

Archaeological Preservation Research Laboratory Report 15:

**Conservation of Devitrified Glass with Methylhydrocyclosiloxanes and
Silicone Oils**

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This experiment was conducted to evaluate the relationship between structural integrity and durability of devitrified seventeenth-century glass. Pieces of waterlogged glass were conserved using a methylhydrocyclosiloxane as a cross linking agent in combination with a series of molecular weights of silicone oils. After conservation, all of the samples were exposed to controlled extremes in temperature and humidity and evaluated for durability, aesthetics, surface spalling and changes in weight. Physical aspects such as durability were expected to change within the samples so they are removed from exposure to catalyst fumes and allowed to remain in humid air for approximately one week. The samples will be fully evaluated on a daily basis to document perceptible changes that might occur.

The glass used for this experiment was taken from the partial remains of an unprovenanced onion bottle acquired from excavations at Port Royal, Jamaica. Generally, the glass in these bottles is highly unstable and when taken out of water, the outer surfaces of the glass begin spalling or flaking within minutes. If allowed to dry, an entire bottle can crumble into tiny fragments in a relatively short period. These fragments, like all other glass from the site, are stored in fresh water which also helps to remove soluble salts from the matrix of the glass. For this experiment, five sections of glass were washed in running tap water and then dehydrated in a freezer mounted vacuum chamber with an applied vacuum of 28 Torr for one hour. Following initial dehydration, the samples were placed into a second beaker of fresh acetone and stored in the freezer for 24 hours. The surface dried weights and initial treatment processes for the five samples are listed below in Table 1.

Sample	Pat-dry weight (g)	Process
A	23.4 g	<ol style="list-style-type: none"> 1. Two baths of acetone in a freezer mounted vacuum chamber. 2. Immersion and vacuum treatment in methylhydrocyclosiloxane. 3. Exposure to CT-32 at 52 C.
B	12.8 g	<ol style="list-style-type: none"> 1. Two baths of acetone in a freezer mounted vacuum chamber. 2. Immersion and vacuum treatment in methylhydrocyclosiloxane. 3. Exposure to CT-30 at 52 C.
C	23.2 g	<ol style="list-style-type: none"> 1. Two baths of acetone in a freezer mounted vacuum chamber. 2. Immersion and cold vacuum treatment in PR-10 silicone with 3% methylhydrocyclosiloxane. 3. Half of the sample was exposed to CT-32 and the other half to CT-30 at 52 C.
D	25.4 g	<ol style="list-style-type: none"> 1. Two baths of acetone in a freezer mounted vacuum chamber. 2. Immersion and cold vacuum treatment in PR-12 silicone with 3% methylhydrocyclosiloxane. 3. Half of the sample was exposed to CT-32 and the other half to CT-30 at 52 C.
E	14.2 g	<ol style="list-style-type: none"> 1. Two baths of acetone in a freezer mounted vacuum chamber. 2. Immersion and cold vacuum treatment in PR-14 silicone with 3% methylhydrocyclosiloxane. 3. Half of the sample was exposed to CT-32 and the other half to CT-30 at 52 C.

Sample A was initially dehydrated in two consecutive baths of acetone in a freezer mounted vacuum chamber with an applied vacuum of 28 Torr for thirty minutes for each acetone bath. After dehydration the patted dry weight of the glass sample was 23.4 grams. The sample was then placed into a clean beaker with 500 milliliters of methylhydrocyclosiloxane and a vacuum of 28 Torr was applied for 30 minutes at room temperature. After being removed from the methylhydrocyclosiloxane, sample A was placed into a small containment chamber with a beaker containing 20 milliliters of CT-32 catalyst, and placed into a warming oven which had been preheated to 52 C. The sample was left undisturbed for 24 hours before any evaluations were made.

Sample B was initially dehydrated using the exact same methods that were used for sample A. The pat-dried weight for the sample however was only 12.8 grams after dehydration. This sample was also immersed in methylhydrocyclosiloxane and vacuum bulked at 28 Torr for thirty minutes at room temperature. After removal from the cross

linking agent, the sample was placed into a small containment chamber along with a beaker containing 20 milliliters of CT-30 catalyst, and then placed into the warming oven where it remained at 52 C.

Sample C was initially dehydrated using the same procedures that were used for samples A and B. After dehydration, the pat - dry weight of the sample was 23.2 grams. Sample C was bulked with a solution consisting of PR-10 silicone oil with 3% methylhydrocyclosiloxane added by weight. Sample C was placed in solution into a freezer mounted vacuum chamber and a vacuum of 28 Torr was applied to the glass in solution for eight hours. After vacuum bulking, the sample was allowed to sit in solution in the freezer for twenty-four hours. With bulking completed, the sample was lightly surface wiped to remove free-flowing silicone oils from its surfaces. It was then broken approximately in half. One half was placed into a small containment chamber with 20 milliliters of CT-30 catalyst in a small beaker and the other half of the sample was placed in a small containment chamber with a beaker containing 20 milliliters of CT-32 catalyst. While in their containment chambers, the samples were placed into a warming oven and allowed to cure at 52 C.

Sample D was initially dehydrated using the same procedures as sample A and B. After dehydration, the pat-dried weight of this sample was 25.4 grams. Sample D was bulked with solution consisting of PR-12 silicone oil with 3% methylhydrocyclosiloxane added by weight. The sample was then placed in solution into a freezer mounted vacuum chamber and a vacuum of 28 Torr was applied to the glass in solution for eight hours. After vacuum bulking, the sample was allowed to remain in solution in the freezer for twenty-four hours. With bulking completed, the sample was lightly surface wiped to remove free-flowing silicone oils from its surfaces. The sample was then broken approximately in half; one half being placed into a small containment chamber with a beaker containing 20 milliliters of CT-30 catalyst and the other with a beaker containing 20 milliliters of CT-32 catalyst. While in their containment chambers, the samples were placed into a warming oven and allowed to cure at 52 C.

The pat-dried dehydrated weight of sample E was 14.2 grams and it was noted that this particular sample was slightly thinner than the other samples. Sample E was processed using the exact same procedures as were used for sample D except that PR-12, a heavier molecular weight silicone oil with 3% methylhydrocyclosiloxane was used to bulk the sample. Like samples C and D, sample E was bulked using the exact same procedures except that PR-14 with 3% methylhydrocyclosiloxane was used to bulk the sample. PR-14 is the heaviest molecular weight silicone oil that we have used for artifact conservation to date. Like samples C and D, sample E was removed from the silicone - methylhydrocyclosiloxane solution and lightly surface wiped to remove free flowing silicone oil. The sample was then broken in half and one piece was placed into a small containment chamber with a beaker containing 20 milliliters of CT-32 catalyst. The other half of the sample was placed into a similar containment chamber with a small beaker containing 20 milliliters of CT-30 catalyst. Like samples C and D, the two halves of sample E in their containment chambers, were placed into the warming oven and allowed to cure at 52 C.

Initial Observations

After twenty-four hours of exposure to catalyst fumes in the warming oven, all samples were removed from the oven and evaluated on the basis of appearance, surface flaking and degree of polymerization that appeared to have occurred, judged by the dryness or tackiness of the sample.

Sample A, which had been bulked with methylhydrocyclosiloxane and cured in CT-32 catalyst appeared to be totally dry to the touch when removed from the warming oven. No flaking was observed in the sample and the surfaces of sample A had a slight rainbow coloration, caused by a change in the refractive index of the surface as a result of the very thin coating on the sample. After curation, the sample had decreased in weight from 23.40 grams to 23.00 grams, for a total weight loss of -1.739 percent.

Sample B, which had also been bulked with methylhydrocyclosiloxane and cured in CT-30 catalyst, appeared to be totally dry when removed from the containment chamber. Inspection of the surface of the glass indicated that there were some signs of surface flaking and like sample A, the surfaces of the glass had a rainbow colored patina. This was caused by a change in refraction index of the glass due to a very thin coating that had formed during curing.

Samples C had been broken into two sections after bulking. These sections were denoted as C-32, which was cured in CT-32 catalyst, and C-30, which was cured in CT-30 Catalyst. After twenty-four hours of curation in the warming oven, sample C-32 was glossy in appearance with a very slight rainbow effect on the exterior surfaces of the glass. No flaking was noted in this initial evaluation of the sample and the surfaces of the glass were slightly tacky, indicating that complete polymerization was not complete.

Sample C-30 was equally glossy in appearance and like C-32, the sample was tacky when removed from the warming oven. No flaking was noted on the surfaces of this sample and the surfaces of the glass remained clear, with no rainbow coloration noted. The combined post-treatment weight of C-32 and C-30 was measured at 23.81 grams as compared to the dehydrated weight of 23.20 grams, indicating that the sample had experienced an increase in mass of 2.56% as the result of conservation.

Like sample C, sample D was broken into two pieces for curing in each of the two catalysts. Sample D-32 was cured in CT-32 catalyst and sample D-30 was cured in CT-30 catalyst, following the same procedures as were used for sample C. After twenty-four hours of curing in the warming oven, D-32 appeared to be slightly less glossy than C-32 and C-30, and the surface of the sample was slightly tacky. No flaking was noted during this initial evaluation and a slight rainbow coloration was noted on the exterior surface of the sample.

Sample D-30, which had been cured using CT-30 catalyst was slightly glossy when removed from the containment chamber and the surfaces of the glass were tacky. No

flaking was noted and in contrast to sample D-32, no rainbow coloration was noted in this sample. The dehydrated weight of sample D was 25.40 grams and the post-treatment weight of D-32 and D-30 were recorded at 24.50 grams. This indicates that the sample had decreased in mass by .39% as the result of conservation.

Sample E was broken in half and like the other samples, one half was conserved using CT-32 catalyst and the other half was conserved using CT-30 catalyst. Sample E-32 was slightly gloss and tacky to the touch when it was removed from its containment chamber in the warming oven. No flaking was noted on the surfaces of this sample and the surfaces of the glass were clear.

Sample E-30 was more glossy in appearance than sample E-32. The surfaces of this sample were tacky to the touch and no surface flaking was noted in the sample. The glass remains clear in appearance and no discoloration was noted. The dehydrated weight of sample E was 14.20 grams. After conservation, the mass of samples E-32 and E-30 had increased to 14.25 grams, indicating an increase in mass of .35% which can be attributed to bulking during conservation.

There is a marked contrast in surface appearance between samples A and B, which were treated successfully without a silicone bulking agent and samples C, D and E which incorporated three molecular weights of silicone as part of the bulking process. In samples A and B, methylhydrocyclosiloxane has acted to consolidate and chemically bond the unstable glass. The rainbow coloration noted in both samples is the result of changes in the refractive index of the surface glass as the result of conservation. Aesthetically, the surfaces of these samples appear to be well consolidated although both samples are slightly more translucent than samples C, D and E which were conserved using silicone oils as part of the bulking process. Samples C-30, D-30 and E-30, which were polymerized using CT-30, tended to form non-tacky dry surfaces faster than samples C-32, D-32 and E-32, which were conserved using CT-32 catalyst. All of the samples that were polymerized using CT-30 catalyst were clearer and more transparent than samples conserved with CT-32 catalyst. Based on the limited range of this experiment, it would appear that CT-30 catalyst, which is a liquid stannous compound, may yield better results for this type of glass consolidation.

All of the sample groups conserved in this experiment will be evaluated over time to monitor any changes that might occur. These samples will also be included in a future experiment on accelerated aging. Included in this experiment, the effects of ultra violet radiation as well as the effects of fluctuating temperature and humidity will be assessed as a means of determining the probable conservation life of artifacts conserved using silicone bulking processes.

Table2. Initial Observations - Glass Sample.

