the site of UHU plus quickset with excess hardener.

On one of the slab ends, diffuse bright pink discoloration appeared surrounding an application of properly mixed 1:1 binder: hardener UHU that had been directly wet with deionized water and cured at near 100% relative humidity.

Discussion

The results of the scientific investigation of adhesive samples and of the experimental trials suggest that the pink discoloration is unrelated to secondary materials in contact with the epoxy, that moisture may be a key factor in its formation, and that excess hardener may also influence the formation of the pink staining.

The mechanism of pink stain formation remains unclear, but both analytical results and experimental work indicate that the pink discoloration forms from components present in the epoxy. FT-IR and SEM-EDS analysis of adhesive samples from the stained sculptures detected only epoxy, although there were some additional unidentified peaks in the FT-IR spectrum of the pink-colored portion of the adhesive. On the marble mock-up boards, the pink staining only formed in instances where UHU plus quickset alone had been applied to the marble surface.

The only successful replications of pink discoloration on the experimental marble pieces occurred when the epoxy was cured at high relative humidity, and in one case was directly wet. The marble boards which were not subjected to elevated RH did not exhibit any pink discoloration. The formation of pink discoloration around the UHU plus quickset with excess hardener also suggests that an improper ratio of the two components may contribute to pink staining.

Because of the correlation between moisture and the pink discoloration, its possible relationship to the amine blushing phenomenon may merit exploration. When epoxy resins cure in high humidity environments, amine compounds in the epoxy can combine with airborne carbon dioxide, forming mixtures of ammonium bicarbonate and ammonium carbamate on the surface of epoxy coatings. However, amine blush products are usually described as whitish in color rather than pink.

While this preliminary work has characterized the adhesive associated with the pink discoloration on the JPGM marble sculptures and suggested that exposure to moisture during curing and excess hardener may result in stain formation, additional research into the nature of the staining is necessary. Further analytical investigation is required to clarify the mechanism of the stain formation, and additional study of the most effective stain reversal techniques should be undertaken.