Anti-Graffiti Clearcoat

by **Liza A. Capino**, The Sherwin-Williams Company

Graffiti markings are everywhere. Several types of "anti-graffiti" coatings have been developed over the years to address this ever-increasing problem. Some are one-time-use only; others are semi-permanent. Most are highly durable, crosslinked coating systems. Most can be made graffiti-resistant by the incorporation of surface additives such as fluoro/silane compounds, which orient themselves at the surface providing the marking repellency. All of these encounter some limitations.

A new anti-graffiti coating that addresses some of those limitations has been developed. Being a one-pack moisture-cure, this organosiloxane coating eliminates the inconvenience of mixing multiple components typical of the crosslinked systems such as polyurethanes and epoxies—the two most common types of high-durability anti-graffiti coatings. In addition, unlike the more traditional, economical single-pack coatings such as alkyds and latexes, this coating provides excellent resistance to weathering and moisture penetration. Moreover, it offers some advantages in cleanability. Pressurized water is typically sufficient to wash off the graffiti markings from this coating. However, stronger cleaning agents may also be used for persistent markings due to the coating's excellent solvent (MEK) resistance. Because of its outstanding adhesion, it can be applied over properly prepared fresh or previously coated concrete or masonry. The preparation, property evaluation, and application of this coating are discussed in this article.

INTRODUCTION

Graffiti, defined as "designs, scribbles, writings, drawn on a wall or other exposed surface" by the *Webster Dictionary*, are timeless methods of communication. In prehistoric times, they were considered forms of writing and sacred rituals. In modern times, to some, graffiti is an art form exhibited in the public domain; but to most, they are a nuisance. Any defacement of private or public property as an advertisement of political, religious, social, commercial, personal, or gang-related messages without the consent of the owners or official authority is considered vandalism, and therefore, has to be dealt with accordingly under the law. In large cities such as Philadelphia, New York, Chicago, Los Angeles, and Pittsburgh, anti-graffiti campaigns have been launched since the early 1990s through massive community supported clean-ups, a government database-

This paper was presented at the ACA-sponsored Advancements in Coatings Series on Coatings for Concrete, Las Vegas, NV, 2010.

driven graffiti-tracking system, prevention of sale of spray paints or permanent markers to minors, and more police vigilance.

Several organizations have established efforts to prevent graffiti. The National Council to Prevent Delinquency (NCPD) is a non-profit organization funded by the paint and related industries. Concerned with stopping illegal or harmful use of legitimate paint products, it created the Anti-Graffiti Project. The main goal is to prevent and reduce graffiti vandalism through public awareness, education, and advisory functions for fair regulations of spray paints.[1]

The International Municipal Lawyer Association (IMLA) has published model ordinances on anti-graffiti as a suggested guideline for the local governments in drafting ordinances. Models include provisions on prevention and removal of defacing materials.[2] One such prevention measure is to include the use of protective coatings that facilitate graffiti removal.

TYPES OF ANTI-GRAFFITI COATINGS

Anti-graffiti coatings can be classified according to their service life as sacrificial, semi-permanent, or permanent. Sacrificial coatings are single-use type, typically wax-based coatings that can be removed using a hot water pressure washer. This means that this type has to be applied after every graffiti removal.

Semi-permanent coatings, such as latexes, acrylics, and alkyds, have low-to-mediocre resistance to cleaning solvents that can cause softening, wrinkling, or complete dissolution of the coatings. They can withstand a few repeated graffiti removal processes.

Permanent type coatings are highly durable coatings such as urethanes, epoxies, siloxanes, and other crosslinked systems that can accommodate far more graffiti removal processes than the semi-permanent products. Most can be made graffiti-resistant by the incorporation of additives, particularly fluorinated or siliconized types, which orient themselves at the surface providing marking repellency. Some even have functionalities that attach themselves onto the resin matrices. However, once the thin layers of additives erode from such coatings upon repeated cleaning and scrubbing, the anti-graffiti property diminishes or in some cases disappears completely.

A sub-type of the permanent anti-graffiti coating, which is the subject of this article, is a one-pack, moisture-cure, 100% elastomeric polysiloxane (abbreviated MCE siloxane) that offers an advantage over the traditional permanent type due to the ease of graffiti removal. Pressurized water is typically sufficient to clean off the markings.

Stage 1: **Hydrolysis**

$$\text{R-Si(X)}_2\text{-O-[Si(CH}_3)_2\text{-O]}_n\text{-Si(X)}_2\text{-R} + 2\ \text{HOH}\downarrow \longrightarrow$$

$$\text{OH-Si(R)(X)-O-[Si(CH}_3)_2\text{-O]}_n\text{-Si(R)(X)-OH} + 2\text{HX}\uparrow$$

Stage 2: **Condensation**

$$2\ \text{OH-Si(R)(X)-O-[Si(CH}_3)_2\text{-O]}_n\text{-Si(R)(X)-OH} \longrightarrow$$

$$\text{OH-Si(R)(X)-O-[Si(CH}_3)_2\text{-O]}_n\text{- (R)(X)-}\boxed{\text{Si-O-Si-}}\text{(R)(X)- [O-Si(CH}_3)_2]_n\text{-O- Si(X)(R) OH} + \text{HOH}\uparrow$$

X = hydrolyzable end groups
HX = neutral by-product
OH = condensation site to form silicone group Si–O–Si

Figure 1—Curing mechanism: hydrolysis followed by condensation.

MOISTURE-CURE ELASTOMERIC POLYSILOXANE ANTI-GRAFFITI COATING

Raw Materials

The silicone elastomers consist of three-dimensional polydiorganosiloxanes.[3] The precursor oligomers have some functional units such as hydroxyl, which react with the silane crosslinkers to yield a polymer with terminal hydrolyzable functional groups such as oximino or alkoxy groups that cleave off as neutral moieties on curing. In addition to the silane crosslinkers, filler materials such as pyrogenic or precipitated silicas may also be added for chain reinforcement via hydrogen bonding. Other extender pigments, additives, and solvents may be incorporated to meet specific process and service requirements. Tin catalyst is a popular choice for promoting the crosslinking reaction. The processing is carried out in a practically moisture-free reaction vessel.

Curing Mechanism

Upon application, the MCE siloxane coating cures at ambient condition by reacting with moisture in the air. The first stage is the formation of the silanol groups accompanied by the liberation of the hydrolysis by-products. The second stage is the condensation of the silanol groups with either the starting polymer chain or the silicone macromolecules as illustrated in *Figure* 1.

As water is taken up for the hydrolysis reaction, it is probable that it may also be given off in the condensation process. Therefore, in the limited access to moisture, i.e., underneath the coating surface or in an atmosphere with very low relative humidity, crosslinking still occurs in a reasonable amount of time, as demonstrated by the dry time data in *Figure* 2. The data illustrate that while there are variations in the dry-to-touch and tack-free times, the through-cure times are practically the same. These variations could be just the differences in the rates of evaporation of the solvent

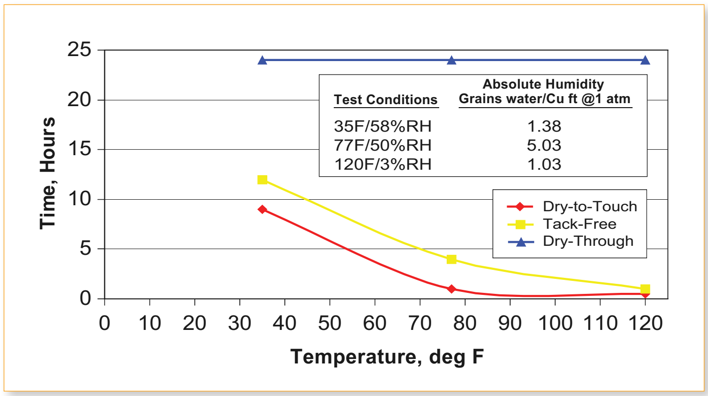

Figure 2—Dry times at various temperature/relative humidity conditions. Although there are differences in the dry-to-touch and tack-free times at various atmospheric conditions, which could be just the differences in the rates of evaporation of the solvent in the coating, the through-cure dry times are practically the same.

in the coating at those various atmospheric conditions. In other words, whether the absolute humidity in grains of water per cu ft at 1 atm pressure is 1.03 or 5.03, the dry-through time still remains the same as manifested in their comparable methyl ethyl ketone (MEK) resistance.

Coating Properties

The properties of the MCE siloxane clearcoat formulation are shown in *Table* 1.

Application Properties

Although the MCE siloxane clearcoat could be applied unreduced by brush or roller over properly prepared fresh or previously coated concrete or masonry, it is recommended that 5% mineral spirits by volume be added for airless spray application. With this amount, the VOC is still maintained at less than 2.1 lb/gal (<250 g/L). In cases when further reduction is necessary, the VOC-exempt reducer p-chlorobenzotrifluoride (PCBTF) is recommended. *Figure* 3 shows the viscosity profile of the clearcoat with the corresponding % volume of solids upon reduction. Test results indicate that beyond 15–20% reduction the drop in viscosity becomes less apparent. Thus, further reduction does not offer additional advantages in the spray application appearance.

Knife-Cut Adhesion

The MCE siloxane clearcoat has excellent adhesion over properly prepared fresh or previously coated concrete, having an 8–10 rating with knife-cut adhesion testing (ASTM D6677-07). It also has good adhesion over itself as seen in *Figure* 4.

Chemical Resistance, Covered-Spot Test

In the chemical resistance, covered-spot evaluation, the reagents are placed on the panels and immediately covered with watch glasses. Panels are inspected for swelling, loss of gloss, and discoloration after 72 hr. Overall, the MCE siloxane clearcoat exhibits better results than the 2K polyurethane and the 2K silane epoxy/amine coatings as shown in *Table* 2 and *Figure* 5.

Heat Resistance

Heat resistance is evaluated by placing the panels in the oven at 300°F for 24 hr and immediately submerging them in tap water. The panels are then examined for any color change, cracking, checking, blistering, or loss of adhesion. *Figure* 6 shows the relative heat resistances of the various coatings. All panels exhibit no film cracking or loss of adhesion. The MCE siloxane and 2K polyurethane show comparable color resistance, which is much better than the 2K silane epoxy/amine wherein severe yellowing occurs.

Table 1—MCE Siloxane Clearcoat Formulation

Properties	
Color	Clear
Gloss @ 60°	Semi-gloss (40-50 units)
Weight solids	75%
Volume solids	72%
Density	7.8 lb/gal (0.94 g/ml)
VOC	1.95 lb/gal (234 g/L)
Brookfield viscosity, #6 spindle	100 poise @ 10 rpm / 30 poise @ 100 rpm
Leneta sag	25 mils (635 microns)
Dry-to-touch/tack-free, 77°F/50% RH	1 hr / 24 hr
Film	Elastomeric
Recommended dry film thickness	6-9 mils; 150–225 microns
Solvent	Mineral spirits
Flash point	105°F (41°C)

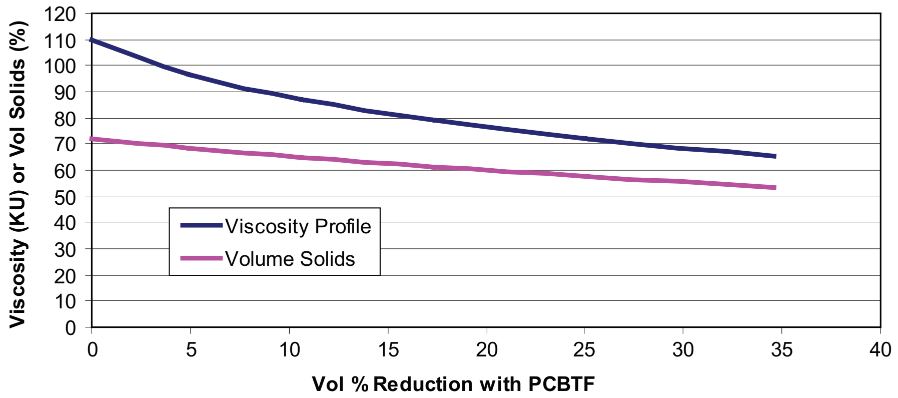

Figure 3—Viscosity profile of the MCE siloxane clearcoat upon reduction with p-chlorobenzotrifluoride.

Figure 4—Adhesion results. After a two-week cure, a second coat is applied at the lower portion of each panel. Both panels have excellent adhesion over the concrete and over the first coats.

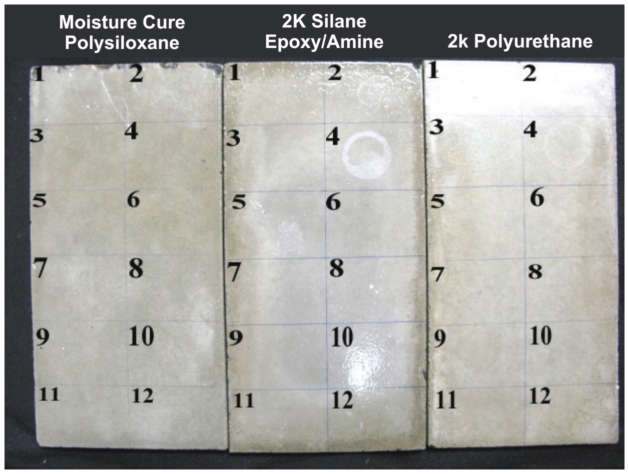

Figure 5—Chemical covered-spot test. After 72 hours of exposure to chemical, the MCE siloxane shows the best overall results, followed by the 2K polyurethane. The 2K silane epoxy/amine ranks last.

Table 2—Results of the Chemical Resistance, Covered-Spot Test

No.	Chemicals	Moisture-Cure Polysiloxane	2-K Silane Epoxy / Amine	2-K Acrylic Polyurethane
1	10% Citric acid	Excellent	Excellent	Fair
2	Tilex™ mildew remover	Good	Good	Good
3	Isopropanol	Excellent	Excellent	Excellent
4	1% Sodium hydroxide	Excellent	Poor	Fair
5	Methyl ethyl ketone	Excellent	Poor	Excellent
6	Crude oil	Good	Excellent	Excellent
7	25% Sodium chloride	Excellent	Excellent	Excellent
8	1% Sulfuric acid	Excellent	Fair	Excellent
9	Industrial degreaser	Excellent	Excellent	Excellent
10	Mild detergent	Excellent	Excellent	Excellent
11	1% Ammonia solution	Excellent	Excellent	Excellent
12	Citrus-based cleaner	Excellent	Excellent	Excellent

Rating: Excellent = No effect; Good = Slight discoloration, gloss drop, or swelling;
Fair = Moderate discoloration, gloss drop, or swelling; and Poor = Severe discoloration, gloss drop, or swelling.

Graffiti Resistance and Cleanability

The graffiti resistance evaluation involves the cyclic QUV exposure, defacing, and cleaning of the panels. This procedure is similar to the one utilized by the Texas Department of Transportation (TX DOT) with the exception of using QUV instead of a Xenon Arc Weatherometer. Coatings are applied by brush over concrete blocks at the recommended film thickness. The panels are cured for 24 hr at 77°F/50% RH and exposed in the environmental chamber for a total of 2000 hr. After each 500 hr of exposure, a graffiti marking is applied that is allowed to cure for 72 hr before cleaning with MEK. A total of four graffiti marking materials are used:

1. Acrylic aerosol spray lacquer
2. Alkyd aerosol spray enamel
3. Epoxy aerosol spray paint
4. Permanent ink marker

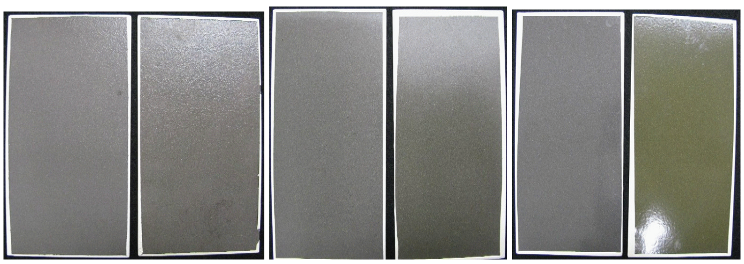

Figure 6—Heat resistance. The left panel of each pair is not tested; the right one, after 24 hr of exposure at 300°F and immersion in water thereafter. No cracking, blistering, or loss of adhesion occurs. MCE siloxane and 2K polyurethane have excellent yellowing resistance; 2K silane epoxy/amine has severe yellowing.

MCE siloxane shows no signs of graffiti staining upon casual inspection and the coating remains intact without any streaking, cracking, pinholing, discoloration, or other obvious coating degradation, as shown in *Figure* 7.

Continuing on to 4600 hr of QUV exposure and defacing process, the relative performance of the MCE siloxane and the 2K epoxy silane/amine is shown in *Figure* 8. The result indicates much better weatherability, graffiti resistance, and cleanability with MCE siloxane than with the 2K silane/epoxy amine.

As mentioned earlier, what differentiates the performance of MCE siloxane anti-graffiti coating from other types of permanent graffiti-resistant coatings is its ease of cleanability with water. *Figure* 9 demonstrates its relative washability compared with the 2K silane epoxy/amine, 2K polyurethane, and sacrificial anti-graffiti clearcoats. Using only a wiper wet with tap water, the aerosol spray paints could be cleaned off from the MCE siloxane. Some ink markers may contain dyes that can penetrate through the coating, leaving some shadowing. Those dyes may eventually fade on exposure to sunlight.

Graffiti markings from the surfaces of the other types of anti-graffiti coatings are only removed, either completely or partially, using a stronger cleaner (MEK). Citrus cleaner does very little in the case of persistent markings. Even after repeated defacing and cleaning with MEK, the MCE siloxane remains intact, graffiti-resistant, and easy to clean, as shown in *Figure* 9A.

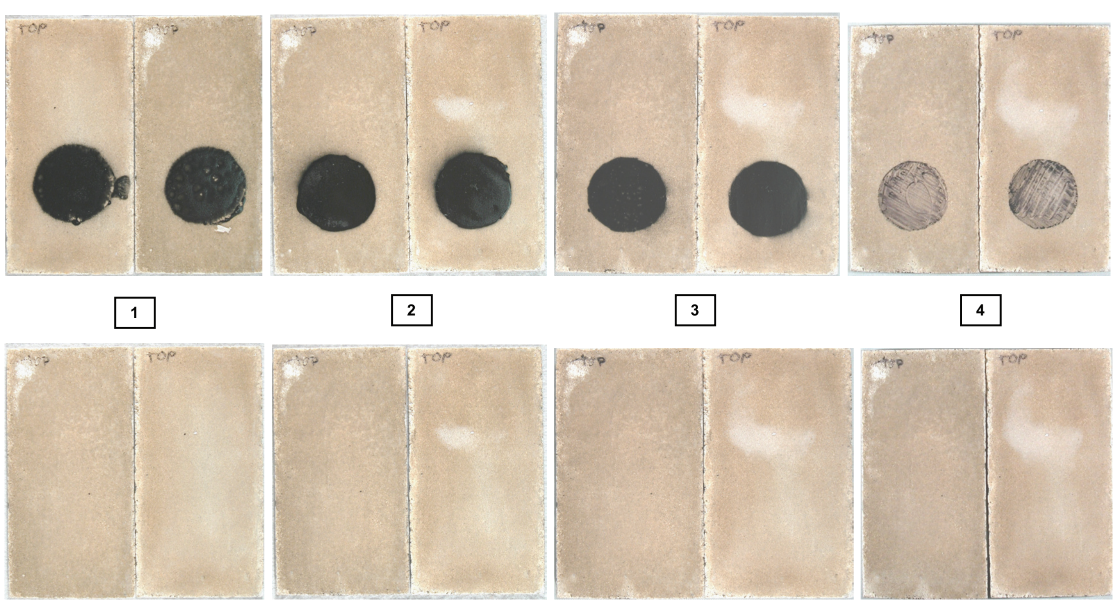

Figure 7—Graffiti cleanability of MCE siloxane clearcoat using MEK. Top row: Graffiti material applied after each 500-hr increment of QUV exposure. (1) Acrylic; (2) Alkyd; (3) Epoxy; (4) Permanent Ink. Bottom row: Panels after cleaning with MEK exhibit no signs of graffiti staining or any film deterioration.

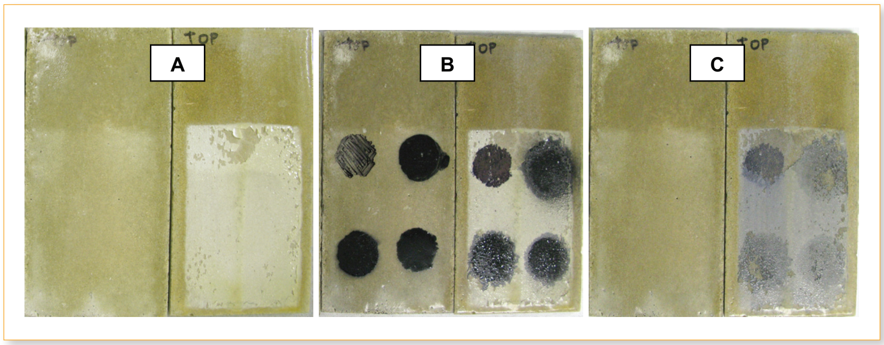

Figure 8—Comparative QUV exposure and cleanability**.** The left panel on each pair is the MCE siloxane; the right one, 2K silane epoxy amine. A = Panels after 4600 hr of QUV exposure; B = Panels after defacing with aerosol spray paints and permanent marker; C= Panels after cleaning with MEK.

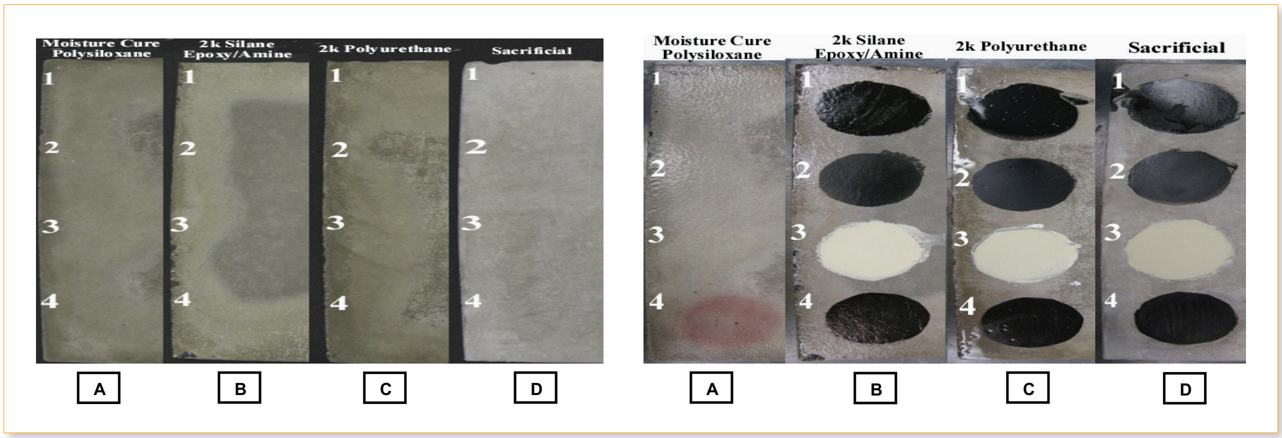

Figure 9—Comparative cleanability with water-wet wipers. Panels on the left photo, before defacing; panels on the right, after defacing and cleaning with water**;** A = MCE siloxane; B = 2K silane epoxy amine; C = 2K polyurethane; D = Sacrificial coating.

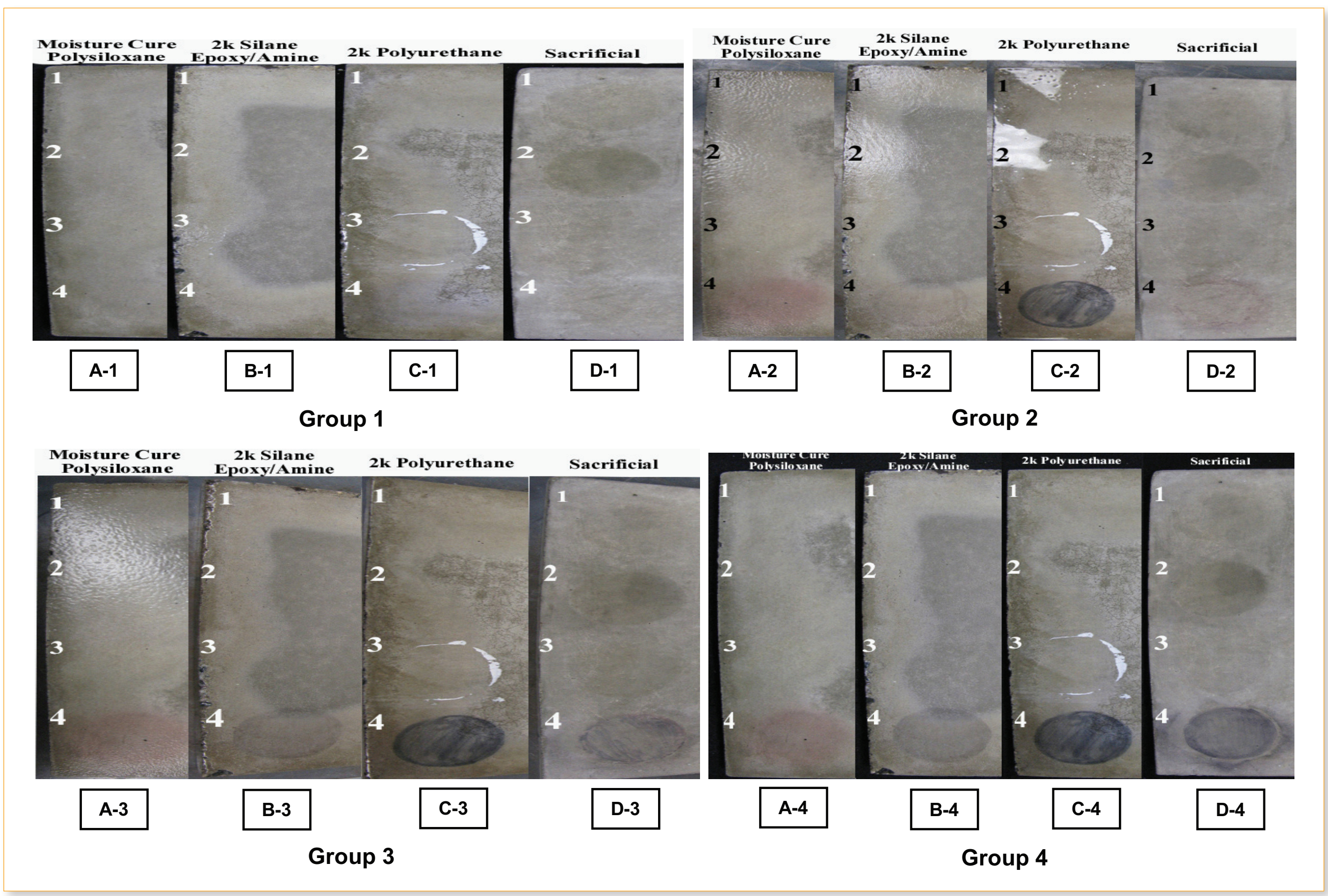

Figure 9A—Comparative cleanability with MEK-wet wipers. Group 1 = Defaced and cleaned once; Group 2 = Defaced and cleaned twice; Group 3 = Defaced and cleaned three times; Group 4 = Defaced and cleaned four times.
A = MCE siloxane; B = 2K silane epoxy amine; C = 2K polyurethane; D = Sacrificial coating.

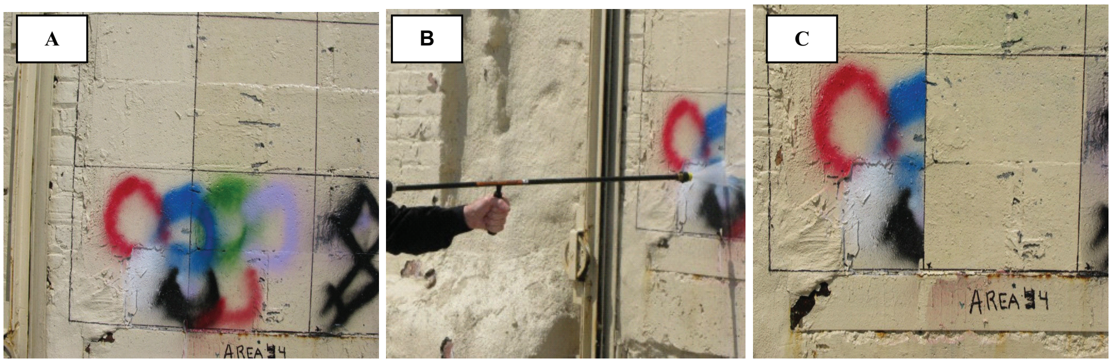

Figure 10—Exterior application, defacing, and cleaning. (A) Defaced with aerosol spray paints; (B) Power washing; (C) Power washed. On left portion of wall without MCU, siloxane graffiti remained; on right portion with MCE siloxane anti-graffiti clearcoat, graffiti was removed.

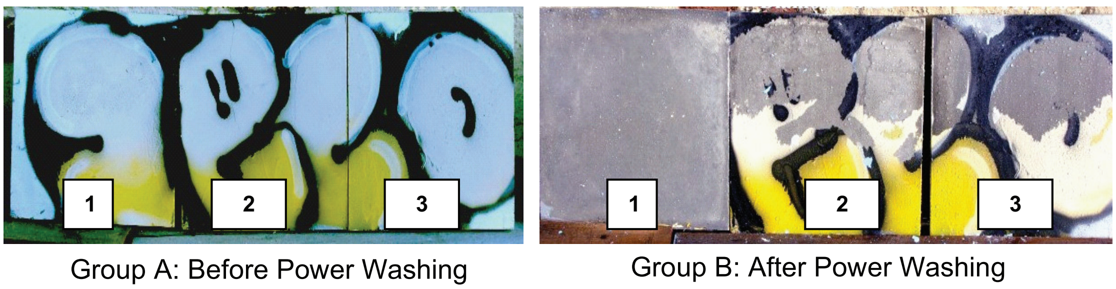

Figure 11—Comparative cleanability using power wash. Clearcoats applied: (1) MCE siloxane, (2) 2K polyurethane, and (3) 2K silane epoxy/amine. Aerosol paints applied one week later. Power washing done one week thereafter. Group A on the left: before power washing. Group B on the right: after power washing.

Exterior Exposure

The MCE siloxane reduced 5% with mineral spirits was applied by airless spray over an exterior concrete wall, as shown in *Figure* 10. The wall was prepared by power washing with a 3000-psi water jet using a 15° tip with a 25-ft hose. The coating was applied and allowed to cure at various times of one day, one week, four weeks, six months, and one year before applying aerosol paints. The graffiti markings were also allowed to cure at different time intervals before power washing. A portion of the wall was not coated with the MCE siloxane as a control. As the results in *Figure* 10 show, the graffiti was barely removed, if at all, from the surface without the MCE siloxane, whereas it was completely removed where the MCE siloxane was applied. It was particularly difficult to clean up the area where the black paint was sprayed. It was necessary to hold the tip very close to the surface—as close as half-an-inch distance—to remove the residual black paint. The graffiti removal process also responded very positively when MEK was used. After the cleaning, the surface was inspected and found to have no visual damage to the MCE siloxane.

The process of defacing and cleaning of the wall continues. This is done to assess the resilience of the paint with the cycle of graffiti application and removal over some period of time.

What Makes It Work?

It is a well-known fact that the flexible nature and weak intermolecular forces of polydimethylsiloxane give rise to its exceptionally low surface energy. Only fluoropolymers have lower values.[4] The non-migratory, crosslinked polymer with low surface energy makes the adhesion of many coatings (graffiti) unusually low. *Figure* 11 demonstrates that MCE siloxane has better cleanability compared with the 2K polyurethane and 2K silane epoxy/amine using power wash.

The analytical data on the surface energies (*Table* 3) support the comparative ease of graffiti

Table 3—Comparative Surface Energies and Contact Angles

Clearcoat	Surface Energy (mN/m)	Contact Angle (°) with Water
MCE siloxane	11.56 + 0.43	110.8 + 1.76
2K polyurethane	19.44 + 0.50	96.4 + 1.26
2K silane epoxy/amine	26.53 + 0.41	103.8 + 2.89

removal results shown in *Figure* 11. The MCE siloxane has the lowest surface energy. Due to the mobility of the hydrophobic methyl groups, which tend to orient at the surface, the contact angle with water is the highest, which results in a high degree of water beading or repellency.

CONCLUSION

The moisture-cure elastomeric anti-graffiti polysiloxane clearcoat has advantages over the traditional permanent and sacrificial coatings because of its outstanding ease of graffiti-marking removal. Power washing is typically sufficient. For persistent defacing, materials with stronger cleaning solvents can be used. It can withstand repeated cleaning processes much better than other types due to its excellent solvent resistance and weathering properties. The MCE siloxane adheres directly over properly prepared concrete or over sound previous coatings. It is convenient to apply because it is a one-pack system. In addition, it can be applied by brush, roller, and airless spray. It is anticipated that this product will find tremendous application opportunities in various markets, in particular, bridges and highways, rails and transit systems, commercial and public buildings, schools, and sports complexes. CT

References

1. http://www.anti-graffiti.org/about.htm
2. Willett, R.T., "A Community Strategy for Combating Graffiti Vandalism," presented at Metropolitan Washington Council of Governments Conference, VA, March 1996.
3. Pachaly, B., et al., "Silicones," Wacker Chemie AG, Wiley-VCH, pp 34-39, 2005.
4. Jones, R.G., et al., (Ed.), *Silicone-Containing Polymers,* Kluver Academic Publishers, Ch 8, 213-231, 2000.

AUTHOR

Liza A. Capino, Protective and Marine Coatings, The Sherwin-Williams Company, Chicago, IL; lxcapino@sherwin.com.