A Re-evaluation of Adhesives Used for Mending Ceramics at Kaman-Kalehöyük: A Final Assessment

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ABSTRACT

In 1999, a series of long-term adhesive testing on ceramic was initiated at Kaman-Kalehöyük. These tests were instigated by the occurrence of slumped ceramic vessels that had been mended with Paraloid® B-72 and exposed to elevated temperatures in storage. Three other adhesives were examined for their suitability as substitutes for Paraloid® B72: Paraloid® B-48N, Butvar® B-98 and Cellulose Nitrate. The tests were designed to study the aging properties of the four adhesives and to evaluate their reaction to varying environmental conditions. The study was concluded with a final assessment of the aged sample in two experiments that explored the adhesives' strength and solubility.

INTRODUCTION

During the 1999 and 2000 excavation seasons, a series of long-term adhesive testing was initiated at Kaman-Kalehöyük (Moy 2000; 2001). These tests were a response to an occurrence of slumping in ceramic vessels that had been reconstructed with Paraloid® B-72. This incident raised questions regarding the resin's suitability as an adhesive in extreme climatic fluctuations, with values ranging from the thirties (°C) to below freezing levels, all common in Central Anatolia throughout the year. Application techniques used at the site were also reconsidered (Moy 2000: 235). The aim of the tests was to evaluate conservation-grade adhesives with respect to their strength, solubility, flexibility, appearance and reaction to varying temperatures and relative humidity conditions over time (Moy 2000; 2001).

1. Objectives in the 1999 Excavation Season

In the first season, the investigation was focused primarily on re-evaluating the use of Paraloid® B-72 (methyl acrylate/ethyl methacrylate co-polymer) as well as investigating the appropriateness of Paraloid® B-48N (butyl acrylate/methyl methacrylate co-polymer) as an adhesive for thick-walled, heavy ceramics and establishing the most successful adhesive application technique (Moy 2000: 242). In addition, the effect of age on the adhesives' strength, flexibility, solubility and appearance was explored. Four tests were conducted utilizing four adhesives (Moy 2000: 239). The adhesives selected were based on what other conservators have used for a variety of materials when excessive heat was a concern at archaeological sites:

1. Paraloid® B-72 (50% in acetone: ethanol (95:5), w/w)
2. Paraloid® B-48N (50% in acetone, w/w)
3. Butvar® B-98 (poly(vinyl butyral)) (25% in ethanol, w/w)
4. Cellulose Nitrate (cellulose polynitrate ester) HMG Heat and Waterproof Adhesive – provided in the tube by the manufacturer

All of the tests consisted of subjecting the test samples to the site's uncontrolled storage environment. It was proposed that the samples would be assessed every season for at least five years (Moy 2000: 235).

2. Objectives in the 2000 Excavation Season

Due to insufficient results from the tests begun in the 1999 excavation season, two groups of tests were initiated during the 2000 excavation (Moy 2001: 206). Both experiments consisted of examining the adhesive failure rate of sets of adhered homemade tiles under conditions that were designed to cause physical stresses (Moy 2001: 206-7). The homemade tiles sought to mimic similar ceramic body types found at Kaman-Kalehöyük, using clay indigenous to Central Anatolia. These tests were aimed at accelerating the failure rate of the adhesives. Fumed silica and possible miscible adhesive mixtures were added in order to study their effect on the adhesives' glass transition temperature. The adhesives tested were the following (Moy 2001: 206-7):

1. Paraloid® B-72 (50% in acetone: ethanol (95:5), w/w)
2. Paraloid® B-72 (50% in acetone: ethanol (95:5) plus a small spoonful of fumed silica, w/w)
3. Paraloid® B-72/Paraloid® B-48N (50% (1:1, w/w) in acetone: ethanol (95:5), w/w)
4. Paraloid® B-48N (50% in acetone: ethanol (95:5), w/w)
5. Butvar® B-98 (25% in ethanol, w/w)
6. Cellulose Nitrate HMG Heat and Waterproof Adhesive – provided in the tube by the manufacturer

It was proposed that the tests would be run and assessed every season, along with those initiated in 1999, for five to ten years (Moy 2001: 208).

3. Objectives in the 2009 Excavation Season

The 2009 excavation season marked the ten-year anniversary of the first set of adhesive tests, a date chosen as appropriate for a final assessment and conclusion on the adhesives' properties. This final evaluation included an update of the current state of the samples and documented test observations as well as results from previous seasons. Additionally, two final tests were carried out on the existing samples which explored the adhesives' strength and solubility properties. The 2009 tests were short-term experiments on the test samples from 1999 and 2000.

EXPERIMENTAL DESIGN

1. 1999 Excavation Season Tests

Reconstructed Modern Ceramic Vessels

In total, 24 modern ceramic vessels, 360 mm tall and 110 mm in diameter, were reconstructed. Sixteen vessels were mended with Paraloid® B-72 and eight were mended with Paraloid® B-48N (Moy 2000: 240). The research conducted in 1999 showed that although Paraloid® B-72 is a favoured adhesive in conservation on account of its reversibility and stability, its low glass transition temperature (Tg) (40°C) has led conservators working in warm climates to prefer Paraloid® B-48N (Tg = 50°C) (Moy 2000: 235-6).

Eight of the sixteen vessels mended with Paraloid® B-72 were completed using the adhesive application method that had been practiced at Kaman-Kalehöyük prior to the initiation of these experiments (Moy 2000: 240). Although ceramic vessels were typically mended by trained technicians rather than conservators, the adhesives made for these experiments and in the past seasons were made by conservators. It must be noted that the exact recipe for making the adhesive prior to 1999 is unknown. The remaining eight vessels mended with Paraloid® B-72 and all of the vessels mended with Paraloid® B-48N were reconstructed using the adhesive application method recommended by Stephen Koob and Tony Sigel (1997) (Moy 2000: 240). Below is an account of the earlier method (after Moy 2000: 238):

1. Clean the joining edges with a brush to remove debris.
2. Apply two coats of 5-10% Paraloid® B-72 [in acetone] (w/v) to seal and [prime] the edges (allowing the [primed] edge to dry for a minimum of 15 minutes).
3. Dispensed from a tube, apply the appropriate adhesive.

This may be compared to the method of adhesive application developed by Stephen Koob and Tony Sigel (1997) (the Paraloid® B-72 was prepared according to Stephen Koob's (1996) directions) (after Moy 2000: 241):

1. Using a soft brush the joining edges were cleaned of all interfering deposits.
2. Two coats of 7.5% solution of Paraloid® B-72 (w/v) in acetone and ethanol were applied to [prime] and seal the join edges. [Each priming coat was allowed to dry for at least 12 hours. In addition,] a minimum of 12 hours [before the second priming layer and 24 hours after the second priming layer] was allowed for the [priming coats] to dry before any attempts at joining were made. The [primed edges] strengthened the adjacent ceramic fabric, creating a like to like bond and preventing premature absorption of the adhesive solvent from the join.
3. The adhesive was [dispensed from a tube and] applied to the join edges, then closed without pressure to evenly distribute the adhesive. It was then pulled apart for a few seconds. The join was then closed and pressure was applied.

Out of the 24 reconstructed vessels, 12 (four from each group) were stored on the highest shelf in the Eski Depo[1]. The remaining 12 vessels (four from each group) were stored on a lower shelf in the same storage depot to test the influence of temperature gradients (Moy 2000: 241).

Strength Test

This test foremost consisted of preparing two types of tiles: 64 home-made red tiles (60 x 40 x 12.5 mm) and 64 store-bought white kitchen/bathroom tiles (60 x 40 x 7 mm) (Moy 2000: 241). Visual examination with the naked eye indicated that the home-made red tiles are more porous than the store-bought white tiles.

The home-made red tiles were made from clay that is commonly found in the Central Anatolian region in combination with 0.1 mm coarse sand (2:1 ratio by volume). A hole was punctured into each tile approximately 10 mm below the edge of one end (length of 40 mm) to allow the tile to be suspended. The shaped tiles were fired at 700ºC. The store-bought white kitchen/bathroom tiles were cut into 64 pieces. A binder clip was adhered to one end (length of 40 mm) with an epoxy adhesive. All of the joining edges were ground with a diamond wheel to ensure a smooth and even surface for good edge bonding (Moy 2000: 241).

After all of the individual tiles from both groups had been prepared, two tiles in each group were adhered together "end-to-end" along one side (length of 4 cm) to form one sample (Moy 2000: 242). In total, each group contained 32 samples. Each of the tested adhesives (Paraloid® B-72, Paraloid® B-48N, Butvar® B-98 and Cellulose Nitrate) was used to make eight tile sets in the group composed of home-made red tiles and eight tile sets in the group composed of store-bought white tiles. Fishing line was applied to the ends of each set: on the home-made red tiles, it was passed through the holes, while on the store-bought white tiles it was passed through the binder clips. The fishing line on one end was used to hold a 250 g weight composed of sand packed in a polyethylene Ziploc® bag and wrapped in cheesecloth. The purpose of the fishing line on the opposite end was to hang the sample sets in a wooden crate (Moy 2000: 241).

Out of the 64 tile samples, 32 samples were placed on the highest shelf in the Eski Depo and 32 samples were placed on a lower shelf along with the reconstructed modern ceramic vessels. The samples were divided so that half of the tile sets (four out of eight) adhered with the tested adhesives from each tile group was placed on the high shelf and the other half on the low shelf in order to test the temperature gradient (Moy 2000: 242).

Flexibility, Solubility and Appearance Tests

The preparation required for these two experiments consisted of making solid film strips from the tested adhesives (Paraloid® B-72, Paraloid® B-48N, Butvar® B-98 and Cellulose Nitrate). This consisted of applying the adhesives with the aid of a syringe onto silicon release Mylar® and leaving them to set for 72 hours. The set adhesive films were exposed to natural light near a window in the Labo[2] (Moy 2000: 241).

In order to test the flexibility of the aging adhe-

[1] The Eski Depo refers to the old storage depot in which the test samples were stored from 1999 to 2004.

[2] The Labo refers to the old conservation laboratory which stored the flexibility, solubility and appearance test samples from 1999 to an unknown date. The laboratory came out of use in the 2009 excavation season.

sives, the film of each tested adhesive was cut into 12.5 x 30 mm strips and bent over a Plexiglas® rod, 10 mm in diameter. Qualitative observations were made on the ease of bending and any signs of cracking or brittleness (Moy 2000: 242).

The solubility test consisted of cutting approximately 5 mm^2 of each adhesive film every excavation season and subjecting it to the specified organic solvent (Moy 2000: 241). Paraloid® B-72, Paraloid® B-48N and Cellulose Nitrate were placed in 1 mL of acetone in a petrie dish with a cover. The process for Butvar® B-98 differed in the organic solvent used, which was ethanol. Qualitative observations were made on the time that the adhesive film strips required to solubilise (Moy 2001: 206).

The appearance test was intended to be a visual assessment on any colour changes of the aged samples as they were undergoing dissolution by means of exposure to the appropriate organic solvents (Moy 2001: 206).

2. 2000 Excavation Season Tests

In a similar manner to the 1999 strength test, the experiments conducted during the 2000 excavation season employed tiles that were home-made. In total, 90 tiles (50 x 30 x 10 mm) were made with the same clay as in the previous season that is commonly found in the Central Anatolian region. Sand inclusions were not added to the mixture due to their unavailability during the 2000 season (Moy 2001: 206). Visual examination with the naked eye revealed these tiles to be less porous than the home-made ones from the previous season. A hole was made near the edge of one side (length of 30 mm). The finished tiles were fired at 700ºC. Each tile was then cut in half with a diamond circular saw and smoothed, resulting in two tiles (25 x 30 x 10 mm) (Moy 2001: 207).

The two halves of each tile were adhered together "end-to-end" along one side (length of 30 mm) with the tested adhesives (Paraloid® B-72 with and without fumed silica, Paraloid® B-72/B-48N, Paraloid® B-48N, Butvar® B-98 and Cellulose Nitrate) to form 90 samples. The joining edges were not primed prior to application of the adhesives (Moy 2001: 206). Each adhesive was used to join 15 pairs of tiles, which were divided into the respective tests. Copper wire was passed through the hole in each tile set so that the tiles could be hung in polyethylene containers (Moy 2001: 207).

High Relative Humidity Test

A total of 36 samples were employed for this test. Six samples with each adhesive were divided into two polyethylene containers: three samples with each adhesive were hung in a container that was stored on the highest shelf in the Eski Depo and three samples with each adhesive were placed in a container that was stored on the lower shelf in the Eski Depo along with the reconstructed modern ceramic vessels and strength test pieces from 1999. Both containers contained cotton that was intended to be saturated with water to form a 99% relative humidity environment (Moy 2001: 207).

Accelerated Aging Tests

This test consisted of subjecting the tiles to three different types of environmental conditions: outdoor, freezing and freeze/thaw. In total, fifty-four samples were employed for this test – nine with each tested adhesive. Three samples with each tested adhesive were hung in three different polyethylene containers. The first container was placed outdoors to be exposed to the natural sun and heat. The second container was placed in the dark interior of a freezer with a temperature of -15ºC. The third container was put through a freeze (-15ºC)/ thaw cycle, whose design consisted of "subject[ing] [the samples] to freezing for 10 hours, and 2 hours to acclimate in a dark room with no environmental controls; followed by 10 hours outside, [in the same location as the outdoor samples,] in direct sunlight, and again two hours to acclimate to room temperature, over a cycle of 14 days." (Moy 2001: 207).

3. 2009 Excavation Season Tests

The experiments conducted in the 2009 excavation season employed the tile samples made in 1999 and 2000. The tile samples from the 1999 excavation season consisted of high and low shelf ambient relative humidity depot samples with weights (295 g). The tests from the 2000 excavation season included the high and low shelf 99% relative humidity microenvironment depot samples and accelerated aging samples that were subjected to outdoor environmental conditions. The surviving 1999 and 2000 tests tiles were removed from their current storage location in the Beton Depo[3] and divided into two groups: one group underwent a strength test and one group underwent a solubility test in 2009. Preference was given to the solubility test on account of its application in conservation; therefore, in cases of an odd number of remaining tiles for a tested adhesive, a greater number of tiles was allocated to the solubility test.

Strength Test

The goal of this experiment was to apply pressure to the tiles to assess the strength of the adhesive compared to that of the ceramic. Breaks were recorded as 'a break along the join', 'a break in the tile', or 'a break in the join and tile'. The experiment consisted of placing each tile at the edge of a tabletop and positioning it so that half of one of the joined fragments (30 mm on the large tiles and 11 mm on the small tiles) was resting on the table; while, the join region and the other end of the ceramic projected off the table edge. The tile was fastened to the table with a C-clamp. In each case, a 1000 g weight was allowed to fall freely onto the tile from a height of 300 mm. Both the mass of the weight and the falling distance were selected. The aim was to impact the tile at a distance of 10 mm from the join on the larger tiles and 5 mm on the smaller tiles. To ensure accuracy, a structure with indicated measurements was used. The structure was constructed using a flat, wooden stick, Ethafoam™, Coroplast™ and an 80 mm scale. This structure was arranged so that, with the aid of a plumb line, it guided the positioning of the weight above the tile. The bottom surface of the weight was positioned at the measured point above the tile by hand. It was released by the hand and allowed to fall onto the ceramic tile and then to the floor. The floor beneath the tile was padded with Ethafoam™ to cushion the fall of the tile and to protect the floor.

Solubility Test

The objective of this experiment was to determine the solubility of the aged adhesives within a set amount of time. The results were recorded either as a 'join failure' or 'no join failure' on each sample. The test consisted of placing all tiles in a sealed solvent vapour chamber. Since all of the tested adhesives are soluble in acetone, it was decided that for the purpose of consistency, all of the tiles were subjected to acetone vapours. The tiles were hung vertically from one end, as they were previously stored this way for the tests that were initiated in the 1999 and 2000 experiments. Additionally, the tiles from the higher and lower shelves from the ambient relative humidity 1999 depot tests retained their 250 g weights during the solubility test. The tiles were tied with spinning line to horizontal bars on a wooden frame, which was specifically designed for this experiment. The frame was enclosed in a clear, polyethylene bag that was tightly sealed with masking tape. Three 200 mL beakers and one 300 mL beaker was filled with cotton batting saturated with approximately 125 mL of acetone and placed in the chamber. In total, 2000 mL of acetone were used. Three additions of 500 mL were made every 24 hours to the initial 500 mL to ensure a complete saturation of the cotton. The beakers were placed at regular intervals around the frame. The tiles were left in the chamber for a period of 188 hours and 15 minutes, during which time they were closely monitored both by one of the authors and by video camera to ensure that an accurate account of the time of adhesive failure was documented.

ENVIRONMENTAL MONITORING

It was initially assumed that the reason for slumping in the ceramic vessels mended with Paraloid® B-72 was that the temperature in the storage environment exceeded the transition glass temperature of the adhesive (40ºC) (Moy 2000: 235). On this account, monitoring of the temperature and relative humidity in the location of the stored samples (the Eski Depo, Beton Depo and Labo) was a vital component of these tests.

1. Eski Depo

During the 1999 and 2000 excavation seasons, a Langan Model L12 Hygrothermograph was employed to monitor the temperature and relative

[3] The Beton Depo refers to the storage depot in which the test samples were stored from 2004 to 2009.

humidity on the two shelf levels (high and low) in the Eski Depo, a corrugated steel siding structure, in which the test samples were stored. This environmental monitoring was only carried out during each season's testing period (Moy 2000: 239-240). The aim was to determine whether the temperatures on these levels ever exceeded 40ºC (the glass transition temperature of Paraloid B-72). In 2000, the maximum recorded value on the high shelf was 45.5ºC, while the maximum temperature on the lowest shelf was seen to have surpassed 40ºC only on two occasions during the testing period (Moy 2001: 208).

2. Beton Depo

From 2004 to 2005, all of the reconstructed pots and test samples (except for the 1999 flexibility and solubility test samples and 2000 freeze and freeze/thaw test samples) were stored in the new storage depot, a concrete structure referred to as Beton Depo. The temperature and relative humidity in this storage depot were monitored from October 2004 to July 2005 with two HOBO® Temperature Relative Humidity 1996 Onset Data Loggers; one was placed in an unsealed cabinet and one was placed in a sealed cabinet. The recorded results between the two data loggers demonstrated that Kaman-Kalehöyük's collection was exposed to great fluctuations in the environmental conditions throughout the year. In terms of the temperature, the maximum recorded value was 30.31ºC in July, while the minimum value was -1.06ºC in February. This equals to a difference of 31.37ºC. With respect to the relative humidity, the maximum recorded value was 77.90% in February, while the minimum value was found to be 23.5% in July. This results in a difference of 54.4% between the two dates.

3. Labo

The temperature and relative humidity in the Labo, a corrugated steel siding structure, was monitored from July 2008 to July 2009. It was found that the maximum temperature value that the laboratory reached was approximately 33ºC, while the minimum value was approximately -5 ºC. This results in a difference of 38ºC to which the samples may have been annually subjected. The maximum relative humidity value was recorded to be approximately 88%, while the minimum value was approximately 25%. This results in a difference of 63% to which the samples may have been annually subjected.

RESULTS AND OBSERVATIONS

1. 1999 Excavation Season Tests

Reconstructed Modern Ceramic Vessels

With respect to the vessels adhered with Paraloid® B-72, both on the high and low shelves, an equal number of vessels mended by the method employed at Kaman-Kalehöyük prior to the initiation of the 1999 experiments and the Koob-Sigel method was found to be stable (62.5% for each). Regarding the effect of temperature on the vessels' stability, 50% of the vessels stored on the high shelf (subjected to higher temperatures) were found to be in a stable state; while, 75% of vessels stored on the low shelf (subjected to lower temperatures) were found to be stable. These results indicate that temperature rather than the method of adhesive application affect the stability of ceramic vessels that have been mended with Paraloid® B-72. In terms of the more appropriate adhesive, Paraloid® B-72 versus Paraloid® B-48N, to be used on ceramic artifacts in warm climates, Paraloid® B-48N has proven to have greater success in providing stability to the re-assembled artifacts.

Strength Test

None of the tiles from both the higher and lower shelves failed during the ten-year period. These results indicate that the tested adhesives (Paraloid® B-72, Paraloid® B-48N, Butvar® B-98 and Cellulose Nitrate) are equally capable of bearing a load over a long period of time. It was hoped that the adhesives would exhibit their differences in strength over time (Moy 2000: 239); however, this was not the case.

Flexibility, Solubility and Appearance Tests

The flexibility and solubility test samples from 1999 were stored in the Labo. Unfortunately, the samples could not be located during the 2009 excavation season. It is believed they may have been discarded sometime between 2002 and 2009.

The observations for the flexibility test conducted during the 1999, 2000 and 2002 excavation seasons indicate that after one year, the only adhesive out of the tested adhesives (Paraloid® B-72, Paraloid® B-48N, Butvar® B-98 and Cellulose Nitrate) to lose its flexibility and become brittle was Paraloid® B-48N. Only Butvar® B-98 and Cellulose Nitrate retained their flexibility even after three years of aging in natural light.

The solubility tests conducted during the 2000 and 2002 excavation seasons have shown a general trend for all four tested adhesives (Paraloid® B-72, Paraloid® B-48N, Butvar® B-98 and Cellulose Nitrate): an increase in age resulted in slower dissolution. Based on the results, the order of reversibility, from the most to the least reversible, of the aged adhesives has been determined to be Paraloid® B-72, Cellulose Nitrate, Paraloid® B-48N and Butvar® B-98. Only Cellulose Nitrate discoloured after one year of aging in natural light.

2. 2000 Excavation Season Tests

High Relative Humidity Test

None of the tested adhesives (Paraloid® B-72, Paraloid® B-72 with fumed silica, Paraloid® B-72/B-48N, Paraloid® B-48N, Butvar® B-98, Cellulose Nitrate) on the high shelf experienced failures during the ten-year period; while, only one sample of Cellulose Nitrate failed on the low shelf. The fact that none of the tested adhesives have been classified as water-soluble polymers may support the adhesives' evident success in withstanding high relative humidity conditions (Horie 1987: 50). The initial hypothesis that Paraloid® B-72 and Paraloid® B-48N would remain unaffected in the high relative humidity conditions due to the hydrophobic nature of acrylics has proven to be true (Moy 2001: 207). It must be noted that the high relative humidity levels were not maintained constant throughout the ten-year period; the samples were last humidified during the 2003 excavation season.

Accelerated Aging Tests

Paraloid® B-72 without fumed silica proved to be the most capable adhesive out of those tested (Paraloid® B-72 with and without fumed silica, Paraloid® B-72/B-48N, Paraloid® B-48N, Butvar® B-98 and Cellulose Nitrate) of withstanding extreme conditions (11.1% of the samples failed) and Cellulose Nitrate to be the least capable (88.9% of the samples failed). Out of the failed samples, 34.5% failed in the freeze environment, 31.0% failed in the outside environment and 37.9% failed in the freeze/thaw conditions. Therefore, the freeze/thaw conditions were the most stressful conditions for the tested adhesives; while, the outdoor environment was the least damaging. It may be suggested that it is the wide temperature fluctuations experienced within a short time frame that cause the greatest amount of stress to a join, thereby increasing the adhesive failure rate.

3. 2009 Excavation Season Tests

Strength Test

The results from the tiles that had been subjected to the 1999 strength test (*Fig. 1 to Fig. 4*) indicate that the tested adhesives (Paraloid® B-72, Paraloid® B-48N, Butvar® B-98 and Cellulose Nitrate) were generally weaker than the ceramic. Out of the 16 store-bought white tiles, 62.5% of the breaks occurred in the join, 12.5% of the breaks occurred along the tile and 25.0% occurred both in the join and along the tile (*Fig. 1 and Fig. 2*). The breaks were often clean and there was an equal amount of adhesive residue and a minimal amount of ceramic residue on both joining edges. Out of the 16 home-made red tile samples tested, 56.3% of the breaks occurred in the join, 31.3% along the tile and 12.5% both in the join and along the tile (*Fig. 3 and Fig. 4*). Breaks in the join were usually very rough and a large, unequal amount of adhesive and ceramic residue from one joining edge remained on the other joining edge. Overall, the tiles of red clay with sand inclusions appear to be a weaker ceramic than the white tiles (31.3% versus 12.5% breakage through the ceramic of the red and white tiles respectively). The different shelf levels do not appear to have had an effect on strength of the tested adhesives, although Paraloid® B-48N seems to have performed better from the higher shelf based on *Fig.1 to Fig. 4*.

The tiles that had undergone the 2000 high relative humidity and outdoor environment accelerated aging tests all yielded the same results: the tiles broke in the join. In all cases, the break was clean.

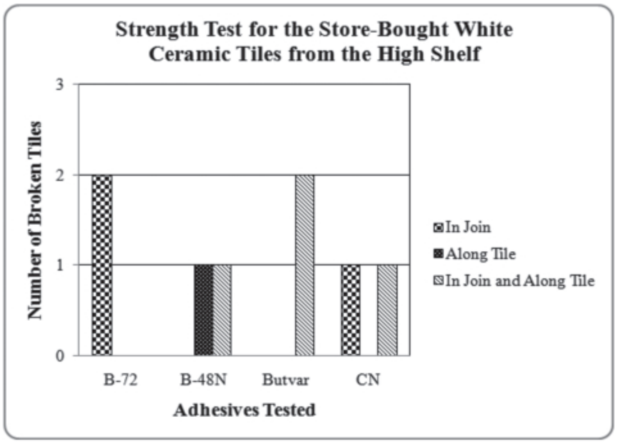

Fig. 1 Broken store-bought white tiles from the 1999 high shelf strength test during the 2009 strength test.

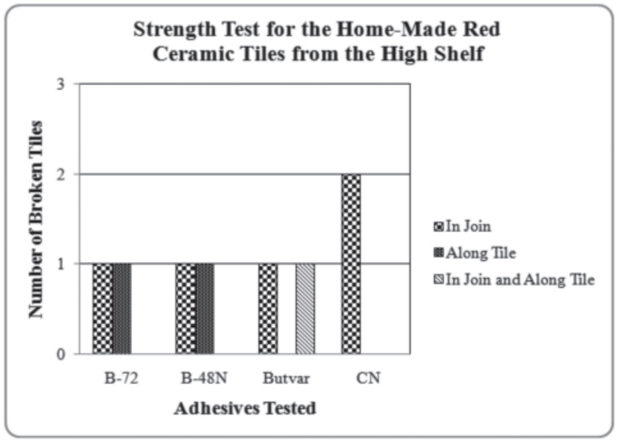

Fig. 3 Broken home-made red tiles from the 1999 high shelf strength test during the 2009 strength test.

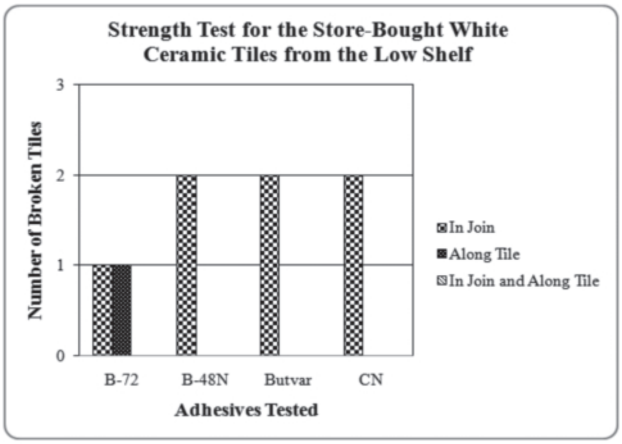

Fig. 2 Broken store-bought white tiles from the 1999 low shelf strength test during the 2009 strength test.

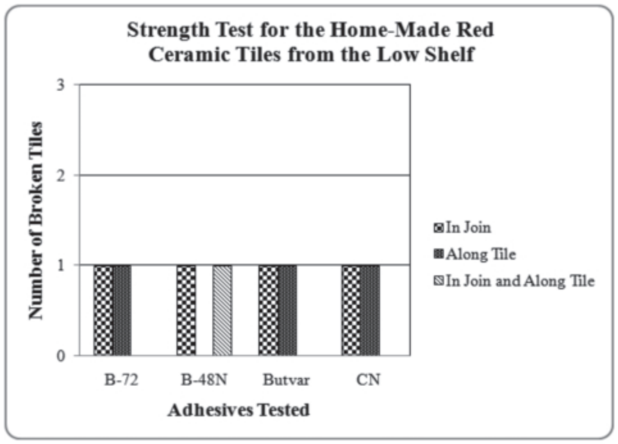

Fig. 4 Broken home-made red tiles from the 1999 low shelf strength test during the 2009 strength test.

An equal amount of adhesive and ceramic residue was usually found on both join edges. These results indicate that the tiles were stronger than the adhesives tested (Paraloid® B-72 without fumed silica, Paraloid® B-72 with fumed silica, Paraloid® B-72/B-48N, Paraloid® B-48N, Butvar® B-98 and Cellulose Nitrate). It is believed that rather than the environmental conditions, to which the samples were subjected, the small size of the tiles and decreased porosity of the red clay without sand inclusions led to such an outcome.

Solubility Test

The failure rate of the tiles formed two groups: the first group consisted of tiles that had been subjected to the 1999 strength test (*Fig. 5 and Fig. 6*); the second group was composed of tiles from the 2000 high relative humidity (*Fig. 7*)[4] and outdoor environment accelerated aging (*Fig. 8*) tests. The tiles from the strength test failed first. It is believed that this may be attributed to the load that these tiles bore rather than the environmental conditions to which they had been exposed. Also, the difference in the porosity of the tiles seen in the home-made red tiles versus the store-bought white tiles did not have an effect on the failure rate of the adhesives.

Furthermore, unlike the rest of the tiles, the tiles that had been subjected to the 1999 strength test

[4] Although three samples from the higher shelf failed (two samples containing Paraloid® B-72 with fumed silica and one with cellulose nitrate), the great uncertainty in the time of failure deemed the results unusable; only the samples from the lower shelf gave meaningful results.

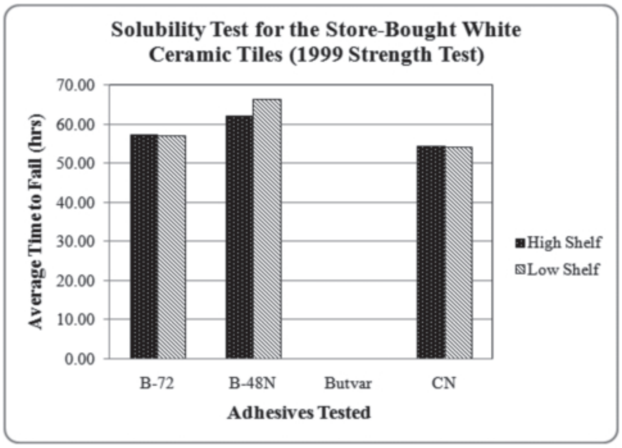

Fig. 5 **Time (hrs) that it took for the store-bought white tiles from the 1999 strength test to fail.**

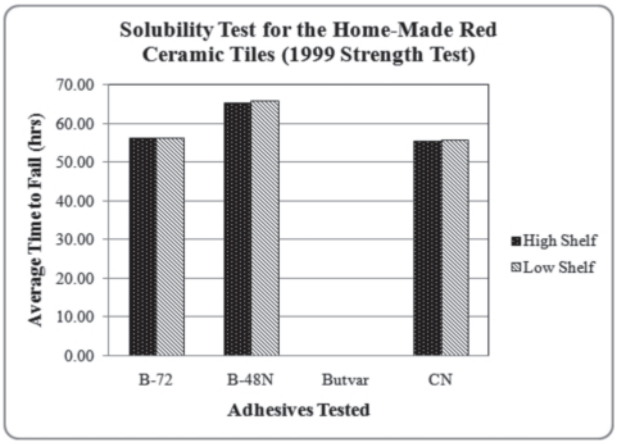

Fig. 6 **Time (hrs) that it took for the home-made red tiles from the 1999 strength test to fail.**

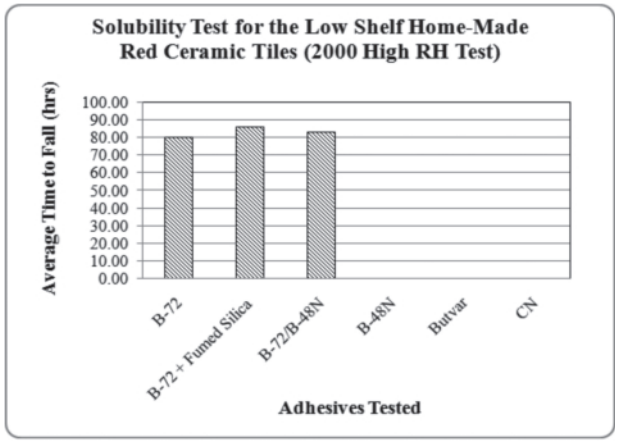

Fig. 7 **Time (hrs) that it took for the low shelf home-made red tiles from the 2000 high RH test to fail.**[6]

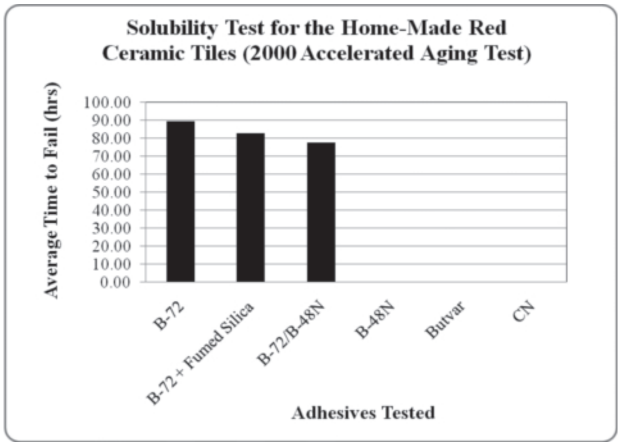

Fig. 8 **Time (hrs) that it took for the home-made red tiles from the 2000 accelerated aging test to fail.**[7]

displayed a distinct pattern in the adhesive failure. The order in which the adhesives failed is Cellulose Nitrate, Paraloid® B-72 and Paraloid® B-48N. Butvar® B-98 did not fail at all. These results follow the same trend as the solubility test results conducted in 2000 and 2002. They confirm the reversibility of the tested adhesives over time: cellulose nitrate has proven to be the most reversible adhesive in acetone; while, Butvar® B-98 has shown to be the least reversible adhesive in acetone.[5] On account of its reputation for reversibility, it was believed that Paraloid® B-72 would be the first to fail. The results, however, have questioned this characteristic.

[5] It must be noted that acetone is classified as a borderline solvent for solubilizing Butvar® (Horie 1987: 199). A more appropriate solvent for testing the solubility of Butvar® would have been ethanol (Horie 1987: 199); however, it was considered important for all of the adhesives to be tested under the same conditions.

[6] No distinctive failure pattern was observed for the tiles that had undergone the 2000 high relative humidity test on the lower shelf. The home-made red ceramic tiles experienced failures in the order of Paraloid® B-72, Paraloid® B-72/B-48N and Paraloid® B-72 with fumed silica. Paraloid® B-48N, Butvar® B-98 and Cellulose Nitrate did not fail during the testing period.

[7] The 2000 outdoor environment accelerated aging test also resulted in a varied failure pattern. Paraloid® B-72/B-48N failed first, followed by Paraloid® B-72 with fumed silica and Paraloid® B-72. The remaining adhesives (Paraloid® B-48N, Butvar® B-98 and Cellulose Nitrate) did not fail during the testing period.

CONCLUSION

The finalization of this ten-year study has revealed information on the studied adhesives that had not been foreseen when the testing was begun in 1999. The natural aging of the test samples has given us a unique opportunity to study the stresses to which archaeological collections are subjected.

Based on the priming tests of ceramic prior to adhesion, the different modes of application did not affect the tendency for the vessels to slump in elevated temperature using Paraloid® B-72 as the primer and adhesive.

With regard to the suitability of Paraloid® B-48N for use in adhering ceramic vessels, while it did perform better at higher temperatures than Paraloid® B-72, it was found that the primary concern was the adhesive's decreasing solubility with age. In the two solubility tests conducted, the results placed Paraloid® B-48N in third place. This is a potential problem as it hinders the treatment's reversibility – a vital concept in conservation.

It is believed that the results from this ten-year study may aid conservators in their decision-making processes when considering the application of different adhesives to conservation treatments. It is also hoped that this work will encourage testing of current adhesives to determine their appropriateness for different materials in a range of environments.

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SUPPLIERS

Paraloid® B-72 and Paraloid® B-48N: Rohm and Haas Ltd.
Butvar® B-98: Solutia Inc.
Cellulose Nitrate: HMG (H. Marcel Guest) Ltd.

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