The Use of Siloxane-Based Cleaning Systems to Clean Water-Sensitive Painted Surfaces

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Introduction

John Scott's "Thornbush Blues Totem" was made in 1990 and entered the collection of the Smithsonian American Art Museum in 1994. The large sculpture is made of formed and welded steel, aircraft cable, and copper alloy fittings. All surfaces of the piece were primed and painted with the exception of the cables and fittings. The painted surfaces appear to have been brush applied: there is significant variation in paint thickness throughout, visible brush strokes, and scattered drips of paint. The painted surfaces have a shiny appearance.

The sculpture came to the conservation lab from storage previous to display in the exhibition *African American Art. Harlem Renaissance. Civil Rights Era and Beyond* presented by the Smithsonian American Art Museum in 2012. A preliminary examination of the sculpture in storage identified the conservation treatment priorities as removing residues of adhered urethane foam residues as well as large strips of an adhesive foam tape.

The large passages of adhesive foam tape that were found along the sides of the sculpture, at the bottom edges of the base, appear to have been on the sculpture in 1994. It is speculated that the tape was applied in the past to facilitate moving the large, heavy sculpture and/or to protect a floor surface. The residues of adhered urethane foam were due to a packing decision made by the museum registrars department without consulting conservators.

The surface of the sculpture had a light layer of dirt and grime overall. In areas where foam residue and tape were found on top of the paint film it was clear that a combination of solvent and mechanical action would be needed. Before treatment took place there was no time for analysis of paint media. This took place during and after treatment. As with the majority of conservation treatments, analytical support is not readily available and treatment decisions must be made without this knowledge.

The paint surfaces were tested for solubility in a wide range of solvents including filtered tap water, pH 7 buffered water (Bis-Tris), petroleum benzine, xylene, ethanol, and benzyl alcohol. In all cases the paint was soluble. Based on previous experience by one of the authors using silicone-based materials for cleaning water-sensitive surfaces it was decided to test that class of materials [1].

Silicone-Based Materials

It is worth reviewing the nomenclature of silicone-based materials as it can be confusing. Silicon is the free element listed on the periodic table. The element silicon does not exist in nature as a free element and must go through a chemical reaction to be released from silica or quartz (silicone dioxide: Si-O2).

The silica is heated with a carbon source such as wood in a carbothermic reaction. The reaction isolates silicon which can then be reacted with methyl chloride in the Rochow-Muller direct process producing methylchlorosilanes. These silicon compounds contain both methyl groups and chlorine and can be distilled to dimethyldichlorosilane which is hydrolyzed to produce siloxanes and silicones.

The term silicone was first used to describe synthetic polymers containing a Si-O backbone in 1857 [2]. Technically the term is applied to materials with the Si-O bond however the term is now widely used to refer to substances that contain a silicon atom.

Silicone fluids, more accurately described as linear and cyclic volatile methylsiloxanes (VMS), are characterized by their special surface properties. Their low surface tension is related to the length of the Si-O and Si-C bonds which are able to adopt low energy configurations at interfaces [3]. This property has made them ideal for release agents.

Silicone fluids are used in the cosmetic industry to formulate water-in-oil emulsions. Silicone materials are extremely non-polar making them suitable for cleaning applications on water-sensitive surfaces. Their low-surface tension means they are able to wet out surfaces and undercut soiling material. The neat VMS materials are characterized by low toxicity and no odor [4].

In testing silicone-based materials for cleaning applications in conservation our approach has been to start with the neat silicone solvents and then explore building emulsions or micro-emulsions by adding low HLB surfactants (either polyether modified polysiloxanes or trisiloxanes or ethoxylated aliphatic alcohols) to the silicone solvents [5]. Some dimethicone crosspolymers, e.g. Velvesil, come mixed in a dense gel form to which polar solvents (including water) may be added creating an emulsion.

Testing and Treatment

On the John Scott sculpture, testing was carried out in order to determine which silicone-based material or combination of materials would allow for removing the foam adhesive tape without solubilizing the original, water-sensitive paint surfaces.

The solvent cyclomethicone D5 was tested first since it had a slow evaporation rate which would give us working time to observe the behavior of the solvent and interaction with the paint surface. Cyclomethicone D5 is a pure form of the solvent where there is a ~~5~~ ten-member ring of alternating silicon and oxygen atoms with each silicon atom having two methyl groups attached.

While there was no immediate reaction with either the paint films or the adhesive of the tape other than wetting the surface, the slow evaporation rate appeared to lend itself to slowly undermining the adhesive of the foam tape.

The use of a shaped and sharpened wooden applicator was the primary mechanical tool required to remove the tape and carrier.

The cyclomethicone D5 made the physical manipulation of the scalpel easy due to the slick interaction of the solvent with all surfaces: the scalpel blade could more easily slide over the slightly uneven paint surface and under the foam adhesive tape.

Hexamethyl disiloxane, a linear form of a silicone solvent, was also tested. The supplier of our hexamethyl disiloxane, Shepard Brothers Inc. in La Hambra, CA, uses the abbreviation DMF for their line of linear silicone solvents (not to be confused with dimethylformamide). The 0.65 indicates viscosity (measures in units of stokes at 25 degrees C), a parameter that is used widely for distributing linear silicone fluids. This material was able to wet well onto the surface and appeared to penetrate into the plastic carrier of the tape. The process of mechanically removing the tape and foam adhesive was similar to that described above, however the working time was less because it has a much faster evaporation rate than the cyclic silicone solvents.

As the silicone solvents did not appear to have much of a solubilizing effect on the adhesive itself it was decided to explore using the commercially prepared silicone-based gels. These gels are crosspolymers that contain silicone. They are supplied in a concentrated gel form and the solvents are generally cyclomethicones. When we used these gels we first diluted them using small amounts of the silicone solvents. The gels were tested alone and then as emulsions with water or another solvent.

Figure 1. Mixing solvent with gel

A dimethicone / polyethylene glycol (PEG) crosspolymer commercially named KSG-210 by Shin Etsu was emulsified with a small amount of 1-methoxy-2-propanol. A second test was carried out with another emulsion by substituting the emulsified phase with n-butanol. The paint did not show any sensitivity to either mixture. The adhesive bond of the tape was undermined to some degree. The tape and foam adhesive had to be removed mechanically. The area was rinsed with hexamethyl disiloxane and cyclomethicone D5.

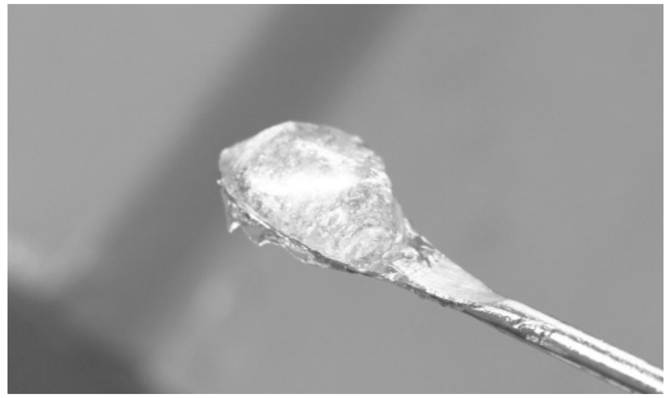


Figure 2. Gel and solvent mixed for application

Lastly, another dimethicone / polyethylene glycol (PEG) crosspolymer commercially named USG-107A by Shin Etru was used. The USG-107A has reportedly greater phenol substitution groups and vinyl functional groups than the KSG-210 which were described to us by the manufacturer as lending to better spreading/wetting properties.

The silicone gel USG-107A was thinned with the linear silicone solvent hexamethyl disiloxane. While this mixture wet on to the surfaces as others had, it was found to have the most effective working time. As no solvent combination was found to dissolve the foam adhesive easily, mechanical action was required to remove the tape. This mixture was found to be the most effective at providing physical proper-

Figure 3. Mechanical removal after the adhesive bond of the tape is weakened by the solvent gel.

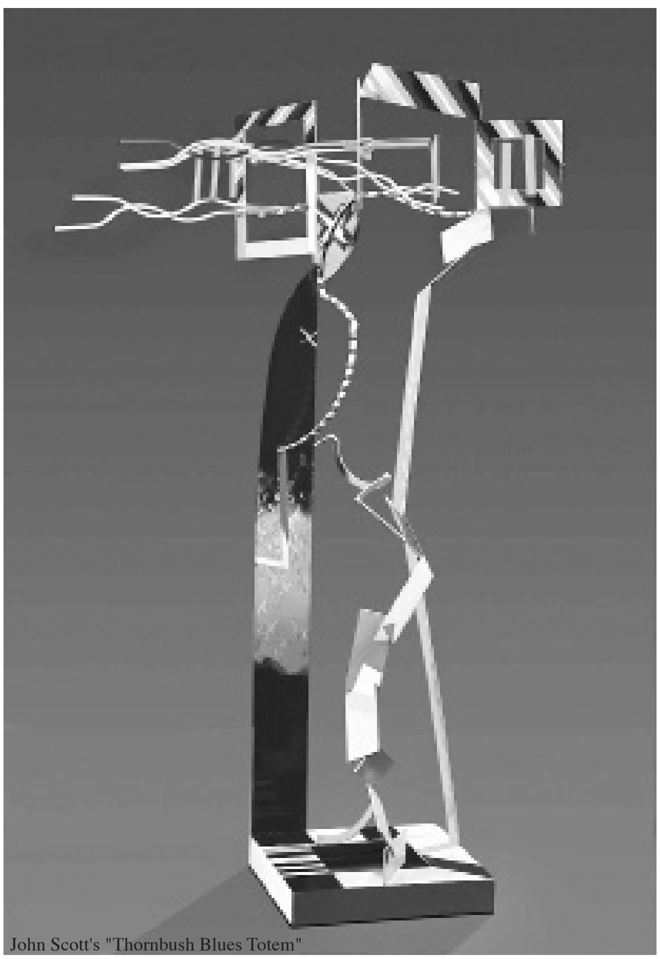
ties to facilitating moving a scalpel over an uneven surface. The gels and emulsions tested were cleared with repeated applications of solvent (either the cyclomethicone D5 or the hexamethyle disolixane). Cyclomethicone D5 has a very slow evaporation rate, and it is normally the major component in the solvent blends. The low molecular weight straight-chained silicone solvents, such as the hexamethyldisiloxane evaporate much faster. In addition, the linear forms of the solvent pose less of a threat to the environment [6].

Conclusion

The treatment of the sculpture was effective in allowing us to remove different forms of residues from a water-sensitive surface. Due to limitations in time and access to analytical equipment, samples were taken after cleaning was underway for analysis of the paint. The paint was characterized as a methyl methacrylate-butyl methacrylate-alkyd mixture by FTIR and Py-GC-MS [7].

While the paint surfaces of the John Scott have been described as shiny, it is important to note that they are very uneven due to the hand application of the paint layers. Thus, working mechanically over the uneven surface under the foam tape was challenging since one could not see the surface of the object. The silicone-based materials were very useful in both allowing for us to physically manipulate materials safely while also not solubilizing the original painted surface.

We look forward to the results of ongoing PhD research into the efficacy and clearance of silicone, currently being carried out by Professor Richard Wolbers [8].



John Scott's "Thornbush Blues Totem"

Acknowledgements

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Endnotes

1. In the summer of 2009 Richard Wolbers introduced this material during a Cleaning Acrylic Paintings meeting. The meeting was a collaboration between the Getty Conservation Institute, the Getty Museum, the Tate, and Winterthur/University of Delaware Program in Art Conservation. The subsequent use of cyclomethicone and Velvesil Plus are described in “Developing cleaning systems for water-sensitive paints by adjusting pH and conductivity” by Tiarna Doherty, Chris Stavroudis, and Jennifer Hickey. *Paintings Specialty Group Postprints*. American Institute for Conservation 2010. Forthcoming.

2. “The Evolution of Silicones,” http://www.chemistry-explained.com/Ru-Sp/Silicone.html (Accessed 27 August 2012).

3. O’Lenick, Anthony J. Jr. “Basic Silicone Chemistry – A Review” in *Silicone Spectator*, First published in August 1999. www.siliconespectator.com/articles/Silicone_Spectator_January_2009.pdf (Accessed 27 August 2012)

4. Cull, Ray A. and Stephen P. Swanson. “Volatile Methylsiloxanes: Unexpected New Solvent Technology,” *Handbook for Critical Cleaning*, Barbara Kanegsberg, Ed. CRC Press, 2001. 147-156.

5. For more information about these surfactants see Chris Stavroudis, A Surfeit of Surfactants, *WAAC Newsletter*, Volume 34. Number 3. September 2012: 24 – 27.

6. “Octamethylcyclotetrasiloxane (cyclomethicone D4) has been identified as bioacumulative and therefore potentially harmful to the environment. Because of its silicon content, it is recycled differently from hydrocarbon solvents. This means that the solvent should not be mixed with other solvents for hazardous waste but disposed of separately unless explicitly instructed otherwise by your waste hauler. In general, the family of volatile methylsiloxanes are considered safe for human exposure but there is growing concern over long term exposure, particularly in women, and particularly those with silicone-based implants. The decamethylcyclopentasiloxane (cyclomethicone D5) and polydimethylsiloxanes remain widespread in personal care products.” See “Developing cleaning systems for water-sensitive paints by adjusting pH and conductivity”

7. Email correspondence with Jennifer Giaccai and the Analytical Report in object record file, Conservation Department, Smithsonian American Art Museum.

8. Personal communication with Richard Wolbers. October 2012.