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Cyclododecane in Paper Conservation Discussion

ABSTRACT

Cyclododecane is a relatively new material to conservation that has been used as a temporary consolidant, fixative, masking material, and barrier layer in many different areas of specialization. The material's most attractive characteristic is its ability to slowly sublime, converting from a solid to a gas, thereby eliminating any additional chemical or physical treatment steps for removal. To begin the session, the moderators reviewed the material's basic physical and working properties, described methods for its application, presented its use in treatments for works of art on paper and textiles, and commented on health and safety issues. Discussion followed these general themes, although there was an emphasis on methods of application. Techniques that had success or failure were discussed. Participants shared their experiences and general observations working with cyclododecane. Focus was placed on its role in paper conservation, though its application in other fields of conservation was touched upon. Generally, cyclododecane was found to have mixed success as use as a temporary fixative for works of art on paper and it was agreed that cyclododecane should be used cautiously. Treatment application should be determine on a case-by-case basis and preliminary tests on similar materials of non-value should be conducted. A sample of cyclododecane, application tools, paper samples impregnated with the material, and treatment facsimiles were passed around the group.

This open discussion took place on June 10, 2002, during the AIC 30th Annual Meeting, June 6–11, 2002, Miami, Florida. The moderators organized and led the discussion and recorded notes. Readers are reminded that the moderators do not necessarily endorse all the comments recorded and that although every effort was made to record proceedings accurately, further evaluation or research is advised before putting treatment observations into practice.

PHYSICAL AND WORKING PROPERTIES

Cyclododecane is a volatile cyclic alkane ($C_{12}H_{24}$) and is comparatively inert, as it is exclusively carbon and hydrogen compounds and is non-polar. It is a colorless, translucent material and has a wax-like consistency and good film-forming properties. Cyclododecane is solid at room temperature and is sold in the form of irregularly formed crystals. It has a melting point of 58-61°C and a boiling point of 243°C. Cyclododecane has a vapor pressure of about 0 at 20°C, 1hrPa, which is high enough to cause volatilization. It is highly soluble in non-polar and aromatic solvents and poorly soluble in polar solvents.

Cyclododecane's most attractive characteristic is that it sublimes, eliminating additional treatment steps to remove it. There was some discussion regarding how long it takes the material to completely sublime. It has been observed that a solid film of cyclododecane sublimed at a rate of 0.03 mm per 24 hours (Hangleiter et al., 1995). However, the sublimation rate is contingent upon many factors including film thickness and density, substrate porosity, atmospheric temperature and pressure, and air exchange over the surface of the film. Participants agreed that sublimation of cyclododecane takes a relatively long time, from several days to several weeks to complete. The film will begin to noticeably diminish along the edges where surface area is at its greatest. Sublimation is encouraged with increased air exchange over the surface and/or with increased temperature. This may be achieved by placing the treated object in an operating fume hood or by directing a hair dryer on a warm setting over the surface of the treated area. Conversely by reducing the airflow over the surface of the object, sublimation is retarded. For example, plastic sheeting may be used to cover or seal the object. Cyclododecane can be reduced with non-polar solvents. Trace amounts of cyclododecane can remain behind for an extended period of time, but ultimately sublime and visually disappear. Negligible deposits of a polymeric residue have been found to remain behind after sublimation is

complete. Alternative conservation materials, however, would also leave behind residues.

Some desirable working properties of cyclododecane in conservation include its film-forming properties. The hydrophobic solid has been used as a fixative for moisture-sensitive media on paper during aqueous treatment. It is non-polar and therefore could be used to protect polar solvent-sensitive material during local solvent treatment. Cyclododecane forms a relatively rigid solid at room temperature and has been used to secure flaking paint or friable substrates during cleaning in surrounding areas or during transportation. It has also been used to isolate the surface of an object during mold making.

APPLICATION METHODS

Cyclododecane can be applied as a melt or a solvent solution. In selecting an application method, the condition of the intended substrate should be considered. For example, a participant mentioned that using a brush to apply cyclododecane could cause disruption or movement of friable material. For works of art on paper, cyclododecane is generally reapplied between treatments. It was noted that cyclododecane acts as a solvent and can solubilize like materials. Caution of course should be taken to avoid applying cyclododecane to materials that are sensitive to non-polar solvents, such as wax-based media, and latex and acrylic paint. The method of application affects the film formation characteristics and, ultimately, its treatment performance. In this case, the cooling or the solvent evaporation rate could affect the film formation. Generally, it was agreed that a denser film provides a better barrier layer.

Molten

Cyclododecane melts at approximately 60°C and can be applied with a heated spatula, wax-melting stylus, such as a kistka (Ukrainian egg decorating tool) or a batik tool, hot-spraying machine, and by melting the solid in situ with aid of a heat source such as a hot air pencil. The temperature of the application tools may be controlled with a rheostat. Brush application is not recommended unless a solvent is added to lower the melting point. The kistka and batiking tools are preferred for controlled application. Upon cooling, cyclododecane will solidify to form a film. A quick temperature transition will form a dense, homogenous film. A film produced from a melt is considered to produce a thicker and denser film than that formed from a solution and therefore to have a slower sublimation rate.

The temperature of the environment, working surface, and application tool can affect the behavior of cyclododecane and therefore its film-forming properties. For example, if the environment or the substrate is too low in temperature, cyclododecane will not flow well from the heated implement or may solidify on the surface of the object rather than penetrating into it. This may be advantageous if one desires to control the flow of molten cyclododecane. However, for the temporary fixing of water-soluble media on paper, it was agreed that cyclododecane should penetrate through the paper to the verso, protecting the area throughout. One participant suggested using a heating pad to slightly warm the verso of the paper to promote penetration of cyclododecane into the paper. Molten application is particularly attractive as it eliminates the need to employ additional solvents. Avoid applying to heat-sensitive media and non-polar materials.

Solvent Solutions

Cyclododecane can be dissolved in non-polar and aromatic solvents and applied by brush, syringe, or aerosol-spray. Solvent solutions are commonly applied by brush. It is often difficult to produce a uniform film and multiple applications are often required to build up the film. Additional use of a heated spatula may be used to work it further into the support. A saturated solution should be used to produce a film layer. Concentration of solid varies with solvent choice and use of a heated stirring apparatus may be necessary to put the solid into solution. A film produced from a solvent solution is thought to produce a thinner and perhaps less dense film then that produced from a melt and therefore to sublime more quickly than a melted application.

The film characteristics are often shaped by the solvent choice. It was discussed that use of a fast-evaporating solvent can make it difficult to apply cyclododecane, as the solid can crystallize out on a brush, clog a needle and spray apparatus, or solidify out on the surface of the object. It was also noted that the size and pattern of particles formed on the object's surface appear to vary with solvent choice. A fast-evaporating solvent is more likely to form a denser, homogenous film and penetrate less into the substrate, whereas a slow-evaporating solvent appears to encourage the formation of longer needle-like particles with a more open lattice network. Application of the solvent solution to a non-porous surface will cause particles to slowly form on the substrate. Conversely, application to a porous surface will absorb the solvent and allow a dense film to form on the surface. Additional health and working hazards introduced by the solvent should be considered as well.

TREATMENT CONSIDERATIONS

Evaluate the stability of object materials and the treatment objectives. Sensitivity of object materials to heat or to hydrocarbon solvents should always be taken into consideration. Although cyclododecane is relatively transparent there is a reduced clarity in areas that are covered with cyclododecane, which could make it difficult to monitor

treated areas. It was discussed that the cyclododecane layer could develop breaks if the surface flexes or expands. For works of art on paper, paper characteristics, such as fiber length, coating, and sizing, appear to affect the way cyclododecane functions. Caution should be taken when exposing a thin paper locally treated with cyclododecane to strong force or pressure, such as that from a suction table, as it could cause irreversible deformation in paper. It was noted that tidelines, possibly from selective movement or removal of paper components, have been observed under ultraviolet illumination in areas where cyclododecane was applied. Treatments should be monitored under visual light and ultraviolet illumination.

TREATMENT CASE STUDIES

Cyclododecane has been used as a temporary fixative for water-sensitive media on paper that will undergo aqueous treatment. It has been found to offer considerable though not always complete protection during aqueous treatment. In one treatment of a water-sensitive watercolor with substantial impasto, cyclododecane was applied to highly soluble areas of media with a kistka. The drawing was then blotter washed. Cyclododecane needed to be reapplied before additional aqueous treatments were performed. In this instance, sublimation occurred quickly. Cyclododecane proved to be effective in preventing the bleeding of the media.

In another instance, as an experiment, cyclododecane was applied to paper with patches of highly soluble dye-based ink in the molten state using a kistka. On some samples cyclododecane was applied only to one side and in other samples to both sides. The samples were subject to various conservation treatments including humidification, blotter washings, and washing on a suction table and evaluated for the efficacy of cyclododecane as a fixative. In these samples, cyclododecane was a poor performer. Lateral bleeding occurred and there was substantial distortion of the paper sheet. This experiment brought to discussion the numerous variations in application that could change the results. For example, it was suggested that perhaps improved performance could be achieved upon a suction table in an effort to control the movement of the water through the paper during treatment and subsequent drying, avoiding building-up the cyclododecane layer as to possibly cause deformation of the paper. The study also emphasized that cyclododecane is not a good fixative in all cases, regardless of the application method. In these samples, cyclododecane did not appear to have dissipated over the course of a single treatment step and did not sublimate readily.

Cyclododecane was used to protect embroidery decoration containing water-sensitive dyes in a textile sampler during local aqueous treatment. Cyclododecane was melted and applied with a kistka to the embroidery decoration, saturating the embroidery threads. Then, upon a suction disk, water was introduced to textile areas adjacent to the embroidery to locally reduce liquid staining and former bleeding of the dye. Cyclododecane was reapplied between treatments. The embroidery was successfully protected during treatment.

One participant mentioned using cyclododecane to protect the back of a daguerreotype plate during cleaning of oxidation or tarnish. Cyclododecane was applied to the plate by warming it in a Marvelseal pouch, then by cutting a hole in the pouch and pouring it onto the plate. After cleaning treatment, cyclododecane was allowed to sublime. It took one month to completely sublime from the non-absorbent surface. Cyclododecane did not effectively protect the back of the plate from the cleaning treatment, though it was thought that the results were better than if cyclododecane had not been applied.

Other uses for cyclododecane that were discussed included its use as a facing adhesive. A very thin sheet of non-woven polyester was placed over an unstable area and brushed with a saturated solvent solution of cyclododecane. Cyclododecane has been used most often (and successfully) as a consolidant on inorganic materials. In the treatments discussed, cyclododecane was generally applied molten to help with the temporary stability of objects, particularly in excavation or onsite situations. Cyclododecane was cast into sheets so that small flakes could be broken off to slip under unstable areas and then melted with a heat source.

HEALTH & WORKING HAZARDS

The Material Safety and Data Sheet (MSDS) classifies cyclododecane as having low toxicity. Contact may cause skin irritation or rash and eye irritation, such as tearing, discomfort, or blurring of vision. Breathing vapors and mist should be avoided and a respirator should be worn when judged appropriate. Eye protection, such as safety glasses, is recommended when the possibility exists for eye contact through splashing or spraying of the material. Additionally, neoprene gloves should be used when handling solvents. Cyclododecane should be kept away from sparks and flames, as it has a flashpoint of >93°C, and caution should be taken when heating the material, as it can release combustible vapors. Cyclododecane should not be mixed with strong oxidants. It is important to note that the MSDS does not indicate the Permissible Exposure Limit and the Threshold Limit Value for cyclododecane. Concern was expressed that areas remain to be studied regarding the effects of the material. A member of the group pointed out that cyclododecane has been used in the chemical industry as an additive for fragrances and synthetic waxes. It was generally agreed that further study is

needed before any definitive information could be given and that one should err on the conservative side when handling and using cyclododecane. It should also be noted that when introducing another solvent, the health and working hazards for that solvent should be considered.

STORAGE

Cyclododecane is sold in plastic bags within metal containers. The material should be stored well sealed, with the plastic bag tied and the metal container tightly closed, and in a well-ventilated, cool place. This will prevent unnecessary sublimation of the material and amalgamation of the crystals. One participant asked what to do if the crystals amass in the storage container and a suggestion was made to use a heated spatula to scoop out the material.

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