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Residues from cyclododecane consolidation following desalination

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1500 Central and South American archaeological ceramics in the Field Museum of Natural History, Chicago, required desalination treatment. Cyclododecane (CDD) was investigated as a temporary consolidant for extremely friable ceramics during desalination, leading to an investigation of post-sublimation residue. Watch glasses, new unglazed terracotta saucers, and thick potsherds from the archaeological collection were treated and desalinated. No residues were detected after sublimation on watch glasses, the saucers, and archaeological potsherds that did not undergo desalination. Residues were found on all archaeological potsherds that were desalinated. Microscopical study and infrared spectroscopy (ATR–FTIR) indicated the residue to be primarily of biological origin. Its presence could result from the growth within the CDD of bacteria, mould and yeast present in the archaeological ceramic. There was no evidence of CDD remaining in the residue. Residues on desalinated potsherds consolidated with molten CDD were thin, lightly cohesive sheets. The residue could be lifted off with electrostatically charged nylon brush or polyester film. Residues formed in the CDD applied as a solution were less cohesive and could only be removed by brushing. In most cases, some ceramic particles were lost. It was concluded that temporary consolidation with CDD was not useful in desalination treatments.

1 Introduction

Use of cyclododecane (CDD) for consolidation of extremely fragile ceramics prior to desalination was investigated. Its insolubility in water and its ability to sublime at room temperature without leaving residues are CDD's primary advantages. However, there have been published and anecdotal reports of residues remaining after sublimation. The present investigation attempts to identify CDD residues, evaluate CDD application methods for ceramic consolidation, and develop effective methods for removal of any residues after desalination and sublimation. CDD consolidation is evaluated in comparison with the more standard resin solution consolidation procedures.

2 Background

With generous funding from the Institute of Museum and Library Services (IMLS), the Conservation Laboratories at the Field Museum of Natural History conducted a two-year project to address deterioration from salt contamination in its collection of over 15,000 Southern Andes archaeological ceramics. While some underfired ceramics and composite organic and ceramic objects required microclimate housing to immobilise the soluble salts, an environmental solution was not feasible for all of the affected objects. Desalination was the primary approach taken to stabilising the collection. Desalination was achieved by immersion of an object through a series of deionised water baths until conductivity readings indicated that salts are no longer significantly migrating into the soak bath (this was defined as three 24-hour baths with a conductivity below 50 μmho/cm (0.5 μS/m)). Objects with flaking or friable ceramic, slip or residues were consolidated prior to immersion. Most objects could be consolidated by introduction of conventional consolidants (acrylic resin and acrylic dispersion) by capillary action from the tip of a brush loaded with consolidant. A small percentage of objects were so badly flaking and friable that consolidation was required before the object could be moved from its shelf in storage. CDD was tested as a possible consolidant in this situation. Figure 1 is a detail of an example of this condition.

CDD was introduced to conservation in 1995 (Rowe and Rozeik 2008) and has proved to be a versatile temporary and reversible consolidant, binding medium, isolating layer and support material for conservation of a wide variety of materials. Preliminary work at the Field Museum proved that CDD could be safely applied in storage, did not significantly slow down the diffusion of salts into the soak water, and remained intact

Figure 1 Detail of severely deteriorating ceramic on a shelf in collection storage. Photo: ©The Field Museum, catalogue number 169921, Whistling vessel, Chanchan, Moche Vallery, Peru, photographer Ruth Norton.

during immersion. However, in some tests, a white residue remained after sublimation that was difficult to remove because of the friable nature of the salt-damaged surface.

The successful use of CDD as a temporary consolidant for stabilisation of fragile museum objects and archaeological ceramics has been reported by several authors. Research in preparation for moving the British Museum's ancient Egyptian ceramic collection to an upgraded storage facility led to an investigative study on methods for stabilising unstable low-fired pottery (severe delamination, flaking and powdering due to soluble salts) prior to their transfer. Based on the British Museum's preliminary testing, a vessel was successfully stabilised in place using hot-melt CDD applied with brushes (the gentlest technique) and could then be safely moved off a high shelf in a cramped storage area without loss of material (Cleere 2005). Likewise, Muros and Hirx discussed the use of CDD as a temporary barrier for water-sensitive ink on archaeological ceramics during desalination (Muros and Hirx 2004). The results of their experiments and case study showed that CDD, when applied as a melt, offers considerable protection for water-sensitive ink during the desalination of archaeological ceramics and is a viable alternative to other materials commonly used for this purpose.

Caspi and Kaplan reported, however, that CDD does not sublime completely and thereby leaves a residue (Caspi and Kaplan 2001). They described a study in preparation for the Smithsonian National Museum of the American Indian's planned move of over 800,000 artefacts from the Museum's Research Branch in New York, to the new Cultural Resources Center in Maryland. Transport tests on mock-ups and treatment of one artefact demonstrated that CDD can protect unstable areas during transport. However, test applications of CDD on glass microscope slides showed that some material, possibly an impurity, remained after sublimation. Using Fourier-transform infrared spectroscopy (FTIR) and gas chromatography–mass spectrometry analysis (GC–MS), Tissier and Bruhin also discerned small quantities of CDD residues, as well as other elements remaining after sublimation (Tissier and Bruhin 2009).

On the other hand, several studies have demonstrated that CDD sublimes completely from the substrates after treatment without leaving any residue (Brückle *et al.* 1999; Stein *et al.* 2000; Kuvvetli *et al.* 2007). Confer specifically addressed the question whether CDD sublimes completely or leaves a residue on textiles after a measured period of time (Confer 2006). Her samples were analysed for residues using optical microscopy, FTIR and gas chromatography with flame ionisation detection (GC–FID), as well as measuring changes in gloss by means of a handheld glossmeter. She found that, after as little as one week, any residues remaining were too small to be detected by the analytical methods used, and that essentially all CDD had sublimed.

As part of The Field Museum's treatment of Southern Andes archaeological ceramics, we conducted further investigation into the development and nature of the residue found during our preliminary tests, means of reducing its formation, and means of removing it.

3 Preparation and treatment of samples

CDD products were used from four different suppliers (refer to Products list). Two products (Tokyo and Kremer) were readily available in moderate quantity, two (MP Biomedicals and Aldrich) were highly expensive, rare research chemicals and only small quantities were purchased. The Tokyo and Kremer products were applied to watch glasses, transparent glass spot plates, new unglazed terracotta saucers, and

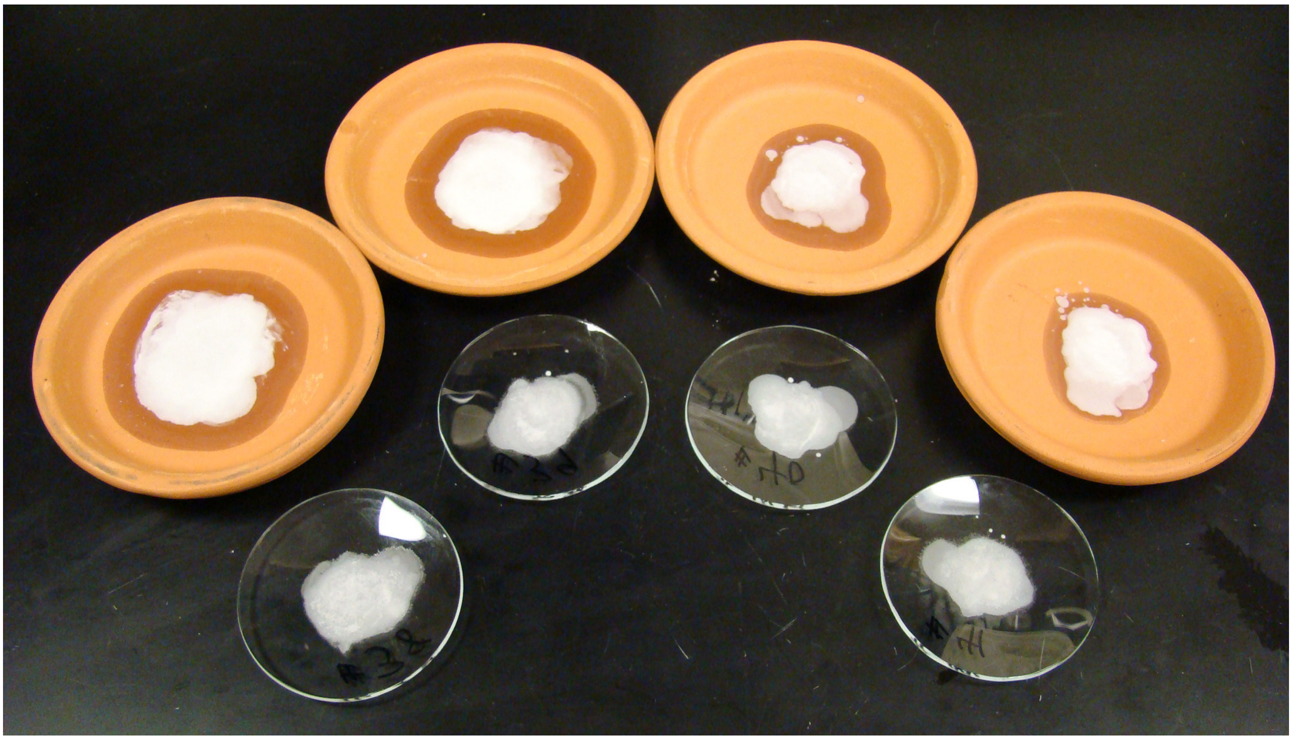

Figure 2 Earthenware saucers and watch glasses treated with various thicknesses of CDD applied molten or molten with 10% odourless mineral spirits, before soaking in water. Photo: ©The Field Museum, photographer Richard Bisbing.

potsherds and a ceramic vessel from the Southern Andes archaeological collection. Methods of application included CDD melt, CDD melt with 10% odourless mineral spirits, and 68% v/v solution CDD in odourless mineral spirits heated to <80°C, all applied by brush. As quantities of the MP Biomedicals and Aldrich products were limited, these were applied only to the transparent glass spot plates.

To test for residue after sublimation, the watch glasses, spot plates and terracotta saucers were treated with various thicknesses of CDD melts or CDD melts with up to 10% odourless mineral spirits (Figure 2). Half of the watch glasses and saucers were soaked in deionised water for between 8 and 15 days, with no water changes. All the treated substrates were allowed to sublime in either the chemical fume hood or the laboratory until the CDD film had disappeared. The potsherds were treated on one surface with CDD melts with up to 10% odourless mineral spirits (Figure 3). Half of the treated potsherds were allowed to sublime in the laboratory (without desalination) while the other half were desalinated using standard procedures followed by sublimation in the laboratory. The duration of desalination ranged from 9 to 34 days with daily changes of bath water. Finally, a deteriorated ceramic vessel was consolidated in different areas with Paraloid B72, Rhoplex/Primal B60A acrylic emulsion prepared as a 50% stock solution in water, molten CDD, and CDD as a heated 68% solution in mineral spirits. The vessel was then desalinated (Figure 4).

Residues were detected by stereomicroscopy and analysed by FTIR using a Smiths Detection IdentifyIR portable spectrometer. Samples were lifted from the ceramic surface and transferred to the diamond internal reflection element in the sample interface and analysed by attenuated total reflection (ATR). The resulting spectra were compared with an in-house spectral library of common conservation materials. Samples were also transferred to microscope slides and studied using polarised light microscopy (PLM), both unstained and stained with various histochemical reagents.

4 Experimental results

No residues were detected from 3 of the products when samples were not desalinated, whether on a watch glass, spot plate, unglazed terracotta saucer or potsherd, regardless of the preparation and

Figure 3 Potsherds treated with CDD applied molten with 10% odorless mineral spirits, before desalination. Photo: ©The Field Museum, catalogue number 170560.G,H,I,K, Majoro Chico, Nazca Valley, Peru, photographer Richard Bisbing.

Figure 4 Vessel consolidated with Paraloid B72 10% in acetone, Rhoplex/Primal B60A 50% stock solution in water, CDD melt, 68% v/v solution CDD in odourless mineral spirits heated to 80°C. The CDD was applied by dripping from an eyedropper and by dabbing and stroking with a brush, both directly on the ceramic and on ceramic that was first soaked with ethanol to reduce penetration of the CDD. Photo: ©The Field Museum, catalogue number 154969, Santa Marta, Magdalena, Colombia, photographer Alexander Dittus.

application of the CDD. The only exception was with the Aldrich CDD, where visible particulate residues were evident when the melt was prepared and remained after sublimation. The product was dirty and the residue was unrelated to the issue of complete sublimation of CDD. In addition, no residues were detected even when the watch glasses and unglazed ceramic terracotta saucers were immersed in a water bath as if for desalination.

A residue was found on all archaeological ceramics that had been desalinated (Figure 5). The residue on potsherds 170560 was characterised as a thin, lightly cohesive sheet of material when it developed on samples where the CDD was applied molten. It was much less dense and cohesive when it developed where the CDD was applied as a heated 68% solution. These characteristics were less distinct on the residue from vessel 154969, indicating that factors other than the method of application of CDD may be influencing the residue form (Figure 6). Microscopical study and FTIR–ATR indicated the residue to be primarily of biological origin. In one instance, the infrared absorption spectra were consistent with ground yeast and some other biological materials. The infrared absorption spectrum of CDD is distinctly different from the spectrum of the residue (Figure 7). Histochemical staining using dilute methylene blue in water and diluted Lugol's iodine confirmed the presence of yeast in the residue on one potsherd and fungal hyphae in the residue from the ceramic vessel (Figures 8 and 9). There was no evidence of CDD remaining in the residue. In a second run of the experiment using more potsherds from the same catalogue number, the residue stained like a protein and the FTIR spectra were consistent with a substance containing protein and carbohydrate-like absorptions such as chitin, yeast and similar biological residues (see Figure 10 and compare with Figure 7). It was therefore concluded that the residues on desalinated objects after sublimation of CDD could be described as biofilms. Biological growth would not be an unreasonable expectation given prolonged immersion in water of a material that had been exposed to biota during use and hundreds of years of burial.

To investigate this theory further, another experiment was conducted. Small terracotta flower pots were buried with a little piece of

Figure 5 Potsherds with residue following desalination and sublimation of the CDD. Photo: ©The Field Museum, catalogue number 170560.G-H, Majoro Chico, Nazca Valley, Peru, photographer Richard Bisbing.

meat (to simulate a grave content and attract microorganisms) in different soils (stony, limy ground; sandy soil, forest floor (under pine); swamp; pebbles; compost/humus; grassland soil). Another flower pot was placed on top of the soil so that it could be determined whether potential microbiological growth in the CDD is due to the soil's microfauna or the microclimate in and near the soil. After being buried for over a month, the pots were excavated and CDD was applied as a melt. Afterwards the pots were desalinated for one month in deionised water with the water being changed eleven times. Several months later, and after the CDD had sublimed, some residue remained on every pot. This was investigated by optical microscopy and staining with naphthol blue black, a protein indicator. The residue on some of the pots was very thin and fine and did not stain. The residue that remained on the pot from the forest soil showed clear fibrous structures. As these structures absorbed some blue stain, and therefore contained some protein, it was concluded that these were hyphae from fungal organisms growing in the CDD during desalination. Although not all the samples have yet been analysed, it appears that the desalination process promotes both development of a non-biological residue as described by Bruhin (2008: 102) and growth of microorganisms like fungi within the CDD structure. The hyphae remain as a residue when the CDD has sublimated. The fact that only some of the samples of this test showed such microorganisms suggests that they originated from the soil rather than from the laboratory environment or the CDD itself.

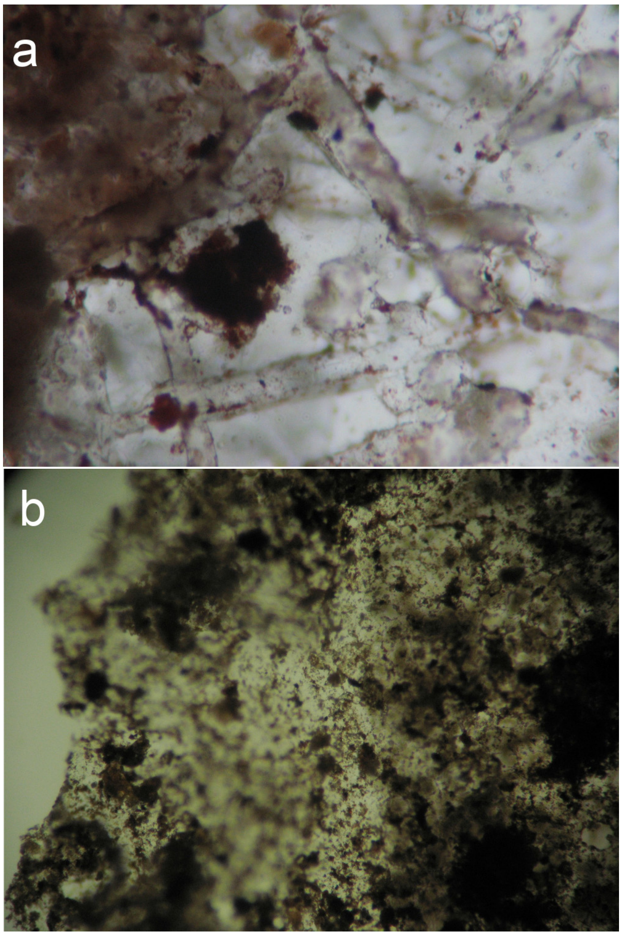

Figure 6 Photomicrographs of the two different characters of residue found on potsherds, catalogue number 170560. Characteristics were less distinct on residue from vessel catalogue number 154969, indicating that the method of application of CDD may not be the dominant factor: a) residue following desalination and sublimation. CDD applied as 68% v/v solution of CDD in odourless mineral spirits. Structure amorphous with branching tubular structures. Formed a cohesive layer. ×100 original magnification; b) residue following desalination and sublimation. CDD applied molten. Structure amorphous with no biological structures visible. ×100 original magnification. Photo: ©The Field Museum, photomicrographer Alexander Dittus.

Methods to remove the residue without touching the surface of the ceramic were compared using the desalinated potsherds and vessel. The cohesive sheets formed after desalination of ceramics treated with molten CDD could be lifted off with an electrostatically charged nylon brush or polyester film, with the nylon brush being more effective. The fluffier residue formed after treatment with CDD applied as a solution was less cohesive and could only be removed by brushing (Figure 11). Removal from

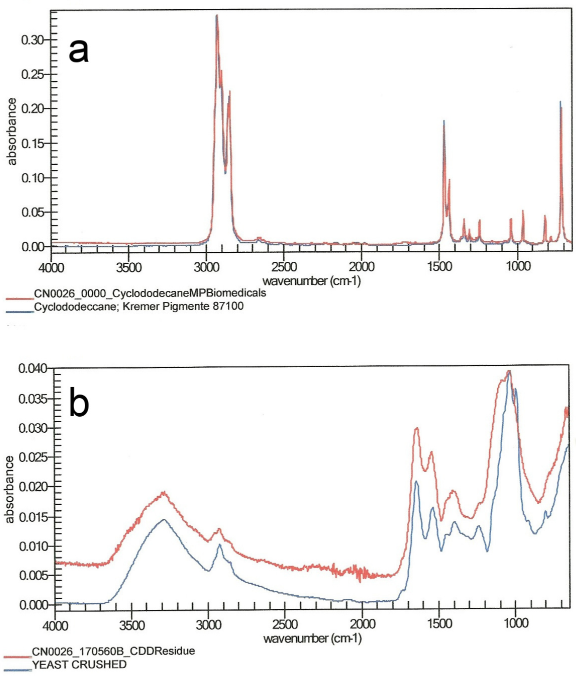

Figure 7 Spectrum of CDD compared to spectrum of residue on potsherd after desalination and sublimation of CDD: a) FTIR spectra of two samples of CDD; b) FTIR spectrum of residue from desalinated potsherd compared to spectrum of yeast. Photo: ©The Field Museum, spectroscopist Richard Bisbing.

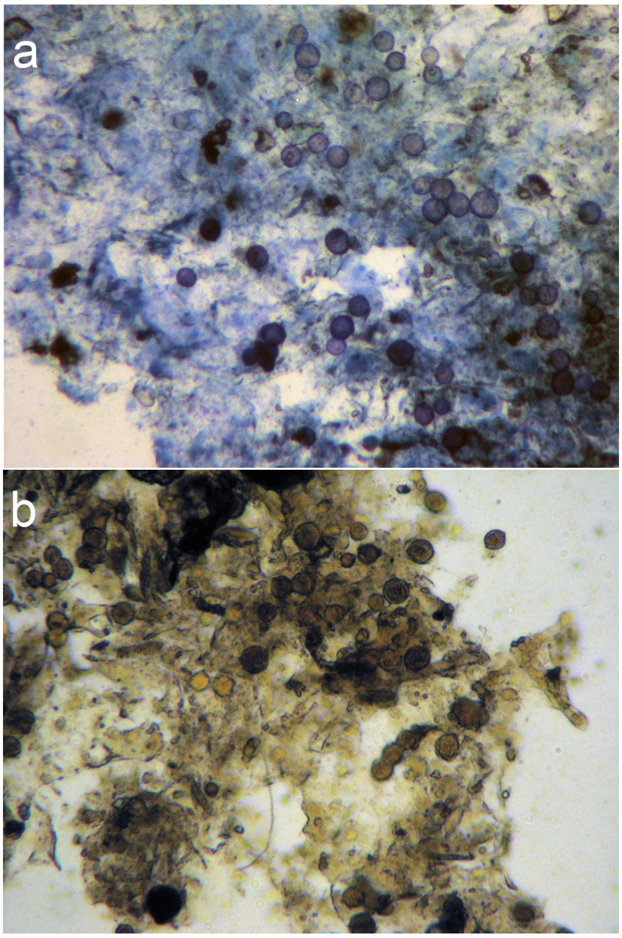

Figure 9 Photomicrographs of yeast in residue from desalinated potsherds 170560 stained with methylene blue and Lugol's iodine: a) potsherd residue stained with methylene blue, ×100 original magnification; b) potsherd residue stained with Lugol's iodine, ×100 original magnification. Photo: ©The Field Museum, photomicrographer Richard Bisbing.

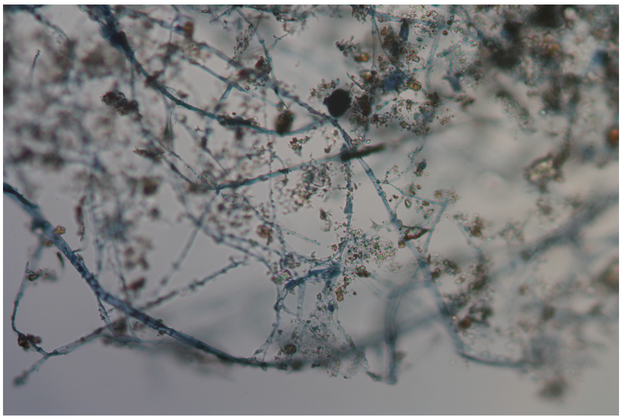

Figure 8 Residue from buried flower pot stained with naphthol blue black; protein in fungal hyphae stained blue. ×40 original magnification. Photo: ©The Field Museum, photomicrographer Alexander Dittus.

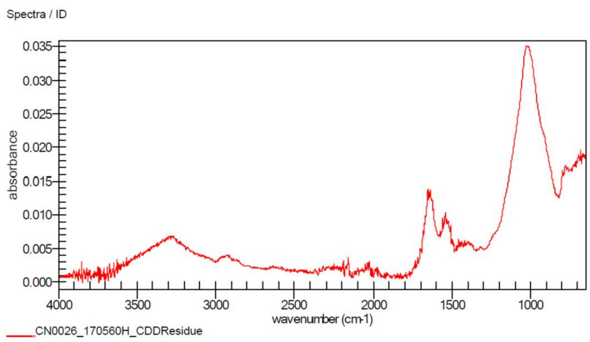

Figure 10 FTIR spectrum of residue from desalinated potsherd, catalogue number 170560.H. Compare with Figure 7. Photo: ©The Field Museum, spectroscopist Richard Bisbing.

intact potsherds was effective, but removal from extremely friable and flaking ceramic surfaces resulted in some dislodgment of particles and flakes, a significant drawback to the practical use of CDD as a consolidant for desalination.

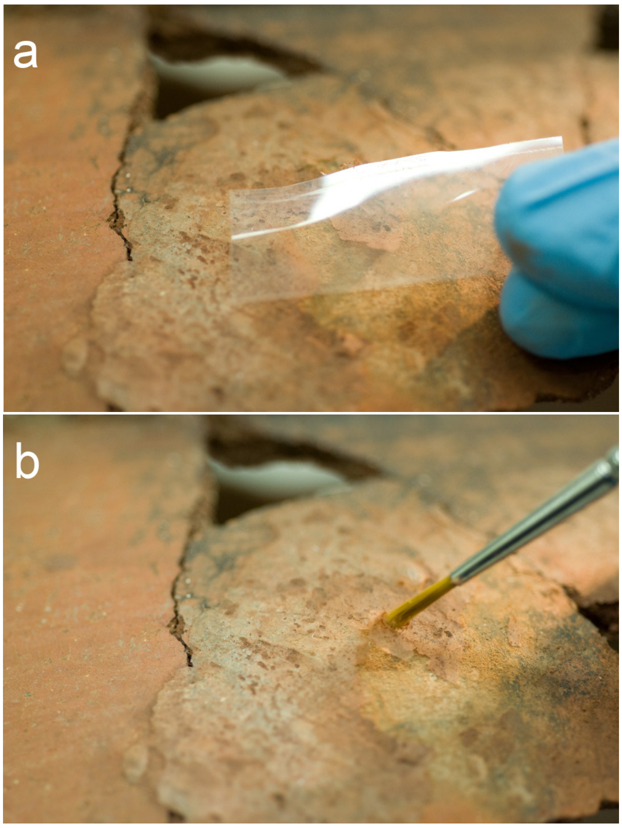

Figure 11 Removal of residue: a) CDD had been applied molten resulting cohesive residue layer. Residue removed with electrostatically charged polyester film; b) CDD had been applied in solution resulting in fuzzier less cohesive residue layer. Residue removed with brush. Photo: ©The Field Museum, catalogue number 154969, Santa Marta, Magdalena, Colombia, photographer Alexander Dittus.

5 Conclusion

Published reports indicate variability in the presence or absence of residue after sublimation of CDD. In our study, regardless of the CDD source and preparations, no CDD residues were detected after sublimation on watch glasses, spot plates, clean unglazed terracotta saucers and archaeological potsherds which did not undergo desalination. Non-CDD residue was left after sublimation of one CDD product on a spot plate, but the residue was clearly a contaminant in the CDD. CDD residue was found only on archaeological potsherds and vessels that were desalinated. The residue appears to be partly of biological origin, forming a biofilm under, within or on the CDD during desalination. The CDD then sublimes completely, leaving only the biofilm.

Initially, it was hoped that applying molten CDD in storage would provide a safe method of consolidation of extremely flaking and friable ceramics that did not introduce solvents into the collection storage room. Applying CDD to extremely friable and flaking ceramics for desalination required touching the damaged surface with the brush tip, resulting in some movement or loss of material. The residue formed on all desalinated deteriorating ceramics proved difficult to remove without some loss of ceramic particles or flakes. After desalination and sublimation of the CDD, it was still necessary to consolidate the ceramic for long term stability. It was therefore concluded that CDD was not a feasible procedure for interim consolidation, and that consolidation with the eventual consolidant material, Paraloid B72, at the beginning of treatment was the most effective approach. Application using a stationary paper wick did not disturb ceramic flakes and particulates. The primary drawback of using Paraloid B72 in storage before moving an object to the laboratory – working with solvents in a confined storage area – was addressed through the use of portable activated charcoal filter vapour extractors.

Biographies

Ruth Norton was, until her retirement in 2016, McCarter Chief Conservator at The Field Museum in Chicago. She has an MS in Art Conservation from the University of Delaware. She practised and provided conservation training at the Bishop Museum, Honolulu, the National Museum of the Philippines, Manila, the University of Sydney excavation at Pella-in-Jordan, Museum of Applied Arts and Sciences, Sydney, and National Museum of Ethnology, Leiden. She taught objects conservation at the University of Canberra, Australia, and at Buffalo State College, and conducted consultancies for UNESCO, ICCROM, the US Department of State and the Australian government. She is a co-author of *The Conservation of Artifacts Made From Plant Materials*.

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Alexander M. Dittus graduated from the objects conservation programme of the State Academy of Fine Arts in Stuttgart, Germany, with an award-winning Master's thesis on the RTI investigation of transparent materials in 2014. During his studies he worked with archaeological and ethnographic materials in conservation laboratories in Germany, Austria and the USA, as well as on excavations in Romania. In 2012–13, as a visiting researcher at the Field Museum in Chicago, he joined the Southern Andes Ceramic Desalination Project. Alexander is currently employed at the Swiss National Museum on the conservation of archaeological fresh finds.

Richard E. Bisbing is a chemical microscopist and uses microscopes to solve chemical problems, most often a combination of polarised light microscopy (PLM), micro-scale techniques of qualitative analytical chemistry, and infrared microspectroscopy (FTIR). As a graduate of Michigan State University, he was trained by Dr Walter C. McCrone, and for 40 years he practised forensic microscopy at the Michigan State Police and McCrone Associates laboratories. After 25 years at McCrone Associates, Inc., Westmont, Illinois, he retired as Executive Vice President. He currently volunteers in the conservation laboratory at The Field Museum.

Material list

Cyclododecane samples:

- Tokyo Chemical Industry Company, LTD (TCI). Catalogue number C0554, www.tcichemicals.com
- Kremer Pigments, Inc., 228 Elizabeth Street, New York, NY 10012, USA. Catalogue number 87100. www.kremer-pigmente.com
- MP Biomedicals, LLC, 29525 Fountain Parkway, Salon, OH 44139, USA. Catalogue number 211172; Lot number 13969. www.mpbio.com
- Aldrich Chemistry (Sigma-Aldrich), 6000 N. Teutonia Avenue, Milwaukee, WI 53209, USA. Catalogue number S436402. www.sigmaaldrich.com

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