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Abstract

Contemporary mural paintings are complex artworks for several reasons, including the heterogeneity of the materials used to make them, and the different types of substrate on which the painting layers can be applied. Currently we are focused on a technical-scientific research aimed to solve the issues related to the long-term care and maintenance of murals, by evaluating the performance of several protective coatings applied on these artworks. This paper deals with a preliminary experimentation aimed to: a) study the interaction of antigraffiti products on common synthetic paints; b) test the effectiveness and efficiency of several commercial products used as antigraffiti; c) define of the best procedure to remove vandalism spray from a coated surface, without damaging the underlying painting layers. Tests have been carried out on laboratory specimens and the performances of different antigraffiti agents have been evaluated by optical and electron microscope observations, as well as by colorimetric measurements.

Keywords	Antigraffiti; Street art Artwork; Protection
Taxonomy	Materials Characterization Techniques, Coatings
Manuscript category	Analysis and Diagnosis of the State of Conservation and Restoration
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Dear Editor-in-Chief,

I would like to submit our manuscript entitled “Comparative study of protective coatings for the conservation of Urban Art” to be considered for publication in Journal of Cultural Heritage. Authors are listed below:

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The paper represents a contribution to YOCOCU 2018 held in Matera (22-26 May).

The research deals with the application of antigraffiti products for the protection of urban art artwork against vandalism.

With my best regards,
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Comparative study of protective coatings for the conservation of Urban Art

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Abstract

Contemporary mural paintings are complex artworks for several reasons, including the heterogeneity of the materials used to make them, and the different types of substrate on which the painting layers can be applied. Currently we are focused on a technical-scientific research aimed to solve the issues related to the long-term care and maintenance of murals, by evaluating the performance of several protective coatings applied on these artworks. This paper deals with a preliminary experimentation aimed to: a) study the interaction of antigraffiti products on common synthetic paints; b) test the effectiveness and efficiency of several commercial products used as antigraffiti; c) define of the best procedure to remove vandalism spray from a coated surface, without damaging the underlying painting layers. Tests have been carried out on laboratory specimens and the performances of different antigraffiti agents have been evaluated by optical and electron microscope observations, as well as by colorimetric measurements.

Keywords: Antigraffiti; Street art Artwork; Protection

Introduction

Acrylics and partially fluorinated acrylics, perfluoropolymers, siloxanes are the main classes of polymers used for the protection of outdoor architectural elements [1-8]. An "antigraffiti" coating is a layer of material applied on the surface of another material, usually stone, with the intent to limit possible vandalism phenomena [9]. These coatings should cover the surface and penetrate through the pore system of the treated stone forming a protective barrier against the colorants and dyes contained in the sprays, markers and other materials used to make graffiti [10]. Three main classes of anti-graffiti can be defined [11-12]: sacrificial, semi-permanent and permanent. The first class of coatings is removed from the surface during the graffiti cleaning, thus such products have to be reapplied after the cleaning process. The second class includes products that generally have to be reapplied after two or three cleaning cycles, while a permanent coating is still effective after up to 10 cleaning cycles. But what happens if the vandalism itself becomes innovative art? Today, many graffiti are undoubtedly considered urban art, and then they should be protected, also against vandalisms. It has been highlighted by the ISCR (Rome Institute of Conservation and Restoration) the difficulty to clean properly vandalism on murals, because solutions which dissolve the vandalism, would dissolve the substrate as well. The protection of murals could make it possible a proper cleaning process, and can be made by using products already available in the cultural heritage sector. These products have been already studied, then, their characteristics in terms of stability and compatibility are well known. The paint used to realize the mural could change the polarity of surface and to limit the adhesion of an antigraffiti product, which is usually used for a bare stone substrate. In this situation, conservators need to perform a set of tests on the substrates to be protected, in order to determine the suitability of anti-graffiti products prior to the final

application. However, currently there are not any standardised methods for the evaluation of performance of protective treatments on murals.
The aim of this paper is to check the suitability of antigraffiti product to protect murals, and also to provide a procedure and resulting criteria for the acceptance or rejection in their use [13]. For this purpose, several products have been considered, applied on laboratory specimens, then colorimetric measurements, cleaning tests, microscopic and spectroscopic investigation have been carried out.

Materials and methods

Specimens reproducing a street art artwork have been prepared as follows. Twelve ceramic tiles measuring 20x20 cm have been covered by a layer of about 1 cm of a premixed mortar. After 30 days, a whitish fine quartz acrylic based paint for exterior coating (Covema Vernici s.p.a., Italy) was applied by two steps, the second application has been carried out after one day after the first one. In order to reproduce the painting layer, two coloured paints have been used: a water-based styrene acrylic orange coloured paint (Kerakover Eco Quarzite, Kerakoll) and an acrylic water-based red paint (ACRIMAX, MaxMeyer) (Fig. 1). The orange paint, when applied appears matt, while the red one shows a gloss effect. Each paint has been applied on six specimens. In the first phase of the research, a screening activity has been carried out in order to choose the best antigraffiti suitable for a deeper investigation. Several products (permanent and sacrificial antigraffiti) have been applied on the specimens, and then, some macroscopic evaluations have been highlighted, as summarized in Table 1.

Product name	Producer	Composition	Type	Applicability	Macroscopic observations
Prostone	Pelicoat	Fluorinated acrylic	permanent	good	no surface alteration
Sandtex Graffiti Prevention	Harpo	siloxane emulsion	permanent	good	glossy and milky surface
Wallgard graffiti barrier	Mapei	Wax emulsion	sacrifical	poor	glossy and yellowing surface
AG09W	Keim	Fluorinated polymer and wax emulsion	sacrifical	good	no surface alteration
Antigraf Permanent	CIR	Polyurethane	permanent	good	glossy surface

Table 1. List and feature of antigraffiti used for the screening phase

According to these results, Prostone (Pelicoat) and AG09W (Keim) products have been selected. Each tile (Red and Orange painted) has been divided in 4x4 cm^2 area, one has been treated with Prostone, and the other one with Keim AG09W. All treatments have been carried out threefold. Then, some portions of surface have been sprayed with a modified alkyd resins based black spray paint (MNT94, Montana Colors, S.L.) in order to simulate vandalism. For comparison purpose, some tiles (Red and Orange) have been left without Prostone/Keim coating. All specimens' features are summarized in Table 2.

Underlying layers	Coloured layer	Antigraffiti
Mortar + white paint	Matt Orange	-
	Glossy Red	-
	Matt Orange	Keim
	Glossy Red	Keim
	Matt Orange	Prostone
	Glossy Red	Prostone

Table 2. Summary of specimens' features.

Removal tests of the vandal black layer have been performed by using poultices with cotton and hydro-alcoholic mixtures (20% and 70% v/v of ethanol) with a drop of ethyl acetate, applied on the surface (contact time 0.5 and 24 hours), after that, the surface layer has been removed by gently wiping with a cotton swab for 5 minutes. Each test has been carried out threefold on a 4x4 cm^2 area. The percentage of cleaned area was calculated using Image J software.
In order to assess the colorimetric variation induced by the antigraffiti coating on the treated surface, as well as the difference between the original colour and the colour obtained after the black removal, colorimetric measurements have been carried out using a CM-2600d Konica Minolta spectrophotometer, to assess chromatic variations. Chromatic values are expressed in the CIE L*a*b* space, where L* is the lightness/darkness coordinate, a* the red/green coordinate (+a* indicating red and −a* green) and b* the yellow/blue coordinate (+b* indicating yellow and −b* blue).
Observation by optic and electron microscope were performed to characterize the stratigraphy and the interactions among layers, heterogeneities and to check the penetration of the between the vandal black painted paint layer the underlying red/orange one. For this purpose, samples were collected from the specimens, and then observed at different magnifications under a Zeiss Axiolab 40 microscope equipped with a digital camera, and under Scanning Electron Microscope (360 Cambridge Instruments Stereoscan), using secondary electron (SE) and backscattered electron (BSE) modes, at the following operating conditions: 20-kV 138 accelerating voltages, 0.2-mA beam current.
The presence of protective layer residues after the cleaning of the surfaces has been checked by collecting a sample from the surface and analysing it by FT-IR technique. For this purpose it has been used a Perkin Elmer Spectrum 100 spectrophotometer, equipped with an attenuated total reflectance (ATR) accessory. Infrared spectra were recorded in ATR mode, in the range of 500–4,000 cm^{-1} at a resolution of 4 cm^{-1}.

Fig. 1. Making of the specimens simulating a street art artwork

Results and discussion

In Table 3 it has been reported the percentages of vandalism layer removal after cleaning procedures. The black paint cannot be removed properly on those specimens that are not treated with an antigrafitti protective layer. According to the results, an increasing of the ethanol into the cleaning mixture induces a slightly improvement of the removal. On the contrary, the application time has a little influence on the performance, then it can be stated that in laboratory conditions, 30 minutes of application can be considered a sufficient amount of time for the cleaning process. Regarding the antigraffiti, Prostone treatment has shown a better behaviour with respect to Keim. Significant differences have been detected between the specimens with Red and Orange paints. On those surface having the glossy red layer, the removal of the vandalism appears to be easier. This is probably due to the different surface of those materials, because a matt paint has a higher pigment/volume ratio (PVC), which lead to a lower resistance toward the mechanical stresses [14], due in this case by cotton swabbing.

Paint	Antigraffiti	Time of application (h)	Ethanol/ Water %	% of removal σ = ±5
Glossy Red	NO	0.5	20	7
		0.5	70	7
		24	20	5
		24	70	5
	KEIM	0.5	20	70
		0.5	70	93
		24	20	72
		24	70	93
	PROSTONE	0.5	20	65
		0.5	70	85
		24	20	64
		24	70	86
Matt Orange	NO	0.5	20	5
		0.5	70	7
		24	20	3
		24	70	4
	KEIM	0.5	20	60
		0.5	70	80
		24	20	62
		24	70	78
	PROSTONE	0.5	20	55
		0.5	70	65
		24	20	65
		24	70	70

Table 3. Summary of the results of cleaning tests

In Table 4 it has been reported the difference of chromatic coordinates measured before and after the application of antigraffiti layer, as well as the colour differences between surfaces cleaned by the hydro-alcoholic solutions (70% v/v for 0.5h) and those just coated with the antigraffiti. The application of the antigraffiti induces a colorimetric variation (ΔE) which is always lower than 5, Prostone induces lower chromatic alterations with respect to Keim (Fig. 2). Regarding the colorimetric variations after the removal of the vandalism layer, very high values are revealed, especially for orange surface (Fig. 2). This can be due to the alteration of the painted surface after the mechanical action, but also to the partial dissolution of the pictorial layer, this result would suggest that the hydro-alcoholic solution is able to remove the thin protective layer interacting directly with the surface.

Coating / Sample	Specular component	After-Before Antigraffiti Coating								After Graffiti Removal – After Antigraffiti Coating							
		ΔL*	σΔL*	Δa*	σΔa*	Δb	σΔb	ΔE	σΔE	ΔL*	σΔL*	Δa*	σΔa*	Δb	σΔb	ΔE	σΔE
KEIM	Included	0.86	1.42	0.53	1.43	0.51	0.62	1.13	1.16	0.39	1.35	-0.97	1.19	-1.36	0.63	1.72	1.06
Glossy Red	Excluded	2.24	0.88	-1.30	1.45	-3.90	0.86	4.68	1.06	2.98	0.93	-4.26	1.40	-5.72	0.67	7.73	1.00
PROSTONE	Included	-1.31	0.99	3.11	1.18	2.50	0.57	4.70	0.91	2.12	1.22	-2.76	1.29	-3.08	0.48	4.65	1.00
Glossy Red	Excluded	1.12	0.89	0.66	1.26	-1.43	0.74	1.93	0.96	4.23	1.04	-5.92	1.36	-8.54	0.61	11.22	1.00
KEIM	Included	0.65	1.44	-2.36	1.64	-4.28	1.27	4.93	1.45	3.50	1.58	-9.93	1.56	-7.51	1.01	12.93	1.38
Matte Orange	Excluded	0.46	1.50	-2.70	1.70	-3.96	1.16	4.55	1.45	3.63	1.71	-9.98	1.40	-7.85	0.91	13.21	1.34
PROSTONE	Included	-1.08	1.32	0.99	1.64	2.25	1.40	2.68	1.46	6.25	1.76	-13.68	1.32	-14.12	1.07	70.63	1.38

Matte Orange	Excluded	-1.12	1.33	1.05	1.65	3.26	1.17	3.60	1.38	6.24	1.67	-13.65	1.32	-15.17	0.82	21.34	1.27

Table 4. Results of colorimetric measurements expressed as differences

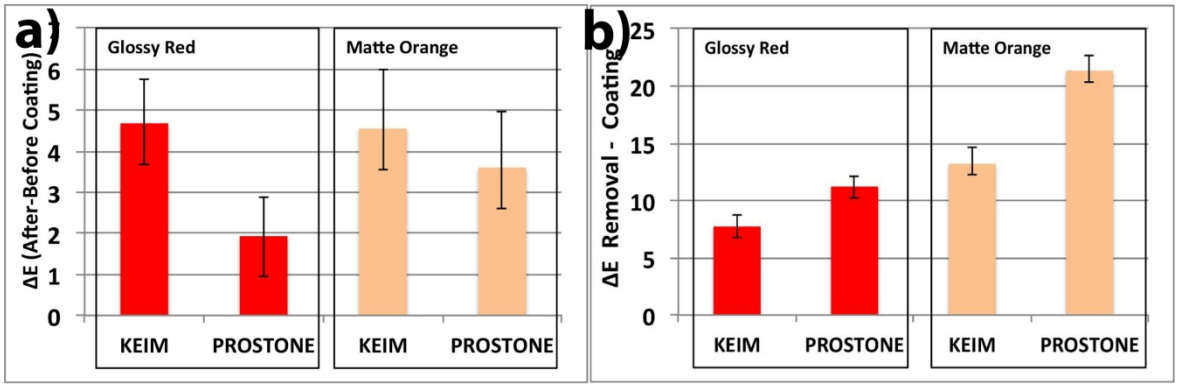


Fig. 2. Colorimetric variations a) before - after antigraffiti coating and b) before-after surface cleaning.

Fragments have been collected from each specimen, and then, analysed in cross section, by means of SEM observations to assess the interaction among the different layers. When the black paint is applied directly on the Red/Orange layer without any antigraffiti treatment, there is a clear penetration of the Montana product (Fig. 3a-3d). This is due to the ethyl-acetate used as thinner in the Montana spray, which dissolves the binder of the underlying layer. In specimens treated with antigraffiti there are clearly distinguishable the stratigraphy Red/Orange paint-Antigraffiti-vandalism layer (Fig 3b-c-e-f), this suggests there is not any penetration of the black paint within the underlying layers. Moreover, there is not any penetration of the antigraffiti product into the red/orange paints. This occurs because the antigraffiti are water-based emulsions, then, not any dissolution of the Red/Orange layer is expected. In addition, the surface of Orange painted specimens is much rougher with respect to the Red painted surface, this has an effect into the cleaning procedure, as the roughness made it difficult to remove the overlying black.

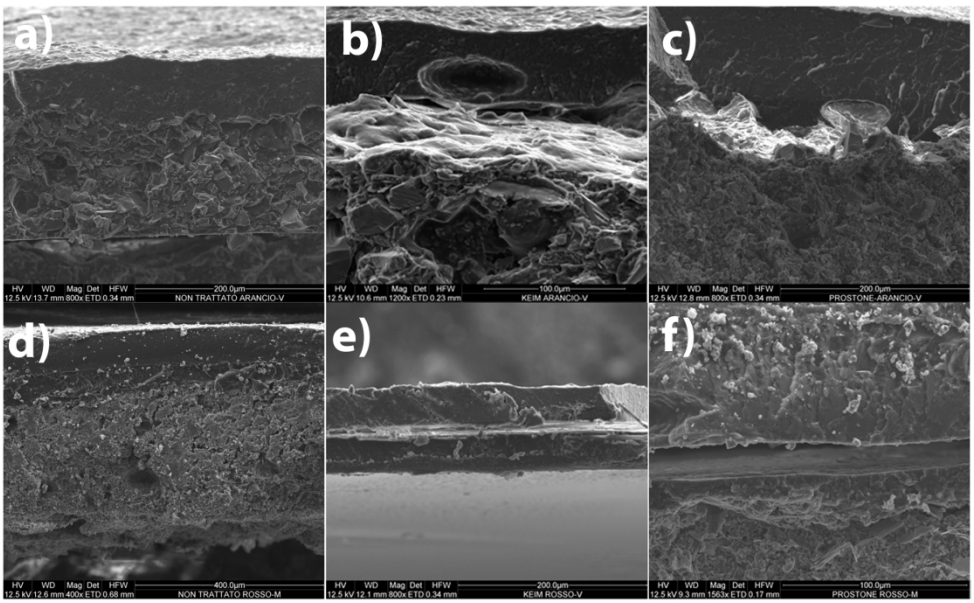


Fig. 3. SEM images of the paint/antigraffiti/vandalism, interfaces. Matt Orange a) untreated and sprayed with Montana; b) treated with Keim and sprayed with Montana; c) treated with Prostone and sprayed with Montana; Glossy Red d) untreated and sprayed with Montana; e) treated with Keim and sprayed with Montana; f) treated with Prostone and sprayed with Montana

The cleaned surfaces (ethanol/water 70/30 v/v for 0.5h) have been analysed by FTIR measurements in order to check if there was any antigraffiti left. In the case of Orang paint, the high number of its peaks in infrared spectrum did not allowed to recognize the signal related to Keim and Montana.
On the contrary, the analysis of the residues on the Red paints shows that both Keim and the Prostone layers are still on the surface (Fig. 4), although Keim is a sacrificial antigraffiti and would not be left on the surface after graffiti removal.

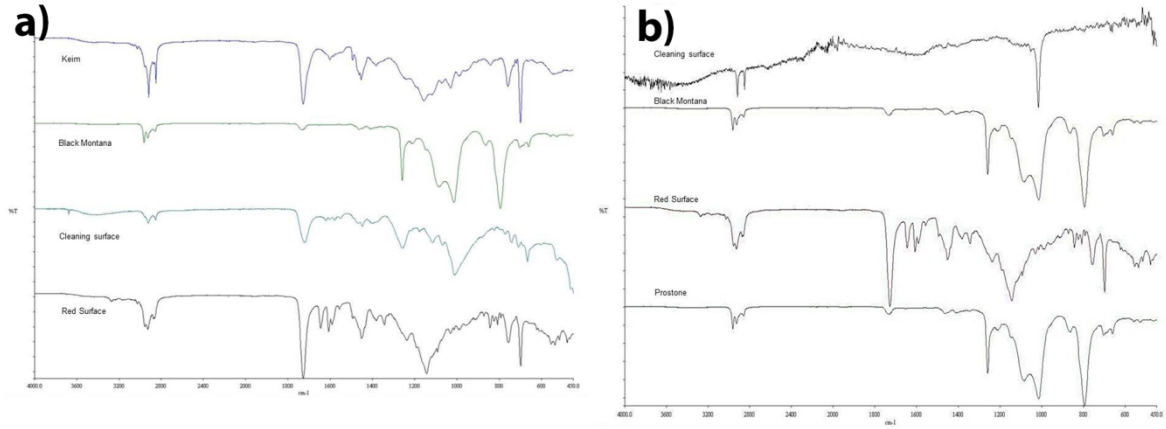


Fig. 4. FTIR spectra of the Glossy Red paint treated with a) Keim and b) Prostone sprayed with Montana and cleaned with ethanol/water 70/30 v/v for 0.5h. Reference spectra of Glossy Red, Black Montana, Keim and Prostone are also reported.

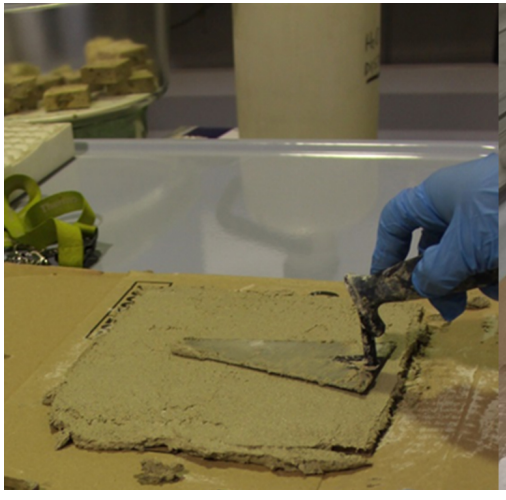
Conclusions

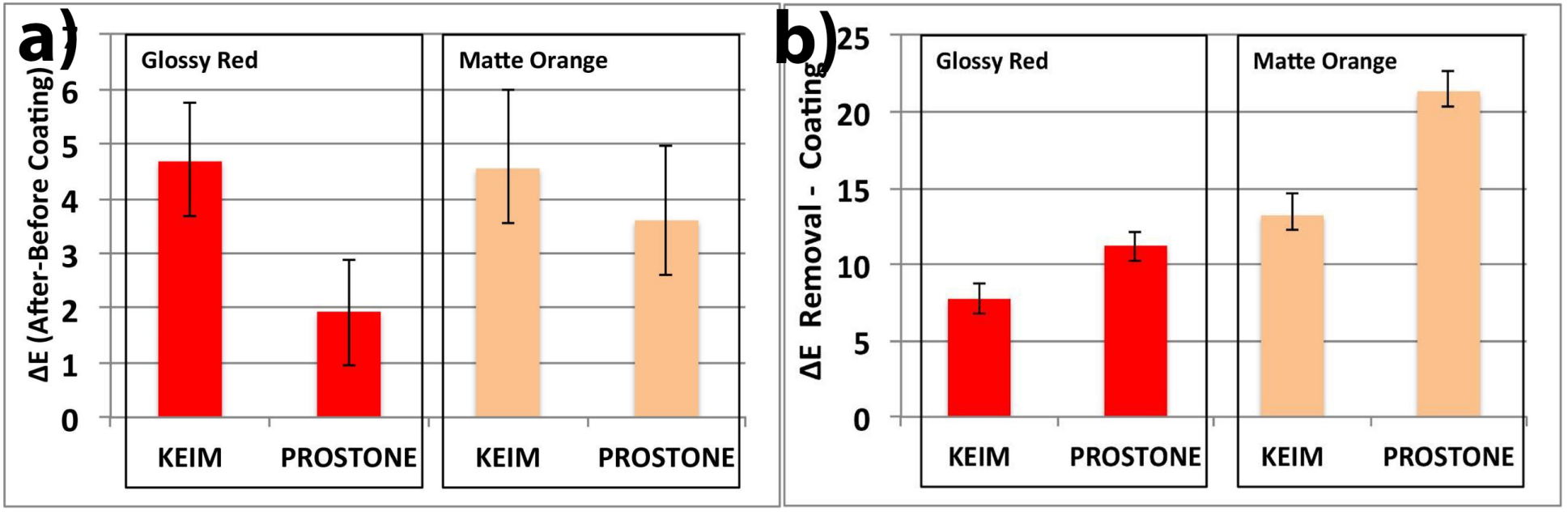
This study was aimed to assess the applicability of antigraffiti commonly used for stone materials, for the protection of street art artworks. Results suggest that the antigrafitti do not penetrate into the underlying paints and do not produce a significant colorimetric alteration of the surface. A solution of water/ethanol 30/70 v/v applied for 30 minutes by poultice, followed by gentle swabbing is able to remove a vandalism layer, although for the matt paint an alteration of the colour is revealed after the cleaning procedure. Prostone product, which is a permanent antigraffiti based on a fluorinated polymer showed the best performance. Results suggest that antigraffiti can be successfully used for the protection of street art artworks against vandalism. Further studies are needed to optimize the original formulations to make them more suitable to our purposes.

References

[1] P.N. Manodius, A. Tsakalof, I. Karapanagiotis, I. Zuburtikudis, C. Panayiotou, Fabrication of superhydrophobic surfaces for enhanced stone protection, Surf. Coat. Technol. 703 (2009) 1322–1328.
[2] P.N. Manodius, I Karapanagiotis, A. Tsakalof, I. Zuburtikudis, B. Kolinkeová, C. Panayiotou, Superhydrophobic films for the protection of outdoor cultural heritage assets, Appl. Phys. A-Mater. 97 (2009) 351–360.
[3] G. Alessandrini, M. Aglietto, V. Castelvetro, F. Ciardelli, R. Peruzzi, L. Toniolo, Comparative evaluation of fluorinated and un fluorinated acrylic copolymers as water-repellent coating materials for stone, J. Appl. Polym. Sci. 76 (2000) 962–977.
[4] M. Licchelli, M. Malagodi, M.L. Weththimuni, C. Zanchi, Water-repellent properties of fluoroelastomers on a very porous stone: Effect of the application procedure, Prog. Org. Coat. 76 (2013) 495–503.
[5] M.F. La Russa, N. Rovella, M. Alvarez De Buergo, C.M. Belfiore, A. Pezzino, G.M. Crisci, S.A. Ruffolo, Nano-TiO_2 coatings for cultural heritage protection: the role of the binder on hydrophobic and self-cleaning efficacy, Prog. Org. Coat. 91(2016) 1–8.
[6]] M.F. La Russa, S.A. Ruffolo, N. Rovella, C.M. Belfiore, A.M. Palermo, M.T. Guzzi, G.M. Crisci, Multifunctional TiO_2 coatings for Cultural Heritage, Prog. Org. Coat. 74 (2012) 186–191.
[7] L. Toniolo, T. Poli, V. Castelvetro, A. Manariti, O. Chiantore, M. Lazzari, Tailoring new fluorinated acrylic copolymers as protective coatings for marble. J. Cult. Heritage 3 (2009) 309–316.
[8] M. Stefanidou, A. Karozou, Testing the effectiveness of protective coatings on traditional bricks. Constr. Build. Mater. 111 (2016) 482–487.
[9] N. Ashurst, S. Chapman, S. MacDonald, R. Butlin, M. Murry, An investigation of sacrificial graffiti barriers for historic masonry, English Heritage Research Transactions, 2, Stone, James and James, London, 2002.

[10] D. Urquhart, The treatment of graffiti on historic surfaces – Advice on graffiti removal procedures, anti-graffiti coatings and alternative strategies, Historic Scotland, Edinburgh, 1999.
[11] C. Borchard-Tuch, Beschichtungen contra Graffiti, Chem. Unserer Zeit, 39 (2005) 355–357.
[12] B. Lubelli, R.P. J. van Hees, T.G. van de Weert, The drying behaviour of building materials treated with anti-graffiti, in: Aedificatio Publishers, Proceedings of the Hydrophobe V Fifth International Conference on Water Repellent Treatment of Building Materials, Brussels, April 15–16, Freiburg, 2008, 85–94.
[13] O. García & K. Malaga, Definition of the procedure to determine the suitability and durability of an anti-graffiti product for application on cultural heritage porous materials. Journal of Cultural Heritage 13 (7012) 77–82.
[14] W. K. Asbeck, M. Van Loo, Critical Pigment Volume Relationships, Ind. Eng. Chem., 41 (7) (1949) 1470–1475.

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Glossy Red
Matte Orange
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PROSTONE
KEIM
PROSTONE
b)
ΔE Removal - Coating
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Glossy Red
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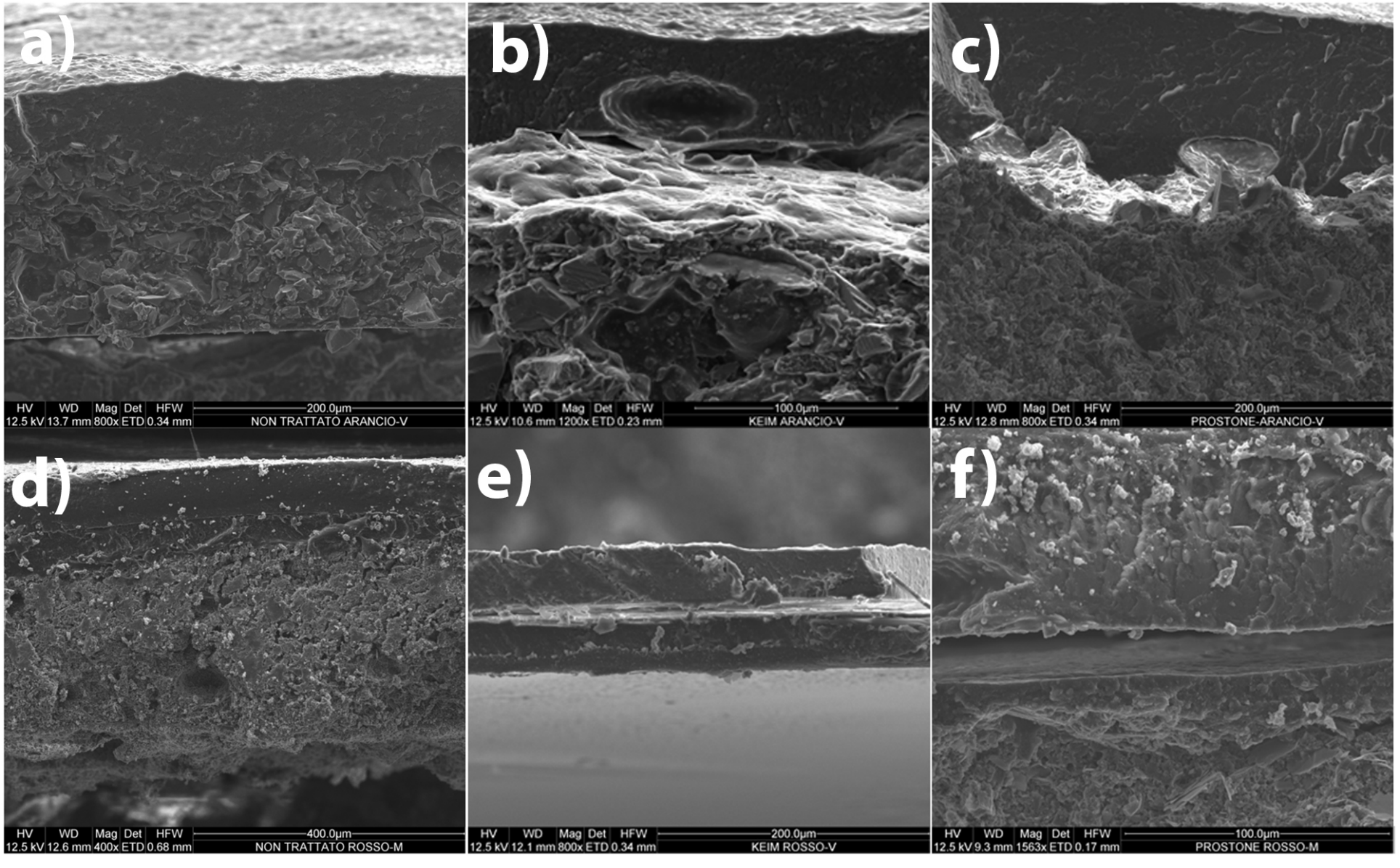
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KEIM ARANCIO-V
c)
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200.0µm
PROSTONE-ARANCIO-V
d)
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NON TRATTATO ROSSO-M
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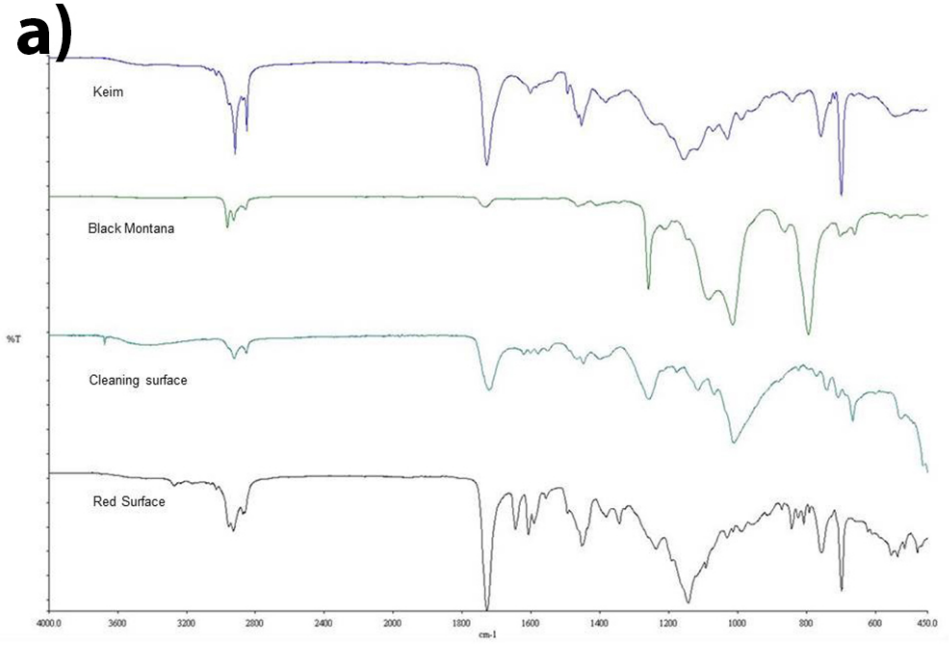
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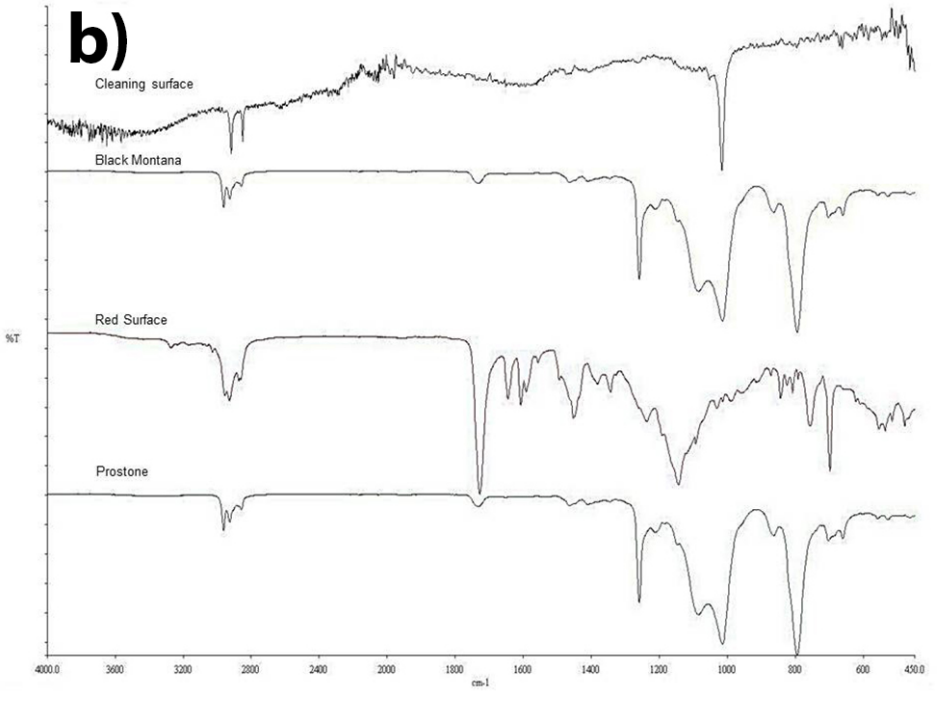
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