

A COMPARATIVE STUDY OF ETHYL-SILICATE-BASED CONSOLIDANTS ON EARTHEN FINISHES

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ABSTRACT—Comparative evaluation was performed on three commercially available ethyl silicates as possible consolidants for earthen finishes: uncatalyzed Silbond 40 in a 1:1 solution with ethanol, Conservare OH100, and Funcosil SAE 300E. Of particular interest was the compatibility of ethyl-silicate-based consolidation with water-based reattachment treatments. The testing program utilized facsimile coupons representing earthen finishes found at Mesa Verde National Park in Colorado and measured exposure to changing relative humidity, response to liquid water, surface cohesion, and effect on appearance. Samples were subjected to measurement with a linear variable differential transformer, environmental scanning electron microscopy, time-lapse photomicrography, observation during wet-dry cycling, water drop absorption testing, colorimetry, and photographic recording. A comparison of the three ethyl-silicate-based consolidants clearly demonstrated that they can perform very differently on the same earthen substrate, and that careful selection should be made prior to use. Many questions remain regarding the influence of the finish composition, finish condition, and environmental conditions on the effectiveness of consolidation; further test development and testing are recommended.

TITRE—Une étude comparative des consolidants à base de silicate d'éthyle pour les revêtements en terre. **RÉSUMÉ**—Une évaluation comparative a été effectuée sur trois silicates d'éthyle disponibles comme consolidant pour les revêtements en terre: le Silbond 40 non-catalysé dans une solution 1:1 avec de l'éthanol; le Conservare OH100; et le Funcosil SAE 300E. Une caractéristique intéressante des consolidants à base de silicate d'éthyle réside dans leur compatibilité avec les traitements adhésifs à base d'eau. Le programme de tests a été effectué à l'aide d'échantillons fac-similés représentatifs des revêtements en terre du *Mesa Verde National Park* (parc national du Mesa Verde) au Colorado, pour évaluer les changements face aux fluctuations d'humidité relative, la réponse à l'eau liquide, la cohésion de la surface et l'effet sur

l'apparence. Les échantillons ont été évalués à l'aide d'un transformateur différentiel à variation linéaire, un microscope électronique à balayage environnemental, de la microphotographie vue par vue, des observations lors de cycles d'assèchement et de mouillage, des tests d'absorption de gouttes d'eau, des tests de colorimétrie, ainsi que d'une documentation photographique. Une comparaison entre les trois consolidants à base de silicate d'éthyle démontre clairement qu'ils agissent de façon très différente sur les substrats en terre et qu'une sélection méticuleuse doit être effectuée avant de les utiliser. Plusieurs questions demeurent concernant l'influence de la composition du fini et de son état, ainsi que des conditions environnementales sur l'efficacité de la consolidation; des tests supplémentaires sont donc recommandés.

TITULO—Estudio comparativo de consolidantes basados en silicato de etilo sobre acabados de barro

RESUMEN—Se realizó una evaluación comparativa de tres silicatos de etilo que se consiguen comercialmente como posibles consolidantes para acabados de barro: Silbond 40 sin catalizar en solución 1:1 en etanol, Conservare OH100, y Funcosil SAE 300E. La compatibilidad de los consolidantes basados en silicato de etilo con tratamientos acuosos de reacoplamiento fue de particular interés. El programa de pruebas utilizó cupones facsímiles que representaban acabados de barro encontrados en el *Mesa Verde National Park* (Parque Nacional Mesa Verde), en Colorado, y se midieron los cambios frente a variaciones en la humedad relativa, la respuesta frente al agua líquida, la cohesión superficial y los efectos sobre el aspecto. Las muestras se sometieron a mediciones con un transformador para variaciones lineales diferenciales y con un microscopio electrónico de barrido ambiental, además de fotomicrografía secuencial, observación durante el ciclado húmedo/seco, pruebas de absorción de humedad por gota de agua, y registro fotográfico. Una comparación de los tres consolidantes basados en silicato de etilo demostró claramente que se pueden comportar de manera muy diferente sobre el mismo substrato de barro, y que debe realizarse una selección cuidadosa antes de su uso.

Quedan muchas preguntas relacionadas a la influencia de la composición del acabado, la condición del acabado, y las condiciones medioambientales sobre la efectividad de la consolidación. Se recomiendan el desarrollo y la realización de más pruebas.

TÍTULO—Estudo comparativo de consolidantes à base de silicato de etila em revestimentos de terra
RESUMO—Foi realizado estudo comparativo entre três silicatos de etila disponíveis no mercado, como possíveis consolidantes para revestimentos em terra: Silbond 40 não catalítico em solução de 1:1 com etanol, Conservare OH100 e Funcosil SAE 300E. Especialmente interessante foi a compatibilidade da consolidação à base de silicato de etila com os tratamentos de rejunte em base aquosa. O programa de teste utilizou cópias de certificados exemplificando revestimentos de terra encontrados no *Mesa Verde National Park* (Parque Nacional Mesa Verde) no Colorado e mediu a exposição frente à variação da umidade relativa, reação à água no seu estado líquido, coesão da superfície e efeitos no aspecto. As amostras foram submetidas a sensores para medição de deslocamento linear, microscópio eletrônico de varredura ambiental, fotomicrografia time-lapse, observação do ciclo molhado-seco, teste de absorção de água, colorimetria e registro fotográfico. Uma comparação entre os três consolidantes à base de silicato de etila demonstrou claramente que eles podem atuar de maneira muito diferente no mesmo substrato de terra e que uma seleção cuidadosa deveria ser feita antes de usá-los. Ainda restam muitas questões a respeito da influência dos componentes, do estado de conservação e das condições ambientais dos revestimentos sobre a qualidade da consolidação; são recomendados o desenvolvimento e a realização de testes adicionais.

1. INTRODUCTION

The use of ethyl silicate for the conservation of building materials, specifically stone, was developed and publicized in Great Britain from the mid 19th to the early 20th century (Royal Institute of British Architects 1861; Laurie 1924; Schaffer 1932; Weiss 1995). Its popularity is in part due to its ability to form polymers that can bridge small gaps in the material being treated, making it suitable for consolidation, i.e., the reestablishment of grain-to-grain cohesion. These polymeric chains are formed

through a process of hydrolysis and condensation, in which linkages are made between alternating silicon and oxygen atoms. All of the four alkyl groups on each ethyl silicate molecule are available for these bonds, creating a three-dimensional structure that can be very strong. Ethyl silicate is less toxic than other potential consolidants with similar bridging abilities (Wheeler 2005), and its low viscosity allows for good penetration of the treated surface. These properties have made it popular for consolidation (Wheeler 2005) and the consolidant of choice for most porous inorganic building materials.

Ethyl silicate was named as a soil consolidant in a patent filed in 1940 (Stone and Teplitz); that same year, the United States National Park Service reported interest in its use for the conservation of archaeological sites (United States National Park Service). The mention of National Park Service trials on adobe structures in a technical publication (Cogan and Setterstrom 1947) was cited to support later use on earthen archaeological remains in Iraq (Bruno et al. 1969). Many publications describing the use of ethyl silicates on earthen materials followed (Steen 1971; Torraca 1971; Munnikendam 1976; Clifton 1977). In 1980, Chiari became the first to publicize the use of ethyl silicates on earthen architectural surface finishes (e.g., washes and plasters) on earthen reliefs in Peru. At the same conference Schwartzbaum, Silver, and Wheatley described the use of ethyl silicate on an earthen substrate during their treatment of a mural in Jordan (1980). Consolidation treatments of earthen finishes with ethyl-silicate-based consolidants have continued in Peru (Morales Gamarra 1985; Jerome 1995), and in the southwestern United States (Bohnert 1990; Silver 1990; Silver et al. 1993).

Despite the reported success of these consolidation treatments, many questions remain regarding their long-term performance in an outdoor environment. Laboratory and field-based research such as the Getty Conservation Institute (GCI) project at Fort Selden (Agnew 1990; Caperton 1990; Coffman et al. 1990; Selwitz et al. 1990; Taylor 1990; Oliver 2000; Selwitz and Oliver 2002), and investigations into the long-term behavior of ethyl silicates (Lewin and Schwartzbaum 1985; Chiari 1988; Chiari 1990; Dayre and Kenmogne 1993) have begun to provide some information. Whereas these investigations have focused on mud brick and similar materials that serve primarily structural purposes, little scientific research has been specifically performed on the consolidation

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of earthen surface finishes. For these types of materials, there are no established methods for sample preparation or testing.

Although a limited visual assessment of ethyl silicates for the consolidation of earthen finishes at Mesa Verde National Park has been performed (Silver 1987), it is still unknown what effect their application would have on the material under changing environmental conditions, especially exposure to moisture. Additionally, consolidation is often performed in combination with other treatments for surface finishes, such as reattachment, that may employ the use of water, other dispersants, or solvents. In this case, an ideal consolidant should not only reestablish good internal cohesion (assuming the finishes were originally well formulated), but also allow for their rewetting and replasticizing to allow manipulation back onto the wall surface.

A fundamental consideration for all earthen materials, and specifically thin applications prepared with clay binders is the effect of ethyl silicates as a class of consolidants on water absorption and plasticity in addition to the assumed increases in cohesive strength. In order to explore this fundamental consideration, evaluation criteria and laboratory testing methodologies for assessment of consolidants for earthen finishes were developed.

At the outset of this study, several critical properties were identified in the evaluation of these consolidants. As an initial measure of its functionality, any consolidant must improve grain-to-grain cohesion. For the purposes of this research, an ideal consolidant for earthen finishes should also have the following performance properties:

- Continued plasticity (even if reduced) of the clays, a property that may be measured by hygric expansion (hygric being defined as relating to water vapor)
- Durability under conditions of wet-dry cycling or hydric response, a necessity in a partially exposed outdoor environment
- Limited effect on appearance, including color and texture
- Ability to absorb sufficient water to allow reattachment treatments to be performed

The first two requirements are open to interpretation. One way to stop moisture-related deterioration

is to render the finishes insensitive to moisture (a preventive measure) while improving their cohesive strength (remedial). This, however, is a risky proposition since it is precisely the ability of the clay-based finishes to respond to moisture that allows them to be replasticized for reattachment after years of exposure has caused them to detach or deform. This last consideration directly addresses the issue of retreatability and is further discussed in section 6.2.

In order to test the selected commercial consolidants for these properties, a set of facsimile coupons were produced to replicate one common type of earthen finish found at Mesa Verde National Park. Original wash and plaster samples from numerous park sites were analyzed for clay mineralogy and particle size distribution. Facsimile samples were then made in small squares measuring 5 x 5 cm to meet minimum requirements for cohesion testing and 1 mm or 7 mm in depth. Discs measuring 6 mm in diameter and 1 mm in thickness were made for tests where a smaller sample size was preferable. These samples were then treated with several selected consolidants and allowed to cure, after which they were subjected to specific physical tests, and the results evaluated.

2. CHARACTERIZATION OF SOILS FOR SAMPLE PRODUCTION

More than twenty years of field study and laboratory research of the finishes at Mesa Verde reveal a limited range of soil types used as architectural surface finishes (Dix 1996; Hartzler 1996; Slater 1999; Mueller 2001; Carr 2002; Matero et al. 2002; Zinn 2005; Ferron 2007; Hall 2007; Collum 2008). At Mesa Verde, finishes are divided into two basic typologies: thin colored washes, which measure 1 mm or less in thickness, and plasters, usually found having a thickness of approximately 5–15 mm. The granulometry of these finishes is reflective of their thickness and function, and presumably shrinkage control, with plasters averaging 54% sand: 46% silt and clay, and washes averaging 16% sand: 84% silt and clay. Clay mineralogy of Mesa Verde plasters and washes is usually high in kaolinite (70%–90%) with some illite (10%–20%) and smectite (10%). Illite/smectite mixed layer clays have also been found (up to 40%), often in association with friable plasters and washes such as those at Kiva Q in Cliff Palace and Kiva F in Long House. Illite/smectite mixed layer clays are known to be relatively expansive (Brady and Weil 2008), so it should not be surprising to find them

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in a friable condition, due to the stresses that would be induced by any introduction of water into their environment.

Based on these results, facsimile samples were prepared with two layers representing a plaster and wash, or one layer representing a wash, as appropriate to each test. The soil mixtures used to produce these layers, one for washes and the other for plaster, were prepared from soils found within or adjacent to Mesa Verde. These natural soils were combined in proportions to produce mixtures with the target particle size distributions described above. The mineralogy of the clay-size fraction of the soil wash mixture was quantitatively analyzed by the Mineral Lab, Inc., using x-ray diffraction. This soil mixture contained predominantly smectite (73%) with some kaolinite (7%) and illite (< 5%). Although such a high percentage of smectite alone is not typically found in Mesa Verde washes, the benefits of using a naturally occurring local soil and the guaranteed reactivity of a smectitic soil argued for its use in this case.

The presence of soluble salts in the facsimile wash soils was analyzed by chemical spot tests (Odegaard 2000) and Merckoquant test strips. Nitrates, sulfates, carbonates, and calcium were identified in the soil mixture; the results were consistent with previous analyses for the friable original finishes at Kiva F, Long House. Because the composite samples containing both plaster and wash layers were used only for observations of surface effects, a property that was visible on the wash layer only, the soil mixture for plaster production was not analyzed for clay mineralogy or the presence of salts.

3. SAMPLE PRODUCTION

Facsimile sample production is one of the challenges of designing a testing program for the consolidation of earthen finishes. It is important both to replicate the original methods of plaster and wash application and to produce a sample set that is sufficiently consistent, particularly in thickness, across cohorts.



Fig. 1. Planar distortion of samples after drying. Samples were prepared in a laser-cut acrylic mold for optimal control of their dimensions. Two layers were applied—a 6 mm-thick plaster, topped by 1.5 mm of wash layer. A second set of samples was produced with only the thin wash layer.

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Table 1. Consolidants

| Consolidant | Abbreviation | Manufacturer | Composition | Solvent added in this testing program | Application |
|--|--------------|------------------------------|---|--|---|
| None (Control) | Control | — | — | — | Nothing applied to samples |
| Water | Water | — | Deionized water | None | Brushing: 2 passes of 1-5 brushstrokes each |
| Silbond 40 | S.40 | Silbond Corporation | TEOS monomers and oligomers with an average chain length of five, uncatalyzed | Mixed with ethanol in 1:1 solution (by volume) | Brushing: 2 passes of 1-5 brushstrokes each |
| Conservare OH-100 | C.OH | Prosoco, Inc. | TEOS oligomers, dibutyltindilaurate catalyst | None | Brushing: 2 passes of 1-5 brushstrokes each |
| Funcosil SAE 300E | F.E. | Remmers Baustofftechnik GmbH | TEOS oligomers, dibutyltindilaurate catalyst | None | Brushing: 2 passes of 1-5 brushstrokes each |
| Funcosil Antihydro & Funcosil SAE 300E | F.A.+E. | Remmers Baustofftechnik GmbH | TEOS oligomers, dibutyltindilaurate catalyst, unidentified elasticizing materials forming linear, flexible segments | None | Brushing: 2 passes of 1-5 brushstrokes each, Funcosil Antihydro treatment applied 9 days prior to consolidation |

The method that was developed utilized a mold constructed from acrylic sheets of specific depth to match Mesa Verde wash and plaster thicknesses. The top sheet was cut to exact dimensions, using a laser cutter to excise 5 x 5 cm squares or 6 mm circles as suitable for each test method, then stacked and bolted onto a solid acrylic sheet backing. In this way all sample dimensions, especially thickness, could be carefully controlled. The molds, containing approximately 45 samples each, proved to be useful not only for production of the samples, but also for storage, consolidant application, and transportation while the testing program was being performed. One of the major drawbacks of using this system was the impermeability of the acrylic, which allowed only the top of the sample to evaporate moisture. This caused the samples to curl because the sample surface dried more quickly and non-uniformly than the rest of the sample (fig. 1). A more porous backing material

alleviated this problem, an option that had been explored during a trial of various backing materials prior to sample production. However, the acrylic sheet was selected over the porous backing materials, because the acrylic sheet is a material on which the laser cutter may be used, it allowed for samples to be removed more easily from the molds, and the acrylic sheet-to-sheet connection is the most compatible.

4. CONSOLIDATION

Ethyl-silicate-based consolidants included in the research were uncatalyzed Silbond 40 (in a 1:1 v/v solution with ethanol), Conservare OH100, and Funcosil SAE 300E (table 1). Funcosil Antihydro, a companion product to the Funcosil consolidant marketed as a pretreatment to limit expansion and shrinkage of clays, was also included in the testing program. Water was included as a possible consolidant

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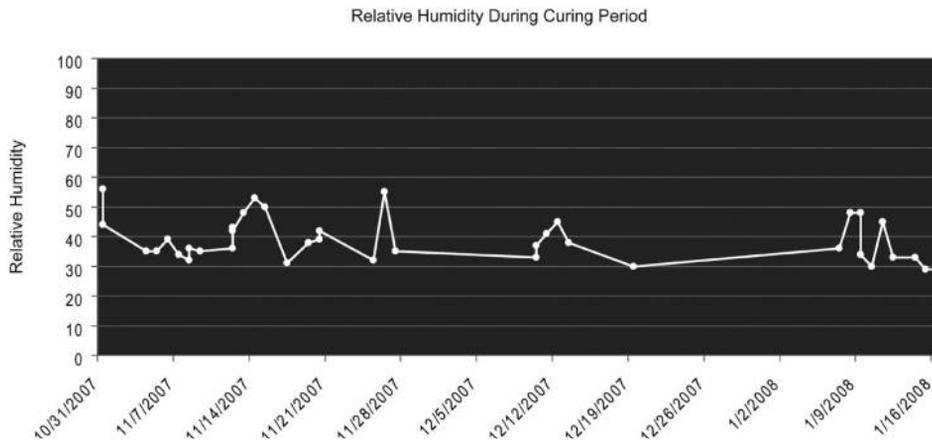


Fig. 2. Relative humidity in ambient laboratory conditions during the curing period, lasting 11 weeks total. Temperature during the curing period remained in the range of 18°–24°C (65°–75°F).

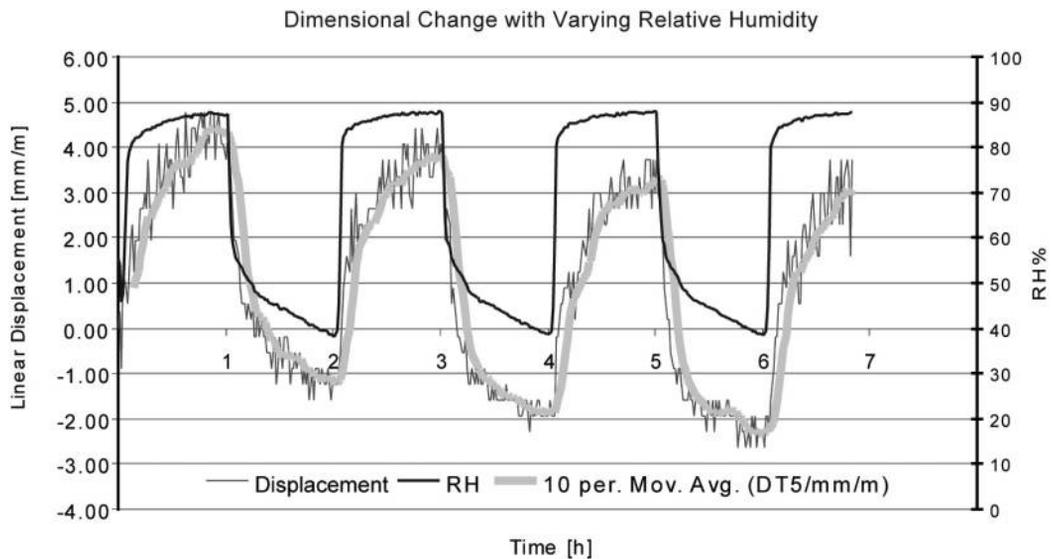


Fig. 3. RH cycling of untreated sample WD-1-1 (in black) and resulting dimensional changes (in dark gray) with trend line (in light gray), plotted over time (labeled in hours). The peaks and valleys were used to calculate average dimensional change per sample.

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since it has been suggested that one of the effects of rehydration is to improve mechanical properties by reactivating the clays present in earthen materials (Silver 1987), a possibility that has yet to be assessed in a laboratory environment. A control set was left untreated and used for comparison during analysis of test results. Six sets of 27 samples each were assembled and five were treated accordingly.

The Silbond 40, Conservare OH100, and Funcosil SAE 300E products all utilize tetraethoxysilane but differ in their degree of pre-polymerization, catalyst, and additives. Silbond 40 is generally believed to have a greater degree of prepolymerization than the other two and is available without a catalyst or additives, while Conservare OH100 and Funcosil SAE 300E contain the catalyst dibutyltin dilaurate (Wheeler 2005). Funcosil SAE 300E contains an additional elasticizing component, such as polymerized siloxane or polyurethane, which provides some linear segments to reduce the rigidity seen in the three-dimensional forms produced during the curing of ethyl silicate (Wendler 1997). Laboratory investigations of mechanical properties after consolidation have shown that Funcosil SAE 300E may be compatible with earthen materials (Richter 2004).

The absence of solvents and catalysts from Silbond 40 allows the user greater control in application. Ethanol, water, and hydrochloric acid are suggested by the manufacturer as potential additives to improve the curing time and flexibility of the cured gel. Silbond Corporation also makes a catalyst TMB-70 (trimethyl borate) available for use with Silbond 40. Field use reports the addition of ethanol to Silbond 40 (Bruno et al. 1969; Rossi Manaresi and Chiari 1980; Morales Gamarra 1985; Chiari 1990; Chiari et al. 2000; Selwitz and Oliver 2002). Most literature describing use of Silbond 40 does not mention water, but it is possible that a small amount of water is included if the ethanol used was less than 200 proof. The addition of as little as 5% water will affect curing time. Field application has been performed both with and without an acid catalyst. Use of the methyl borate catalyst has been shown to make the treated material brittle (Selwitz and Oliver 2002). In consideration of this history of use, the formulation of the Silbond 40 consolidant solution was a 1:1 mixture of Silbond 40 and 190-proof ethanol. It was not known how long curing would take for this formulation, but it was expected that it would be longer than the three

weeks listed in product literature for Conservare OH100 and Funcosil SAE 300E.

During consolidation, samples were treated by brushing in two application sessions of 1 to 5 brushstrokes each, separated by 30 minutes of absorption. After nine days, samples that had been pretreated with Funcosil Antihydro were treated with Funcosil SAE 300E in the same manner as the other samples. It would have been preferable to treat all samples with consolidant on the same day, but lack of time made this difficult. To minimize exposure of students and staff to solvent fumes, consolidation was performed in an outdoor environment, where temperatures during application were approximately 7°–13°C (45°–55°F) and the relative humidity was 40–50%. These conditions are not ideal for consolidation, as specified by the consolidant manufacturers. Samples were moved into the laboratory approximately two hours after consolidant application. Relative humidity was recorded periodically during curing. Due to ambient conditions in the laboratory, relative humidity often fell below the 40% minimum recommended by consolidant manufacturers during the eleven-week curing period (fig. 2), which may have slowed the curing process. Temperature remained in the range of 18°–24°C (65°–75°F).

5. ASSESSMENT AND EVALUATION

Treatment performance criteria established at the outset of the testing program were: 1) improved grain-to-grain cohesion, 2) limited effect on appearance, 3) ability to absorb water, 4) durability under conditions of wet-dry cycling, and 5) continued plasticity of the clays (table 2). Due to scheduling constraints, linear variable differential transformer (LVDT), environmental electron scanning microscopy (ESEM), and time-lapse photomicrography were performed 29 days after sample consolidation, and 20 days after consolidation for the samples with the Funcosil Antihydro pretreatment. It should be noted that, in addition to the samples treated with uncatalyzed Silbond 40, these samples treated with Funcosil Antihydro may have not been able to cure to the same degree as the samples treated with Conservare OH100 and Funcosil SAE 300E without Antihydro pretreatment.

The results for surface cohesion, hygric dimensional change, wet-dry cycling, colorimetry, surface effects, and microdrop absorption are compared in

Table 2. Test Specifications

| Property | Continued plasticity of the clays: hygric dimensional change | Continued plasticity of the clays: hygric dimensional change | Continued plasticity of the clays: hygric dimensional change | Continued plasticity of the clays: hygric dimensional change | Continued plasticity of the clays: hygric dimensional change | Durability to wet-dry cycling | Improvement of grain-to-grain cohesion | Limited effect on appearance: color | Limited effect on appearance: surface effects | Ability to absorb water: microdrop absorption |
|------------------------------|--|--|--|--|--|----------------------------------|--|---|---|---|
| Test method | LVDT | ESEM | Time-lapse photography | Wet-dry cycling | ASTM D4214-97, modified | Colorimetry | Photography and observation | RILEM test II.8b | | |
| Temperature | 19–22°C | 2–5°C | 21°C | 18–24°C while wetting, 60°C while drying | 18–24°C | 24°C | 7–13°C during treatment | 18–24°C | | |
| Relative humidity | 39–89% | 17–95% | 18% | 29–48% while wetting | 30% | 51% | 40–50% | 36% | | |
| Curing period before testing | 4 weeks, 1 day | 3 weeks, 5 days | 3 weeks, 5 days | 10 weeks | 11 weeks, 2 days | 34 months | Immediate | 11 weeks, 2 days | | |
| Sample type | Wash layer only | Wash layer only | Wash layer only | Wash layer only | Wash and plaster | Wash layer only | All samples | Wash layer only | | |
| Sample dimensions | 6 mm diameter x 1.5 mm thickness | 6 mm diameter x 1.5 mm thickness | 6 mm diameter x 1.5 mm thickness | 5 cm x 5 cm x 1.5 mm | 5 cm x 5 cm x 7.5 mm | 5 cm x 5 cm x 1.5 mm | 5 cm x 5 cm x 7.5 mm and 5 cm x 5 cm x 1.5 | 5 cm x 5 cm x 1.5 mm | | |
| Sample condition | Not wet-dry cycled | Not wet-dry cycled | Not wet-dry cycled | — | 2 sets: Wet-dry cycled and not wet-dry cycled | Before and after wet-dry cycling | After treatment | 2 sets: Wet-dry cycled and not wet-dry cycled | | |
| Duration of test | 7 hours | 30 minutes—3 hours for each sample | 5 minutes—1 hour for each sample | 8 days, 40 cycles of 1.5–2.5 hours | — | 30 minutes | — | 2 seconds—1 hour | | |
| Repetitions | 2.5 RH cycles | — | — | 40 wet-dry cycles | — | 3 measurements per sample | — | — | | |
| Instrumentation | Trans-Tek linear variable differential transformer Series 200 DC, controlled by a Campbell scientific signal processor | FELI30 ESEM-FEG, gaseous secondary electron detector (GSE), with Peltier cooling stage | Leica MZ12 stereoscope | Laboratory oven and trigger-type spray bottle | Olympus c-5060, Permacel J-LAR Superclear Tape | Minolta CR-221 | Olympus c-5060 | — | | |
| Specifications | — | 2.0 kV, 1.2–7.2 Torr, and 1.8–5.0°C, with a magnification range of 150–2000x | samples photographed every 5–6 seconds | — | — | — | — | — | | |

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Table 3. Summary of Results

| Test method | ASTM D4214-97, modified | LVDT | Hygic dimensional change, average linear displacement in mm/m (standard deviation) | Resistance to wet-dry cycling | Color change compared to the control, after wet-dry cycling in ΔE^*_{94} ^a | Surface effects, after treatment | Microdrop absorption, in seconds, after wet-dry cycling (standard deviation) |
|----------------------------------|----------------------------|-----------------------------|--|----------------------------------|---|-------------------------------------|---|
| | | | | Wet-dry cycling | Colorimetry | Photography and observation | RILEM test II.8b |
| Control (Untreated) | 41% (20%) | 6.04 (0.72) | | Unstable | 0.0 (0.0) | No change | 3.3 (0.90) |
| Water | 60% (11%) | 3.41 (0.62) | | Unstable | 1.5 (1.0) | Very little change | 2.6 (0.26) |
| Conservare OH-100 | 8% (9%) | 5.00 (0.35) | | More stability | 0.4 (0.3) | Very little change | 4.8 (1.8) |
| Silbond 40 | 69% ^b (18%) | 5.53 ^b (0.68) | | Most stability ^b | 0.4 (1.3) | Very little change | 20.4 ^b (23.2) |
| Funcosil SAE 300E | 74% (9%) | 5.09 (0.25) | | More stability | 1.8 (0.7) | Very little change | 9.3 (5.4) |
| Funcosil Antihygro & SAE 300E | 71% (7%) | 4.43 ^c (0.39) | | Most stability | 1.4 (0.8) | Texture lost | 12.7 (2.5) |

a. Standard deviation for ΔE^*_{94} reflects the relative homogeneity of each sample.

b. These results for Silbond 40 are not directly comparable due to the slower curing time of the uncatalyzed consolidant.

c. These results for hygic dimensional change of samples treated with Funcosil SAE 300E with Antihygro pretreatment should be distinguished from results for the other samples due to the shorter curing time at the time of testing.

table 3. When a property was measured both before and after wet-dry cycling, the results obtained after wet-dry cycling are displayed.

While all results are listed, many of the results for Silbond 40 are not directly comparable due to the slower curing time of the uncatalyzed consolidant. Prior to consolidant application and testing, it was not known how long the curing for this solution of Silbond 40 would take. The progress of curing of the Silbond 40 may be inferred from observations of hydrophobic behavior, since ethyl silicate is hydrophobic in its uncured state, a property that subsides as the consolidant cures. Considering the observations of sample behavior during wet-dry cycling and the results for water drop absorption, it can be concluded that this Silbond 40 formulation had not cured after 11 weeks. The results listed for Silbond 40-treated samples should therefore be viewed as a representation of the consolidant's performance at that point in the curing process, rather than as an indication of the behavior of the cured consolidant.

Similarly, the results for hygric dimensional change (through LVDT and ESEM) of samples treated with Funcosil SAE 300E with Antihydro pretreatment should be distinguished from results for the other samples due to the shorter curing time at the time of testing. All tests other than for hygric dimensional change were performed after 11 weeks of curing, ample time for the Funcosil SAE 300E to completely cure.

5.1 CONTINUED PLASTICITY OF THE CLAYS: HYGRIC DIMENSIONAL CHANGE

5.1.1 Linear Variable Differential Transformer

LVDT has been used to measure the dimensional change of adobe samples with changing relative humidity (Bourgès and Simon 2003) and it was therefore used for these earthen finishes as well. Since plasticity has been shown to be related to hygric expansion, the LVDT measurements of hygric dimensional change provide an indication of this property. LVDT testing was designed and performed at the Getty Conservation Institute (GCI) with a Trans-Tek linear variable differential transformer, Series 200 DC. The LVDT was controlled by a Campbell scientific signal processor. Because 12 transmitters were available in the LVDT, two samples of each of the six consolidation types were subjected to simultaneous cycling

ranging from 39%–89% RH on two-hour cycles. For each sample tested, relative humidity fluctuations were recorded in tandem with vertical dimensional changes (fig. 3) covering 2.5 complete RH cycles in 7 hours. The data produced is obscured by noise due to the small sample size, so a trendline (included in figure 3) was calculated as a running average with a period of ten, and used to determine the dimensional change during each cycle and the average dimensional change per type. Figure 3, showing the results for an untreated sample (#WD-1-1), includes typical data produced for each sample: RH, vertical dimensional fluctuations, and trendline. Figure 4 summarizes the results for LVDT testing of all 12 samples.

Results indicate that all treated samples had a reduced dimensional response to hygric conditions as compared to untreated samples. Most notable was the muted response of the water-treated samples, which showed a decrease in dimensional change of 44%. One potential explanation for this behavior is that the water treatment may have produced microcracks which then absorbed dimensional changes during hygric cycling. Of the chemically treated samples, those treated with Silbond 40 showed the least decrease in dimensional change, which may have been a result of their slow curing time. The Funcosil SAE 300E with the Antihydro pretreatment imparted the greatest decrease in dimensional change, an expected finding because it is marketed as a treatment to reduce the expansion and contraction of clays.

5.1.2 Environmental Scanning Electron Microscopy

The use of ESEM allowed for high magnification imaging of the expansion and contraction of the clay-based materials in the samples under varying relative humidity conditions (Doehne et al. 2005; Doehne 2006). Testing was performed at the GCI using an ESEM with a Peltier cooling stage at 2.0 kV, 1.2–7.2 Torr, and 1.8–5.0°C, with a magnification range of 150x–2000x. Since the changes that occurred were very slow and difficult to see, they were recorded on video, compressed, and played back at high speed to detect periods of change. Wetting and drying of the samples was achieved through manipulation of the temperature in order to observe changes in the material under these varied conditions. Movement direction, type, and time period were correlated with drying or wetting periods in the samples, allowing for comparison between consolidation types.

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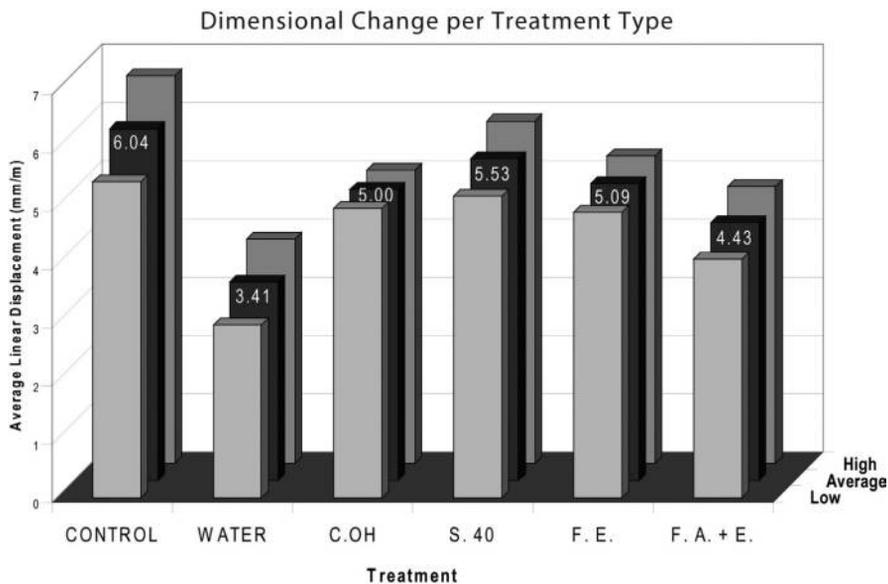


Fig. 4. Dimensional change per consolidation type with average measurements in dark gray in the middle, flanked by the low and high measurements in front and behind, respectively. From left to right they are: untreated (control), water, Conservare OH100 (C.OH), Silbond 40 with ethanol in a 1:1 solution by volume (S.40), Funcosil SAE 300E (F.E.), and Funcosil Antihydro pre-treatment with Funcosil SAE 300E (F.A.+E.).

Observation of treated and untreated samples using this method provided for a new and more complex understanding of the expansion and contraction of these earthen materials. In general, the samples exhibited immediate widening of cracks and shrinking of sample portions after relative humidity was lowered (figs. 5, 6). The degree of movement was not consistent for each type of sample, however, because the level of magnification with the ESEM is such that the area observed cannot be considered to be representative of the whole. This variation in observed movement held true even when different areas of the same sample were viewed. While consistent conclusions cannot be drawn for each of the consolidation types, ESEM did improve understanding of the behavior of these earthen materials when exposed to a range of humidity.

5.2 CONTINUED PLASTICITY OF THE CLAYS: HYDRIC RESPONSE

Hydric response was visible by observing the wetting and absorption behavior of treated and untreated samples with time-lapse photomicrography using a Leica MZ12 stereoscope at the GCI. In this case, a sample was photographed every 5–6

seconds while wetting with one drop of water, then allowing the water to be absorbed into the sample and subsequently evaporate. The testing period for each sample, lasting from five minutes to one hour, was considered to be concluded when the sheen from the water drop was no longer visible. One observation period was performed for each sample tested. Dimensional and surface changes were observed and recorded to provide information on the nature of expansion and contraction at that scale, as well as the process of crack formation.

During application of the water drop, the formation of small cracks measuring approximately 1–10 μm in width could be seen on the samples that were untreated, treated with water, and treated with Silbond 40. For all samples, the silica aggregate appeared more prominently after one cycle of wetting and evaporation, suggesting that binder may have been washed from the sample surface. One of the primary benefits of this test is that it allows for viewing changes to the samples at a micro-scale over real time. The results are difficult to measure and compare between consolidant types, but they provide a new understanding of the nature of the material as it responds to water.

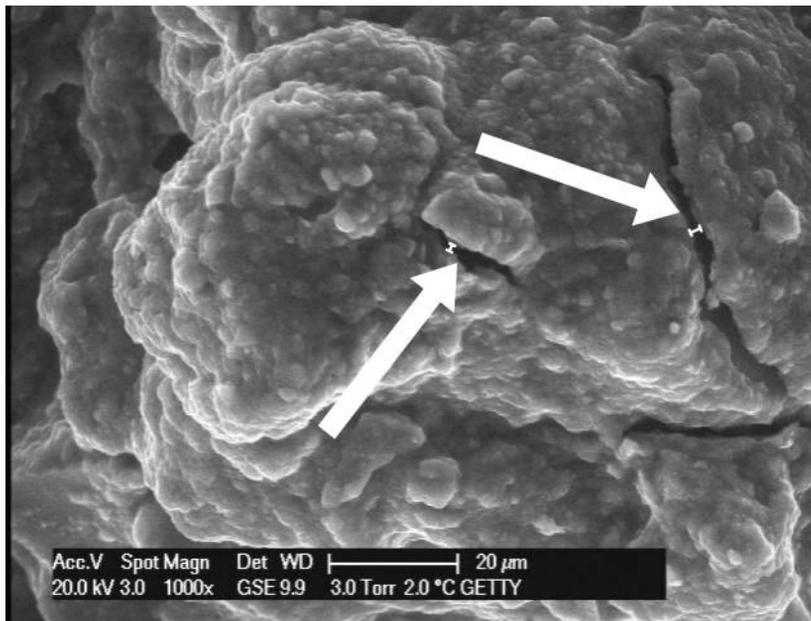


Fig. 5. Fungosil Antihydro-treated sample viewed with environmental scanning electron microscopy before movement. Arrows point to cracks where movement can be seen. Lines mark the dimensions of the crack openings before movement.

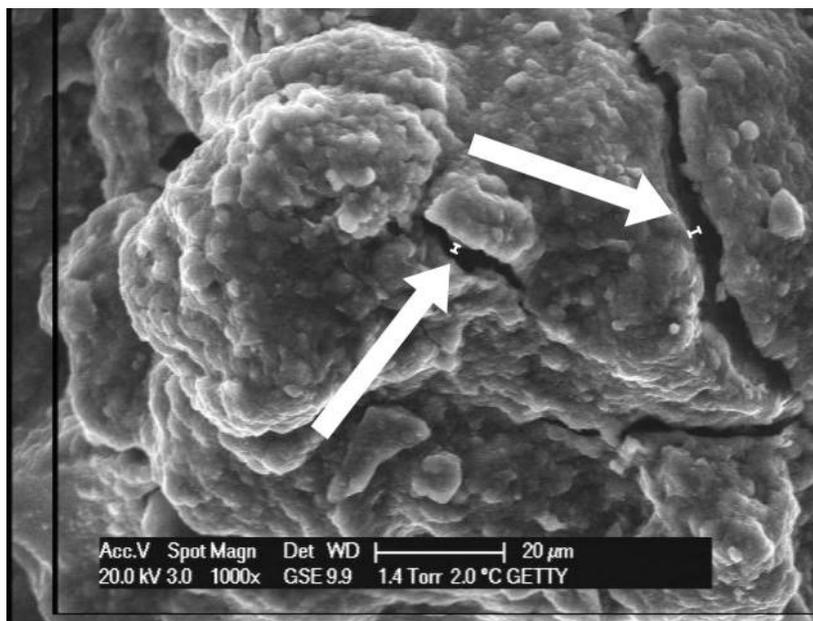


Fig. 6. Fungosil Antihydro-treated sample after movement responding to lowered relative humidity. Arrows point to cracks where movement can be seen. Lines mark the dimensions of the crack openings before movement.

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Fig. 7. Samples before wet-dry cycling viewed from above. Each column contains samples treated with the same consolidant. From left to right they are: untreated (control), water, Conservare OH100, Silbond 40 with ethanol in a 1:1 solution by volume, Funcosil SAE 300E, and Funcosil Antihygro pre-treatment with Funcosil SAE 300E.

5.3 DURABILITY TO WET-DRY CYCLING

Cycling was performed by spraying the samples with deionized water, allowing the water to absorb and evaporate for 30 minutes in ambient laboratory conditions, and placing the samples in a laboratory oven at 60°C for 1–2 hours. At night, samples were left in ambient laboratory conditions to dry. All samples were placed on a single sample tray, and sprayed or dried simultaneously (fig. 7). Spraying was performed with a common, trigger-type spray bottle, rotating the tray 360° in 45° increments. The number of pumps per interval was kept consistent during each spraying cycle, but ranged between cycles from 15 to 30 pumps. Forty cycles were performed over a period of eight days. Results were assessed by visual inspection of samples in real time and by examination of photographic records made before, during, and after cycling.

After cycling, the untreated and water-treated samples displayed notable cracking and planar deformation, and exhibited a greater response than the chemically consolidated samples (figs. 7, 8). Planar deformation was most prevalent in untreated and water-treated samples but was seen in all samples, most of which formed slightly concave wash fragments. Silbond-treated samples deformed convexly, theorized to have been due to its slower curing time and related hydrophobicity. The more limited absorption of these samples may have resulted in the wetting of only their topmost surfaces, limiting expansion to the upper face of the sample, causing it to deform into a convex shape. Differences in the degree of response of the chemically treated samples were discernible but not obvious. Of the chemically consolidated samples, Silbond 40 and Funcosil SAE 300E with Antihygro pretreatment

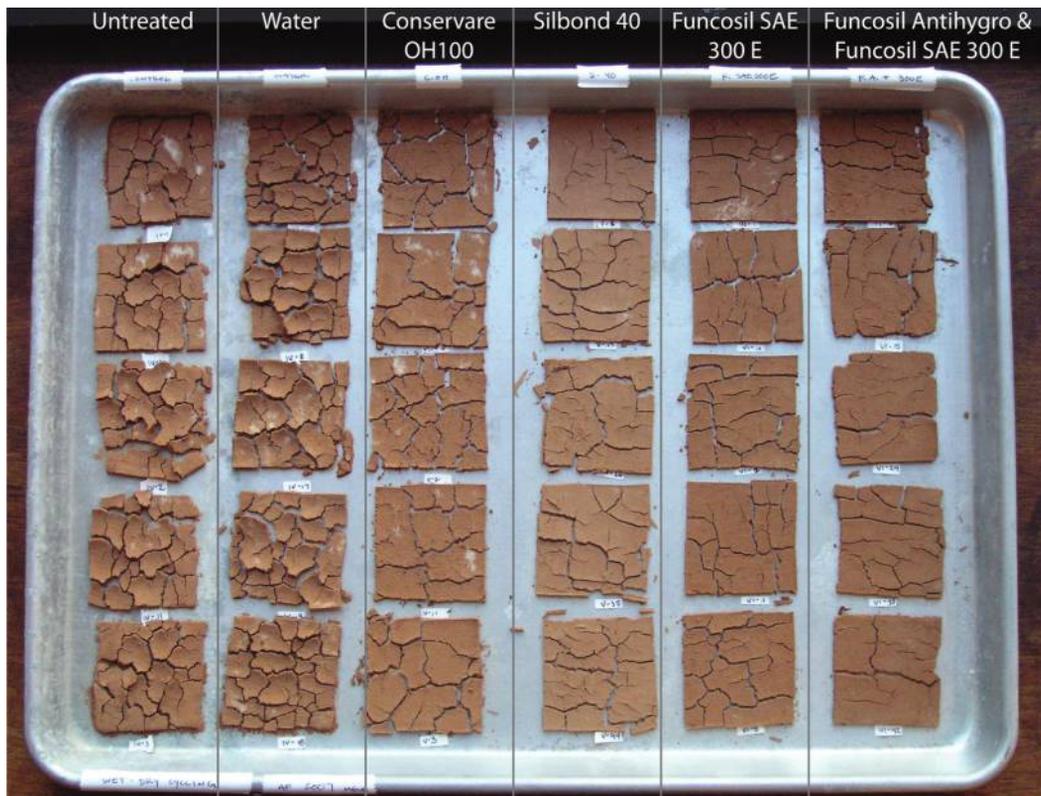


Fig. 8. Samples after wet-dry cycling. From left to right each column of sample consolidants is: untreated, water, Conservare OH100, Silbond 40 with ethanol in a 1:1 solution by volume, Funcosil SAE 300E, and Funcosil Antihygro pre-treatment with Funcosil SAE 300E.

appeared to produce the least response to cycling; Conservare OH100 produced the most noticeable response. While this test method can yield interesting qualitative results for the behavior of finishes under wetting and drying conditions—an important assessment of durability to environmental conditions—a quantitative measure of performance remains to be developed. In this testing program, observation was found to be the best method of test result analysis.

5.4 IMPROVEMENT OF GRAIN-TO-GRAIN COHESION: SURFACE COHESION

Surface cohesion testing was based on ASTM D4214-97, “Standard Test Methods for Evaluating the Degree of Chalking of Exterior Paint Films,” method D (2007), in which a piece of tape is applied to the surface of the sample, gently rubbed, removed, and

placed on a sheet of bright white paper. According to the standard, the tape is then compared to a reference to determine the shade and estimate the amount of material removed. Because the earthen material is removed in larger concentrations than anticipated by this standard for evaluating paint films, the area of removed material is more readily quantified. A photographic record of the material remaining on the tape was made using an Olympus C-5060 camera, and analyzed digitally to quantify the degree of cohesion based on the percentage of the tape area covered by removed finish material (Ferron 2007). The tape used with this test, Permacel J-LAR Superclear Tape, was selected for its superior transparency.

Surface cohesion was measured on samples that had and had not been wet-dry cycled, so that the effect of wet-dry cycling on the durability of the treatments could be observed for each consolidation

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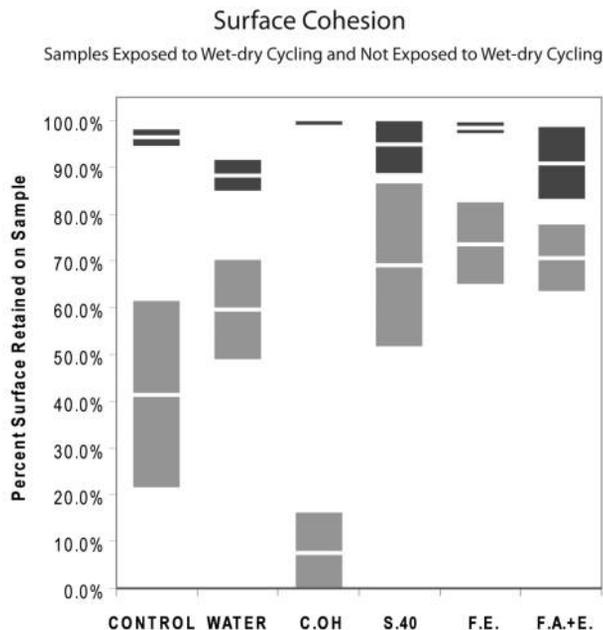


Fig. 9. Surface cohesion tested without wet-dry cycling (in dark shading) and after wet-dry cycling (in light shading), shown as an average with one standard deviation above and below. From left to right the consolidants are: untreated (control), water, Conservare OH100 (C.OH), Silbond 40 with ethanol in a 1:1 solution by volume (S.40), Funcosil SAE 300E (F.E.), and Funcosil Antihygro pre-treatment with Funcosil SAE 300E (F.A.+E.).

type directly. For example, untreated samples had a 56% decrease in cohesion after wet-dry cycling, showing that the cycling had a notable effect on surface cohesion. These results for the control samples were then taken as the baseline for comparison of all treated samples. The percent improvement from the performance of untreated samples is shown in figure 9. On the samples that were not wet-dry cycled, those treated with water had less surface cohesion than those left untreated. On assessments of samples after wet-dry cycling however, water-treated samples had an over 40% improvement in surface cohesion compared to the control, suggesting there may be some benefit to the water treatment as observed by Silver (1987). Conservare OH100 showed very different results, giving an initial increase in surface cohesion without wet-dry cycling that then became a nearly 60% decrease from the control on samples that were wet-dry cycled. This, paired with previous results for wet-dry cycling (Ferron 2007), indicates that Conservare OH100 may perform poorly compared to the other materials tested, when exposed to liquid water and cured under the described conditions. The Silbond 40 (in 1:1 solution with ethanol) showed a slight initial decrease in surface cohesion, possibly because it was slower to cure than the other

consolidants. After wet-dry cycling, however, it had a greater than 60% improvement in surface cohesion compared to results for the control. The elasticized Funcosil ethyl silicate had the highest performance for surface cohesion overall, with initial improvements as well as the most improved surface cohesion after wet-dry cycling. When paired with Antihygro pretreatment, Funcosil SAE 300E did not perform as well, showing an initial decrease in surface cohesion, probably due to the significant surface texture effects produced by the Antihygro (see section 5.5.2). After wet-dry cycling, the combined treatments did not perform as well as Funcosil SAE 300E used alone. In general, all consolidation treatments showed improved surface cohesion compared to the control samples after wet-dry cycling, with the exception of Conservare OH100. Compared to these post-cycling results, initial deviations from the control seem much less significant.

This modified ASTM test can be performed without expensive instrumentation in the field as well as in the lab, and is logistically simple in that it requires measurement at only one point in time. The standard deviation is relatively high (fig. 9), which could be remedied by having a greater number of samples in future testing.

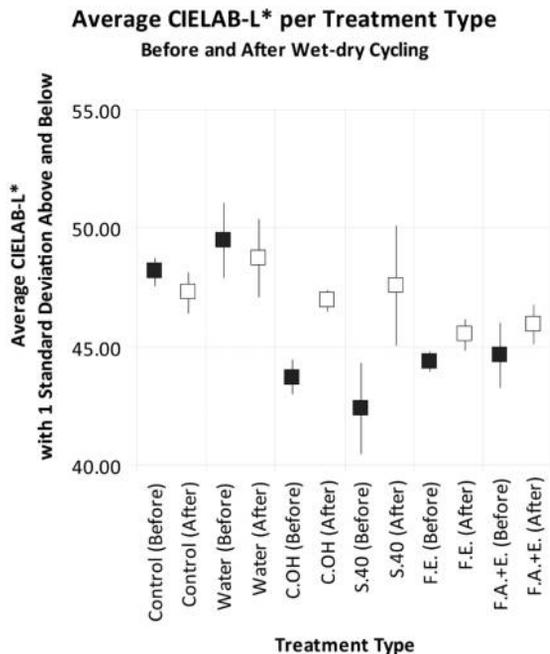


Fig. 10. Colorimeter measurements for CIELAB-L* (lightness-darkness) of treated and untreated facsimile samples. Colorimeter measurements were taken 34 months after treatment, before and after wet-dry cycling, on samples comprised of a 1.5 mm-thick wash layer only. One standard deviation is marked with a black line above and below the averages. The change in L* value recorded for treated samples is an amount that may be noticed before wet-dry cycling, but is not likely to be noticed in the ranges seen after wet-dry cycling.

5.5 LIMITED EFFECT ON APPEARANCE

5.5.1 Color Change

Color of treated and untreated samples was measured with a Minolta CR-221 colorimeter, 34 months after treatment, on samples containing a wash layer only. Three samples of each treatment type were measured in three locations, using CIE L*a*b* color space. Change in overall color was calculated as ΔE^*_{94} , also known as DE94. DE94 is the second in a series of equations created for calculating color differences in CIE L*a*b* color space: CIELAB (recommended by CIE in 1976), DE94 (recommended in 1995), and DE2000 (recommended in 2001). The second equation was chosen in this study because its improved performance over CIELAB is four times greater than the DE2000 improvement over DE94 (Melgosa et al. 2004). The simplification DE94 offers has made it the GCI conservation laboratory's preferred computing metric for visual color difference.

Variation in results was seen almost exclusively in L* (lightness-darkness) values (fig. 10). As expected, the water-treated samples had a slight lightening in color while most treated samples exhibited some

darkening when measured before wet-dry cycling. Possibly more indicative of the color effects these treatments would have in situ are measurements after wet-dry cycling, which indicate that the color of all treated samples partially returned to values seen for the control. Table 3 lists ΔE^*_{94} for each treatment type after wet-dry cycling (using the average of the three samples measured) compared to the average for the control samples. It should be noted that these values reflect the overall magnitude of difference in color but do not indicate the nature of the color change. Since almost all of the color difference for these samples was determined to be in the L* direction, the ΔE^*_{94} values are mostly a reflection of the change in lightness and darkness. The initial darkening effect recorded for these treatments should be visible, because a ΔE^*_{94} measurement of 1 approximates a "just noticeable change" under ideal viewing conditions. However, when the earthen finish surface shows inhomogeneities of color or texture, values of up to 3 or 4 may be more difficult to see with in-situ viewing conditions.

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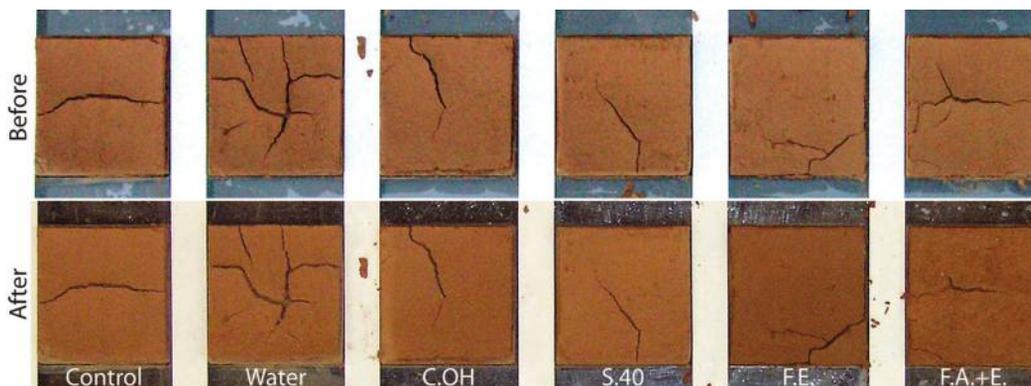


Fig. 11. Plaster and wash samples before consolidation and 20 days after consolidation. During consolidation it was observed that the application of Funcosil Antihydro appeared to alter the surface texture of the samples, creating a mottled texture and closing cracks. Consolidants from left to right in the composite image: untreated (control), water, Conservare OH100 (C.OH), Silbond 40 with ethanol in a 1:1 solution by volume (S.40), Funcosil SAE 300E (F.E.), and Funcosil Antihydro pre-treatment with Funcosil SAE 300E (F.A.+E.).

5.5.2 Surface Effects

Changes in surface texture were noted during trial consolidation and photographed using an Olympus C-5060 camera. The only changes noted were seen on samples treated with Funcosil SAE 300E with Antihydro pretreatment, where a great loss of texture was evident, closing cracks and creating a mottled texture immediately after treatment (fig. 11). Consolidation without pretreatment produced minimal texture changes and generally allowed the samples to maintain a smooth surface. This method allowed for recording of multiple samples simultaneously for ease of comparison. In future testing, more detailed analysis could be performed with macrophotography or photomicroscopy.

5.6 ABILITY TO ABSORB WATER: MICRODROP ABSORPTION

Water drop absorption was measured by RILEM test II.8b on samples that had and had not been wet-dry cycled. Microdrop absorption was found to have decreased for all chemically treated samples that had not been wet-dry cycled (fig. 12). Samples subjected to the Antihydro pretreatment showed slightly higher absorption, possibly due again to their changed surface texture. As expected, control samples had the same absorption index whether they had been wet-dry cycled or not. Water-treated samples had

increased absorption after wet-dry cycling, perhaps because the water treatment produced microcracks in the sample, increasing its porosity and ability to absorb water. All other treated samples showed an increase after wet-dry cycling, the most pronounced seen in samples treated with Conservare OH100, possibly related to its decrease in cohesion. Silbond 40 had the least increase in microdrop absorption from samples that were not wet-dry cycled to those that were, likely due to its slow speed of curing.

One of the primary limitations of this test is that it can only measure the absorption of the area that is covered by the water drop and consequently, variations in the sample can cause deviations in results. Due to the high figures for standard deviation, it may have been preferable to increase the number of samples in each cohort tested for each consolidant type. Despite these concerns, this test is well suited for assessment of finishes because of the small, relatively superficial area tested.

6. DISCUSSION

The development of testing methods for this research and assessment of their effectiveness may serve as a preliminary contribution to the establishment of testing standards for the evaluation of consolidants for earthen finishes, a void within the conservation

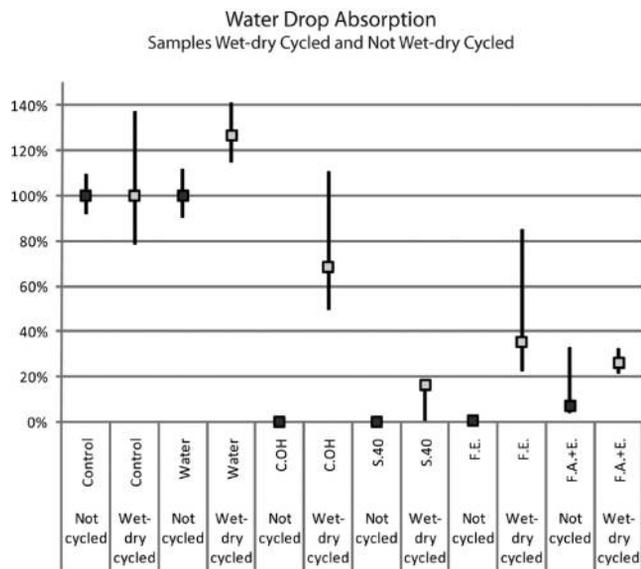


Fig. 12. Microdrop absorption as measured on samples that were and were not exposed to wet-dry cycling. High, low, and average values were calculated based on one standard deviation of the absorption time and are expressed as a percentage of the control as specified in RILEM Test II.8b. Consolidants from left to right are: untreated (control), water, Conservare OH100 (C.OH), Silbond 40 with ethanol in a 1:1 solution by volume (S.40), Funcosil SAE 300E (F.E.), and Funcosil Antihydro pre-treatment with Funcosil SAE 300E. (F.A.+E.)

field that became clear during this research. In addition to the investigation into testing methodology, interpretation of the results provides an opportunity to further consider prioritizing performance properties for friable earthen finishes. As stated, the preferred behaviors for treated samples established at the outset of this research were:

1. Increased cohesive strength
2. Continued plasticity after consolidation
3. Durability under conditions of wet-dry cycling or humidity cycling
4. Limited effect on the appearance of color and texture
5. Continued, albeit possibly reduced, ability to absorb water

The last point is important in allowing associated water-based treatments, such as reattachment or compensation, to be performed on these finishes. In addition to the selection of appropriate consolidants, the establishment of testing methods for this research may serve as a preliminary contribution to a more rigorous evaluation of consolidants for earthen finishes. Additional test development, inclusion of a range of clays and soil types, and comparison of samples that are at the same stages of curing will

provide more definitive results on the effectiveness of these consolidants. Final selection of the most appropriate consolidant at Mesa Verde will rely on the continuation of this laboratory-based testing protocol, in situ assessments, and consultation with tribal affiliates; however, an initial selection to begin the evaluation process is suggested.

6.1 INCREASED GRAIN-TO-GRAIN COHESION

By definition, a consolidant must reintroduce or improve intergranular cohesion within an inherently weak or degraded material; therefore, it was deemed necessary that all consolidants tested perform in this way. This is, in fact, in line with the findings for all consolidants except Conservare OH100. Therefore, Conservare OH100 appears not to be a suitable consolidant for smectite-containing earthen finishes in an environment where the treated material will continue to be exposed to liquid moisture.

6.2 CONTINUED PLASTICITY AFTER CONSOLIDATION

According to the results for hygric dimensional change by LVDT (an indicator for plasticity), Silbond 40 had the least effect on dimensional change as compared to the control, and would appear to be a good selection because it should allow treated samples

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to be replasticized for retreatment whether applied before or after reattachment. Additional testing would need to be performed to more completely assess reattachment after consolidation. In opposition to the preference for continued dimensional change, dimensional stability is another valued performance characteristic, since the problems caused by expansion and contraction of clays are one of the primary difficulties encountered in the conservation of earthen materials. When the tests for hydric change are interpreted with this in mind, water-treated samples, with the least dimensional change, exhibited the best results. Since continued plasticity after consolidation and dimensional stability are both desired properties, yet are in opposition to each other, it must be decided which is more critical to the success of these treatments. In this case, where finishes are situated in a partially protected rock alcove environment, plasticity is more highly valued than dimensional stability and should take precedence.

6.3 DURABILITY UNDER CONDITIONS OF WET-DRY CYCLING

During wet-dry cycling, the most stabilizing consolidants were Silbond 40 and Funcosil Antihydro with SAE 300E. Conservare OH100 and Funcosil SAE 300E also provided an increase in stability from the control, so they can be considered to have improved sample performance. Consolidation with water did not noticeably change the samples' resistance to wet-dry cycling and was therefore considered to have yielded the least preferable results.

6.4 LIMITED EFFECT ON THE APPEARANCE OF COLOR AND TEXTURE

Color change after wet-dry cycling was within a range that would be difficult to notice for all treated samples; thus, all results are acceptable. Surface effects remained stable for all treatments except the Funcosil Antihydro pretreatment, which produced unacceptable results.

6.5 ABILITY TO ABSORB WATER

Microdrop absorption is another property for which the results may be interpreted from multiple perspectives. In general, earthen materials are more durable when they are hydrophobic. For the reattachment treatments used at Mesa Verde,

it is required that the consolidant allow samples to absorb water so that they may be replasticized. Consequently, a greater microdrop absorption rate is more appropriate for this site. At the same time, the increase in absorption seen with water-treated samples after wet-dry cycling is not necessarily a positive response.

6.6 SUMMARY AND ANALYSIS

Although these findings can only be considered preliminary, the results suggest some important differences in the effects of four commercial ethyl silicate consolidants on one class of earthen materials. None of the consolidants had ideal results for all the performance properties tested; selection of a consolidant requires a compromise. Two of the consolidants produced results that are unacceptable for earthen finishes and can be eliminated from consideration. In the first case, Conservare OH100 decreased the sample's cohesion after wet-dry cycling, indicating that it was not able to perform as a consolidant when exposed to liquid water. In the second case, the loss of surface details immediately after pre-treatment with Funcosil Antihydro bars it from serious consideration as a treatment for these finishes, given their important original textural evidence (e.g., fingerprints, handprints, etc.). Poor performance in one category can also be enough to remove a consolidant from consideration. For example, consolidation with water alone was not selected because the results for resistance to wet-dry cycling indicated that the samples had not gained any cohesive stability as compared to the control samples. Silbond 40 performed well for all performance measures except microdrop absorption, a result that is important because it may inhibit subsequent reattachment treatments. Funcosil SAE 300E alone had fair to good results for all tests performed.

7.0 CONCLUSIONS

The behavior of properties of four ethyl-silicate-based consolidants used on earthen finishes and their moisture response, appear to vary widely depending on the type of ethyl silicate used. This, in itself, was an unexpected outcome. According to the results produced in this study, Funcosil SAE 300E may be the preferred consolidant for treating certain friable finishes at Mesa Verde National Park. Consolidation with water and Silbond 40 produced less useful

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behaviors, but none that can eliminate them from consideration completely. It can be concluded, however, that Conservare OH100 and Fungosil Antihygro should not be used on these finishes because they cause visible damage.

The findings outlined here allow for only a preliminary set of conclusions. Further tests and causal explanations for the observed results are necessary; work is underway to better understand the possibilities and limitations of the application of these consolidants to earthen finishes at Mesa Verde and elsewhere. To address the issue of standardization for this type of assessment, further test development will be necessary. Additionally, consolidants other than ethyl silicates, such as animal proteins, natural vegetable extracts, or diisocyanates should be considered in any future testing. As with all sites, any intervention performed should fit within a comprehensive conservation plan that follows a values-led planning model including environmental and cultural impacts developed in consultation with professional cultural resource managers and traditional stakeholders.

ACKNOWLEDGMENTS

This project has been completed with the financial support of Mesa Verde National Park, National Park Service, and the collaborative assistance of the GCI. Thanks to Eric Doehne, Conservation Sciences, Inc., for help with design and performance of ESEM and time-lapse photomicrography. Photo credits for the ESEM images go to him. Thank you to David Carson for assistance with design and performance of LVDT testing. Colorimetry and interpretation of results were performed with Jim Druzik at the GCI. Consolidation products were donated by Silbond Corporation, Prosoco Incorporated, and Remmers Baustofftechnik GmbH. Many individuals have made generous contributions as well, including Jeanne Marie Teutonico, Giacomo Chiari, A. Elena Charola, Claudia Cancino, George Wheeler, Jake Barrow, Linda Towle, Julie Bell, Kay Barnett, Robert Jensen, Tim Hovezak, Preston Fisher, Carolyn Landes, Art Johnson, Doug Yates, Paul Guevin, Dennis Pierattini, Victoria Pingarron-Alvarez, John Hinchman, Suzanne Hyndman, Bruce Campbell, and Lauren Hall.

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