1K permanent Anti-graffiti for Architectural

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Graffiti has emerged as a pervasive issue worldwide, impacting communities on multiple fronts. It contributes to financial losses by causing damage to local businesses, declining ridership on transportation systems, and reducing property values. The removal of graffiti exacerbates the problem, as it is not only a costly process but often requires the use of harsh solvents or chemical cleaners that can adversely affect the environment by emitting VOCs and HAPs.

Free from fluorine- and tin-based compounds, this coating allows graffiti tag removal using high-pressure water without relying on harsh solvents.

Over the years, several types of anti-graffiti coatings have been developed to address the persistent issue of graffiti. However, a significant number of these coatings fall into the sacrificial category. Sacrificial coatings either establish a weak bond with the substrate, facilitating the removal of both the coating and the graffiti tags, or incorporate fluorine-based additives. These additives can migrate to the surface, reducing surface energy and making graffiti removal easier. Since these additives deplete over time, periodic reapplication of the coating becomes necessary. Conversely, commonly available permanent anti-graffiti coatings come with their own set of limitations. Many are presented as two-component (2K) systems, which may not always align with the preferences of end-users. Additionally, some

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one-component (1K) permanent options include fluorine-based additives, making them susceptible to evolving regulations and legislations imposed by environmental organizations.

We have developed a new 1K permanent anti-graffiti coating using elastomeric polysiloxanes, ideal for architectural substrates such as concrete, masonry, and dry walls. As a single-component moisture-cure system, it eliminates the inconvenience of mixing multiple components. Free from fluorine- and tin-based compounds, this coating allows graffiti tag removal using high-pressure water without relying on harsh solvents. Moreover, it maintains anti-graffiti properties even after exposure to artificial and natural weathering.

Introduction

Graffiti, defined as unauthorized writing or drawing on a public surface,[1] poses an escalating issue in urban areas globally. Graffiti is commonly encountered in public places, such as walls facing streets, traffic signs, statues and monuments, bridges, parking garages, park benches, and transportation systems, including trains, subways, buses, and transit stations. Regardless of its message—political, social, religious, personal, or gang related—if defaced without the consent of the property owner or official authority, graffiti is considered an act of vandalism.

Graffiti exacerbates financial losses by harming local businesses, diminishing ridership on transportation systems, and devaluing property. Furthermore, graffiti has a pronounced cumulative impact; its initial manifestation in a location tends to attract additional instances. In cases where a sizable portion of the graffiti is associated with gangs or offensive content, the affected area is more prone to an increased gang presence, leading to heightened crime rates and turf conflicts.

Graffiti vandalism imposes a significant financial burden on communities worldwide.[2]

In the United States, the annual expense for graffiti removal averages around $12 billion. The removal process is intricate, often necessitating the use of potent solvents that can contribute to the emission of volatile organic compounds (VOCs) and hazardous air pollutants (HAPs). Simultaneously, the act of tagging graffiti itself generates VOC emissions. It is reported that approximately 4,862 tons of VOCs were emitted from the graffiti sector in the US in 2008.[3]

This article focuses on the development and evaluation of 1K permanent anti-graffiti coatings based on elastomeric silicones.

Anti-graffiti coatings fall into three categories: sacrificial, semi-permanent, and permanent. Sacrificial coatings can be removed using a high-pressure washer taking the graffiti with it. These single-use coatings are usually wax-based and form weak bonds with the substrate to allow for easy removal. Sacrificial coatings require frequent reapplication to protect the surface. Semi-permanent coatings are usually acrylic or alkyd-based and can withstand a few subsequent graffiti-removal processes before deterioration by the cleaning solvents. Lastly, permanent coatings are usually based on crosslinked polymeric networks such as epoxies, acrylics, and polyurethanes, where sufficient crosslinking reduces the chance of the polymer to swell and absorb graffiti paint.

In most cases, these coatings contain silicone or fluorine-based additives that migrate to the surface and reduce the surface energy, minimizing the adherence of graffiti paints to facilitate the removal. Despite their good initial performance, after multiple graffiti removals, these additives will deplete, reducing the effectiveness of anti-graffiti paint drastically. Moreover, emerging regulations and legislation prohibiting the use of fluorine-based additives are changing the market trends and customer preferences toward fluorine-free coatings. Furthermore, the traditional two-component (2K) nature of these coatings can lead to application errors. Therefore, there is a growing need for one-component (1K) permanent coatings that are fluorine-free and ensure long-term anti-graffiti performance.

Elastomeric silicones offer high water repellency, high gas permeability, and outstanding release properties due to their low surface energy (20 MJ/m^2) and high flexibility of the silicone network. This outstanding flexibility is due to larger bond angles than their carbon counterparts, which enables a high degree of segmental movement and large void volume (The Si–O–Si angle ranges from about 130° to 180°, whereas the C–O–C angle is typically 107–113°).[4] Additionally, Si–O bonds forming the siloxane backbone are stronger than C–O bonds in conventional organic backbones (452 vs. about 360 KJ/mol), resulting in superior exterior durability, gloss and color retention, and heat resistance. These unique properties make elastomeric silicones an exceptional option for the development of durable permanent anti-graffiti coatings that enable graffiti removal with high-pressure water only without the need to use harsh solvents.

This article focuses on the development and evaluation of 1K permanent anti-graffiti coatings based on elastomeric silicones. These siloxane-based anti-graffiti coatings (abbreviated as "siloxane AG") were prepared via reacting hydroxyl-terminated polydimethylsiloxanes with organo-functional silicone crosslinking agents to form a multi-functional network. The coatings were cured under ambient moisture and were evaluated for ease of graffiti removal right after curing, as well as after artificial and natural weathering. The coatings were also studied for hydrophobicity and lipophobicity via contact angle measurements. Finally, the coatings were further evaluated for water uptake and water vapor permeability, as critical indicators for the long-term durability of architectural coatings. Results indicated that siloxane AG coatings exhibited effective removal of graffiti tags using high-pressure water. However, for the benchmarks, chemical graffiti removers were necessary to clean the surface. Additionally, the siloxane AG coatings maintained their high performance even after prolonged weathering. In summary, devoid of tin and fluorine compounds, with less than 150 grams VOCs per liter, and easily removable with high-pressure water, siloxane AG coatings present a prominent and sustainable alternative to current commercial options.

Experimental

Formulation of the Coatings

The formulation of siloxane AG coatings is for the most part similar to other architectural coatings. However, the manufacturing of these coatings can only be carried out under moisture-free and in an inert environment with a nitrogen blanket, which prevents premature gelation. The main ingredients in such coatings are listed below.

Elastomeric Silicone Binder

The polymeric network in these systems consists of hydroxyl-terminated polydimethylsiloxanes, which were reacted with excess amounts of multi-functional organosilane crosslinking agents under moisture-free conditions. As depicted in **Figure 1**, this initial condensation reaction forms tetra-functional structures, where the terminal X groups are hydrolyzable and the stage for subsequent ambient moisture curing. Suitable crosslinkers include alkoxysilanes, oximinosilanes, acetoxysilanes, aminosilanes, amidosilanes, and aminoxysilanes that have at least three hydrolyzable groups.[5]

Reinforcing Fillers

Pyrogenic and precipitated fumed silica can be added to the silicone elastomer to achieve optimal rheology and thixotropy control, as well as enhanced mechanical properties via hydrogen bonding.

Solvents

Aliphatic solvents, such as mineral spirits (MS), and VOC-exempt solvents, such as tert-butyl acetate (TBAc), are the preferred choices for adjusting the viscosity of these coatings. Other solvents may be used; however, all combinations must be tested to ensure clarity of the coating, solvency, and stability. Weak solvent combinations can lead to a loss of cure, clarity, or even precipitation in the coating.

Catalysts

Although tin-based catalysts are a popular choice to accelerate crosslinking in such systems, they can be toxic and cause negative environmental impacts. Therefore, the siloxane AG coatings that are discussed in this paper are tin-free.

Other Ingredients

Other ingredients such as additives, pigments, and extender fillers could be added to these coatings to meet specific service or process requirements.

As an example, **Table 1** provides a baseline formulation for a white anti-graffiti coating.

TABLE 1
Starting Point Formulation for White Anti-graffiti Coating

Ingredient	Function	weight (g)
Siloxane AG	Clear anti-graffiti coating	58.00
HOLCOSIL IP White	Pigment paste	32.35
Tert-Butyl acetate	Solvent	9.65
Total		**100**

Application and Curing of the Coatings

The siloxane AG coating is particularly suitable for mineral building substrates such as concrete, brick, limestone, natural and artificial stone, and plaster. It can be applied either with brushes/rollers or by airless sprayers. This coating should be applied on properly prepared fresh or previously coated surfaces at temperatures above 5 °C, with a wet film thickness of 7 to 10 mils (~178 to 254 microns). It should be noted that dilution with aliphatic solvents such as MS or VOC-exempt options such as TBAc might be required when the spray method is used. **Figure 2** demonstrates the viscosity profile of the siloxane AG coatings as a function of % weight of solvent used for reduction. It should be noted that viscosity readings were done at a shear rate of 13/s after 180 s using an MCR Paar Physica rheometer.

FIGURE 1
Basic synthetic chemistry of elastomeric silicones.

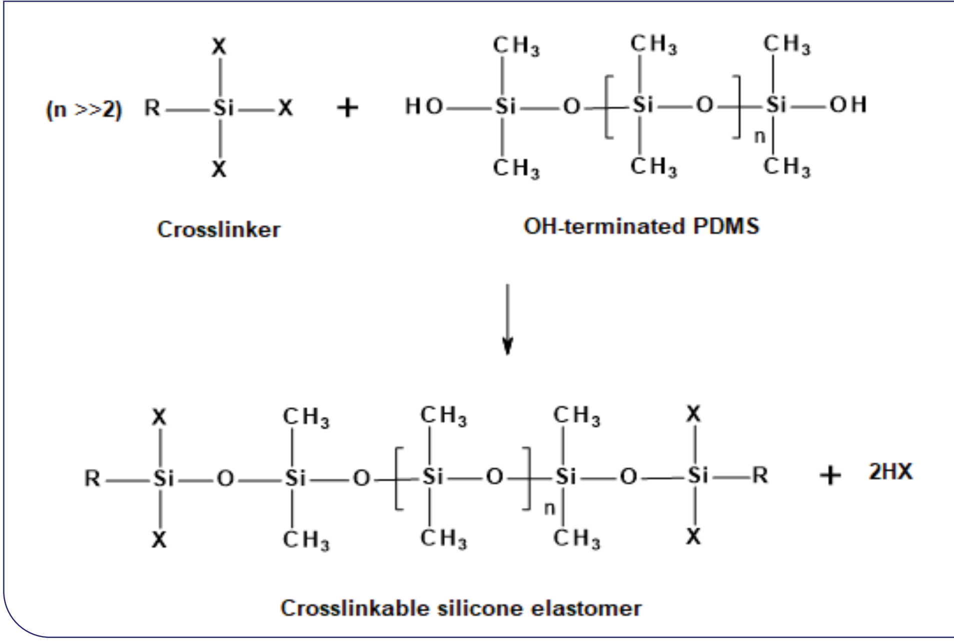


FIGURE 2
Effect of solvents on viscosity profile of siloxane AG coating.

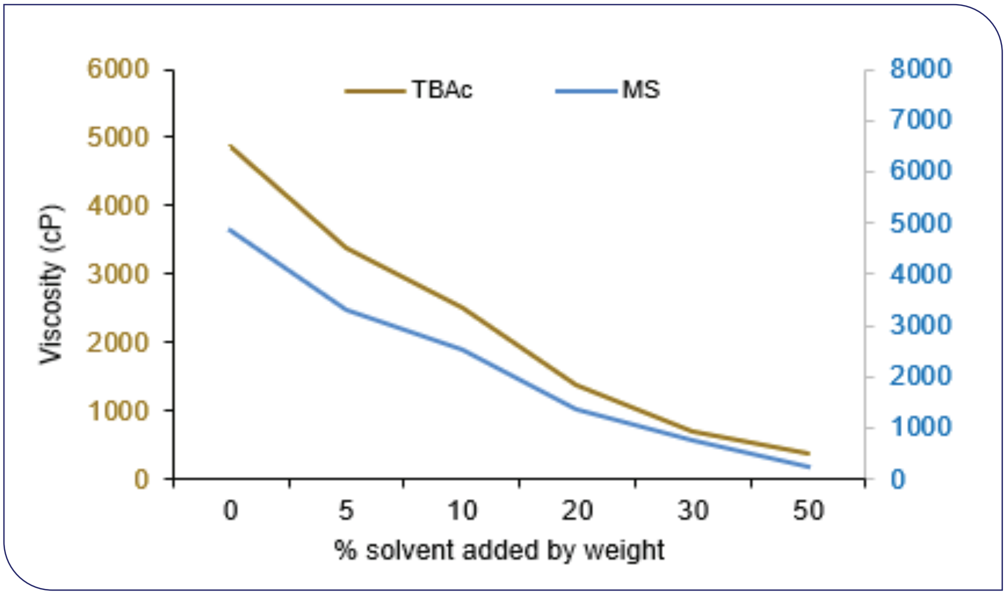
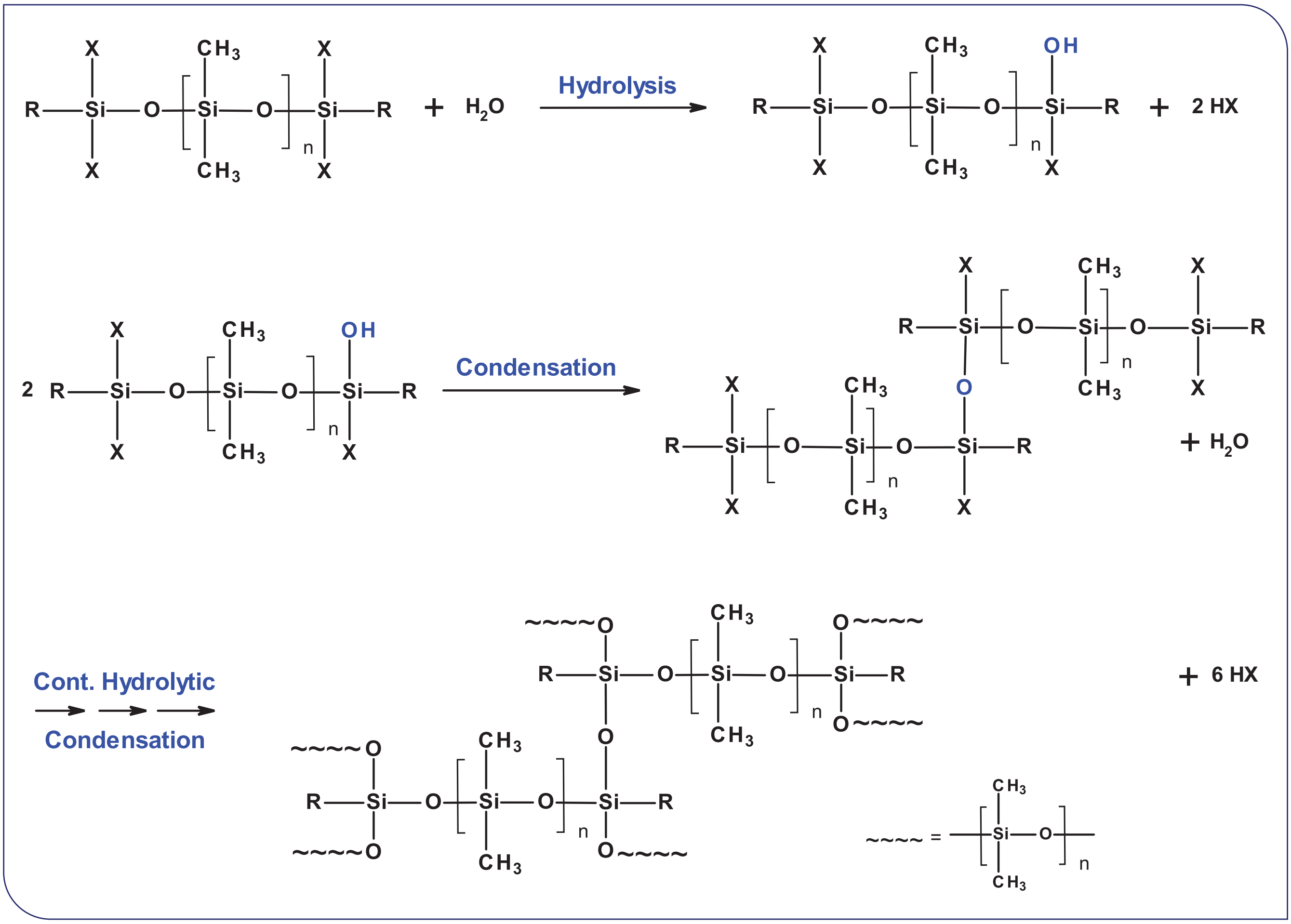


FIGURE 3
Hydrolytic condensation curing of siloxane AG coating.



As illustrated in **Figure 3**, the curing mechanism is based on the hydrolysis of the X groups represented in **Figure 1** in the presence of ambient moisture, followed by condensation of the formed silanol groups to develop polysiloxane networks.

Results and Discussions

Generic Characteristics of the Siloxane AG Coating

Table 2 summarizes the generic characteristics of the permanent siloxane AG coating, which were performed using various ASTM methods as indicated below.

Water Vapor Transmission

Water Vapor Transmission Rate (WVT), or Water Vapor Permeability (WVP), serves as a measure to assess the breathability of coatings. It indicates the amount of water vapor that passes through a material per unit area per unit time. Coatings with low WVT impede evaporation, potentially trapping water within the cementitious substrate, and consequently, significantly reducing its service life. WVT of the anti-graffiti coatings was measured according to ASTM D1653, using the wet cup method at 23 °C and 50% relative humidity. WVT for the siloxane AG coating was calculated to be 8.5809 grams per m^2 per 24 h (0.5125 grains per ft^2 per 1 h), while the WVP was calculated to be 20.7018 perms.

Graffiti Resistance and Removal

The effectiveness of siloxane AG coating for its anti-graffiti properties on concrete was evaluated by pressure washing according to ASTM D6578 as described below.

Removal of Freshly Applied Graffiti Tags from Coatings That Have Been Subjected to Artificial Weathering.

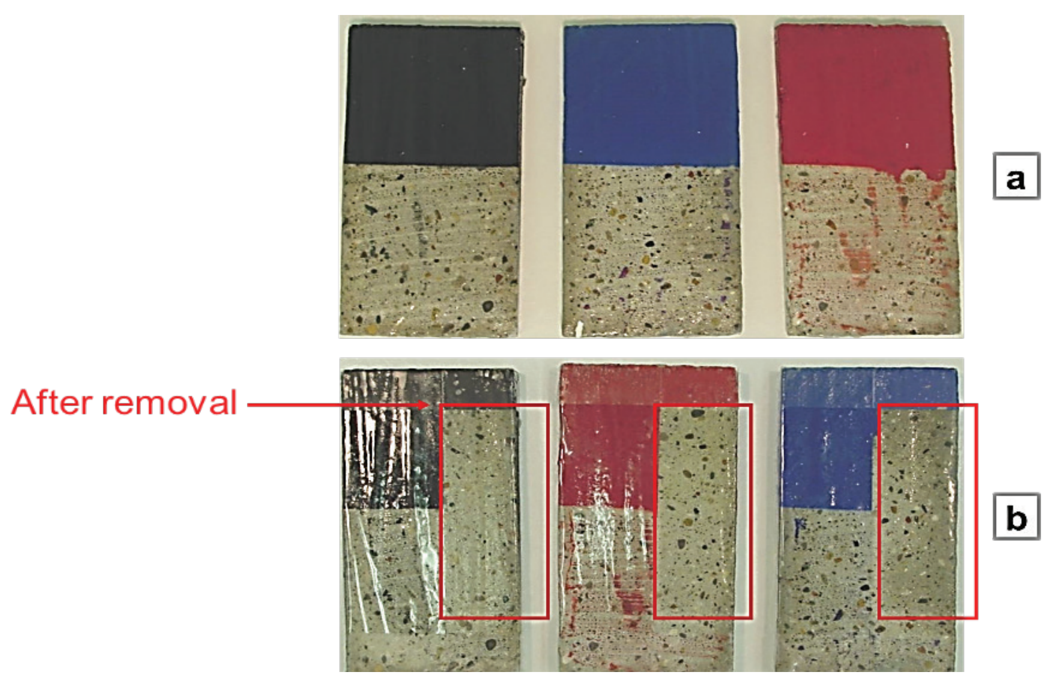
Coatings, applied on concrete panels with a wet film thickness of 7 to 10 mils using rollers, were cured under ambient conditions for 24 h. Subsequently, the coatings were weathered for 1500 h in a QUV-A tester following ASTM G 154 standards, involving alternate cycles of 8 h of UV exposure at 60 °C and 4 h of condensation at 50 °C. Afterward, the coatings were tagged with various graffiti, including red, blue, and black spray paints and permanent markers. The graffiti tags were allowed to dry at ambient conditions for 72 h. The tags were then removed with high-pressure water and were visually rated for the effectiveness of graffiti removal, color change, and loss of gloss. As demonstrated in **Figure 4**, the graffiti tags on artificially weathered samples were effectively removed by power washing. This signifies the enduring effectiveness of the siloxane AG coatings in graffiti removal even after prolonged artificial weathering.

The graffiti removal evaluation also involved the investigation of color change (delta E) and gloss retention during the QUV exposure via spectrophotometry. As an example, **Figure 5** illustrates the spectrophotometry results for coatings that were tagged with black spray after every 250-h increment of QUV-A exposure. The readings were

TABLE 2
Characteristics of the Permanent Siloxane AG Coating

Properties		Test Methods
Appearance of the coating	Translucent viscous liquid	N/A
Appearance of the film	Clear Elastomeric film	N/A
Weight Solids (%)	90 ± 5	ASTM D2369
Volume Solids (%)	85 ± 5	ASTM D2697
Specific gravity	0.9571 ± 0.0015	ASTM D1875
VOC (g/L)	< 150	ASTM D3960
Dynamic viscosity (cP), 25° /13 1/s	~ 5000	ASTM D445
Flash Point (°C)	37	ASTM D3278
Sag resistance (mils)	30	ASTM D4400
Tack-free time (h), 25° / 50% RH	< 4	ASTM D5895
Tensile strength (psi)	91	
Elongation (%)	218	ASTM D412
Modulus (psi)	56	
T_g (°C)	-120 ± 5	ASTM D3418

FIGURE 4
Removal of fresh graffiti from artificially weathered coatings. (A) Tagging the weathered coatings with graffiti after 1500 h of QUV-A exposure. (B) Graffiti removal with high-pressure water after 72 h.



In the United States, the annual expense for graffiti removal averages around $12 billion.

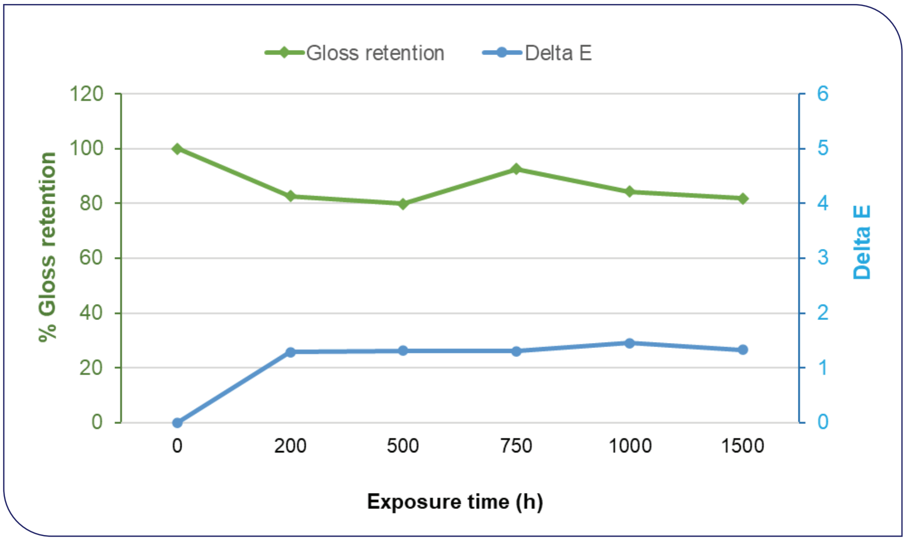


FIGURE 5
Color change and gloss retention of the siloxane AG coating as a function of exposure time.

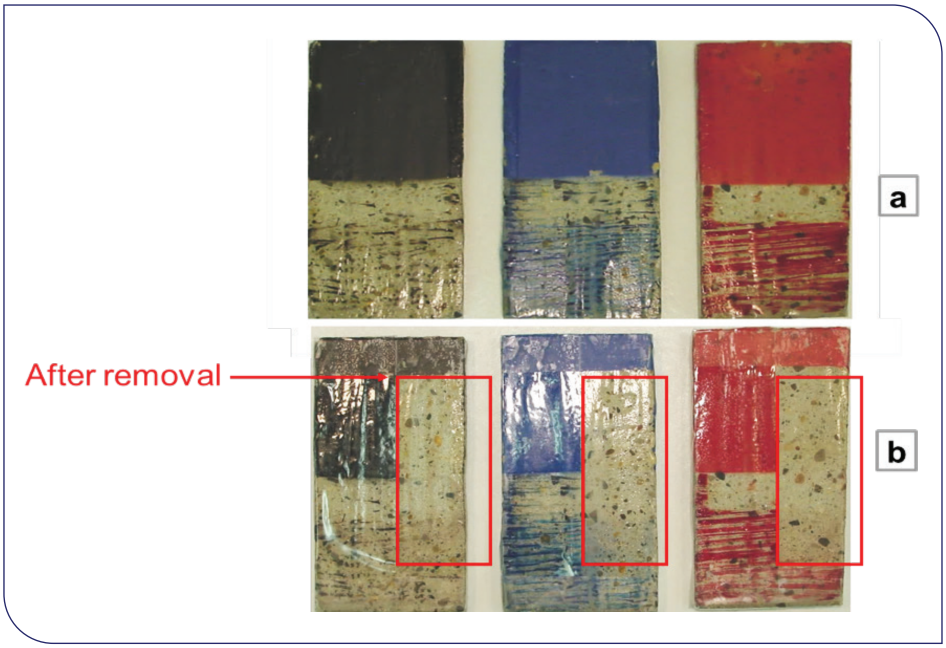


FIGURE 6
Removal of aged graffiti from siloxane AG coatings. (A) Tagged coatings, which were aged for 1500 h under QUV-A exposure. (B) Graffiti removal with high-pressure water.

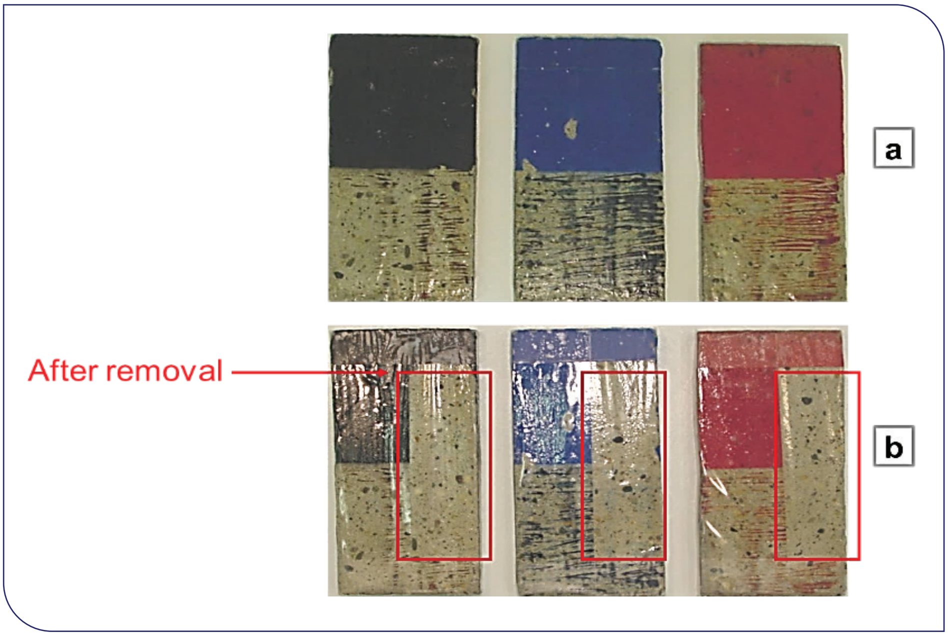


FIGURE 7
Removal of graffiti from naturally weathered siloxane AG coatings. (A) Tagging the coatings after 30 days of outdoor exposure. (B) Graffiti removal with high-pressure water.

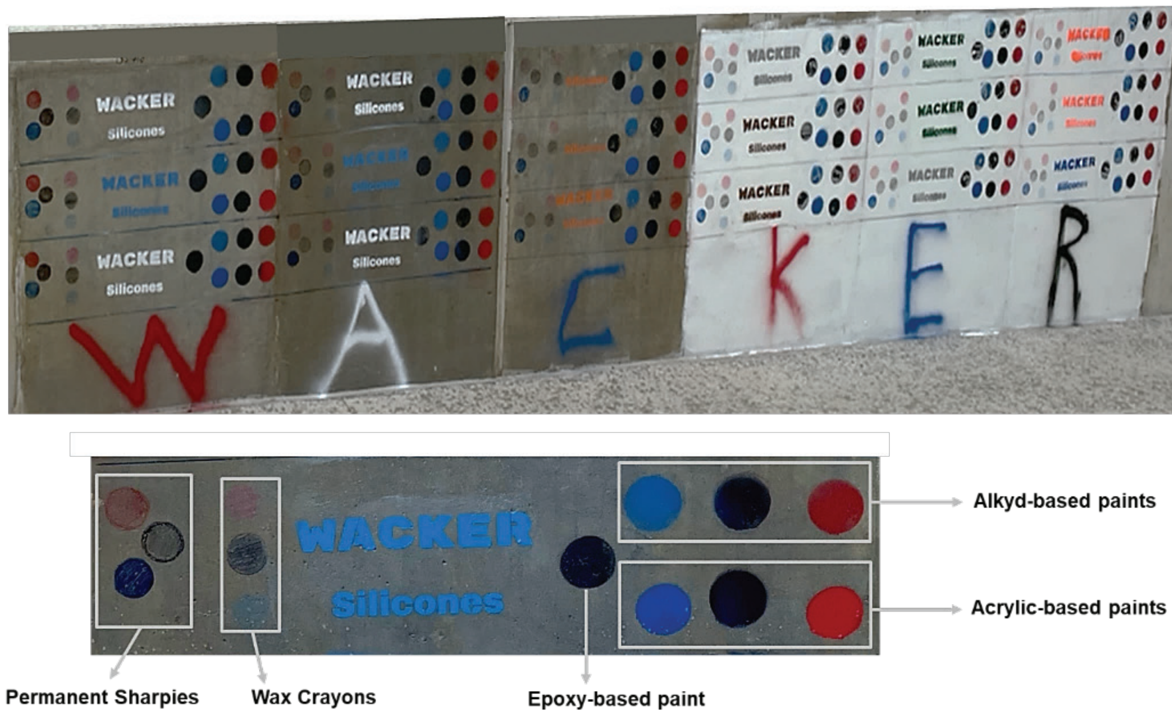


FIGURE 8
Tagging the siloxane AG coatings applied on a vertical wall, facing south, Ann Arbor, MI.

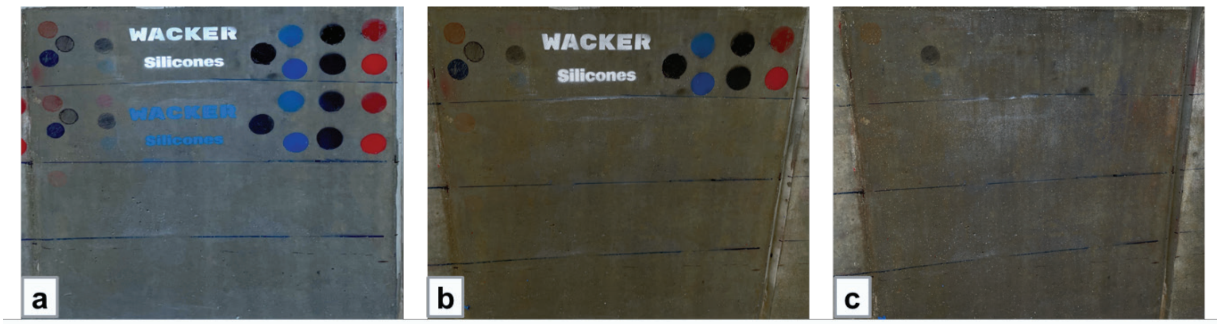


FIGURE 9
Removal of graffiti from the vertical wall shown in Figure 7. (A) after 1 week, (B) after 3 weeks, (C) after 5 weeks of outdoor exposure.

performed after graffiti removal and before placing the samples back in the QUV for continued weathering. The results showed that the coatings retained more than 80% of their initial gloss, while demonstrating color change values of less than 2. This outstanding weathering is probably due to the strong Si-O bonds, which make polysiloxanes extremely resistant to photooxidation.

Removal of Aged Graffiti Tags After the Tagged Panels Have Been Subjected to Artificial Weathering.

The coatings were applied, cured, and tagged as described in section 3.3.1. The tagged samples were then artificially weathered for 1500 h under the conditions described in section 3.3.1. As shown in **Figure 6**, the aged graffiti tags were successfully removed by power washing with minimal color or gloss change. This further substantiates the enduring anti-graffiti performance over time.

Removal of Freshly Applied Graffiti Tags from Coatings That Have Been Subjected to Natural Weathering.

The coatings were applied, cured, and exposed to outdoor conditions for 30 days in Ann Arbor, MI, facing south at an angle of 45°. After this aging period, the coatings were tagged with graffiti and subjected to high-pressure water washing after 72 h. As demonstrated in **Figure 7**, the graffiti tags on naturally weathered samples were effectively removed through power washing, with minimal change in appearance.

Removal of Aged Graffiti Tags After the Tagged Panels Have Been Subjected to Natural Weathering.

The coatings were applied to a vertical wall facing south in Ann Arbor, MI. After curing for 7 days under ambient conditions, various graffiti, including acrylic- and alkyd-based spray paints, permanent Sharpie, and wax crayons in red, blue, and black colors, were applied to the coatings. Additionally, black epoxy-based spray paint was used for tagging (**Figure 8**). Subsequently, the graffiti tags were subjected to natural weathering for 1 week, 3 weeks, and 5 weeks before removal using high-pressure water. As depicted in **Figure 9**, the power washer effectively removed all spray and Sharpie graffiti. Minimal color change caused by red Sharpie after 3 and 5 weeks of aging also diminished over time with exposure to sunlight. Although wax crayons were not entirely removed by power washing, they could be easily wiped off with a wet cloth.

Comparison to Benchmarks

Two commercial anti-graffiti coatings, one based on an acrylic fluoropolymer and the other on polyurethane, were employed as benchmarks. These benchmark coatings were applied and cured according to the recommended procedures before being subjected to graffiti tagging.

Anti-graffiti Performance

The cured coatings were tagged using alkyd-based aerosol sprays in red, blue, and black colors, and allowed to dry for 72 h before tag removal. As demonstrated in **Figure 10**, the tags on the polyurethane benchmark proved entirely non-removable with high pressure water, while only partially removable on the acrylic fluoropolymer. Subsequently, a commercial graffiti remover chemical was used to remove the graffiti on benchmarks. Although it yielded partial tag removal, it fell short of complete effectiveness, particularly for the black color. Conversely, the siloxane AG, enabled complete and effortless removal of tags in all colors.

FIGURE 10
Graffiti removal. From left to right: polyurethane, acrylic fluoropolymer, and siloxane AG coatings. (A) Coatings after curing, (B) coatings after tagging, (C) tag removal with power wash, (D) chemical tag removal.

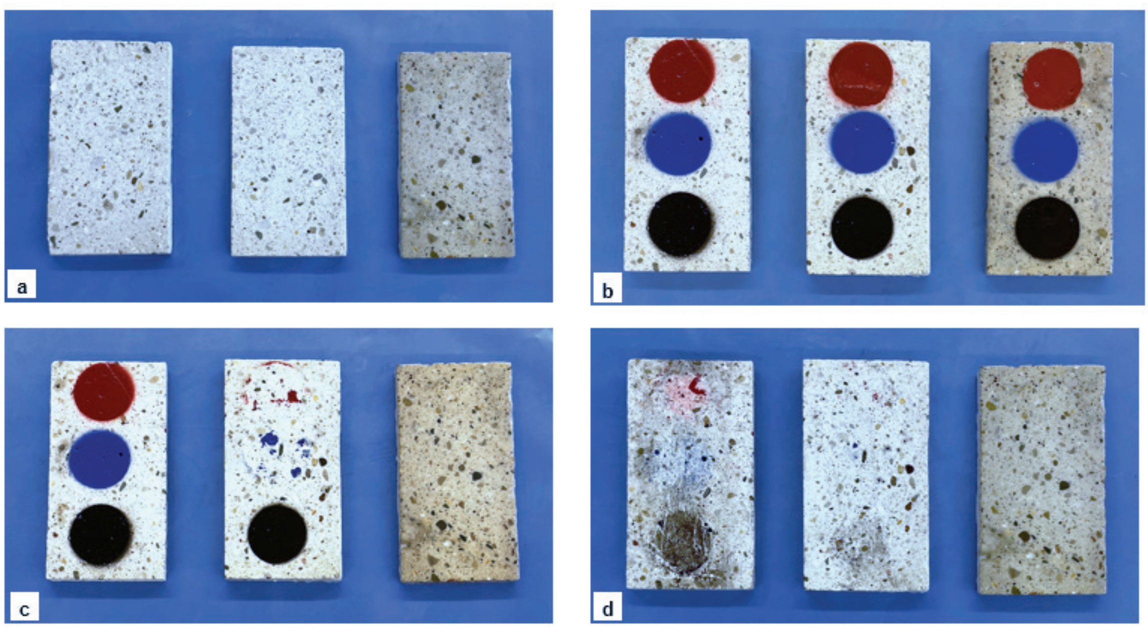
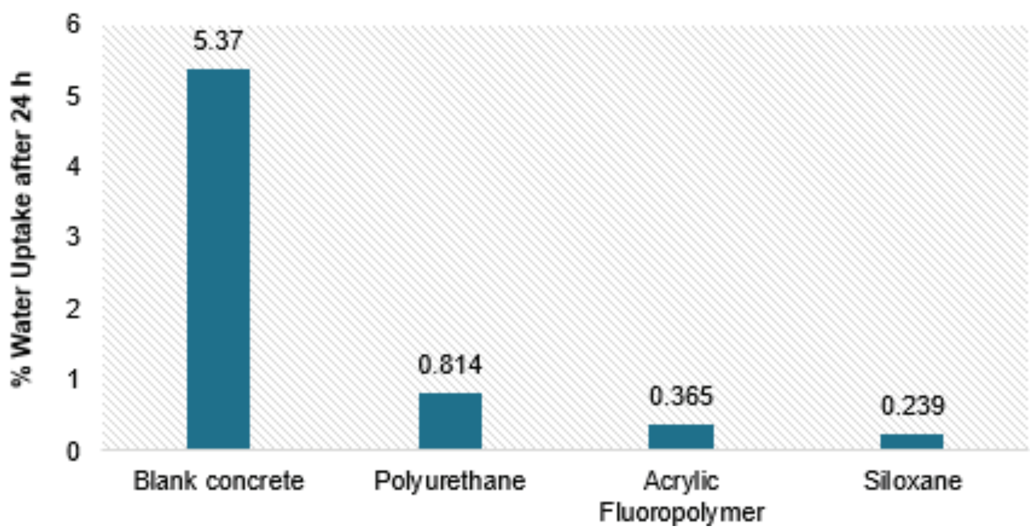


FIGURE 11
Water uptake of the coated samples versus blank concrete.



Water Uptake

Absorption of water by coatings, aka water uptake, leads to the reduction of their protective properties and eventually their degradation. Therefore, coatings with lower water uptake are preferable for long-term protection of architectural surfaces. The water uptake test followed the Wacker internal test method, involving placing coated concrete panels (two replicates for each sample) and blank concrete on a sponge submerged in a water bath. The water level was adjusted to the top of the sponge, exposing only the coated surfaces of the concrete panel to water. Continuous water exposure for 24 h was followed by removing the panels and wiping off any excess water. The coated concrete panels were then weighed to determine the water uptake, and the percentage of water uptake after 24 h (G) was calculated according to **equation 1**.

$$G = \frac{W_1 - W_2}{W_2} \times 100 \qquad \textit{Equation (1)}$$

As indicated in **Figure 11**, the siloxane AG coating exhibited a markedly lower water uptake in comparison to other coatings. This characteristic contributes to its long-term durability and extended protection of cementitious substrates.

Static Contact Angle and Surface Free Energy

A mobile surface analyzer was employed to measure water and diiodomethane contact angles, along with surface free energy, utilizing the sessile drop method. **Table 3** highlights superior performance of the siloxane AG coating, which shows higher hydrophobicity and lipophilicity, combined with a lower surface energy.

TABLE 3
Contact Angles and Surface Free Energy of the Anti-Graffiti Coatings.

	Siloxane	Acrylic Fluoropolymer	Polyurethane
Water contact angle (°)	105.73 ± 1.26	81.33 ± 1.24	73.41 ± 1.14
Diiodomethane contact angle (°)	83.42 ± 2.28	75.87 ± 3.54	50.75 ± 3.53
Surface free energy (mN/m)	15.91 ± 1.26	28.46 ± 2.94	41.41 ± 2.79

Conclusion

In conclusion, the development of one-component permanent anti-graffiti coatings based on elastomeric silicones has shown exceptional results in various aspects including graffiti removal. These coatings, free from undesirable tin and fluorine compounds, exhibit sustainable characteristics with a VOC of less than 150 g/L. Through a comprehensive evaluation process, including graffiti tagging, artificial and natural weathering, and subsequent removal, the siloxane AG coatings exceeded the benchmarks.

Additionally, the coatings exhibited enduring anti-graffiti properties, with effective removal of graffiti tags using high-pressure water even after extended periods of weathering. Notably, the coatings displayed resilience against a variety of graffiti types, including spray paints, permanent markers, and wax crayons. The hydrophobic and lipophobic nature of the siloxane AG coating was evident through contact angle measurements, highlighting its repellent properties against water and diiodomethane.

Furthermore, the coatings demonstrated superior water vapor permeability and minimal water uptake, highlighting their breathability and resistance to water absorption. Comparative analyses with commercial benchmark coatings underscored the favorable attributes of the siloxane AG coating, contributing to enhanced graffiti removal efficacy.

In summary, the siloxane AG coating emerges as a new eminent solution for durable, sustainable, and effective anti-graffiti protection on architectural surfaces, providing a robust defense against graffiti while maintaining long-term aesthetic and protective qualities. ❊

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