Visualizing Cyclododecane on Porous Materials Using Cryogenic Scanning Electron Microscopy

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Subliming Surfaces: Volatile Binding Media in Conservation Conference and Workshop, University of Cambridge

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ABSTRACT

This study explores the interaction of cyclododecane with porous substrates commonly encountered among cultural materials. Untreated samples of paper, wood, and clay were imaged using conventional SEM. A second set of substrate samples was treated with a solvent application of cyclododecane and imaged under cryogenic conditions. Comparing SEM and cryo-SEM images of the samples reveals that cyclododecane forms a coating that closely mimics the surface topography of a given substrate. Due to instrumental limitations, only the topmost surface of each substrate was observed. It was therefore not possible to qualify the depth of penetration of the consolidant or the force exerted by the consolidant upon the substrate. The close correspondence between untreated and treated surfaces suggests that a thorough consolidant coating was achieved.

INTRODUCTION

Since its introduction in the mid-1990's, cyclododecane (**Figure 1**) has found increasing use in the field of conservation. Publications describe its use on a variety of porous and non-porous substrates to facilitate stabilization, transport, and treatment procedures. However, the physical effects of deposition and sublimation of the cyclododecane on porous substrates remain somewhat unexplained.

The present study, building upon a 1998 publication by Riedl and Hilbert,[4] attempted to better understand the interaction between the consolidant and three commonly encountered porous substrates-paper, wood, and clay- using scanning electron microscopy (SEM).

Due to its low vapor pressure, cyclododecane cannot be imaged with conventional SEM, because the vacuum conditions force sublimation. Cryogenic (cryo) conditions in the SEM enable imaging of the material, since cyclododecane remains in a solid physical state at low temperatures.

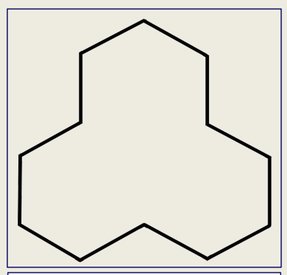

Figure 1. Cyclododecane ($C_{12}H_{22}$) molecule

METHODOLOGY

Substrate Materials:
- Whatman Filter Paper #3
- Unfinished oak veneer, transverse plane
- Self-hardening Critter® clay

Sample Prep:

1. Samples of the paper and wood were taken using a 1.3 mm Harris Uni-Core punch and placed into BAL-TEC gold flat-bottomed planchettes with well diameters approximately 1.4mm(**Figure 2**). The clay was directly inserted into the planchette and allowed to harden.
2. A fourth planchette, intended to represent a single pore of an inert substance, was left unfilled and prepared for imaging.

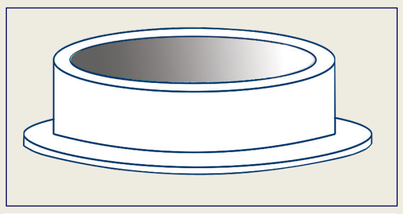

Figure 2. Schematic of a BAL-TEC (Leica Microsystems) gold, flat-bottomed planchette.

Imaging Uncoated Samples with Conventional SEM:

3. The four samples (paper, wood, clay, and single pore) were sputter-coated with 10nm of chromium, using a Denton DV602 sputter coater. The samples were examined using a Topcon DS-130F Field Emission SEM with an in-lens imaging system.[5] Samples were placed in the upper stage of the microscope to decrease the path length of the electron beam, reducing noise and improving resolution.[6]
4. Images of each sample were digitally captured at 500x, 1000x, 2000x, and 5000x using an Orion Lichtenstein capture board. The accelerating voltage was 10 or 15 kV for all images.

Consolidation with Cyclododecane:

5. Samples of wood, paper, and clay were prepared as described above. A supersaturated solution of cyclododecane (0.5 µL , 80% w/v in Shellsol® OMS[7]) was applied to the top surface of each sample with a glass micropipette. The fourth, empty planchette was filled with the same solution.
6. The samples were placed onto an ECHOtherm Model IC20 chilling/heating plate at 30°C for 30 minutes, while the solvent was allowed to evaporate.

Imaging with Cryo-SEM:

7. Prepared samples were plunge-frozen in liquid ethane (-183°C) and were then transferred to a Gatan CT-3500 cryo-preparation stage.
8. Surfaces were fractured with a pre-chilled blade and were sputter-coated with 10nm of chromium under vacuum conditions at less than -170°C in a Denton DV-602 coater.
9. The cryo-preparation stage with sample was transferred to the pre-cooled Topcon DS-130F Field Emission SEM. The stage temperature was gradually raised and allowed to equilibrate with that of the microscope for 30 minutes. Imaging was performed at -120°C.
10. The microscope was operated at 10 or 15 kV, and images were digitally captured as above at 500 - 5000x magnification and compared with images of the uncoated substrates.

Figure 3. Taylor inserting the cryo-stage into the SEM.

RESULTS

Self-Hardening Critter® Clay

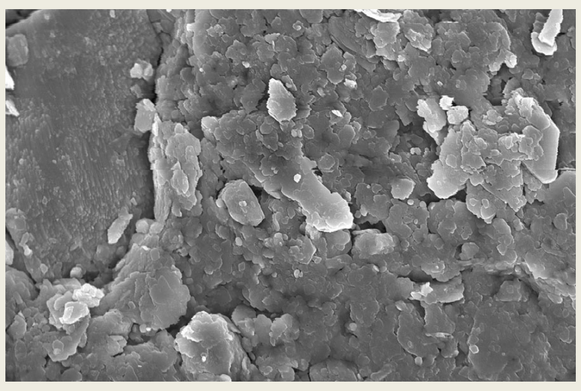

Figure 4. Critter® Clay, uncoated, 10 kV, 5000x

Figure 5. Critter® Clay, coated, 10 kV, 2000x

Oak Wood

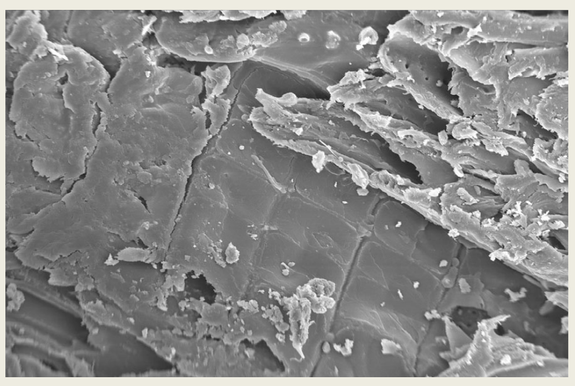

Figure 6. Oak wood, uncoated, 10 kV, 1000x

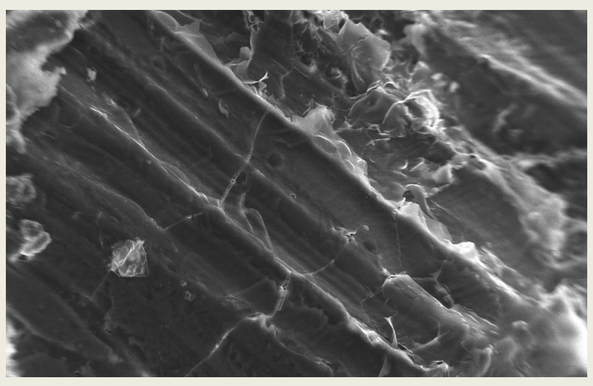

Figure 7. Oak wood, coated, 10 kV, 1000x

Whatman Filter Paper #3

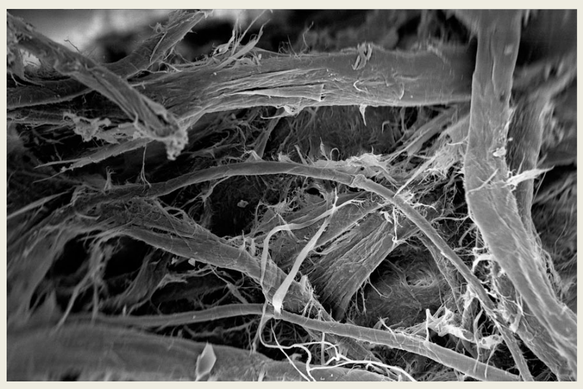

Figure 8. Filter paper, uncoated, 10 kV, 1000x

Figure 9. Filter paper, coated, 10 kV, 1000x

Cyclododecane

Figure 10. Untreated gold planchette, 10kV, 50x

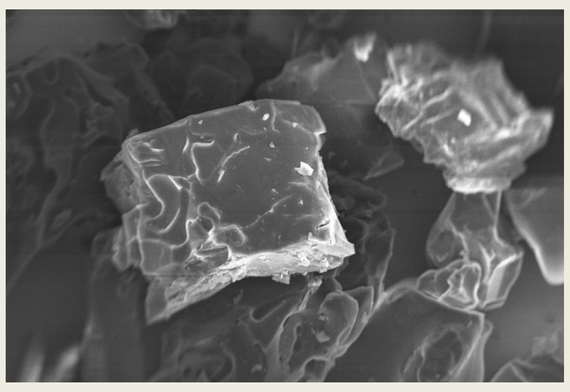

Figure 11. Cyclododecane in gold planchette, 10kV, 500x

DISCUSSION AND CONCLUSIONS

Comparing images of untreated and treated clay, wood, and paper samples reveals that the cyclododecane forms a fairly uniform coating that closely mimics the topography of the substrate. The fine clay surface was completely covered with a smooth, tile-like coating of cyclododecane (**Figures 4, 5**). The characteristic cellular structure of wood could be seen through the cyclododecane coating layer, which closely follows the contours of the porous substrate (**Figures 6, 7**). The intertwined and projecting fibers of the paper were individually encased in cyclododecane (**Figures 8, 9**). Cracking and delamination were sometimes observed within the coating layers and may be related to plunge-freezing process. Only a small amount of cyclododecane was seen within the well of the gold planchette intended to represent a single pore. It seemed that the cyclododecane was not easily retained by the smooth metal surface and plunge freezing in liquid ethane was enough to dislodge the majority from the well. The cyclododecane that remained appeared crystalline and angular (**Figures 10, 11**).

Cryo-SEM proved limited in its ability to peer into the pores of the treated substrates because the cryogenic stage does not offer enough rotation to make it possible to significantly alter the viewing angle. The treated samples themselves were too small to be easily manipulated and/ or cross-sectioned, particularly while maintaining frozen conditions. Because only the topmost sample surfaces were observed, it was not possible to assess the depth of consolidant penetration or the force exerted by the consolidant upon the substrate. With a different cryo stage, it might be possible to position samples to allow a cross-sectional view of the porous substrates.

This study permitted an assessment of the physical interaction between cyclododecane and the surfaces of treated substrates, revealing a close correspondence and suggesting thorough coverage of porous materials when the consolidant is applied as a saturated solvent solution.

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[4] Riedl, N. and G. Hilbert. 1998. Cyclododecan im Putzgefuge. *Restauro* 7 (1998): 494-499.

[5] All SEM analysis was performed at the Robert P. Apkarian Integrated Electron Microscopy Core, Emory University.
[6] This in-lens imaging utilizes only SE-1 and SE-2 secondary electrons nearest to the surface of the sample.
[7] CAS # 64741-65-7. Shellsol® OMS is an isoparaffinic solvent synthesized from selected hydrocarbons (predominantly C9-C12). Also sold as ShellSol 71. Produced by Shell Chemicals.