
CYCLODODECANE: Observations on Residues and Substrate Interactions

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Cyclododecane Use in Conservation

Since its introduction in the mid-1990s, cyclododecane has found increasing use globally in the field of conservation. Conservation publications describe cyclododecane's use on a variety of substrates to facilitate stabilization, transport, and treatment procedures. Several means of application are described, including molten and solvent systems. Spray methods are employed with increasing frequency, noting a more uniform and continuous coating result.

Since Rozeik and Rowe compiled a thorough summary of the relevant conservation literature in *Reviews in Conservation* in 2008, articles about the practical uses of cyclododecane continue to be published. Recent articles cite the successful use of cyclododecane as a consolidant and facing material for painted surfaces (Ryan 2009; Borgioli 2009), as a protective coating to enable revised or difficult treatment (Rozeik 2009; Sahmel, et al. 2012), as a fixative for friable media (Balzarotti-Kämmlin 2010), and to temporarily stabilize fragile materials during excavation and transport (Ma 2011; Bayer 2011; Davidson 2010). Additional articles will be published as postprints to the "Subliming Surfaces: Volatile Binding Media in Heritage Conservation" conference, held at the University of Cambridge in April 2015.

Published discussions generally focus on the application method and treatment scenario, with repeated acknowledgement of concerns about sublimation rate as well as health and safety. Rate of sublimation has been shown to be influenced by external environmental factors such as temperature, ventilation, and pressure (Bruhin 2012) and has been explored by nuclear magnetic resonance (NMR) profilometry and Fourier transform infrared spectroscopy (FTIR) with the conclusion that the rate of sublimation is quasi-linear and dependent on film thickness (Anselmi 2011). Though some ecotoxicological data exist, long-term health effects and permissible exposure limits for cyclododecane have not been determined (Vernez 2011).

Additional concerns are repeatedly raised about the presence of residual compounds and interaction of cyclododecane with various substrates.

It is important to distinguish between residual cyclododecane and residues of other compounds. Tissier and Bruhin observed residues using FTIR and gas chromatography-mass spectrometry (GC-MS) after visual and weight assessment suggested complete sublimation from various materials. These residues were not detected in the stock cyclododecane and their mass was less than 1% of the cyclododecane applied during treatment (2009). Jägers reported that observed white residues were linked to the polyethylene pipettes used to apply the cyclododecane as well as to saponified wax compounds present in the substrate, suggesting that cyclododecane mobilized these compounds (2012).

Cyclododecane Chemistry and Manufacture

The chemistry of cyclododecane predicts that the pure compound should sublime completely. The cyclic, semi-crystalline hydrocarbon has a melting point of 60°C (NIST 2012), low vapor pressure of 0.1 hPa (Watters 2007), and a relatively low enthalpy of sublimation, $\Delta H^{\circ}_{\text{sub}}$: 76.4 +/- 1.7 kJ/mol (NIST 2012), which permits sublimation at room temperature. As a monocyclic saturated alkane, it has numerous conformations and thus demonstrates its somewhat malleable semi-crystalline character.

Cyclododecane converts from solid to gas through the disruption of intermolecular forces, causing intact rings to separate from the aggregate without breaking into smaller fragments. This sublimation occurs spontaneously at ambient conditions of temperature and pressure.

A series of US patents granted in the late 1960s and early 1970s describe the synthesis of cyclododecane by selective hydrogenation of cyclododecatriene (Misono 1973; Gosser 1970; Levaie 1968; Mcalister 1968; Smith 1963). The patent literature indicates that solid cyclododecane is relatively stable and unreactive, typically requiring a catalyst and increased temperature and pressure to react with other compounds. Patent authors consistently noted difficulty with the control of side reactions and product purity but by 1968 were able to demonstrate 99% product purity (Leviae).

It is assumed that synthesis of cyclododecane is today achieved via this method or a similar variation, but current suppliers Sigma Aldrich and Kremer Pigments could not offer product preparation details. Samples from several cans of cyclododecane were tested as part of a study by Caspi and Kaplan (2001); one was found to contain very small amounts of fatty acid and hydrocarbons, but the source of these contaminants was not identified.

Experimental Observations

In the present study, questions about residues and substrate interactions were further investigated through four analytical and practical experiments. A series of high magnification cryogenic Scanning Electron Microscopy (cryo-SEM) images were taken following the sublimation of cyclododecane from a gold planchette. GC-MS was conducted following the sublimation of cyclododecane from an aluminum foil weighing pan. Objects previously treated with cyclododecane were re-examined macroscopically. Finally, cyclododecane was applied to glass slides that had been treated with a variety of materials commonly used as adhesives, consolidants, or coatings in conservation.

The experimental procedures were designed to minimize variables and to limit possible contamination. The same stock of cyclododecane, purchased from Kremer Pigments in 2005, was used for all four experiments. Cyclododecane was applied in its molten state to avoid contamination from solvents.

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1. Cryo-SEM imaging

A new BAL-TEC gold planchette with a flat-bottomed well measuring 1.4mm in diameter was first cleaned by sequential sonication for approximately five minutes in distilled water, reagent grade acetone, and finally reagent grade methanol. The empty planchette was placed in the cryo-preparation stage, cooled under liquid nitrogen, chromium-coated, inserted in the field emission SEM, and imaged at -120°C.¹ The microscope was operated at 10kv and images were digitally captured at increasing magnifications from 40x to 10,000x.

Once removed from the microscope, this planchette was re-cleaned, and a small piece of solid cyclododecane was placed into the well with stainless steel tweezers. The planchette was heated on a hot plate at 70°C for a few minutes to melt the cyclododecane. It was covered with an inverted shallow plastic dish to prevent dust accumulation and was allowed to sit at room conditions. After seven days, the planchette was again chromium-coated and imaged under cryo conditions.

Comparing images of the planchette before and after treatment with cyclododecane and its subsequent sublimation, it was evident that the bulk of consolidant had readily departed. The surface area of the planchette well was too small to flush with solvent for further analysis.

2. GC-MS analysis

An aluminum foil weighing pan was rinsed with acetone, allowed to evaporate and then warmed on a hot plate at 100°C to dry. The empty pan was weighed on a digital scale to one-hundredth of a gram, and one gram of solid cyclododecane was placed into each pan using stainless steel tweezers.

The pan was heated on a hot plate at 70°C to melt the cyclododecane, and the temperature was raised to 85°C for one minute to produce a more level layer. The pan was placed under an elevated plastic box to limit dust accumulation while also promoting air circulation. The cyclododecane was allowed to sublime at room conditions for approximately eight weeks until it was no longer visible to the naked eye and the pan had returned to its empty weight.

The pan was rinsed with 500uL of hexanes, and this rinse solution was analyzed via GC-MS.²

Comparison spectra were also collected from the hexanes, an unused pan rinsed with hexanes, and solid cyclododecane dissolved in hexanes. The detection limit was estimated to be approximately 100ppb. The spectra from the treated and untreated pans were the same within instrumental precision. All impurities in the samples were also seen in the solvent and were therefore determined to originate from the solvent or the column. These results suggest that the cyclododecane was uncontaminated, sublimated completely, and did not leave behind derivative compounds.

3. Re-evaluation of objects previously treated with Cyclododecane

Several objects that were previously treated with cyclododecane in preparation for transport were visually evaluated for the presence of surface alterations such as a deposit, bloom, or haze that might relate to their prior treatment with cyclododecane.

A limestone column capital in The Cloisters/ Metropolitan Museum of Art was treated in 1999 with cyclododecane, applied both in 3:1 Shellsol OMS:xylenes solution and as a melt (Stein, et al. 2000). Ceramic vessels in the National Museum of the American Indian were treated in 2001 with molten cyclododecane (Caspi and Kaplan 2001). A painted linen fragment with glue and textile backing in the Michael C. Carlos Museum of Emory University was faced in 2010 with molten cyclododecane on tissue. None of the conservators who examined these objects at the authors' request observed any visible surface alterations on the previously treated objects.

4. Glass slides coated with conservation materials and treated with Cyclododecane

Glass microscope slides were washed with Aquet glassware soap, rinsed with acetone, and dried with Kimwipes. Using a glass stir rod, an approximately 1-inch area of each slide was coated with one of several conservation materials (see Table 1).

1. Cryo-SEM imaging was accomplished at the Robert P. Apkarian Integrated Electron Microscopy Core at Emory University. Procedures for imaging cyclododecane under cryogenic conditions in a scanning electron microscope were developed for a separate study to examine how the temporary consolidant interacts with porous substrates (Murray et al., 2015).

2. GC-MS analysis was conducted by Applied Technology Services, Inc. The agilent GC-MS system consisted of a model 7890A gas chromatograph with split/ splitless injection port and a model 5975C mass selective detector. A HP-5MS 5% Phenyl Methyl Siloxane column (30m, 250µm diameter, 1µm film

thickness) was used with helium as the carrier gas at a flow rate of approximately 1ml/min and linear velocity of approximately 36.6 cm/sec. The injection port temperature was 280°C at 8.16 psi and a total flow rate of 1ml/min. Injections were carried out in split mode with a split ratio of 20:1 and split flow rate of 20ml/min. The temperature was held at 55°C for 2.5 minutes, then ramped at 20°/min to 115°C and then 10°/min to 280°C, and held at the final temperature for 2 minutes, giving a total run time of 24 minutes. MS analysis was carried out in scan mode with a transfer line temperature of 230°C and temperature of the quadrupole ion source at 150°C. Scan parameters were low mass 29.0 and high mass 352.0 with a threshold of 50.

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The coated slides were allowed to dry overnight and were digitally photographed. A small piece of cyclododecane was placed on each slide with stainless steel tweezers and then melted in place with a heated spatula, forming a layer that partially covered both coated and uncoated areas of the slide. As this experiment was designed to be practical, the amount of cyclododecane delivered to each slide was not weighed, and the thicknesses of the resulting layers were not measured.

The treated slides were digitally photographed. The cyclododecane was allowed to sublime under room conditions. After approximately three weeks, the slides were examined through a stereobinocular microscope and compared with images taken before sublimation.

A thin deposit remained on the coated and uncoated areas of the slides with PVA-AYAF, B-72, Multiwax, and Bowling Alley Wax. The slides coated with the waxes clearly appeared to have a more generous application of cyclododecane, which would require longer to sublime. It is also possible that the sublimation was slowed by the presence of the chemically similar waxes.

The uncoated and coated areas of the other slides appeared unchanged by the application and subsequent sublimation of the cyclododecane. The surfaces of the glass and the conservation materials were not visibly deformed, etched, or otherwise physically altered. No haze, film, or residue appeared to be present.

Figure 1 presents a detail of the glass slide coated with carnauba wax and treated with cyclododecane, viewed

under magnification after more than three weeks of sublimation. Less cyclododecane appears to remain on the uncoated glass than on the carnauba wax coating. The partially sublimated cyclododecane layer has a very porous gauzy appearance, more so on top of the carnauba wax. Streaks in the carnauba wax coating are visible through the cyclododecane layer.

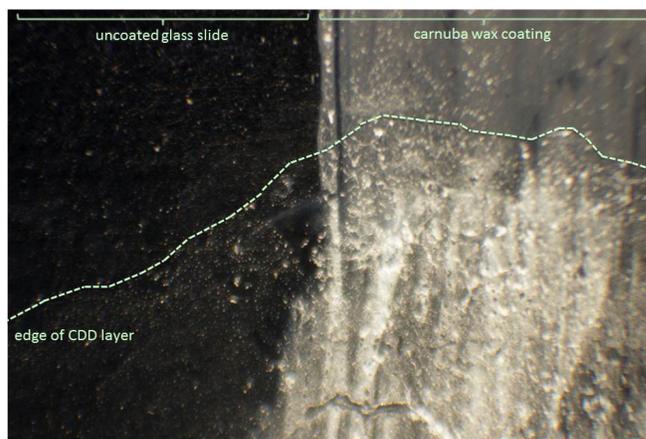


Figure 1

Conclusions

The cryo-SEM imaging and GC-MS analysis indicate that cyclododecane sublimates completely. Objects previously treated with cyclododecane do not appear to be altered as a result of the treatment, suggesting that the temporary coating does not react with substrate materials nor causes changes to them over time.

The porosity of the treated surface as well as its chemical affinity for hydrocarbon compounds may influence cyclododecane's rate of sublimation, as do the amount and thickness of cyclododecane applied.

The very "quick-n-dirty" tests with coated glass slides suggest that the cyclododecane does not visibly interact with a variety of commonly used conservation materials; further analytical investigation would be worthwhile.

It is important to distinguish between residual cyclododecane and residues of other unknown compounds. The chemistry of cyclododecane and these experimental results indicate that residual cyclododecane will sublime with time. Anything left behind after complete sublimation could be a contaminant.

As with any material manipulated for use in conservation, there is opportunity for contamination by manufacturing, tools or equipment, solvents, and handling. The heat, solvent, and/or movement of the consolidant system within a substrate could also cause interactions with materials present in the substrate.

Table 1. Adhesives and Preparation Methods

Adhesive	Preparation Method
Jade 403	commercially prepared, undiluted
Rhoplex AC234	commercially prepared, undiluted
Fish Glue (Veritas)	commercially prepared, undiluted
Butvar B-98	dissolved in ethanol
Klucel G	1% (w/v) in ethanol
PVA-AYAF	15% (w/v) in ethanol
Paraloid B-72	40% (w/v) in acetone, diluted
Aquazol 200	20% (w/v) in 1:1 ethanol:deionized water
Multiwax X-145A	as purchased
Bowling Alley Wax (100% Carnauba wax)	as purchased

Note: Commercially prepared adhesives had been previously opened. Other adhesive solutions were not prepared for this experiment, so could have been contaminated through prior use.

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Cyclododecane itself may act as a solvent for nonpolar compounds (e.g. oils, fatty acids, soaps, resins, and plasticizers) within the treated object, causing them to move. Such potential for contamination and substrate interaction exists with cyclododecane just as it does with any other system encountered in conservation treatment, whether used for temporary or long-term cleaning, consolidation, or adhesion, etc. The extent to which these potential effects can be predicted, prevented, mitigated, and reversed is an essential evaluation in choosing all treatment materials and methods.

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