

Work Package 4: Tests on selected products Final Report | June 2020

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1 Introduction

The introduction gives a brief overview of the aims of work package 4, the partners involved and the products used.

The following chapters contain the results of all research groups participating in WP4.

1.1 Work package overview

The main objective of Work Package 4 was to identify several products, both in terms of cleaning and in terms of protection of surfaces.

One focus was on carrying out solubility tests and evaluating those cleaning treatments analytically, both with non-invasive techniques and with invasive techniques after sampling.

The other focus was on testing protecting methods and evaluating those protecting treatments analytically to look at different compositions of possible coatings to find out the best protection and the best aesthetic appearance.

Additionally tests on consolidating products were carried out.

All tests were carried out either on-site or on ad hoc samples within the companies/research centres.

This WP also planned mobility activities between the Academy of Fine Arts in Warsaw and the Cologne Institute of Conservation Sciences and between the University of Torino and the Sisak Municipal Museum, with the collaboration of the University of Split.

1.2 Partners involved

- University of Turin (Italy) and Conservation and Restoration Centre "La Venaria Reale" (Italy)
- CESMAR7 (Italy) and ANTARES (Italy)
- University of Vigo (Spain)
- Academy of Fine Arts in Warsaw (Poland)
- University of Split (Croatia), Sisak Municipal Museum (Croatia) and METRIS (Croatia)
- Cologne Institute of Conservation Sciences (Germany) and Schmincke (Germany)

All the teams, following the instructions of the WP leader, produced two or three reports depending on the type of products tested (cleaning, protection and consolidation products), with the exception of the team formed by the University of Split (Croatia), Sisak Municipal Museum (Croatia) and METRIS (Croatia). Due to unforeseen reasons, the Sisak Municipal Museum, which has the task of leading the preparation of model samples and the testing of cleaning and protection products and methods, out the was unable to carry activities on schedule. The partner University of Split has meanwhile contributed to WP4 with the following activities:

- planning of research (a) on methods for the removal of aged coatings from painted steel sculptures, and (b) on coating systems for outdoor steel sculptures
- purchase and analysis of ISO standards

• participation in the drafting of a methodology for the research of coating systems for use in conservation-restoration of metal outdoor sculptures.

The reports of the various teams, except the Croatian team, are part of this document and are here reported after the introductory part.

The full report of the Croatian team will be attached later to this report as an appendix.

1.3 Product information

WP 4 aimed to identify several products, both in terms of cleaning and in terms of protection of surfaces.

Several products have been selected in advance. As far as products for cleaning are concerned, they have been selected in order to remove dirt and alteration products, while respecting constituent materials.

The requirements on products for coating were high stability against atmospheric weathering but also vandalism like graffiti.

The following tables show selected products for cleaning methods (Table 1) and protective coatings (Table 2).

The tables are intended as an example of how you can compile your own product table with the relevant product data.

The products listed in the tables are to be seen as examples. In the reports of the individual partners a number of other products have been mentioned and investigated. The data on these products can be found in the individual reports.

Table 1: Information on products for cleaning

CAR	S	Version 1.3	march 201	9															
	WP4.1: Information on products for cleaning																		
	Chemical base				On surface							To remove				Application with			
Product- number	Product	Order number	Class	Mixture	Metal	Plastering	Wood	Oil	Colour Acrylic	Alkyd	Miscellaneous, comments	Dirt	Particle	Old colour	Old	Brush	Airbrush	Paintroll	Miscellan eous
1	Picture Cleaner	50018	Solvent	Y	N	N	N	Y	N	Y	most for oil pictures	Y	Y	Ν	N	Y	N	N	Cloth
2	Brush cleaner	50051	Solvent	N	Y	N	N	Y	Y	Y	most for artist brushes	Y				Y		Y	
3	C6 Gel Graffitireiniger	1175	Solvent	Y	Y	Y	N	Y	Y	Y	good in combination with e.g. Fluorosil Premium protection	Y	Y	Y	N	Y	N	Y	
		ANSVE005C-									Graffiti remover for unpainted plasters and stones. To be carefully evaluated if it is to be used on street art paintings if they are not protected by antigraffiti								
4	Stain remover 804N	E-D	Solvent	Y	Y	Y	Y	N	N	N	coating	N	N	Y	Y	Y	N	N	

References		Experience		Pa		Application rate	Safet	y data sheet	Manufacturer						
Object	Year	Object	Year	Туре	Quantity	Unit	Available	Safety precautions required	Name	Address	Phone number	Web address	Entry in base by		
				Tube	35ml	1ml/10mm ²	Y	Gloves, Glasses	H.Schmincke	Germany Ottohahn-Str. 2 Erkrath	'+492112509474	info@schmincke.de	H. Schmincke		
				Glass bottle	60,200,1000ml		Y	Gloves, Glasses	H.Schmincke	Germany Ottohahn-Str. 2 Erkrath	'+492112509474	info@schmincke.de	H. Schmincke		
				Plastic can	1, 5, 10 liter	0,2 - 1 kg/m²	Y	Gloves, Glasses	Scheidel by Schmincke	Germany Ottohahn-Str. 2 Erkrath	'+492112509474	info@schmincke.de	H. Schmincke		
				Bucket	1-5-15 kg	1ml/4000 mm2	Y	Gloves, Glasses	An.t.a.res srl	San Lazzaro di Savena, Italy	+390516259816	info@antaresrestauro.it	An.t.a.res		

Table 2: Information on products for protection

CA	PS	Version 1.3	march 2019												
	WP4.2: Information on products for protection														
	· · · · · · · · · · · · · · · · · · ·		Chemical base						Applica	ation on			aqA	lication w	ith
Product-									Colour						
number	Product	Order number	Class	Mixture		Plastering		Oil	Acrylic	Alkyd	Miscellaneous / comments				Miscellaneous
1	Acryliclaquer	50586	Acrylic, waterbased	Y	Y	Y	Y	N	Y	N	in-/outdoor	Y	Y	Y	
2	Acryliclacquer, semi-mat	50587	Acrylic, waterbased	Y	Y	Y	Y	N	Y	N	in-/outdoor	Y	Y	Y	
		50.400									in-/outdoor ;under development; hard-		l		
3	ACPU-Clearlaquer	50199	Acrylic-Polyurethane, waterbased	Y	N	Y	Y*	N	Y	N	elastic film	Y	N	Y	
4	Tutto Prom bright	214052	Polysilazan, solvent based white spirit	Y	Y	Y*	N	N	Y	Y	permanent	Y	Y	Y	
5	Tutto Prom matt HD	214053	Polysilazan, solvent based BAC	Y	Y	Y* V	N	N	Y	Y	permanent	Y	Y	Y	
6	Fluorosil Premium	3765	C6-Fluorocompounds, waterbased	Y	N	Y	N	N	Ŷ	N	permanent	Y	Ŷ	Ŷ	
7	HydroGraff OS-A AGS creme		Silane-Siloxane-Fluoracrylate, waterbased	Y	N	Y	N	N	Y	N	RAL proof, non film	Y	N	Y	
8	Wachs (Wax)	3760	Microwax emulsion	Y	N	Y	N	N	N	N	non permanent	Y	N	Y	
9	Anti-Stain	ANANT007A-7	Fluoropolymers and waxes, waterbased	Y	*	Y	*	*	*	*	Sacrifical anti-graffiti for stones	Y	Y	Y	
10	HEXAFORTM SA-6320	n.a.	Fluorinated silicon polymer, waterbased	Y	*	Y	*	*	*	*	anti-graffiti for stones	Y	Y	Y	
11	Pro-stone	n.a.	Fluorinated acrylic polymer, waterbased	Y	*	Y	*	*	*	*	sacrifical anti-graffiti for stones	Y	Y	Y	
12	ProtectGuard TC	2160	Nanofluorinated, waterbased	Y	*	Y	*	N	Y	*	anti-stain coating for acrylic paintings	Y	Y	Y	
13	Ector® RG-10	n.a.	Nanosilica, water based Blend based on fluorinated acrylic	Y	N	Y	N	*	Y	*	anti-graffiti for stones	Y	Y	Y	
14	HEXAFOR™ AGR60	PRCAGR600050-200	5	Y	*	Y	*	*	*	*	Concentrated anti-graffiti for stones	Y	Y	Y	
15	HEXAFOR™ 6392	PRC63920050-200	Fluorinated acrylic polymer, waterbased	Y	*	Y	*	*	*	*	Concentrated anti-graffiti for stones	Y	Y	Y	
16	HEXAFOR™ 6232	PRC62320050-200	Fluorinated acrylic polymer, waterbased	Y	*	Y	*	*	*	*	Concentrated anti-graffiti for stones	Y	Y	Y	
17	Multisurface acrylic lacquer	N.A.	Acrylic waterbased	Y	N	Y	Y	Y	Y	Y		Y	Y	Y	
18	SB Acrylic lacquer	N.A.	Acrylic solventbased	Y	Y	Y	Y	Y	Y	Y		N	N	N	Aerosol
19	Barniz al agua satinado	BV000	waterbased varnish	N	N	N	Y	N	Y	Y	applied on paints on concrete and brick	Y	N	N	
20	Carlux agua	EGA-352-M00-01-FT	waterbased varnish	N	N	N	Y	N	Y	Y	applied on paints on concrete and brick	Y	N	N	
21	Emulsione anti-graffiti 15%	n.a.	non-ionic wax emulsion with polymer	Y	Y	Y	*	*	*	*	anti-graffiti and anti-pollution coating for stones	Y	N	Y	
	* to be evaluated														

References	·'	F	Experience		Package	Application	Safety	y data sheet		Manufacturer		'	1
Object	Year. entry by	Objec	t Year, entry by	/ Type	Quantity	Unit	Available	Safety precautions required	Name	Address	Phone number	Web address	Product entry b
		(200ml	150ml/m ²	Y			Erkrath, Germany, Otto-Hahn-Str. 2	'+492112509474		H. Schmincke
,	· ['	-			200ml	150ml/m ²	Y			Erkrath, Germany, Otto-Hahn-Str. 2	'+492112509474		H. Schmincke
,	·'			Glass bottle.		f ''''''''''''''''''''''''''''''''''''	1	0.0	f	+	1	+	1
,	1 '	1 '			200. 1000ml	150ml/m ²	Y	Gloves	H.Schmincke	Erkrath, Germany, Otto-Hahn-Str, 2	'+492112509474	info@schmincke.de	H. Schmincke
,	·			Metal bottle			Ý	Gloves		Erkrath, Germany, Otto-Hahn-Str. 2	'+492112509474		H.Schmincke
,	·'		· †'	Metal bottle			Ý			Erkrath, Germany, Otto-Hahn-Str. 2	'+492112509474		H.Schmincke
,	· · · · · ·			Plastic can	1, 10	100 - 130ml/m ²	Y			Erkrath, Germany, Otto-Hahn-Str. 2	'+492112509474		H.Schmincke
	1'	\square'	'	Plastic bucket		150 - 400g/m²	Y	Gloves	Scheidel by Schmincke	Erkrath, Germany, Otto-Hahn-Str. 2	'+492112509474	info@schmincke.de	H.Schmincke
,	↓ '	+ '	·'	Plastic can		100 - 250ml/m ²				Erkrath, Germany, Otto-Hahn-Str. 2	'+492112509474		H.Schmincke
,	+'	+ '	·'		5-10	150ml/m2	Y			San Lazzaro di Savena, Italy	+390516259816		An.t.a.res
,	+'	+ '	·'		50-200 kg	300 g/m2	Y			Castelli Calepio, Italy	+390354494301		An.t.a.res
,	+'	4'	·'	tank	5-25	100-300 ml/m2	Y	Gloves	Pelicoat	Rome, Italy	+39068126722	info@pelicoat.it	An.t.a.res
/	 '	 '	ļ'	Plastic tank	51	100 ml/m2	Y	Gloves	GUARD INDUSTRIE S.A.S	Montreuil, France	+330155861760	info@guardindustrie.com	An.t.a.res
ready used for protection of 'Barba ide' in Vicenza, Italy	a ?, An.t.a.res	 '	_ _ '	tank	5-10 I	50-33 ml/m2	N	Gloves	R & R Group S.r.I	Thiene (VI), Italy	0445366572	info@ectorlab.com	An.t.a.res
′	↓ ′	 '	'	Drum	50-200 kg	*	Y	Gloves	Maflon SPA	Castelli Calepio, Italy	+390354494301	maflon@maflon.com	An.t.a.res
′	↓ ′	 '	<u> </u>	Drum	50-200 kg	*	Y	Gloves, glasses	, Maflon SPA	Castelli Calepio, Italy	+390354494301	maflon@maflon.com	An.t.a.res
'	└── ′	⊥ _'	<u> </u>		50-200 kg	*	Y			Castelli Calepio, Italy	+390354494301		An.t.a.res
'	↓ '	 '	'		5-10L	100ml/m2	Y			Sant Vicenç de Castellet, Spain	+34938332787		MONTANA
,	↓ '	4 '	·'	Aerosol	400ml	160ml/m2	Y	Gloves, mask	MONTANA COLORS	Sant Vicenç de Castellet, Spain	+34938332787	montana@montanacolors.com	MONTANA
/	1'	1_'	'	Plastic can	750 ml	100ml/m2	Y	Gloves	Industrias PROA S.A.	San Salvador de Budiño, Gándaras de Prado 36475 Porriño, Pontevedra, Spain	·+34986346525	proa@pinturasproa.com www.pinturasproa.com	UVIGO
!	<u> </u>		'	Metal can	750 ml	125ml/m2	Y	Gloves		Campo de los Palacios, 16 01006 Vitoria-Gasteiz, Spain	'+34945136737	info@pinturasega.com www.pinturasega.com	UVIGO
,	· · · ·	· · · ·		Plastic tank	125	28ml/m2	Y	Gloves	An.t.a.res srl	San Lazzaro di Savena. Italy	+390516259816	info@antaresrestauro.it	An.t.a.res

1.4 Content of the report

The following table is intended to give an overview of the methodological approaches followed by all partners.

Partner	methods/material	Tested on
CLEANING		
Unito & Restoration Centre "La Venaria Reale"	 Solvents with thickeners and supporting agents laser cleaning 	 12 mock-ups - concrete - cement-based mortar substrate
CESMAR & ANTARES	 Dry cleaning materials aqueous solutions solvents, blends and emulsions with thickeners and supporting agents 	 38 mock-ups two layered supports four paint layers among chromatically stable and unstable colours.
Acadamy of Fine Arts Warsaw	 Dry cleaning materials aqueous solutions solvents 	 2 objects Plaster - lime mortar, lime and cement mortar with quartz filler; black charcoal Paint layer: acrylic and vinyl paints Plaster - lime mortar with quartz filler Paint layer: acrylic, polyester, phthalic, vinyl, and tempera paints
PROTECTION		
CESMAR & ANTARES	 - 5 anti-graffiti coating - 1 protective coating - 1 varnish 	 130 and 144 mock ups on microscope slides on cement mortar
Acadamy of Fine Arts Warsaw	- 2 varnishes	 2 objects Plaster - lime mortar, lime and cement mortar with quartz filler; black charcoal Paint layer: acrylic and vinyl paints Plaster - lime mortar with quartz filler Paint layer: acrylic, polyester, phthalic, vinyl, and tempera paints
CICS	- 1 anti-graffiti coating	• 50 mock-ups - brass plates
University of Vigo	- color protectors	mock-ups
CONSOLIDATION	I	1
Unito & Restoration Centre "La Venaria Reale"	- microemulsion - dispersion	• 34 mock-ups
Acadamy of Fine Arts Warsaw	- dispersion - casein - mortar	• 2 objects

- Plaster - lime mortar, lime and cement
mortar with quartz filler; black charcoal
Paint layer: acrylic and vinyl paints
- Plaster - lime mortar with quartz filler
Paint layer: acrylic, polyester, phthalic, vinyl,
and tempera paints

2 Report on the analytical evaluation of cleaning methods

2.1 University of Turin (Italy) and Conservation and Restoration Centre "La Venaria Reale" (Italy)

NUMBER OF PARTNER	COUNTRY	NUMBER OF OBJECTS	NUMBER OF SAMPLES
P1-P2	Italy		12

2.1.1 Information on tested cleaning methods carried out on mock up samples within the companies/research centres and on-site based on the selected sculptures (output wp2 and wp3).

Describe your experimental setup, including details on sample preparation, instruments and experimental conditions used. Take into account to name the objectnumber and sample identification.

Both chemical and laser cleaning were tested on mock-ups. 12 mock-ups were prepared either with a concrete or with a cement-based mortar substrate, with (mock-ups from n. 5 to 12) or without a primer (n. 1, 2 and 3), in order to simulate some common supports of murals. Based on the most common paints identified during WP3, both acrylic brush paints and alkyd spray paints were selected for the preparation of mock-ups. In order to test the selectivity of each cleaning procedure in case of unwanted paint materials (e.g. tags, vandalic act) overlapping the artwork, two to three red and green paint layers were overlapped. The selection of these two different contrasting colours was made with the intention of making as easy as possible the observation of the result of the cleaning tests. All overlapping combinations were considered:

- Alkyd paint + alkyd paint¹
- Alkyd paint + acrylic paint²
- Acrylic paint + acrylic paint³
- Acrylic paint + alkyd paint⁴

Before the application of paint, half portion of each mock-up was protected by applying a protective waterproofing coating, placed between the first and the second paint layers from the inside out; then,

¹ Green Belton[®] spray alkyd paint + Red Belton[®] Spray Alkyd Paint

² Green Belton[®] spray alkyd paint + Red AlphaAcryl Sikkens[®] Paint

³ Red AlphaAcryl Sikkens[®] Paint + Green AlphaAcryl Sikkens[®] Paint

⁴ Red AlphaAcryl Sikkens[®] Paint + Green Belton[®] spray alkyd paint

the protective coating was let dry for one week. The coating used was SILO 112 by CTS, composed by a water-based mixture of reactive organosiloxane olygomers⁵.

The cleaning tests were carried out after one week from the application of the paint with both laser and chemical cleaning methodologies. The aim of the tests consisted in a evalutation of the best, if any, system to selectively remove the outer painting layer, considering the eventually contribution of the protective layer.

Regarding the use of laser for the cleaning, an EOS 1000 Long-Q-Switch mode (LQS) laser, working at 1064 nm, was selected on the basis of previous research carried out at the Centro Conservazione e Restauro "La Venaria Reale". Experimental conditions used for tests will be detailed below for each mock-up.

Regarding chemical cleaning tests, different methodologies have been settled up, according to a recent, but poor, bibliography on cleaning and protection of contemporary outdoor paitings. The main difficulty, in this perspective, consists in the willing to preserve the painting layer(s) underlying the superficial layer intended to be removed. In fact, studies and researches mainly deal with the removal of graffiti from unpainted surface such as stone of architectural surfaces, often covered with synthetic filming materials such as protective layers, water-repellents or anti-graffiti coatings. Removing painting layers from layers, with similar chemical composition and therefore similar response to solvents, require to deeply observe the interactions among the different materials and settle specific methodologies, aimed to reduce the penetration of solvents through the superficial painting layer(s), as well as being both selective and effective. In order to set up tailored solutions and methodologies, an innovative cleaning system, based on nanotechnologies, has been compared with pure solvents or solutions, applied either through little swab or gels.

According to the technical data sheet, the nanotechnology cleaning consisted in the application of a water based, nanostructured fluid (Polar Coating S), containing anionic surfactant and a solution of 1-pentanol, ethyl acetate and propylene carbonate. The solvent solution, merged 9% of ethylene carbonate, has then been thicked with a Nanorestore Gel[®] - Medium Water Retention – MWR, a chemical hydrogel with high retentive properties.

Other solvents and solutions include:

- Propylene carbonate,
- Diethyl carbonate,
- Ethylene carbonate,
- N-Butyl propionate,
- Metyl Ethyl Ketone,
- Acetone,
- Isopropyl alcohol,
- Ethanol,
- Water

Differently thickened with:

- Agar
- Poly(vinyl alcohol)-borate gel

⁵ Spepi, A., Pizzimenti, S., Duce, C. et al. *Chemico-physical characterization and evaluation of coating properties of two commercial organosilicons*. J Therm Anal Calorim 138, 3277–3285 (2019). https://doi.org/10.1007/s10973-019-08830-4

- Kelcogel Gellano[®]
- Ethyl cellulose

Applied directly on the painting surface or a sheet of Japanese paper, to reduce the solvent penetration through the layers.

The evaluation of the effects of each cleaning test was carried out by means of:

- observation by stereomicroscope, with a OLYMPUS SZ X10 microscope;
- contact angle measurements, with a DSA100 drop shape analyzer (Krüss GmbH, Hamburg, Germany);
- colour measurements, with a CM-700d Konica Minolta spectra photo colorimeter: measurements were made in SCI (specular component included) mode; a total of 15 measurements (5 points of measure, 3 meaurements for each point) were acquired for each cleaning test area, then the average values were calculated. The change of color *delta E* was calculated for each area comparing colour coordinates L*, a*, b* respectively obtained after the cleaning test (aiming to remove the outer paint layer, while preserving the underlying layer) and before the application of this outer paint layer: thus, the measure of *delta E* gives a clue about the perceptive variation of the background before and after the treatment.

The table below summarizes names and stratigraphy of all the mock-ups and cleaning test	sts achieved:
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# mock-up	Stratigraphy	Cleaning test
1	P (protective coating) Green acrylic Red acrylic Green alkyd Concrete	Chemical cleaning - <i>P portion:</i> test areas 2, 3, 5p, 10p, 11 - <i>noP portion:</i> test areas 1, 4, 5, 6, 7, 8, 9, 10
2	P noP (protective coating) Green acrylic Red acrylic Green alkyd Concrete	Chemical cleaning - <i>P portion:</i> test areas 1p, 2p - <i>noP portion:</i> test areas 1, 2
3	P (protective coating) (unprotected) Red acrylic Green alkyd Concrete	Laser LQS - <i>P portion:</i> test areas A , B , C , D , E , F , G - <i>noP portion:</i> test areas Gp , Gp' , Gp''

4	P (protective coating) Green acrylic Red acrylic Green alkyd Primer Concrete	Laser LQS - <i>P portion:</i> test areas A, B, C - <i>noP portion:</i> test areas Ap, Bp
5	P (protective coating) Red acrylic Green alkyd Primer Concrete	Chemical cleaning - <i>P portion:</i> test areas 1p, 3, 4p - <i>noP portion:</i> test areas 1, 2, 4
6	P (protective coating) Red acrylic Green alkyd Primer Concrete	Chemical cleaning - <i>P portion:</i> test areas 2p, 3 - <i>noP portion:</i> test areas 1, 2, 2', 2'', 4
7	P (protective coating) Green Alkyd Red acrylic Primer Concrete	Laser LQS - <i>P portion:</i> test areas A, B - <i>noP portion:</i> test areas Ap, Bp, Cp
8	P (protective coating) Green alkyd Red acrylic Primer Concrete	Chemical cleaning - <i>P portion:</i> test areas 1p, 2p - <i>noP portion:</i> test areas 1, 2

9	P noP (protective coating) Green alkyd Red acrylic Primer Concrete	Chemical cleaning - <i>P portion:</i> test areas 1p, 2p - <i>noP portion:</i> test areas 1, 2, 3, 4, 5
10	P (protective coating) Red Alkyd Green alkyd Red acrylic Primer Cement-based Mortar	Chemical cleaning - <i>P portion:</i> test areas 1p, 3p - <i>noP portion:</i> test areas 1, 2, 3
11	P (protective coating) (unprotected) Red Alkyd Green alkyd Red acrylic Primer Cement-based Mortar	Chemical cleaning - <i>P portion:</i> test areas 1p, 2p, 3, 4, 6 - <i>noP portion:</i> test areas 1, 2, 5
12	P (protective coating) Red Alkyd Green alkyd Red acrylic Primer Cement-based Mortar	Laser LQS - <i>P portion:</i> test areas A , B , C - <i>noP portion:</i> test areas Ap , Bp , Cp

2.1.2 What were the results of the optical and analytical observation of the different cleaning methods on the ad hoc samples? (table) How did you get the results?

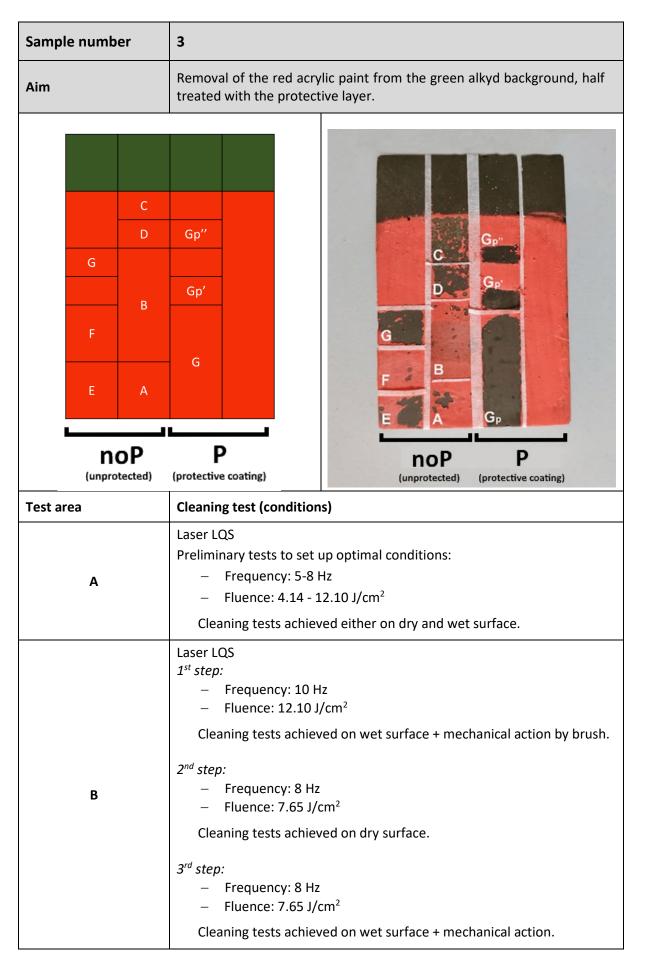
Sample number	1		
Aim	Removal of the green acrylic paint from the red acrylic, applied on a background green alkyd layer (half treated with the protective layer).		
5 6 8 10 4 7 NOP (unprotected)	5p II 10p 3 2 P (protective coating)	6 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	P (protective coating)
Test area	Cleaning test (conditions)		
1	Propylene carbonate, applied o	n the surface wit	h a micro-swab.
2	Diethyl carbonate, applied on the surface with a micro-swab.		
3	Diethyl carbonate, thickened with ethylcellulose (4%) and applied on the surface for 1 minute. Final rinse with diethyl carbonate applied with a swab.		
4	Diethyl carbonate, thickened with ethylcellulose (4%) and applied by interposing a sheet of Japanese paper, for 10 minute.		
5 - 5p	Nanorestore gel extradry [®] with a 90% solution of polar coating S [®] in Ethylene carbonate (30 minute application), followed by a water rinse with a micro-swab.		
6	N-Butyl propionate, applied on	the surface with	a micro-swab.
7	Metyl Ethyl Ketone, applied on the surface with a micro-swab.		
8	Acetone, applied on the surface	with a micro-sw	ab.
9	Isopropyl alcohol, applied on th	e surface with a r	micro-swab.

10 - 10p	Nanorestore gel extradry [®] with a 90% solution of polar coating S [®] in Ethylene carbonate (5 minute application), followed by a micro-swab rinse with a solution 30% of ethanol in water.		
11	Solution of Ethanol (18%), Metyl Ethyl Ketone (18%), Diethyl carbonate (10%) and water (54%), applied on the surface with a micro-swab.		
Analytical Results			
МО			
Contact angle	The average value of contact angle measured on the red acrylic paint layer was $62^{\circ}\pm13^{\circ}$. After all cleaning tests, the surface showed to become superhydrophilic (the drop of water was absorbed and θ <5°), unless for the portion 5p , whose average value of contact angle is $85^{\circ}\pm2^{\circ}$. This is probably due to the fact that in this area, the 30 minutes application of the Nanorestore gel extradry [®] caused the swelling of the two acrylic layers, letting the green alkyd background appear, which in this area of the mock-up presented also the protective coating (therefore explaining the increase of contact angle value).		
Optical results &			
general observations			
1	Very poor solubilization of the green paint that consistently remains on the surface; only a very thin portion of the upper layer has been removed.		
2	Combining the mechanical action of the micro-swab to the physical action of the solvent, the whole green layer can be solved and removed with the swab; due to the common chemical nature of the green and red paints (both of them are acrylic), very poor selectivity of the solvent solution has been attested. The system gradually removes also the underlying red paint.		

3	The compress seems to have action on both the acrylic layers, the following cleaning with the swab remove unselectively the green and the red paint.
4	The solvent is very aggressive towards the two acrylic paints and the lower alkydic layer. After the removal of the Japanese paper, the paint seems to be blistered but, rinsing with a micro swab, both of the acrylics result to have been completely detached from the lower alkyd layer, that appears partially solubilized.
5	Gel application has caused swelling of the two acrylic layers, that are both removed during the final water rinse. In the noP area, a strongest interaction between red acrylic and underlying green alkyd resin is attested.
6	At first the action seems to be gentle and selective, but after few seconds, the solvent penetrates the superficial layers and solubilizes the two layers of acryl paints.
7	No selectivity in the removal of the acryl paints: both of them are solubilized.
8	No selectivity in the removal of the acryl paints: both of them are solubilized.
9	At first the action seems to be gentle and selective, but after few seconds the solvent penetrates the superficial layers and solubilizes the two layers of acryl paints.
10	Partial removal of the green paint, that has been swelled by the gel. On the back of the green painting scales traces of the red acrylic paint are visible.
11	No selectivity in the removal of the acryl paints: both of them are solubilized.

Sam	ple number	2	
Aim Removal of the green acrylic paint from the red acrylic, applied or background green alkyd layer (half treated with the protective layer).			
	2	2 p	2 2p
	1	1p	
	noP (unprotected)	P (protective coating)	(unprotected) P {protective coating}
Test	area	Cleaning test (condition	ns)
	1 - 1p	Nanorestore gel extradry [®] with a 90% solution of polar coating S [®] in Ethylene carbonate (1 hour application), followed by a water rinse with a micro-swab.	
	2 - 2p	Agar gel with a solution 30% of ethanol in water, followed by a gently swab rinse with the same solution.	
Analytical Results			
MO			

	1 1 1 1 2 200 Jm 200 Jm		
Contact angle	The average value of contact angle measured on the red acrylic paint layer was 62.4 ± 13 . After the cleaning test, the portion 2p (use of agar gel with a solution 30% of ethanol in water) became superhydrophilic (the drop of water was absorbed and θ <5°).		
Optical results & general observations			
1 - 1p	Due to the action of the swab, both of the paints are removed during the final rinse, especially in the unprotected area, where possibly the red acrylic paint had deeply interacted with the lower green alkyd one.		
2 - 2p	The final rinse with water and ethanol seems to stop the action of the solvent embedded in the gel, improving the selectivity of the system; despite so, on the back of the green acrylic detached film, little traces of red paint are visible.		



С	Laser LQS 1 st step: – Frequency: 8 Hz – Fluence: 7.65 J/cm ² Cleaning tests achieved on wet surface 2 nd step: – Frequency: 5 Hz – Fluence: 4.14 J/cm ²	
D	Cleaning tests achieved on wet surface Laser LQS – Frequency: 5 Hz – Fluence: 4.14 J/cm ² Cleaning tests achieved on wet surface + mechanical action by brush	
E	Laser LQS – Frequency: 5 Hz – Fluence: 4.14 J/cm ² Cleaning tests achieved on wet surface, covered with polyethylene film in order to slow down water evaporation + mechanical action by brush	
F	Laser LQS – Frequency: 5 Hz – Fluence: 4.14 J/cm ² Cleaning tests achieved on a portion of surface, covered with Nanorestore Gel Dry	
G	Laser LQS – Frequency: 7 Hz – Fluence: 4.14 J/cm ² Cleaning tests achieved on wet surface, covered with polyethylene film in order to slow down water evaporation + mechanical action by brush	
Gp	Laser LQS – Frequency: 7 Hz – Fluence: 4.14 J/cm ² Cleaning tests achieved on wet surface, covered with polyethylene film in order to slow down water evaporation + mechanical action by brush	
Gp'	Laser LQS – Frequency: 6 Hz – Fluence: 2.65 J/cm ² Cleaning tests achieved on wet surface, covered with polyethylene film in order to slow down water evaporation + mechanical action b brush	

Gp"	* No laser action - Mechanical action by dry cotton swab
Analytical Results	
МО	Cleaning tests on the unprotected portion:
	G d d d d d d d d d d d d d d d d d d d
	Cleaning tests on the portion with protective coating:
	Gp' Gp' DEC #

	Gp			20	00 µm		
Colour	Sample	delta L	delta a	delta b	delta E	delta E00	
	3_noP_G	3.80	3.76	1.79	5.63	6.03	
	3_P_Gp	8.44	5.50	2.03	10.27	10.37	
Contact angle	perception of be taken in	of the surfactor to account he mock-up	ce clearly vi that colo o, thus sugg	sible to the r measure gesting the	e naked eye. ments were	g a change of However, it m made on sn pe representat	nust nall
5	120 110	Contact a	ngle	we the for	re made onle cleaning te	measurement y in the case c ests G and Gg rently the bes tained.	of p ,
	100	I		me inc	gle close easured, rease of the mpared to th	ting) a contac to 90° wa	ct as in ty o n
	30 — 20 — 10 — 0 —	noP_G	2 P. Gp	las no the	er LQS for th t show to rer	•	id ct
		aint layer 📕 A	3_P_Gp				

Optical results & general observations	
	 The use of laser LQS on a dry surface proved to provide only a thinning of the red acrylic paint layer and a slight chromatic alteration.
A-B-C	 To wet the surface prior to the use of laser allowed a partial removal of the red paint layer; the increase of the frequency and fluence of the laser was helpful, however this made some visible laser spot marks appear on the surface.
	 Following steps with the laser and the mechanical action of a trimmed brush helped in the removal of the red paint scales.
D	The selection of the operating conditions was based on the evidence of previous tests (A-B-C). The use of laser on a wet surface and the help of mechanical action by a trimmed brush provided a partial removal of the upper paint layer; however, the removed red scales presented some traces of green paint on their back, thus showing a limited selectivity of the cleaning procedure.
E	The same operating conditions of the cleaning area D were repeated, however the application of a polyethylene film onto the surface was added, in order to slow down water evaporation. This made the use of laser more controllable and reduced the risk of chromatic alteration on the lower green paint layer.
F	The same operating conditions of the cleaning area D were repeated and a scrap of a Nanorestore Gel dry was tested to slow down the water evaporation from the surface. However, the method did not result optimal for its complexity and lack of control in the use of laser.
G	The same operating conditions of the cleaning area E were repeated; an increase of the laser frequency up to 7 Hz allowed to obtain a decent result, even if not optimal.
Gp	The best operating conditions tested on the unprotected portion of the mock-up (cleaning area G) were tested on the portion with protective coating. The method resulted quite selective, even if some traces of the protective coating were observable on the back of the red paint scales removed. Acceptable result.
Gp'	The use of laser with lower frequency and fluence than for the cleaning area Gp seems to better preserve the protective coating layer.
Gp"	The mechanical action by a dry cotton swab confirmed the effect of the presence of the protective coating, which created a separation layer between the green and the red paint layers, thus making the removal of the upper paint easier.

Sample number	4					
Aim	Removal of the green acrylic paint from the red acrylic, applied on a background green alkyd layer (half treated with the protective layer).					
B A C	BpApP					
noP (unprotected)	(protective coating)					
Test area	Cleaning test (conditions)					
A	 Laser LQS Frequency: 7 Hz Fluence: 4.14 J/cm² Cleaning tests achieved on wet surface, covered with polyethylene film in order to slow down water evaporation + mechanical action by dry cotton swab. 					
В	Laser LQS 1 st step: – Frequency: 7 Hz – Fluence: 4.14 J/cm ² Cleaning tests achieved on dry surface. 2 nd step: – Frequency: 4 Hz – Fluence: 4.14 J/cm ² Cleaning tests achieved on dry surface.					

с	 Laser LQS Frequency: 7 Hz Fluence: 7.65 J/cm² Cleaning tests achieved on wet surface, covered with polyethylene film in order to slow down water evaporation + mechanical action by dry cotton swab.
Ар	 Laser LQS 1st step: Frequency: 7 Hz Fluence: 4.14 J/cm² Cleaning tests achieved on wet surface, covered with polyethylene film in order to slow down water evaporation + mechanical action by brush. 2nd step: Frequency: 7 Hz Fluence: 4.14 J/cm² Cleaning tests achieved on dry surface.
Вр	Laser LQS 1 st step: – Frequency: 6 Hz – Fluence: 4.14 J/cm ² Cleaning tests achieved on dry surface. 2 nd step: – Frequency: 7 Hz – Fluence: 4.14 J/cm ² Cleaning tests achieved on wet surface.
Analytical Results	
Analytical Results MO	Cleaning tests on the unprotected portion: A C C C C C C C C C C C C C

Colour	Color measurements were not performed since the results of the cleaning tests were very heterogeneous, thus making it harder to find a representative portion of the surface.					
Contact angle	The contact angle measurements were not performed since the results of the cleaning tests were very heterogeneous, thus making it harder to find a representative portion of the surface.					
Optical results & general observations						
A-B-C	 None of the three cleaning areas showed a selectivity of the laser in the removal of the outer green acrylic paint layer from the lower red acrylic one, which resulted to fully adhere one to the other (the green acrylic layer having been layered before that the red one was completely dry). In the cleaning area A, the same operating conditions of the cleaning area G of the mock-up #3 were repeated; In the cleaning area B, a second step with a lower frequency provided a thinning of the green acrylic layer, but with heterogeneous results; In the cleaning area C, the use of a higher fluence for the laser and the mechanical action by a dry cotton swab showed damages to all paint layers, letting the substrate appear. 					
Ар	Despite the presence of the protective coating layer, the results obtained are similar to those of the cleaning area A .					
Вр	For the cleaning area Bp , the mechanical action by a dry cotton swab showed to completely remove the two acrylic paint layers (respectively green and red), letting the lowest green alkyd paint layer appear;					

Sample nu	mber	5						
Aim	Aim Removal of the red acrylic paint from the green alkyd background, h treated with the protective layer.							
2	4	4p 3 Ip	274	4p Jp				
_	10P	P (protective coating)	noP (unprotected)	P {protective coating}				
Test area		Cleaning test (condition	ons)					
1 - :	1p	-	-	n of polar coating S [®] in ed by a water rinse with a				
2		micro-swab						
		micro-swab		-borate gel (10 minutes				
3		micro-swab Propylene carbonate application)		-borate gel (10 minutes				
3		micro-swab Propylene carbonate application) Diethyl carbonate, app	in a Poly(vinyl alcohol)	-borate gel (10 minutes				
	4p	micro-swab Propylene carbonate application) Diethyl carbonate, app Solution of 50% ethance	in a Poly(vinyl alcohol) lied on the surface with a ol in water, applied on the	-borate gel (10 minutes micro-swab				
4 - 4	4p - 4p	micro-swabPropylene carbonate application)Diethyl carbonate, appSolution of 50% ethanceFinal rinse with a solut	in a Poly(vinyl alcohol) lied on the surface with a ol in water, applied on the	-borate gel (10 minutes micro-swab surface with a micro-swab				

	1			1р Эсыт 4р			2000 μπ
Colour	Sample	delta L	20 delta a	delta b	delta E	delta E00	2000 µm
	5_1	0.04	1.07	0.29	1.10	1.49	
	 5_4	-0.31	0.19	0.65	0.75	0.61	
	_ 5_1p	-0.45	1.12	-0.16	1.22	1.62	
	5_4p	-0.52	0.11	0.38	0.65	0.53	
		n of the Nar	norestore g	el extradry	[®] , both on	tained after a the unprotec	
Contact angle							

	Contact angle						
	120						
	110						
	100						
	90						
	80						
	50						
	40						
	30						
	20						
	0 5_1 5_4 5_1p 5_4p Original paint layer After cleaning test						
	After a 1 hour application of the Nanorestore gel extradry [®] , both on the unprotected and the protected portion of the green alkyd background (portions 1 and 1p), the surface became superhydrophilic (the drop of water was absorbed and θ <5°).						
Optical results & general observations							
1 - 1p	After a preliminary test, polar coating S was preferred to water, for the final superficial rinse.						
2	Strong action on both the acrylic and alkyd layers.						
3	Good solubilization of the red acrylic paint, but a lot of residues and a white veil became visible on the surface after the test.						
4 - 4p	Good removal of the acrylic red paint, few remains on the green alkyd layer that result glossier.						
2 - 4 - 4p	After the test all the surface has been rinsed with a 30% ethanol-water solution: good results in the protected area, some remains in the unprotected one.						

Sam	ple number	6				
Aim		Removal of the red acrylic paint from the green alkyd background, half treated with the protective layer.				
	4	3	4 3			
2		2p	2 2p			
	noP (unprotected)	P (protective coating)	(unprotected) (protective coating)			
Test area Cleaning test (cond			·			
	1	water, applied on the s	urface with a micro-swab.			
:	 Propylene carbonate, applied on the surface with a micro-swab. In swab has been used to completely remove all the traces of red pain part. absorbed in the underlying green one. In 2", after a prelimin application of Propylene carbonate, a wood toothpick has been user remove any remaining of red paint. 					
	 Nanorestore gel extradry[®] with a 90% solution of polar coating S[®] Ethylene carbonate (30 minutes application), followed by a water riwith a micro-swab. 					
	 Nanorestore gel extradry[®] with a 90% solution of polar coating S Ethylene carbonate (1 hour application), followed by a water rinse w micro-swab. 					
Analy	ytical Results					
МО						

Colour	Sample		20	00 µm		
Colour	Sample					
		delta L	delta a	delta b	delta E	delta E00
	6_2p	-0.56	0.34	0.29	0.72	0.70
	6_2	0.04	0.50	1.02	1.13	1.00
	6_3	1.84	1.14	2.05	2.98	2.63
	6_4	8.18	2.92	4.16	9.62	8.61
	minutes o observed (portion 3 4; 1 hour a was obtai portion 3,	r for 1 hou and confirr ; 30 minute application ned. This i thus show	r), a clearly ned by col es applicati) of the gre ncrease w ing perhap	visible cha or measure ion) and the en alkyd ba as more re os a positive	nge of colo ements. Bo e unprotec ockground, elevant for e effect of	adry [®] (eithe or of the sur oth on the p cted portion a delta E00 r portion 4 the presence ne of applica
Contact angle						

	Contact angle						
	120 110						
	100 —	90					
	90 —						
	70 —		1	T T	-		
	60 —		Ť.		I I		
	50 -						
	40 -						
	30 — 20 —						
	10 -						
	0						
	0	6_2p	6_2	6_3	6_4		
		O I	iginal paint layer	After cleaning tes	t		
	After the application of Nanorestore gel extradry [®] on the portion 3 (red acrylic paint on green alkyd background with protective coating) a relevant reduction of the contact angle value was measured (the surface, initially hydrophobic, became hydrophilic). Conversely, a minimal variation of the contact angle value was measured on the portion 4 (red acrylic paint on unprotected green alkyd background). For both cases, θ <70°. For portions 2 and 2p , cleaned by using Propylene carbonate, a little higher average value of the contact angle was measured, if compared to portions 3 and 4 .						
Optical results &	3 and 4.						
general observations							
	The red	acrylic paint i	s still partially sol	uble in water, pr	obably because of		
			• •	•	e, water does not		
1					f the presence of a		
	layer of interaction (mainly visible in the unprotected area) between the red acrylic and the green alkyd paint.						
	Good re	emoval of the	red acrylic paint	, insisting in the	final rinse causes		
2 - 2' - 2" - 2p	Good removal of the red acrylic paint, insisting in the final rinse causes solubilization of the lower alkyd green paint. A soft mechanical action,						
2-2-2-20	after a preliminary application of Propylene Carbonate, seems to be						
		ful of the gree					
			-		e gel, appear to be olvent and the red		
3			-		30 minute, results		
	very eff				ected one required		
	-		the test provides	effective remov	al of the red acrylic		
4	-		-		elated with some		

interferences between the two painting layers, are attested after the cleaning.
0

Sample number	7
Aim	Removal of the green alkyd paint from the red acrylic background, half treated with the protective layer.
B	Ср Вр Ар
noP (unprotected)	P (protective coating)
Test area	Cleaning test (conditions) Laser LQS 1 st step: – Frequency: 7 Hz
 Fluence: 4.14 J/cm² Cleaning tests achieved on wet surface, covered with polyethylen in order to slow down water evaporation + mechanical action by A 2nd step: Some conditions than 1st step 3rd step: - Frequency: 2 Hz - Fluence: 1.04 J/cm² Cleaning tests achieved on dry surface. 	

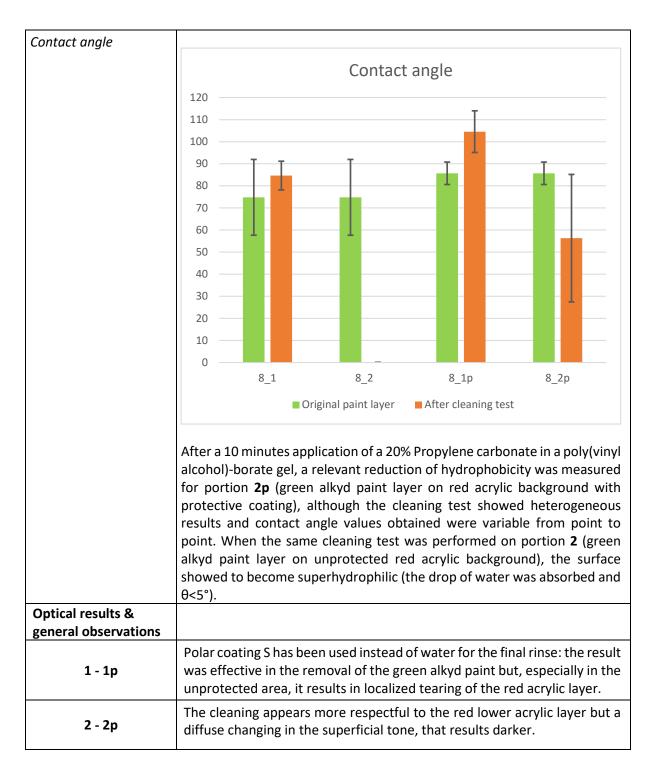
	Laser LQS
В	– Frequency: 6 Hz
D	 Fluence: 4.14 J/cm²
	Cleaning tests achieved on dry surface.
	Laser LQS
	1 st step:
	 Frequency: 7 Hz
	 Fluence: 4.14 J/cm²
	Cleaning tests achieved on wet surface, covered with polyethylene film
Ар	in order to slow down water evaporation + mechanical action by brush.
	2 nd step:
	– Frequency: 3 Hz
	 Fluence: 7.65 J/cm²
	Cleaning tests achieved on dry surface.
	Laser LQS
	 Frequency: 6 Hz
Вр	 Fluence: 4.14 J/cm²
	Cleaning tests achieved on dry surface
	Laser LQS
	 Frequency: 3 Hz
Ср	 Fluence: 7.65 J/cm²
	Cleaning tests achieved on dry surface
Analytical Results	
МО	Cleaning tests on the unprotected portion:
	Cleaning tests on the portion with protective coating:

	Ap Ap Cp Cp
Colour	Color measurements were not performed since the results of the cleaning
	tests were very heterogeneous, thus making it harder to find a representative portion of the surface.
Contact angle	The contact angle measurements were not performed since the results of the cleaning tests were very heterogeneous, thus making it harder to find a representative portion of the surface.
Optical results & general observations	
А	The same operating conditions of the cleaning area G of the mock-up #3 were repeated, here too without good results. Neither repeated steps, nor to keep the surface dry, showed to improve the selectivity of the laser.
В	A thinning of the green alkyd paint is obtained, but, although the cleaning test seems to provide slight better results than the cleaning test A , a good selectivity of the laser is not provided.
Ар-Вр-Ср	The presence of the protective coating layer did not help the selectivity of the laser cleaning. Either a thinning or an uncomplete removal of the green alkyd layer were obtained, but the results of the cleaning tests were heterogeneous; the protective coating showed to fully adhere to the lower red acrylic layer and the damage threshold was reached for the latter.

Samp	ole number	8	8			
Aim		_	emoval of the green alkyd paint from the red acrylic background, half reated with the protective layer.			
	2	lp 2p	2	Ip 2p		
	noP (unprotected)	P (protective coating)	noP (unprotected)	P (protective coating)		
Test a	area	Cleaning test (conditio	ns)			
	1 - 1p	Ethylene carbonate (30 coating S, applied wit	Nanorestore gel extradry [®] with a 90% solution of polar coating S [®] in Ethylene carbonate (30 minutes application), followed by rinse with polar coating S, applied with a micro swab and final application of water combined with the gentle action of a micro-swab.			
	2 - 2p	20% Propylene carbonate in a Poly(vinyl alcohol)-borate gel (10 minutes application).				
Analy	tical Results					
МО						

[Hier eingeben]

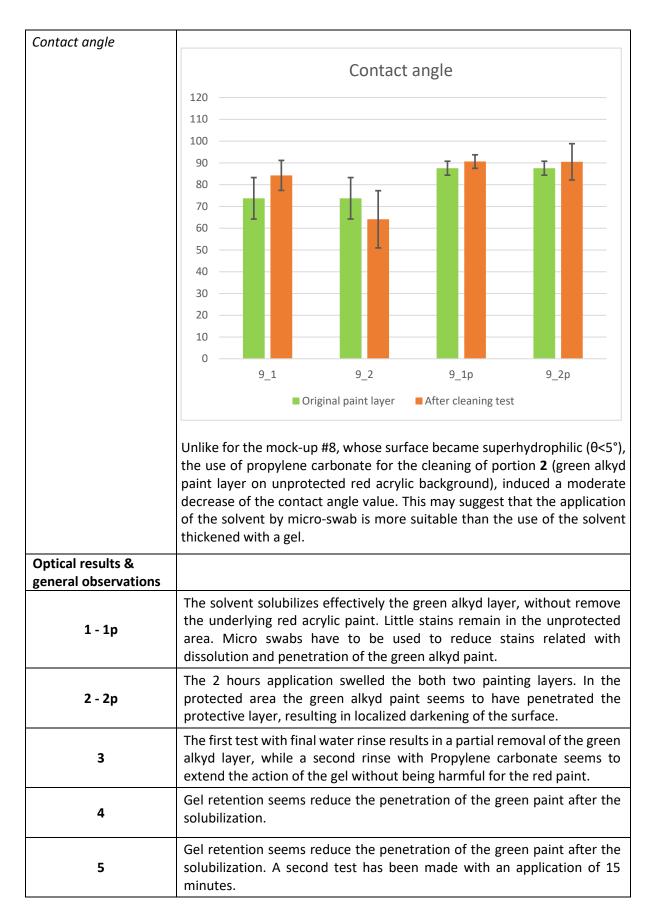
	1p 2p	3	20	1 50 um 2 50 um			2000 µm
Colour	Sample	delta L	delta a	delta b	delta E	delta E00	
	8_1	-0.91	-5.72	-3.17	6.60	2.28	
	8_2	-0.67	-2.64	-0.40	2.75	1.22	
	8_1p	-1.10	-2.56	-0.60	2.85	1.41	
	8_2p	-1.13	-1.44	-0.41	1.88	1.18	
	20% Propy application	lene carbo	onate in a p change of	oly(vinyl a	lcohol)-bo	ites applicat rate gel (10 surface visit	minut

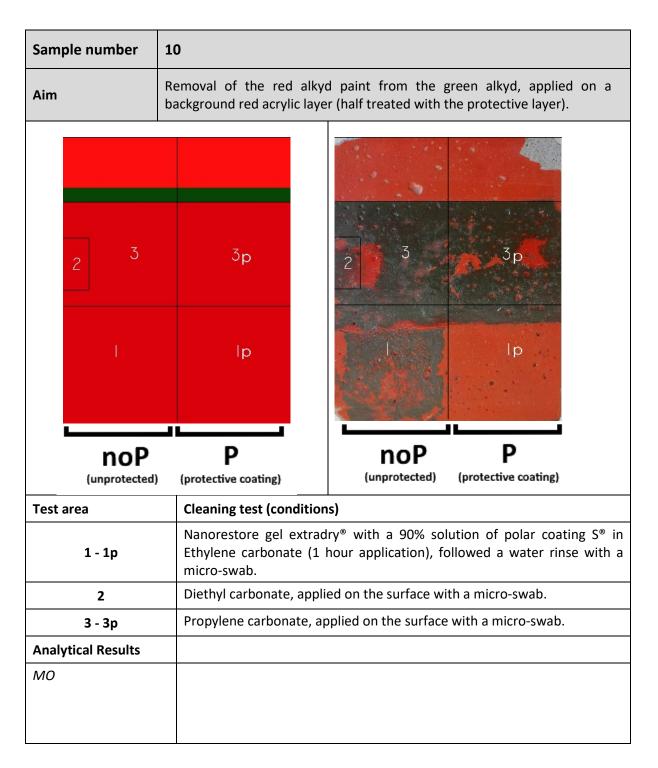


Sample number	9			
Aim	Removal of the green al treated with the protect	kyd paint from the red acrylic background, half ive layer.		
3 4		3 4		
	۱p	l lp		
5)				
2	2p	2 2p		
noP (unprotected)	P {protective coating}	(unprotected) (protective coating)		
Test area	Cleaning test (condition	s)		
1 - 1p	Propylene carbonate, ap	plied on the surface with a micro-swab.		
2 - 2p	_	Nanorestore gel extradry [®] with a 90% solution of polar coating S [®] in Ethylene carbonate (30 minutes application), followed a water rinse with a micro-swab.		
3	Single application of Propylene carbonate applied by brush, followed by the application of Agar gel with 1% (w/w) of Propylene carbonate (10 minutes application).			
4	20% Propylene carbonate in a Poly(vinyl alcohol)-borate gel (10 minutes application), applied on a sheet of Japanese paper.			
5	20% Propylene carbonate in a Poly(vinyl alcohol)-borate gel (10 minutes application).			
Analytical Results				
МО				

[Hier eingeben]

	1p 2p		20	1 50 um 20 um			2000 µm
Colour	Sample	delta L	delta a	delta b	delta E	delta E00	
	9_1	-0.71	-4.21	-2.60	4.99	1.69	
	9_2	-0.37	-7.14	-4.17	8.28	2.71	
	9_1p	-1.65	-0.30	1.02	1.96	1.65	
	9_2p	-2.07	-8.33	-5.01	9.94	3.71	
	2p) and the a change of	e use of pro of color of t	pylene car	bonate (po visible to t	rtion 1 and	adry [®] (porti 1 1p) proved eye (delta EC	to cau

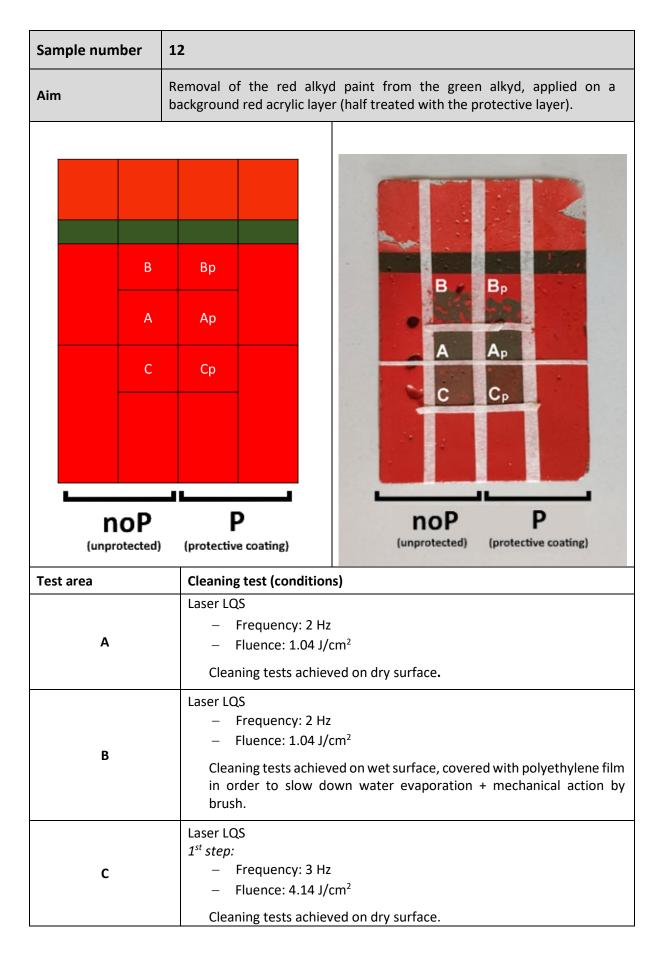




	1 1		
Contact angle	The average value of contact angle measured on the green alkyd paint layer was $60^{\circ}\pm 5$.		
	After the cleaning test with the Nanorestore gel extradry [®] , the surface became superhydrophilic (the drop of water was absorbed and $\theta < 5^{\circ}$) when unprotected (1), while the presence of the protective coating allowed to preserve a good hydrophobicity of the surface (1p). After the cleaning with Propylene carbonate , both the unprotected portion (3) and the portion with protective coating (3p) showed to be hydrophilic, with respectively a little ($55^{\circ}\pm2^{\circ}$ for 3) and a relevant ($60^{\circ}\pm18^{\circ}$ for 3p) reduction of the average contact angle value.		
Optical results & general observations			
1 - 1p	The selective removal of the superficial alkyd layer is impossible; the two alkyd layers are immediately solubilized by the solvent. In the protected area, the test results in a complete removal of the two alkyd layers.		
2	No selectivity or control of the action of the solvent is attested, even in the test with Japanese paper.		
3 - 3p	The action results more gradual and respectful to the lower alkyd layer. Any mechanical action with the swab should be avoid.		

Sample number	11		
Aim	Removal of the red alkyd paint from the green alkyd, applied on a background red acrylic layer (half treated with the protective layer).		
2 5 ا noP (unprotected)	P (protective coating)		
Test area	Cleaning test (conditions)		
1 - 1p	Nanorestore gel extradry [®] with a 90% solution of polar coating S [®] in Ethylene carbonate (2 hours application), followed a water rinse with a micro-swab.		
2 - 2p	Propylene carbonate, applied on the surface with a micro-swab.		
3	Diethyl carbonate, applied on the surf	face with a micro-swab.	
4	Ethylic alcohol, applied on the surface with a micro-swab.		
5	Diethyl carbonate applied with a little brush on the surface, followed by the application of Kelcogel [®] rigid gel with Propylene carbonate (10 minutes application).		
6	20% Propylene carbonate in a Poly(vinyl alcohol)-borate gel (10 minutes application), applied on the painted surface.		
Analytical Results			
МО			

	1 1 1 1 1 1 1 1 1 1 1 1 1 1	
Contact angle	The average value of contact angle measured on the green alkyd paint layer was $60^{\circ}\pm5^{\circ}$. After the cleaning test with the Nanorestore gel extradry [®] , the surface became superhydrophilic (the drop of water was absorbed and θ <5°) both when unprotected (1) and with the protective coating (1p). After the cleaning with Propylene carbonate , both the unprotected	
	portion (3) and the portion with protective coating (3p) showed to be hydrophilic, with comparable average contact angle values (respectively $68^{\circ}\pm4^{\circ}$ for 3 and $68^{\circ}\pm9^{\circ}$ for 3p).	
Optical results & general observations		
1 - 1p	Any selective removal of the two alkyd paints is impossible: the solvent immediately solubilizes the two layers; moreover, even a gentle mechanical action results in scratches and thinning of the green alkyd paint and of the underlying red acrylic one.	
2 - 2p	The two alkyd paints have been softened and partially solubilized by the solvent: with a gentle action, a partial removal of the red alkyd seems to be possible but the lower green alkyd paint becomes sticky and tears off the cotton fibers of the swab.	
3	The two alkyd paints are immediately solubilized by the solvent, only with a very thin and dry swab a partial removal of the red alkyd paint is possible.	
4	No selectivity: the two alkyd paints are immediately solubilized and the surface results in localized bleaching.	
5	No selectivity, the solvent immediately solubilizes the two paints, even if embedded in a gel.	
6	No selectivity, the solvent immediately solubilizes the two paints, even if embedded in a gel.	



	2 nd step:				
	– Frequency: 2 Hz				
	 Fluence: 2.65 J/cm² 				
	Cleaning tests achieved on dry surface.				
	3 rd step:				
	– Frequency: 2 Hz				
	 Fluence: 2.65 J/cm² 				
	Cleaning tests achieved on wet surface.				
	Laser LQS				
	Preliminary tests to set up optimal conditions:				
Ар	– Frequency: 2-6 Hz				
	 Fluence: 1.04 J/cm² 				
	Cleaning tests achieved on dry surface.				
	Laser LQS				
	– Frequency: 2 Hz				
Вр	– Fluence: 1.04 J/cm ²				
55	Cleaning tests achieved on wet surface, covered with polyethylene film				
	in order to slow down water evaporation + mechanical action by				
	brush.				
	Laser LQS				
	1 st step:				
	 Frequency: 3 Hz Fluence: 4.14 J/cm² 				
Ср	Cleaning tests achieved on dry surface.				
	2 nd step:				
	– Frequency: 2 Hz				
	 Fluence: 2.65 J/cm² 				
	Cleaning tests achieved on dry surface.				
Analytical Results					
МО	Cleaning tests on the unprotected portion:				
	A				
L					

	Cleaning tests on the portion with protective coating:
	Ap Cp Cp Cp Cp Cp Cp Cp Cp Cp C
Colour	Color measurements were not performed since the results of the cleaning tests were very heterogeneous, thus making it harder to find a representative portion of the surface.
Contact angle	The contact angle measurements were not performed since the results of the cleaning tests were very heterogeneous, thus making it harder to find a representative portion of the surface.
Optical results & general observations	
A-B-C	Either on a dry or a wet surface, the use of laser proved no to be selective in the removal of the outer red alkyd paint layer from the lower green alkyd layer. Even the use of moderate frequency and fluence of the laser allowed the partial removal of red scales, presenting some traces of green paint on their back. The red alkyd paint and the green alkyd one resulted to fully adhere one to the other (the red paint having been layered before that the green one was completely dry) and the damage threshold was reached for the lowest green layer.
Ар	The use of laser for repeated steps allowed an acceptable removal of the outer red alkyd paint; however, it seems that the protective coating layer suffered some damages.
Вр	The same operating conditions of the cleaning area B were repeated; in this case, the presence of the protective coating allowed a higher selectivity in the removal of the outer red alkyd paint. The removed red scales, indeed, presented fewer traces of green paint on their back.
Ср	As in the cleaning area C, a thinning of the outer red alkyd paint was obtained, but its complete and selective removal was not possible.

2.1.3 Which of the applied cleaning methods were most effective? (lowest impact on the surface, best cleaning result,...test winner) Why? What was your criteria for the evaluation?

None of the cleaning methods tested proved to be fully effective and to have no impact on the surface in all cases considered. As attended, the most challenging tests were performed for those cases of overlapping of two paint layers belonging to the same class of products (i.e. acrylic + acrylic; alkyd + alkyd).

In terms of effectiveness in the removal of the outer paint layer, observation by stereomicrocope was used to assess the cleaning result and the quantity of the residues on the surface:

- Among the chemical cleaning methods, cleaning tests resulted significantly vary, relating to the single chemical class of the paint: generally, the removal of acryl paint, overlaid on an alkyd one, and vice-versa, was found to be easier that the separation of paints belonging to the same chemical class. Moreover, the use of poultice and gels didn't increase the selectivity of the cleaning systems, enhancing, on the contrary, solvents penetration and uncontrolled solubilisation of the two painting layers.

The presence of a protective layer seems to increase the chance to remove the single layers selectively, limiting the interaction beetween the different paints. In these perspective, decreasing of interaction appears to be related with an increase of selectivity of the cleaning system: cleaning test in the protected area of mocks-up 5, 6, 8 and 9 resulted more effective than the ones realised in the unprotected ones. On the other side, when the stratigraphy is more complex –mocks-up 1 and 2(alkyd layer/protective/red acryl paint/green acryl) or mocks-up 10 and 11 (Acryl paint/protective layers/green alkyd/red alkyd paint)-, the presence of the protective layers results in the preferential detachment of the two superficial layers, without possibility to remove them selectively. In general, propylen carbonate was found to be effective for alkyd removal, on an acrylic background, even if a significant increase in superficial hydrophilia has been attested by contact angle measurements. Ethyl alcohol-water based solution was found to easily remove the acrylic red paint, even thus a relevant change in the gloss of the lower green alkyd paint is visible.

In the cleaning of green acrylic paint from red acrylic background, the 30-70 ethanol-water solution shows positive results when tickened in agar gel; as mentioned before, in the protected areas, removal preferentially involve the two superficial acryl layers, instead of the single green acrylic one. Worst results were obtained with alkyd-on- alkyd painting layers where any attempt to remove the upper red alkyd paint ended in a, more or less, visible solubilisation of the lower green alkyd one.

Concerning the use of the LQS laser, different conditions were tested (in terms of frequency, fluence, either dry or wet surface) and best results were obtained for the removal of red acrylic paint from the green alkyd background (mock-up #3) with the following parameters: frequency 7 Hz; fluence 4.14 J/cm². The same conditions for the laser cleaning did not result as much effective for the mock-up #7 (green alkyd paint on a red acrylic background), not allowing a complete removal of the green paint layer, but only a thinning of it.

In terms of impact on the surface, the measure of contact angle and the change of colour (if applicable) were adopted as criteria of evaluation of the main cleaning methods tested:

- For all the mock-ups the use of the Nanorestore gel extradry[®] with a 90% solution of polar coating S in Ethylene carbonate was tested, with a variable application time from 5 minutes up to 2 hours. Results provided by this cleaning method were heteogenous in terms of removal of the outer paint layer, however

an application time longer than 30 minutes induced in most cases a complete loss of hydrophobicity (the surface was defined as superhydrophilic, with a θ <0.5°).

Regardless of the application time, the use of Nanorestore gel extradry[®] cause a change of the visual perception of the surface clearly visible to the naked eye (delta E00 >1).

- The use of propylene carbonate showed to induce a moderate decrease of the contact angle value, thus allowing to define the surfaces after the cleaning test as hydrophilic. However, the use of the same solvent thickened by a gel of poly(vinylalcohol)-borate, induced a superhydrophilic behavior of the surface (total absorption of the water drop, θ <0.5°).
- Similarly to the propylene carbonate, the cleaned areas showed to be hydrophilic after the use of a solution of (30-50%) of Ethanol in water, except for the case of the solution thickened with agar gel, for which a contact angle θ <0.5° was obtained, suggesting a superhydrophilic surface.
- The use of the LQS laser induced a visible to the naked eye delta E00>1, while did not consistently affect the contact angle measured on the surface before and after the cleaning test.
- 2.1.4 Was it possible to transfer the methods/products on the objects on-site? If not, what has been different? Are there indications of a trend whether or not the behaviour of the product/method is the same on-site as under laboratory conditions? If not, what has been different?

No cleaning methods were tested on artwork on-site yet, some tests have to be done in 2020 summer internship with students.

2.1.5 How is the monitoring of the objects planned on-site?

No monitoring of the objects has been planned so far.

2.1.6 What were the benefits of the students and staff mobility?

Learning mobility activities performed in 2019 involved 5 students and one staff member of the University of Torino (P1), who attended a workshop at the Sisak Municial Museum (P13) on preventive conservation, sampling and graphic documentation of outdoor sculptures. The workshop was organised in collaboration with the University of Split (P10) and consisted of theoretical lessons and practical work in the field. Students and staff of UNITO had the opportunity to deal with contemporary metal sculptures, that is works of urban art of a different type than those studied by the UNITO-CCR team in Turin (i.e. murals).

Major benefits of the students and staff members were the sharing of different conservation methodologies (e.g. about creating a safety environment for the sculptures and the visitors, setting up a maintenance plan specific for each art object, looking for the best compromise between conservation and fruition-aesthetics, taking advantage of the collaboration with local public services) and teaching approaches (e.g. field research, brainstorming and open discussions).

2.1.7 Deviation of the work plan.

WP4 activities focused mainly on the testing and evaluation of cleaning methods (Task 1) and consolidation of the painting layers (Task 3). As regards the cleaning methods, investigations were carried out on mock-ups and not on-site. Some on-site activities (Task 2) will be carried out during the internship for students of the Master Degree in Conservation and Restoration of Cultural Heritage of the University of Turin, scheduled for summer 2020. As for the consolidation treatments they were carried out both on mock-ups and on-site during the internship held in summer 2019.

As the characterization of the case studies analysed in WP3 showed only a sporadic use of protective coatings, while significant problems of degradation of the painting and grounding layers emerged, it was decided not to develop fully Task 4 and 5, concerning the selection and testing of protective coatings, and to concentrate efforts on Tasks 1 (cleaning) and 3 (consolidation).

As part of Tasks 4 and 5, the UNITO-CCR team participates with other partners in a collaborative study on the stability of the protective products selected by the business partners Montana Colors, Schmincke and ANTARES. In particular, the UNITO-CCR team is in charge of performing FTIR, SEM and the determination of intrinsic reversibility.

Due to the delays had in the previous WPs and to unexpected personnel changes, the activities of WP4 were closed with an overall delay of 6 months.

2.1.8 Problems encountered and implemented or proposed solutions.

The main problems concerned:

- the delay in completing the activities compared to the initial scheduling: due to the delays had in the previous WPs and to unexpected personnel changes, the activities of WP4 were closed with an overall delay of 6 months; - the withdrawal from the project of partner P9, which was supposed to supply a novel product patented by the partner itself, to be tested as a protective coating for urban artworks. The other business partners (Montana Colors, Schmincke and ANTARES) dealing with the production and supply of painting and restoration materials selected other products for testing. Moreover, a collaborative work involving Montana Colors, Schmincke, ANTARES, CESMAR7, the University of Vigo and the UNITO-CCR team was planned to evaluate the stability of the protective products following accelerated aging treatments. This study is still on-going and will be possibly completed in April 2020.

2.1.9 Comments or short conclusion.

A selective cleaning of unwanted paint materials overlapping the original paint layers of the artwork resulted extremely hard, because of the chemical affinity of paints (often the products used are the same) and the recent application of all paint layers of the mock-ups. The use of gels resulted usefull to extend the contact time between the solvent solution and the paint to remove, even thus this might led to decrease the selectivity of the cleaning systems. Micro-swab application of single solvents are found to be effective and reduce the risk of uncontrolled penetration of the solvent; in these case, further tests might be done in order to stop the action of the solution (evaluating, for instance, specific rinse solutions) or to increase the retention of the gels.

Further tests may be interesting in the case of application of unwanted paint materials on aged artworks; in that case, interactions between different painting layers will presumably be different, causing different rensponses in cleaning tests.

The use of a protective coating composed by a water-based mixture of reactive organosiloxane olygomers provided heterogenous results in terms of effectiveness of the removal of unwanted paint materials without damaging the original paint layers.

2.2 CESMAR & ANTARES

NUMBER OF PARTNER	COUNTRY	NUMBER OF OBJECTS	NUMBER OF SAMPLES
P3-P4	ITALY	-	38

2.2.1 Information on tested cleaning methods carried out on mock up samples within the companies/research centres and on-site based on the selected sculptures (output wp2 and wp3). Describe your experimental setup, including details on sample preparation, instruments and experimental conditions used. Take into account to name the objectnumber and sample identification.

Cleaning tests were carried out on mock up samples based on Milan (3 artworks: Object 12 and 13 a,b) and Reggio Emilia mural artworks (5 artworks, Objects from 2 to 7). We have selected:

- two layered supports
- four paint layers among chromatically stable and unstable colours.

After staining mock ups with soil and nine graffiti materials, several surface cleaning and removal methods were performed in order to find suitable solutions in terms of effectiveness and respect of the paint layers; we also looked at green products and we considered whether these products could be easy used on-site.

In particular, experimental approach was based on the study of selected cleaners currently available on the market, focusing on the following key parameters:

- a. physical-mechanical selective removal
- b. conductivity and pH of aqueous solutions
- c. solubility parameters of solvents, blends and emulsions
- d. viscosity and diffusion rate of thickeners and supporting agents.

Optical examinations of the surfaces by using stereomicroscope were carried out before and after cleaning.

Below the details of the experimental set up adopted by CESMAR7 and ANTARES on Milan and Reggio Emilia samples, respectively.

NOTE: for cleaning tests performed on protected paint layers see Wp4 report – part 2.

CESMAR7

Materials

Table 1 Product list with acronyms and information provided by manufacturers/dealers

Support	Primer	Paint layers	Standard dirt	Graffiti materials
Concrete 1,2	Sikkens® Quartz Full Farbe W05 ¹ SFF	Montana Colors MTN 94 Bright Red RV3001 ² MCR Sikkens Alpha Acrylmat Light blue S0.05.05 ¹⁵ SLB	 Carbon black³ (2,0 g) Iron oxide-ochre⁴ (0,5 g) Micronized Silica⁵ (1,75 g) Kaolin⁶ (20 g) Gelatin Powder⁷ (10 g) Soluble starch⁸ (10 g) Cement⁹ (17,5 g) Olive oil¹⁰ (10 ml) Mineral oil¹¹ (20 ml) White spirit D40¹²(500 ml) SD 	Fabbrica Chimica Unione - Reflex Nero d'inferno dye 726 ¹³ MI Molotow – Coversall Signal black 360PI marker 360000 ¹⁴ MC Molotow – Coversall Bitumen black matt 132692 SB Montana Colors MTN 94 Revered Violet RV-274 ¹⁶ SV Molotow – Burner 400 chrome 940422 SC

12 mock up samples were realized on two sides (dimension 49x19 cm) of two concrete blocks (1,2) similar in composition to those used in Niguarda anti-fascist artwork (Object 12) (**Table 1**, Figure 1-3 – appendix)

- ⁵ Aerosil 200, provided by Antares Italy
- ⁶ ANCAO002, Provided by Antares Italy
- ⁷ Vwr NDH chemicals co.24350.262

Pyrrolidone.

¹ Sikkens[®] Quartz Full Farbe W05: acrylic white primer with siliceous aggregates and pigment resistant to light and alkalis in water dispersion. EBT Encapsulated Biocide Technology).

² MTN 94 – Bright Red –RV3001: Alkyd and solvent based spray paint containing Xylene (mixture of isomers),

Ethyl Acetate, Ethylbenzene, n-Butyl Acetate, Acetone, Polyhydroxyalkylamides, 2-Butanone-Oxime.

³ Kremer - 47000

⁴ Kremer - 40010

⁸ ANAMI001, Provided by Antares Italy

⁹ Leroy Merlin - Axton - REF. 36615523: premixed grey cement

¹⁰ Olive oil from l'Oleandra

¹¹ Vwr -life science VWRCJ217

¹² CTS - 01158505

¹³ Fabbrica Chimica Unione - Reflex - Nero d'Inferno 726: Solvent based dye for natural smooth leathers. It contains Acetone ($80 \le x < 90$), 1-Methoxyi-2-Propanol ($9 \le x < 16$), Ethanol, Benzyl Alcohol, n-Methyl-2-

¹⁴ Molotow - Coversall - Signal Black 360PI marker, 360000: alcohol-based synthetic bituminous ink marker.

¹⁵ Sikkens Alpha Acrylmat - Light Blue -S0.05.05: acrylic matt paint, with quartz powder, to use on outdoor surfaces and walls. Math Point Collection, from a W05 base.

¹⁶ MTN 94 – Bright Red – RV-3001: Alkyd and solvent based spray paint containing Xylene (mixture of isomers), Ethyl Acetate, Ethylbenzene, n-Butyl Acetate, Acetone, Polyhydroxyalkylamides, 2-Butanone-Oxime. Samples were named according to the support (block n.1 or n.2) and the products employed to create them and to the type of stain. The name was assigned as follows, using capital letters in each part: (support) - type of primer - paints used - type of dirt or graffiti materials

1-SFF-MCR-SD; 1-SFF-SLB-SD;

2-SFF-MCR-SD-MI; 2-SFF-MCR-SD-MC; 2-SFF-MCR- SD -SB; 2-SFF-MCR- SD-SV; 2-SFF-MCR- SD -SC; 2-SFF-SLB- SD-MI; 2-SFF-SLB- SD -MC; 2-SFF-SLB- SD -SB; 2-SFF-SLB- SD-SV; 2-SFF-SLB- SD-SC

Two layers of the primer were applied by roller on the concrete supports, then, one for each block face, two distinct chromatic paint layers: **MCR** simulating the spray paint used in Niguarda's work and, by brush, **SLB** that was used by Ivan Tresoldi in object no. 13.

The standard dirt was prepared (**Table 1**) according to the simplified recipe provided by Bronwyn Ombsby¹⁷: only 500 ml of White Spirit was used instead of 1 litre in order to simulate outdoor urban dirt. A final removal of the coarse material was carried out using a fine sieve.

After samples drying (about 3 weeks), the artificial dirt was applied by brush to all the painted surfaces and, after a week, only the block n.2 was coated by five graffiti materials (**Table 1**) simulating vandalism and writing.

Products and Methods

Surface cleaning tests (dirt removal) on the soiled surface of the sample n.1 were performed with dry cleaning materials (**Table 2**) and water based methods (**Table 3**).

Dry cleaning materials	Composition
Akapad White AKW	SBR vulcanized rubber
Akawipe White ¹⁸ AKD powder worked with a brush	SBR vulcanized rubber
Make up sponge Kiko MUS	Polyurethane ether
Microfiber cloth Evolon CR EV	Polyester (PET)-polyamide
Smoke sponge SS	Vulcanized Isoprene rubber
Spugna magica OZ SMOz	-
Blitz fix BF	-

Table 2 List of dry cleaning products and abbreviations used in this research

Table 3 List of aqueous and semi-humid products used in this research

	Composition
	1.Demineralized water
Aqueous methods	2.Buffer solution pH 6, conductivity 6 mS/cm (Acetic acid and NaOH)
3.Buffer solution pH 6, cond.10 mS/cm	
	4.Buffer solution pH 6, cond. 20 mS/cm
	5.Buffer solution pH 6, cond. 6 mS/cm + Ecosurf EH-6 0,25%
	6.Buffer solution pH 6, 6 mS/cm + Ecosurf EH-6 0,5%
	7.Buffer solution citric acid 1% and NaOH, pH 6, 6 mS/cm (sodium citrate solution)
	8.Buffer solution (sodium citrate solution) + 0,5% ECosurf EH-6

¹⁷ Ormsby, Soldano, Keefe, Phenix, and Learner, An Empirical Evaluation of a Range of Cleaning Agents for Removing Dirt from Artists' Acrylic Emulsion Paints, AIC speciality Group 23, 2010.

¹⁸ Akawipe White 4351 purchased by Antares

Semi-humid methods	1.Buffer Solution pH 6, 20 mS/cm + Evolon
	2.Buffer solution pH 6, 20 mS/cm on make up sponge
Agar	Agar 4% in water (sol status, stick)
Gels	1.Buffer solution pH 6, 20 mS/cm, 2% Xanthan gum

- Aqueous solutions/blends: applied with cotton swabs (5 rolls).
- Dry cleaning products: each product has been applied by gently rubbing (5 rubs) the surface.
- Akapad White: applied on the panel lying horizontally on the table, and worked with a brush (5 times)
- Agar 4%: prepared with microwave and then, when partially cooled, applied in the sol status on the surface. Removed right after its gelation.
- Agar stick 4%: prepared with microwave, putted into a plastic syringe, and used after its gelation as a sort of rubber (5rubs). Rinse with water has been carried out after its application.
- semi-humid methods/make-up sponge: washed/rinsed in order to eliminate eventual undesirable substances and left to dry. Then it has been wetted with 2ml of the different solutions and rubbed on the surfaces (5 times).
- semi/humid methods/Evolon: the cleaning solutions has been applied on the cloth by brush and then the Evolon has been rubbed on the surfaces (5 times)

Removal of graffiti materials (overpaint) was carried out on sample 2 by using selected organic solvents and thickeners (**Table 4,5**).

Checking the solubility of the materials present through the solubility test $LA - LE^{19}$ (**Table 4**) was the first step.

This test is based on two series of binary mixtures (Ligroin/Acetone and Ligroin/Ethanol) increasing in polarity.

The resistance of the paint layer to the test mixtures was verified as the basis for identifying selective mixtures on the graffiti materials.

In addition to the LA-LE solubility test, the removal tests listed in **Table 5** were carried out.

Name of products	Composition	So	Solubility parameters		
		fd	fp	fh	
L	Ligroin 100%	97	2	1	
LA1	Ligroin 90% - Acetone 10%	92	5	3	
LA2	Ligroin 80% - Acetone 20%	87	8	5	
LA3	Ligroin 70% - Acetone 30%	82	11	7	
LA4	Ligroin 60% - Acetone 40%	77	14	9	
LA5	Ligroin 50% - Acetone 50%	72	17	11	
LA6	Ligroin 40% - Acetone 60%	67	20	13	
LA7	Ligroin 30% - Acetone 70%	62	23	15	
LA8	Ligroin 20% - Acetone 80%	57	26	17	
LA9	Ligroin 10% - Acetone 90%	52	29	19	
А	Acetone 100%	47	32	21	
LE1	Ligroin 90% - Ethanol10%	91	4	5	

Table 4 list of solvents used for solubility test LA – LE

¹⁹ Cemonesi, P., L'uso dei solventi organici nella pulitura di opere policrome, Il Prato Editore, I talenti n.7, 2004

LE2	Ligroin 80% - Ethanol 20%	85	5	10
LE3	Ligroin 70% - Ethanol 30%	79	7	14
LE4	Ligroin 60% - Ethanol 40%	73	8	19
LE5	Ligroin 50% - Ethanol 50%	67	10	23
LE6	Ligroin 40% - Ethanol 60%	60	12	28
LE7	Ligroin 30% - Ethanol 70%	54	13	33
LE8	Ligroin 20% - Ethanol 80%	48	15	37
LE9	Ligroin 10% - Ethanol 90%	42	16	42
E	Ethanol 100%	36	18	46

Table 5 List of free solvents/ gels of solvents/solvent surfactant gels used for stain removal (vandalizations)

1.LE3 on Evolon and Ligroin on Evolon

2-5.Blend of Propylene carbonate (Pc) and Ligroin (L) (L/Pc 75/25, L/Pc 50/50, L/Pc 75/25, Pc)

6. Solvent surfactant gel nr.1

(0,25 g of Carbopol Ultrez 21, 3 g of Ethomeen C12, 25 ml of Ligroin) \rightarrow rinsing with Ligroin

7. Solvent surfactant gel nr. 2

(LA3: 0,25 g of *Carbopol Ultrez 21*, 3 g *Ethomeen C12*, 17,5 ml of Ligroin, 7,5 ml of Acetone) \rightarrow rinsing with free Ligroin

8. Solvent surfactant gel nr. 3

(LE3: 0,25 g of *Carbopol Ultrez 21*, 3 g of Ethomeen C12, 17,5 ml of Ligroin, 7,5 ml of Ethanol) \rightarrow rinsing with Ligroin

9.Benzyl alcohol in Velvesil

(4 g. of Velvesil, 10drops of benzyl alcohol, 20 drops of Cyclopenthasiloxane D5) →rinsing with D5

The blends have been applied with cotton swabs by rolling them for five times on the majority of surfaces. Only on the violet spray (SV) and the markers (MC, SC) have been performed more rolls, respectively fifteen and ten.

- The solvent gels and the thickened blends have been applied and mechanically stressed with a brush for a minute, then removed with a cotton swab and the area has been rinsed with Ligroin.
- The Evolon cloth has been wetted with solvent/blends using a cotton swab and then rubbed on the surfaces for five times.
- The Velvesil Plus gel has been used with an addition of Benzyl Alcohol and applied and worked on the surfaces for two minutes, then removed and rinsed with D5 using a cotton swab.

Instrumentation

The different cleaning tests have been observed under the visible light and with digital microscope. The different cotton swabs have been compared after the treatments

ANTARES

Materials

Support	Finishing layer	Ground layer	Primer	Paint layers	Graffiti materials
Bacchi - Prontomalt- Malta Bastarda Fibrata, on	Saint Gobain - Webercem RS350 ²¹	Rival - Stella Oro - PO3 ²²	LECHLER - Chrèon - Framaton Riveste Prof, white (Q107751) ²³ P	Montana Colors MTN 94 Light Yellow RV 1021 ²⁴ LY	Montana Colors MTN 94 Matt Black R 9011 ²⁵ SB
bricks ²⁰					Montana Cans Montana Gold Silverchrome M1000 ²⁶ SS
				Montana Cans Montana Gold Pure Orange	Pentel Pen - Permanent Marker N60 ²⁸ PM
				G2080 ²⁷ PO	Grog - Squeezer Mini 10 FMP- Diving Blue ²⁹ SM

Two sets of 8 mock-up samples each, prepared in two different times³⁰.

The 16 mock up samples (dimension 7,5x7,5x2 h cm) were realized following the layered structure found in Reggio Emilia artworks (object n. n.5,6.) (**Table 6**).

²¹Saint Gobain - Webercem RS350: hydraulic smoother for finishing and leveling plasters, either indoor and

outdoor.

²² Rival- Stella Oro – Idropittura traspirante opaca per interno: matt water paint for indoor use.

²³ LECHLER – Chrèon - Framaton Riveste Prof: siloxane acrylic water white paint with quartz powder/flour with an additive to prevent mold and algae, for outdoor use.

²⁴ MTN 94 – Light Yellow – RV 1021: Alkyd and solvent based spray paint containing Xylene (mixture of isomers), Ethyl Acetate, Ethylbenzene, n-Butyl Acetate, Acetone, Polyhydroxyalkylamides, 2-Butanone-Oxime.

²⁵ MTN 94 – Matt Black – R 9011: Alkyd and solvent based spray paint containing Xylene (mixture of isomers),

Ethyl Acetate, Ethylbenzene, n-Butyl Acetate, Acetone, Polyhydroxyalkylamides, 2-Butanone-Oxime.

²⁶ Montana Gold – Silverchrome – M1000: solvent based, Nitro-acrylic professional spray paint cotaining Acetone, aliphatic and aromatic hydrocarbons, Buthyl Acetate, Ethyl Acetate, DME, Propane, Butane, Naphta, 2-Propanol, Xylene, Isobutane, 2-Methoxy-1-Methylethylacetate

²⁷ Montana Gold – Pure Orange – G2080: Nitro-acrylic and solvent based spray paint containing DME, Ethyl

Acetate, Acetone, Propane, Butane, Naphta, Xylene, Isobutane, 2-Methoxy-1-Methylethyl Acetate, 2-Propanol, Ethylbenzene.

²⁸ Pentel Pen – Permanent Marker N60, Black: oil based permanent marker, with synthetic chisel tip.

²⁹ Grog – Squeezer Mini 10 FMP – Diving Blue: Alcohol based paint marker. It contains: Ethanol, Methoxy-2-Propanol, 1-Methyl-2-Metoxyethyl Acetate.

³⁰ The mock-ups were painted in October 2019 (see 1c report part 2 Antares). The first set of samples was

²⁰ Bacchi - Prontomalt - Malta Bastarda Fibrata: hydraulic mortar composed by Portland cement (10-13%) and quartz (70-90%).

soiled in mid-November (5 week after the paint application) and cleaned in December 2019-beginning of January. The second set of samples was soiled in the end of October 2019 (2 week after the paint application) and cleaned in February 2020. They were labelled as follows: LY-P-PM (x2); LY-P-SS (x2); LY-P-SB (x2); LY-P-SM (x2); PO-P-PM (x2); PO-P-SS (x2); PO-P-SB (x2); PO-P-SM (x2), in accordance with the acronym of paint layer, primer and graffiti material employed to create them.

On brick tiles, a cement mortar layer about 2 cm thick was applied and smoothed out by plastering trowels. After curing of at least 30 days, a smoothing thin layer then a layer of yellow ground layer were applied by trowels and paint roller, respectively.

After few days, samples were painted with two coats of primer by roller.

After 1 day, samples were sprayed with the two paint colours and, after 16 days, each sample was completely stained with the four graffiti materials (Figure 4-7, Table 1 - appendix).

The selection of LY and PO colours, with different chemical composition, was justified by

- their light colour useful for checking the performance of cleaning
- their likely use in the artwork n. 5,6

Additional 10 samples were prepared on 3 brick slabs (named TAV) (dimension 24x50x2,5 h cm) and painted with a simplified stratigraphy; these samples were useful for the preliminary cleaning tests (both in liquid form and in gel form):

TAV-LYPO:one tile was painted with LY and PO colours (2 samples)TAV-LY-PMSSSBSM: one tile was painted with LY and coated by graffiti materials (4 samples) TAV-PO-PMSSSBSM: one tile was painted with PO and coated by graffiti materials (4 samples)

Products and Methods

Graffiti removal tests were carried out on samples by using selected products:

- 1.1 Organic solvents and blends in liquid form (**Table 7**)
- 1.2 Water-in-oil micro-emulsions in liquid form (**Table 8**)
- 1.3 Gels, thickeners and supporting agents

Below the details of the products employed.

Selected organic solvents and blends³¹ applied in liquid forms (Table 7) by cotton swabs for a well defined times.

Solubility test LA – LE were firstly carried out on the three brick slabs in order to verify a selectivity in terms of polarity between the graffiti materials and the paint layers underneath.

After that, different organic solvents and blends were tested on the two brick slabs TAV-LY-PMSSSBSM, TAV-PO-PMSSSBSM to understand their cleaning efficacy and, at the same time, the compatibility with the paint layers.

Name of products	Composition and rate w/w	Solubility parameters		eters
		f _d f _p		fh
L	Ligroin 100%	97	2	1
LA1	Ligroin 90% - Acetone 10%	92	5	3
LA2	Ligroin 80% - Acetone 20%	87	8	5
LA3	Ligroin 70% - Acetone 30%	82	11	7

Table 7 list of organic solvents and blends tested on mock ups

³¹ Provided by Antares

LA4	Ligroin 60% - Acetone 40%	77	14	9
LA5	Ligroin 50% - Acetone 50%	72	17	11
LA6	Ligroin 40% - Acetone 60%	67	20	13
LA7	Ligroin 30% - Acetone 70%	62	23	15
LA8	Ligroin 20% - Acetone 80%	57	26	17
LA9	Ligroin 10% - Acetone 90%	52	29	19
А	Acetone 100%	47	32	21
LE1	Ligroin 90% - Ethanol 10%	91	4	5
LE2	Ligroin 80% - Ethanol 20%	85	5	10
LE3	Ligroin 70% - Ethanol 30%	79	7	14
LE4	Ligroin 60% - Ethanol 40%	73	8	19
LE5	Ligroin 50% - Ethanol 50%	67	10	23
LE6	Ligroin 40% - Ethanol 60%	60	12	28
LE7	Ligroin 30% - Ethanol 70%	54	13	33
LE8	Ligroin 20% - Ethanol 80%	48	15	37
LE9	Ligroin 10% - Ethanol 90%	42	16	42
E	Ethanol 100%	36	18	46
Solvent 1	Ethyl Acetate 100%	55.9	18.7	25.4
Solvent 2	Buthyl Acetate 100%	61	14.5	24.5
Solvent 3	MEK 100%	53	30	17
Solvent 4	Ethyl Lactate 100%	44.3	21.1	34.6
Solvent 5	Propylene Carbonate 100%	47.5	42.8	9.7
Solvent 6	Benzyl Alcohol 100%	47.9	16.4	35.7
Solvent 7	Limonene 100%	73.8	7.75	18.45
Solvent 8	DMSO 100%	40.9	36.4	22.7
Solvent 9	Dibasic Esther 100%	28.7	55.3	16
Solvent 10	Solvenon DPM 100%	49.8	19.7	30.5
Solvent 11	Loxanol MI 6470* 100%			
Blend 1	Dibasic Esther - DMSO 76% - 24%	31.6	50.8	17.6
Blend 2	DMSO – Ethyl Lactate 70% - 30%	41.9	31.8	26.3
Blend 3	DMSO – Propylene Carbonate 70% - 30%	42.9	38.3	18.8
Blend 4	DMSO – Ethyl Acetate 70% - 30%	45.4	31.1	23.5
Blend 5	DMSO – Buthyl Acetate 70% - 30%	46.9	29.8	23.3
Blend 6	Dibasic Esther – Benzyl Alcohol 85% - 15%	31.5	49.5	19
Blend 7	Dibasic Esther – DMSO – Benzyl Alcohol 75% - 20% - 15%	34	45.6	20.4
Blend 8	DMSO – Dowanol PM 70% - 30%	41.5	31.5	27
Blend 9	DMSO – Dowanol PM – Ethyl Acetate 60% - 20% - 20%	45.3	28.6	26.1
Blend 10	DMSO – Dowanol PM – Buthyl Acetate 60% - 20% - 20%	46.3	27.8	25.9
Blend 11	Dibasic Esther – Dowanol PM 70% - 30%	34.4	43.3	22.3
Blend 12	Dibasic Esther – Dowanol PM – Propylene Carbonate	39.6	39.4	21
	42.5% - 32% - 25.5%		1	
Blend 13	Propylene Carbonate – Ethyl Acetate 70% - 30%	50	35.6	14.4
Blend 14	MEK – 2-Propanol 50% - 50%	47.1	23	29.9
Blend 15	Loxanol MI 6470* - Dibasic Esther 60% - 40%	-	-	-
Blend 16	Dibasic Esther – Loxanol MI 6470* – Propylene Carbonate	-	-	-
	40% - 35% - 25%			

*solubility parameters not found

Nanorestore cleaning³² (Table 8) applied in liquid form using cotton swabs.

"Nanorestore Cleaning" are nanostructured cleaning fluids (water-in-oil micro-emulsions, micellar solutions) substantially based on water, with a drastically reduced solvent content while maintaining cleaning effectiveness. They were applied on the three brick slabs to test the solubility action on the two paint layers and on the different graffiti materials. ^{33,34, 35}

Name of products	Composition
	Water-based nanostructured fluid containing a nonionic alcohol ethoxylate
Nanorestore Cleanin	g surfactant and a mixture of methyl ethyl ketone (MEK) and 2-butanol
Polar Coating B	
	Water-based nanostructured fluid containing a nonionic alcohol ethoxylate
Nanorestore Cleanin	g surfactant and a mixture of MEK, 2-Butanol, Ethyl Acetate, and Propylene
Polar Coating G	Carbonate
	Water-based nanostructured fluid containing an anionic surfactant and a mixture of
Nanorestore Cleanin	g 1-Pentanol, Ethyl Acetate and Propylene Carbonate
Polar Coating S	
Nanorestore Cleani	g Oil-in-water microemulsion containing an anionic surfactant and a mixture of 1-
Apolar Coating	pentanol and xylene

Gels, thickeners and supporting agents

Finally, the most efficient cleaners were applied in gelled forms and by using supporting agents in order to obtain more selective and safer cleaning methods.

Evolon CR ³⁶	non-woven cloth with a micro-filamented structure, used as supportant after wetting with the solvent/blends, was applied on mock-up, slightly
	buffered and removed.
Agar Agar gels	applied in different ways:
	4% aqueous agar gels immersed for at least 24 hours into solvent/blend, then
	dried with blotting paper and applied on the mock ups' surfaces.
	4% agar gel containing a 10% of solvents blend.
Velvesil plus	added with 20% or 30% of solvents and rinsed with Cyclomethicone D5 Solvent
surfactant gels prepare	ed using Carbopol Ultrez 21 and Ethomeen C-12 or C-25, depending on
	the polarity of the organic solvent/blend to gel.
PVA/borax hydrogel p	repared using an aqueous solution of PVA ³⁷ (8%) and an aqueous solution of
	Borax salt ³⁸ (8%) in percentage 4:1 (v/v). 10% of organic solvent/blend on

overpaintings and undesidered graffiti from street art, 2017, Anal Bioanal Chem.

³² Purchased from CSGI w<u>ww.csgi-unifi.it</u>

³³ Baglioni, M. et al., Nanostructured fluids for the removal of graffiti – A survey on 17 commercial spray –can paints, 2017, Journal of Cultural Heritage.

³⁴ Giorgi, R. Et al., Nanofluids and chemical highly retentive hydrogels for controlled and selective removal of

 ³⁵ Baglioni, M., Alterini, M., Chelazzi, D., Giorgi, R., Baglioni, P., Removing polymeric coatings with nanostructured fluids: influence of substrate, nature of the film, and application methodology, 2019, Frontiers Materials, 6:311
 ³⁶ Purchased from Deffner & Johann www.deffner-johann.de

³⁷ Polyviniyl Alcohol purchased by Antares

³⁸ Decahydrated di sodium tetraborate purchased by Antares

respect of the total volume of the gel was added. Rinsing was not necessary because of the very high viscosity of the gel.

Nanorestore gel39HWR gel (1.5 cm2) immersed into the different coatings (B, G, S, Apolar) for at
least 12 hours, then dried with blotting paper and applied on the mock ups.
Rinsing was avoided because, after treatment, a mechanical action using a
cotton swab or a silicon brush for removing graffiti smears was necessary.

Instrumentation

The documentation of the cleaning tests were carried out by using digital camera Nikon - D3100 under Visible (two vtlamp6 by Velleman, 6500 K), Tiffen color separation guide and gray scale (small) and UV light (portable Wood's lamp - model 31200).

Optical observations of the sample surfaces before cleaning, after staining and after cleaning were performed with LFZNT stereomicroscope (Optech) equipped with Digital camera ISDV5003 and led ring light.

³⁹ Purchased from CSGI w<u>ww.csgi-unifi.i</u>

2.2.2 What were the results of the optical and analytical observation of the different cleaning methods on the ad hoc samples? (table) how did you get the results?

Below the optical results of the cleaning tests performed on mock up samples.

CESMAR7

The performance of the cleaning tests was evaluated following a common criterion decided between Cesmar7 and Antares that was adapted to the research need from the one developed by the Cultural Heritage Agency (RCE) of Amsterdam⁴⁰ for dry cleaning.

Six criteria:

- T preservation of the topography integrity
- Cr presence and clearance of the residues
- G preservation of the surface gloss
- Cp cleaning efficiency and evenness
- Am method feasibility
- (Pp pigment pick up)

Score: from 0 (unacceptable result) to 10 (optimal result) were determined to assess cleaning results and reported in excel file.

Test results aimed at define what cleaning method shows the most optimum balance between all these criteria.

The aspect of the paint layers was examined after test (preservation of the topography (T), of the surface gloss (G), of the paint layer aspect.

Cleaning efficiency and evenness (Cp) was assessed of both cleaning materials and tested surface together with the clearance of residues (Cr), which concerns the quantity of particulate residues, their colour, their size and their tenacity on the surface.

About this last criterion, residues are understood as particles and films from the cleaning material still present on the paint layer after brushing and rolling away of the tested sample. To assess this criterion and compare the amount of residues per materials, they were observed under light microscopy after each test.

Preservation of the topography integrity (T) concerned any abrasion, polishing, increasing of micro cracks or losses of micro impasto and flattening. The preservation of the surface gloss (G) studied any increase or decrease in gloss; the preservation of the paint layer aspect under UV fluorescence (UV) focused on whitening, darkening or noticeable change in the original fluorescence (or absence of fluorescence) of the surface.

Method feasibility parameter (Am) deals with cleaning materials transferability on-site in terms of time consumed materials costs and other features (vertical and medium-large areas of application) of real artworks.

Finally, observing the pigment pick up (Pp) on cotton swabs and gels after cleanings was useful to evaluate whether cleaning methods applied was respectful of the paint layer. This is a parameter related to the T criterion and it was not always possible to assess.

⁴⁰ Daudine-Schotte, M., Analysis and application of fry cleaning materials on unvarnished paint surfaces, Quaderno n. 12 Cesmar7, il prato editore, 2012

The **Table 9** shows the results of the surface cleaning tests (dirt removal) carried out on sample 1 (Figure 10 – appendix).

1- SFF-MCR-SD - Dry Cleaning	т	Cr	G	Ср	Am	Рр
AKW	8	8	9	5	8	10
AKD	8	1	9	4	0	10
MUS	5	10	7	10	7	9
EV	8	10	9	9	8	9
SS	8	9	7	9	8	10
SMOz	7	6	8	9	9	10
BF	5	8	6	5	8	10
1-SFF-SLB-SD - Dry Cleaning	т	Cr	G	Ср	Am	Рр
AKW	8	8	9	6	8	10
AKD	8	1	9	4	0	10
MUS	9	10	8	10	7	10
EV	9	10	8	8	8	10
SS	9	9	9	9	9	10
SMOz	9	6	9	7	8	10
BF	5	8	5	6	8	10
1-SFF-MCR-SD – Aqueous methods	т	Cr	G	Ср	Am	Рр
1. Dem. Water	10	8	10	8	10	10
2. buffer solution pH 6, 6 mS/cm	10	8	10	7	10	10
3. buffer solution pH 6, 10 mS/cm	10	8	10	8	10	10
4. buffer solution pH 6, 20 mS/cm	10	8	10	10	10	10
5. buffer solution pH 6, 6 mS/cm +Ecosurf EH-6 0,25%	10	8	10	9	10	10
6. Buffer solution pH 6, 6 mS/cm + Ecosurf EH-60,5%	5	8	10	10	10	10
7. Citric acid+ NaOH pH 6, 6 mS/cm	5	8	10	8	10	10
8. Citric acid+ NaOH 6-6 + ecosurf EH-6 0,5%	4	8	10	10	10	9
1-SFF-SLB-SD - Aqueous methods	т	Cr	G	Ср	Am	Рр
1. Dem. Water	10	8	10	7	10	10
2. buffer solution pH 6, 6 mS/cm	10	8	10	7	10	10
3. buffer solution pH 6, 10 mS/cm	10	8	10	9	10	10
4. buffer solution pH 6, 20 mS/cm	10	8	10	8	10	10
5. buffer solution pH 6, 6 mS/cm +Ecosurf 0,25%	10	8	10	9	10	10
6. buffer solution pH 6, 6 mS/cm + Ecosurf EH-6 0,5%	10	8	10	10	10	10
7. Buffer solution citric acid+ NaOH pH 6, 6 mS/cm	9	8	10	7	10	10
8. Buffer solution citric acid + NaOH 6-6 + Ecosurf EH-60,5%	9	8	10	10	10	10
1-SFF-MRC-SD - Semi humid methods	т	Cr	G	Ср	Am	Рр
1. WS 6-20 on Evolon	10	10	10	8	10	6
2. WS pH 6-20 on MUS	10	10	10	10	10	10
1-SFF-SLB-SD - Semi humid methods	т	Cr	G	Ср	Am	Рр

Table 9 results of the surface cleaning tests on sample 1

1. WS 6-20 on Evolon	10	10	10	8	10	7
2. WS pH 6-20 on MUS	10	10	10	10	10	10
1-SFF-MCR-SD – Agar	т	Cr	G	Ср	Am	Рр
1. Agar by brush	10	10	10	9	10	10
2. Agar stick	10	3	10	7	3	10
1-SFF-SLB-SD – Agar	т	Cr	G	Ср	Am	Рр
1. Agar by brush (fluid)	10	10	10	9	10	10
2. Agar stick	10	3	10	7	3	10
1-SFF-MCR-SD – Gel	т	Cr	G	Ср	Am	Рр
WS 6-20 + Xanthan 2%	10	8	10	10	10	10
1-SFF-SLB-SD – Gel	Т	Cr	G	Ср	Am	Рр
WS 6-20 + Xanthan gum 2%	10	8	10	10	10	10

Regarding the solubility test LA-LE, MCR paint has resulted sensitive from the first mixture of the test (100% Ligroin) and totally soluble from the second.

SLB acrylic paint has shown more resistance starting to dissolve around LA4.

 Table 10 reports the test results for graffiti removal.

Table 10 Results of solubility test (LA-LE) on graffiti materials (Figure 8-9 – appendix).

Sample- number	Staining material	Product- number	Tests*	Optical Results
	МС	LA/LE	5 rolling + 5 rubbing	Removal effectiveness from L (slow) to all the series blends, max. with LE7-8 and AE2-3. LA3 and LE3 best options (respectfully removal)
	MI	LA/LE	5 rolling + 5 rubbing	Removal effectiveness starts from LA3 and LE1, increasing of effectiveness with polarity, max. result with LA8-9, LE8-9, AE1-3. LA3 e LE3 best options (respectfully removal)
2-SFF-SLB- SD	SB	LA/LE	5 rolling + 5 rubbing	Removal effectiveness from L, all the mixtures effective except for LA9, A and E. AE3 less effective than AE1 and AE2. L, LA3 and LE3 very effective and respectfull (total removal)
	SC	LA/LE	5 rolling + 5 rubbing	Less effective from LA1, evident removal from LA6 to A. LA3-LE3 very effective and respectfull (total removal)
	SV	LA/LE	5 rolling + 5 rubbing	Purple color removal from LA2, but effective cleaning from LA6 to A, less effective LE series (no total removal), only partial removal with LE4-6.
	MC	LA/LE	5 rolling + 5 rubbing	Partial results from L (less effective) to all the range. No total removal
2-SFF-	MI	LA/LE	5 rolling + 5 rubbing	Effective from LA3 and LE1, improved by increase in polarity, maximum with LA8-9 LE8-9 AE1-3.
MCR-SD	SB	LA/LE	5 rolling + 5 rubbing	Effectiveness from L to all the test blends , except for LA, A and E. AE3 less effective than AE1-2. L, LA3 and LE3 very effective and respectfull (total removal)
	SC	LA/LE	5 rolling + 5 rubbing	Removal from LA3 and LE1; all the blends are effective
	SV	LA/LE	5 rolling + 5 rubbing	Colour removal from LA3, partially effective from LA7 to A and LE8, all the tests only partially effective

The **Tables 11-13** shows the results of the removal cleaning tests (overpaint removal) carried out on sample 2. Pigment pick up (Pp) by cotton swab was not detected because it was covered by graffiti materials.

2-SFF-SLB-SD-MC	т	Cr	G	Ср	Am
1. LE3 on Evolon	10	10	10	3	10
2. L/Pc 75/25	7	8	10	5	7
3. L/Pc 50/50	7	8	10	5	7
4. L/Pc 25/75	7	8	10	6	7
5. Pc	7	8	10	7	7
6. Solvent surfactant gel 1	9	5	6	5	6
7. Solvent surfactant gel 2	9	5	6	6	6
8. Solvent surfactant gel 3	9	5	6	7	6
9. Velvesil + benzyl alcohol	10	5	6	1	6
2-SFF-MCR-SD-MC	т	Cr	G	Ср	Am
1. LE3 su evolon	10	10	10	3	10
2. L/Pc 75/25	7	8	10	5	7
3. L/Pc 50/50	7	8	10	5	7
4. L/Pc 25/75	7	8	10	6	7
5. Pc	7	8	10	7	7
6. Solvent surfactant gel 1	9	5	6	5	6
7. Solvent surfactant gel 2	9	5	6	6	6
8. Solvent surfactant gel 3	9	5	6	7	6
9. Velvesil + benzyl alcohol	10	5	6	1	6
2-SFF-SLB-SD-MI	т	Cr	G	Ср	Am
1. LE3 su evolon	10	10	10	3	10
2. L/Pc 75/25	7	8	10	5	7
3. L/Pc 50/50	7	8	10	5	7
4. L/Pc 25/75	7	8	10	6	7
5. Pc	7	8	10	7	7
6. Solvent surfactant gel 1	9	5	6	5	6
7. Solvent surfactant gel 2	9	5	6	6	6
8. Solvent surfactant gel 3	9	5	6	7	6
9. Velvesil + benzyl alcohol	10	5	6	1	6
2-SFF-MCR-SD-MI	т	Cr	G	Ср	Am
1. LE3 on Evolon	10	10	10	3	10
2. L/Pc 75/25	7	8	10	5	7
3. L/Pc 50/50	7	8	10	5	7
4. L/Pc 25/75	7	8	10	6	7
5. Pc	7	8	10	7	7
6. Solvent surfactant gel 1	9	5	6	5	6

Table 11 results of the cleaning tests on sample 2

7. Solvent surfactant gel 2	9	5	6	6	6
8. Solvent surfactant gel 3	9	5	6	7	6
9. Velvesil + benzyl alcohol	10	5	6	1	6
2-SFF-SLB-SD-SB	Т	Cr	G	Ср	Am
1. L on Evolon	10	10	10	6	10
2. L/Pc 75/25	7	8	10	5	7
3. L/Pc 50/50	7	8	10	5	7
4. L/Pc 25/75	7	8	10	6	7
5. Pc	7	8	10	7	7
6. Solvent surfactant gel 1	9	5	6	5	6
7. Solvent surfactant gel 2	9	5	6	9	6
8. Solvent surfactant gel 3	9	5	6	8	6
9. Velvesil+ benzyl alcohol	10	5	6	1	6
2-SFF-MCR-SD-SB	т	Cr	G	Ср	Am
1. L su evolon	10	10	10	6	10
2. L/Pc 75/25	7	8	10	5	7
3. L/Pc 50/50	7	8	10	5	7
4. L/Pc 25/75	7	8	10	6	7
5. Pc	7	8	10	7	7
6. Solvent surfactant gel 1	9	5	6	5	6
7. Solvent surfactant gel 2	9	5	6	9	6
8. Solvent surfactant gel 3	9	5	6	8	6
9. Velvesil+ benzyl alcohol	10	5	6	1	6
2-SFF-SLB-SD-SC	т	Cr	G	Ср	Am
1. LE3 on Evolon	10	10	10	3	10
2. L/Pc 75/25	7	8	10	5	7
3. L/Pc 50/50	7	8	10	5	7
4. L/Pc 25/75	7	8	10	6	7
5. Pc	7	8	10	7	7
6. Solvent surfactant gel 1	9	5	6	4	6
7. Solvent surfactant gel 2	9	5	6	7	6
8. Solvent surfactant gel 3	9	5	6	4	6
9. Velvesil + benzyl alcohol	10	5	6	6	6
2-SFF-MCR-SD-SC	т	Cr	G	Ср	Am
1. LE3 su evolon	10	10	10	3	10
2. L/Pc 75/25	7	8	10	5	7
3. L/Pc 50/50	7	8	10	7	7
4. L/Pc 25/75	7	8	10	7	7
5. Pc	7	8	10	7	7
6. Solvent surfactant gel 1	9	5	6	4	6
7. Solvent surfactant gel 2	9	5	6	7	6
8. Solvent surfactant gel 3	9	5	6	8	6

9. Velvesil + benzyl alcohol	10	5	6	6	6
2-SFF-SLB-SD-SV	т	Cr	G	Ср	Am
1. LE3 su evolon	10	10	10	3	10
2. L/Pc 75/25	9	8	10	4	7
3. L/Pc 50/50	9	8	10	4	7
4. L/Pc 25/75	9	8	10	4	7
5. Pc	9	8	10	4	7
6. Solvent surfactant gel 1	9	5	6	4	6
7. Solvent surfactant gel 2	9	5	6	4	6
8. Solvent surfactant gel 3	9	5	6	6	6
9. Velvesil benzyl alcohol??	10	5	6	4	6
2-SFF-MCR-SD-SV	т	Cr	G	Ср	Am
1. LE3 su evolon	10	10	10	3	10
2. L/Pc 75/25	7	8	10	4	7
3. L/Pc 50/50	7	8	10	4	7
4. L/Pc 25/75	7	8	10	4	7
5. Pc	7	8	10	4	7
6. Solvent surfactant gel 1	9	5	6	4	6
7. Solvent surfactant gel 2	9	5	6	4	6
8. Solvent surfactant gel 3	9	5	6	6	6
9. Velvesil + benzyl alcohol	10	5	6	4	6

Table 12 results of the cleaning tests on sample 2

Sample- number	Staining material	Product-number	Optical Results
		BLENDS L/PC	Most effective is L/PC25/75 but with several applications
		Velvesil + benzyl alcohol	Low effectiveness
SFF-MCR-SD		Solvent surfactant gel 1	graffiti partial removal but without a an effective cleaning
		Solvent surfactant gel 2	graffiti partial removal but without a an effective cleaning, several applications are required
	MC	Solvent surfactant gel 3	graffiti partial removal but without a an effective cleaning, several applications are required
		LE3 on Evolon	Low effectiveness, further applications with an higher polarity should be tested
		L/PC blends	Effective PC but several applications are required
		Velvesil + benzyl alcohol	Less effective
	MI	Solvent surfactant gel 1	graffiti partial removal but without a an effective cleaning, several applications are required
		Solvent surfactant gel 2	graffiti partial removal but without a an effective cleaning, several applications are required
		Solvent surfactant gel 3	graffiti partial removal but without a an effective cleaning, several applications are required
		LE3 on Evolon	Low effectiveness, further applications with an higher polarity should be tested

SB	L/PC blends	All very effective
	Velvesil + benzyl	Partially effective, probably two or more applications are
	alcohol	required
	Solvent	Very effective
	surfactant gel 1	
	Solvent	Very effective
	surfactant gel 2	
	Sovlent	Very effective
	surfactant gel 3	
	LE3 on Evolon	graffiti slightly removed but without a an effective cleaning,
		several applications are required
SC	Blends L/PC	All effective
	Velvesil + benzyl alcohol	Partially effective, probably two or more applications are required
	Solvent surfactant gel 1	Poor effectiveness, probably two or more applications are required
	Solvent surfactant gel 2	Effective (good cleaning level) but probably shoul be refined with another application
	Solvent surfactant gel 3	Quite effective, probably two or more applications are required
	LE3 on Evolon	Less effective, probably two or more applications are required
SV	L/PC blends	Poor effectiveness
	Velvesil + benzyl alcohol	Not effective
	Solvent surfactant gel 1	Not effective
	Solvent surfactant gel 2	Not effective
	Solvent surfactant gel 3	Not effective
	Surfactant Sci S	

Table 13 results of the cleaning tests on sample 2

Sample- number	Staining material	Product-number	Optical Results					
		BLENDS L/PC	Most effective is L/PC25/75 but more application are required					
		Velvesil + benzyl alcohol	Poor effectiveness					
SFF-SLB-SD		Solvent surfactant gel 1	graffiti slightly removed but without a an effective cleaning, several applications are required					
		Solvent surfactant gel 2	graffiti slightly removed but without a an effective cleaning, several applications are required					
	мс	Solvent surfactant gel 3	graffiti slightly removed but without a an effectiv cleaning, several applications are required					
		LE3 on Evolon	Poor effectiveness, further applications with an higher polarity should be tested					
		L/PC blends	Effective 25/75 but several applications are required					
		Velvesil + benzyl alcohol	Not effective					
	МІ	Solvent surfactant gel 1	graffiti removed but without a an effective cleaning, several applications are required					
		Solvent surfactant gel 2	graffiti removed but without a an effective cleaning, several applications are required					

		Sovlent surfactant gel 3	graffiti removed but without a an effective
			cleaning, several applications are required
		LE3 on Evolon	Poor effectiveness, further applications with an
			higher polarity should be tested
	SB	L/PC blends	All blends poor effective except PC
		Velvesil + benzyl alcohol	Quite effective, probably two or more
			applications are required
		Solvent surfactant gel 1	Very effective
		Solvent surfactant gel 2	Very effective
		Sovlent surfactant gel 3	Very effective
		LE3 on Evolon	graffiti removed but for an effective cleaning,
			several applications are required
	SC	Blends L/PC	Effective 25/75
		Velvesil + benzyl alcohol	Poor effectiveness, two or more applications are
			required
		Solvent surfactant gel 1	Poor effectiveness, two or more applications are
			required
		Solvent surfactant gel 2	Quite effective but probably should be refined
			with another application
		Solvent surfactant gel 3	Quite effective, two or more applications are
			required
		LE3 on Evolon	Poor effectiveness, two or more applications are
			required
	SV	L/PC blends	Poor effectiveness
		Velvesil + benzyl alcohol	Not effective
		Solvent surfactant gel 1	Not effective
		Solvent surfactant gel 2	Not effective
		Solvent surfactant gel 3	Not effective
		LE3 on Evolon	Not effective
L			···· ·

ANTARES

The performance of the cleaning tests on mock-up samples was firstly evaluated with the naked eye observing the treated paint surfaces, the pigment pick up on cotton swabs, on gels and on supporting agents after cleanings.

Only the tests with better results (see point 3) were observed and documented under stereomicroscope and assessed following the evaluation criterion shared with Cesmar7.

The **Tables 14-21** summarize the cleaning tests results observed with the naked eye on all the mock up samples divided for cleaning product/method.

Each table refers to cleaning tests performed with the same time and method except for the tests performed with gels and with supporting agents.

Each trial has been marked with a colour and/or a symbol that mean:

Red	not respectful cleaning for PO or LY paint layer
Grey	not effective cleaning for graffiti materials (PM, SS, SB, SM) and paint layers (PO, LY)
Green	respectful cleaning for PO or LY paint layer
Х	Total removal of graffiti material (PM, SS, SB, SM)
/	Partial removal of graffiti material (PM, SS, SB, SM)

Cleaning tests directly performed on paint layers have been only marked with a colour that indicates if the cleaner is relatively safe or unsafe for their integrity.

Modern spray paints are generally very sensitive to organic solvents, also at low polarity. This fact is more evident considering fresh and not aged paints materials as those constituent of the samples taken into account in this research. Therefore, it has to be said that the "green lights" must be understood as cleaners less aggressive than others (i.e. in terms of time) but not inherently safe. If effective for removal of overpaints or graffiti materials, these cleaners could be selected and applied in a controlled way (short time application, in at highly viscous gel or micellar solutions, etc) in order to minimize as much as possible the impact on the paint layers.

This was our approach looking for wide spectrum products and methods (i.e. effective for removal in a safety way all the selected graffiti materials on all the paint layers considered).

See the **Tables 2-3 appendix** for all details regarding tests: timing, application methods, cleaning efficacy and respect of the paint layers (**Figure 11-18 appendix**).

Table 14 Results of the cleaning tests on brick samples

ID SAMPLE		SOLUBILITY TEST LA BLENDS												
	L	LA1	LA2	LA3	LA4	LA5	LA6	LA7	LA8	LA9	А			
TAV-PO-PM		Х	Х	Х	Х	Х	Х	Х	Х	Х	Х			
TAV-PO-SS	х	Х	х	Х	х	х	Х	Х	х	х	Х			
TAV-PO-SB			1	1	1	1	1	1	1	1	1			
TAV-PO-SM		1	х	х	Х	х	Х	Х	х	Х	Х			
TAV-LY-PM		Х	Х	Х	Х	Х	Х	Х	Х	Х	Х			
TAV-LY-SS	х	х	х	Х	Х	х	Х	Х	х	Х	Х			
TAV-LY-SB							1	1	х	Х	Х			
TAV-LY-SM			х	Х	Х	Х	Х	Х	х	Х	Х			
TAV-PO														
TAV-LY														

Table 15 Results of the cleaning tests on brick samples

ID SAMPLE				SOLUE	BILITY TES	ST LE BLE	NDS			
	LE1	LE2	LE3	LE4	LE5	LE6	LE7	LE8	LE9	E
TAV-PO-PM	Х	х	Х	х	х	X	X	Х	Х	Х
TAV-PO-SS	Х	х	Х	х	х	X	X	Х	Х	Х
TAV-PO-SB		1	1	1	1	1	1	1	1	/
TAV-PO-SM	Х	х	Х	х	х	Х	X	Х	Х	Х
TAV-LY-PM	х	х	х	х	х	х	x	х	x	х
TAV-LY-SS	х	х	х	х	х	Х	X	х	x	х
TAV-LY-SB									1	/
TAV-LY-SM	х	Х	х	х	х	х	X	Х	Х	х
TAV-PO										
TAV-LY										

Table 16 Results of the cleaning tests on brick samples

ID SAMPLE					S	OLVEN	ITS				
ID SAMPLE	1	2	3	4	5	6	7	8	9	10	11
TAV-PO-PM	Х	Х	Х	/	/	Х	/	/	/	Х	Х
TAV-PO-SS	Х	Х	Х	Х	/	/	/		/	/	1
TAV-PO-SB	1	1	1					1			1
TAV-PO-SM	Х	Х	Х	/	/	Х	/	/	/	Х	Х
TAV-LY-PM	Х	Х				Х				Х	Х
TAV-LY-SS	Х	Х	Х	/		1				/	/
TAV-LY-SB	1	1	1								
TAV-LY-SM	Х	Х	Х			Х				Х	Х

									BLE	NDS						
ID SAMPLES	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
PO-PM	Х	Х	х	Х	Х	Х	х	Х	Х	Х	Х	Х	Х	Х	Х	х
PO-SS	Х	Х	х	х	Х	x	х	Х	х	Х	Х	Х	Х	Х	Х	Х
PO-SB	7	7	7	х	x	1	х	x	Х	Х	7	7	7	Х	Х	Х
PO-SM	Х	Х	х	х	Х	x	х	Х	Х	Х	Х	Х	Х	Х	Х	х
LY-PM	Х	Х	х	Х	x	x	х	Х	х	Х	х	х	х	Х	Х	х
LY-SS	Х	Х	х	х	x	x	Х	х	х	Х	х	х	х	Х	Х	х
LY-SB			1	7	Х	1	7	Х	7	Х		1		Х		1
LY-SM	X	Х	х	Х	x	х	х	х	Х	Х	х	Х	х	Х	х	х

Table 17 Results of the cleaning tests on brick slabs and mock up samples of the $1^{\mbox{\scriptsize st}}$ set

Table 18 Results of the cleaning tests on brick samples

	LE BLENDS and E SUPPORTED													
ID SAMPLE	LE1 solvent gel	LE7 solvent gel	Evolon +E	Agar embedded into E	Velvesil Plus + 20% E	10% E into PVA/Borax gel 4%	10% E into PVA/Borax gel 8%							
TAV-PO-PM	Х	Х	Х	/	Х									
TAV-PO-SS	Х	Х			Х									
TAV-PO-SB	/	/												
TAV-PO-SM	Х	Х	Х	/	Х									
TAV-LY-PM	Х	Х	Х		1									
TAV-LY-SS	Х	Х												
TAV-LY-SB		Х												
TAV-LY-SM	Х	Х	Х		Х									

Table 19 Results of the cleaning tests on brick slabs and mock up samples of the $1^{\mbox{st}}$ set

					BLENDS SU	JPPORTED			
ID SAMP L ES	Velvesil Plus + 30% of blend 5	Agar + 10% of blend 7	Evolon + blend 12	Agar loaded with blend 12	Agar + 10% of blend 12	10% blend 12 into PVA/B gel 8% (hours)	Evolon + blend 16	10% blend 16 into PVA/B gel 8% (hours)	10% blend 16 into PVA/B gel 8% (less time)
PO-PM	х	х	х	x	х	х	x	х	x
PO-SS		х	Х	х	х	х	х	х	x
PO-SB	7	Х	/		х	х	7	х	X
PO-SM	Х	Х	Х	х	х	х	Х	Х	x
LY-PM	Х	Х	х	х	х	х	/	х	/
LY-SS		Х	х	/	х	x	1	х	x
LY-SB	1	/				х		x	x
LY-SM	Х	X	х	Х	Х	Х	х	Х	/

	NANORESTORE COATING [®] and NANORESTORE GEL [®]							
ID SAMPLES	В	HWR loaded wit B	G	HWR loaded with G	S	HWR loaded with S	Apolar	HWR loaded with Apolar
PO-PM	Х	Х	Х	Х	Х	Х	Х	/
PO-SS	Х	х	х	х	Х	х	Х	
PO-SB	Х	Х	х	х	Х	х		
PO-SM	Х	х	х	х	Х	х	Х	/
LY-PM	Х	Х	х	Х	х	х	Х	
LY-SS	Х	/	Х	/	Х	х	Х	
LY-SB	Х	х	Х	х	Х	х		
LY-SM	Х	1	Х	X	Х	х	Х	/

Table 20 Results of the cleaning tests on brick slabs and mock up samples of the $1^{\mbox{st}}$ set

After these tests, in particular the ones carried out on the 1^{st} set of mock-ups, we selected the best cleaning methods in order to test them on the 2^{nd} set of mock-ups⁴¹, to confirm their effectiveness.

	REMOVAL METHODS							
SAMPLES	Velvesil +	Evolon	Velvesil	PVA/B 8%	PVA/B 6%	HWR +	HWR +	HWR +
SAIVIT LES	Ethanol	+	+ Blend	+ blend	+ blend	coating	coating	coating
	20%	Ethanol	16	16 10%	16 20%	В	G	S
LY-P-SM	Х	1	Х	-	-	-	-	-
LY-P-SS	-	-	-	1	Х	Х	Х	Х
LY-P-SB	-	-	-	/	Х	Х	/	/
LY-P-PM	Х	/	Х	-	-	-	-	-
PO-P-SM	/	Х	Х	-	-	-	-	-
PO-P-SS	-	-	-	-	-	-	-	-
PO-P-SB	-	-	-	-	-	-	-	-
PO-P-PM	/	/	Х	-	-	-	-	-

Table 21 Results of the cleaning tests on mock up samples of the $2^{nd}\,\text{set}$

As expected, the solubility tests performed with organic solvents/blends in liquid form have shown a number of effective products for removal the overlapping graffiti materials but few products safe for the paint layers underneath. It has to be said that "safe cleaner" means a cleaning agent less aggressive than others but not inherently safe for the paint layer (see above).

Below the observations on graffiti materials collected during the cleaning tests:

- PM thin layer partially penetrated inside the paint layers. A good extractive cleaning method is necessary to remove it minimizing the penetration of the solvent that would cause the more in depth penetration of the marker's ink. Sensitive to the majority of tested solvents, but in a lesser way to solvents no. 4, 5, 7, 8, 9.
- SS film layer at medium average thickness. Methods that swell it with a mechanical action afterwards are effective to remove it but also extractive methods are not to be excluded for a partial removal. The completely removal of the spray is tricky because of the tiny silver

⁴¹ It is important to highlight that the mock-ups used for the 1st set were cleaned 1 month later the soiling with graffito materials while the 2nd set of samples were cleaned 3 months later the soiling: graffiti to removed were different aged.

particles that remain spread on the surface and are very difficult to remove. Sensitive to the majority of tested solvents, including Ligroin, and in a lesser way to solvents no. 8, 9 and follow to no. 5, 7.

- SB high thick film layer. Methods that swell it with a mechanical action afterwards are effective to remove it. Compared to the other graffiti materials tested, it is the least sensitive to organic solvents/blends and it is the slowest to swell. The most effective solvents on SB are the no. 1, 2, 3 and the blends that contain these: no. 5, 10, 14.
- SM high thick layer without a filming feature. Extractive cleaning methods are necessary to completely remove it otherwise the swelled residues are not easily removable by mechanical tools because of their toughness/hardness and stickiness. Sensitive to the majority of the tested solvents from a medium to high polarity (i.e Ligroin is not effective). In general the less effective solvents are no. 4, 5, 7, 8, 9.

Ligroin (fd97, fh2, fp1) has resulted the only safe solvent for the two paint layers, followed by LA1,LE1 blends (fd92-1, fh5-4, fp3-5). Nevertheless, Ligroin is not inherently safe for PO that is particularly very sensitive, and more active are LA1,LE1 blends.

Compared to PO, the alkydic yellow paint LY has showed a relatively more resistance to solvents.

The tests performed on this paint have allowed to identify three safety ranges in terms of polarity:

fd 97-87 fp 2-8 fh 1-5

fd 91-85 fp 4-5 fh 5-10

fd 42-36 fp 16-18 fh 42-46

The third polarity range has been considered because a lot of solvents generally used in the restoration field are in this range.

This range has been experimentally confirmed by finding Solvenon DPM and Ethanol the most effective solvents in terms of removal of the overlapping graffiti and, at the same time, safety for LY. All the three parameters (fd, fp, fh) should be as close as possible to the ones of the range. Green solvent Loxanol MI 6470 has showed good effectiveness; it has been recently introduced on the market as a paint stripper, but unfortunately the solubility parameters are not known.

However, blends with the best results are not included into the above mentioned range, in particular the fp and fh parameters are higher and lower, respectively. Unfortunately, the parameters of Loxanol MI 6470 blends were not available. In-depth investigation about this aspect is necessary by studying the kind of inter-molecular interactions between these blends and functional groups of the graffiti materials to remove.

Concerning the cleaning on the yellow (LY) samples, the experimentation was carried out by testing the most effective organic solvents and blends thickened or by using a supporting agent: Ethanol and blends no. 16 and 12 are the safest for the operator and have a better profile for the environment.

Depending on the type of graffiti material, supporting agents have shown different efficacy:

- high retentive gels characterized by a slow and controllable release of solvent (PVA/Borax gels) have swelled the graffiti materials film layer with the help of a gently mechanical action afterwards
- Evolon, due to its peculiar micro-structure, acts by sucking. It has performed better on the penetrating and non-filming graffiti (PM, SM).

• Velvesil, thanks to its chemical inertia towards the paint layers and its delicate and superficial action, has better performed on the non-filming graffiti materials (PM, SM, i.e. gel containing Ethanol (20%) on the LY samples soiled with SM.

Finally, the micro-emulsions (containing effective solvents for the graffiti removal) with high retentive and inert gels have showed good and safe cleaning results, in particular on thick and filming graffiti materials: they have been swelled and then mechanically removed.

Because of the extreme sensitivity of the PO paint layer, even the tests with thickeners and supporting agents have shown negative results and have resulted to be too aggressive and dangerous.

2.2.3 Which of the applied cleaning methods were most effective? (lowest impact on the surface, best cleaning result,...test winner) why? What were your criteria for the evaluation?

Same criteria for the cleaning tests evaluation were adopted from CESMAR7 and ANTARES taking into account six key parameters above explained (section 2).

- T preservation of the topography integrity
- Cr presence and clearance of the residues
- G preservation of the surface gloss
- Cp cleaning efficiency and evenness
- Am method feasibility
- (Pp pigment pick up)

from 0/10 (unacceptable result) to 10/10 (optimal result).

Below the evaluation of the most effective cleaning methods.

CESMAR7

Dirt removal

Dry cleaning: dry cleaning tests have shown that the best materials for cleaning standard dirt in our cases are Smoke sponge, Spugna Magica Oz and the makeup sponge, the last two with the best results in terms of effectiveness. The make-up sponge on the surface treated with MCR has slightly removed the colour (probably due to its spray application).

Aqueous solutions: The best buffer solution is the one at pH6, 20 mS/cm, which works better if gelled on the surface with 2% Xanthan gum, reaching an excellent cleaning level on both on the blue and red areas, even in macro porosity of the surface. In general, the approach starting from low conductivity mixtures is good and allows to identify the most suitable cleaning solution. In a proposal of standard solutions to be tested, a pH 5 solution should be added to the list <u>(not used in this study)</u> **Semi humid methods:** the best results have been obtained with the Kiko make-up sponge moistened with the pH 6 buffer solution and a conductivity of 20 mS/cm which had proved to be the best even on its own. Even with Evolon moistened, an excellent cleaning is obtained but a more consistent colour loss occurs on both the red and blue areas.

Agar Agar: fluid agar gives excellent results; it is simple to use, very respectful of the surface and leaves no residue, removing also the embedded dirt into the macro porosity. On the contrary, agar stick leaves the dirt on the surface together with many residues into the micro roughness; residue therefore must be removed with other methods or by multiple applications.

Graffiti removal

Solvent gel No. 3.

Solubility test has shown that starting from LA3 and LE3 all the staining materials start to swell. The Molotow black spray can be completely removed even with simple ligroin while the others need more polar solvents. Markers and purple Montana paint are the most difficult to remove. Using solvents directly on the surface there is the risk of creating halos and tidelines around the treated area. Brushing the solvent over Evolon microfiber cloth and dabbing it gives good results but only after repeating the steps several times. Solvent surfactant gels act faster than Evolon even if they impaste the staining materials and they should be rinsed well so that there are no residues on the surface. Solvent gel No. 3 is the one that has given the best results.

ANTARES

Below the radar graphics that summarizes the better results obtained after the tests carried out on the 1st set of mock-up samples, and in particular on samples LY paint layer (Tables 3-23 – appendix) The score of each parameter has been evaluated by observing the cleaned surfaces under stereomicroscope at different magnifications.

This has allowed to observe in a more detailed way the cleaned surfaces and to adjust some of the evaluations before made by the naked eye.

The best product/methods for removing each graffiti materials, in particular on LY samples have been the following, reported from the more to the less effective:

SM on LY	blend no.16 applied with Evolon, Ethanol 20% in Velvesil, followed by Ethanol on
	Evolon
PM on LY	blend no. 5 on Evolon, followed by blend n. 12 and Ethanol on Evolon, and finally by
	blend no. 16 on Evolon
SS on LY	10% of blend no.16 into PVA/Borax gel 8%
SB on LY	Nanorestore Cleaning [®] Polar Coating B in HWR gel, followed by 10% of blend no.16
	into PVA/Borax gel 8% and finally by Nanorestore Cleaning [®] Polar Coating G in HWR
	gel

Follow the supporting agents used with the different cleaning products that have obtained the best results, in order of effectiveness⁴²:

Evolon: effective on the non-film forming graffiti. Safe and respectful of the paint layer's surface morphology (T) and the gloss (G) without the release of residue (Cr). The cleaning capability (Cp) was sufficient, but only when used on SM and PM, with lower score on the last, because of the major penetration of the black marker into the paint layers. It has been noted that a major cleaning effectiveness has been obtained replacing the Evolon cloth frequently.

Concerning the application, it has been noted that a very thin accumulation of solubilized SM material around the edges of the cleaned zone: this phenomenon can be avoided using cloths of a greater size than the area to clean. It has resulted as very easy to transfer on a real case on-situ, and in a vertical application; it is also cheap. The only aspect that it did not permit to Evolon to reach the maximum on Am parameter is the very short application time (few seconds).

Velvesil: more effective on non-film forming graffiti materials (PM, SM). It is a method that involve a mechanical action so it is less safe for the morphology (T) and gloss (G) of the paint layers' surfaces, however it does not seem to pick-up the pigment. It did not release residues on the surface (Cr) and its cleaning capability (Cp) was satisfactory, but it was not able to clean the micro-pores of the paint layers. The D5 rinse, makes it safe for the selected paint layers.

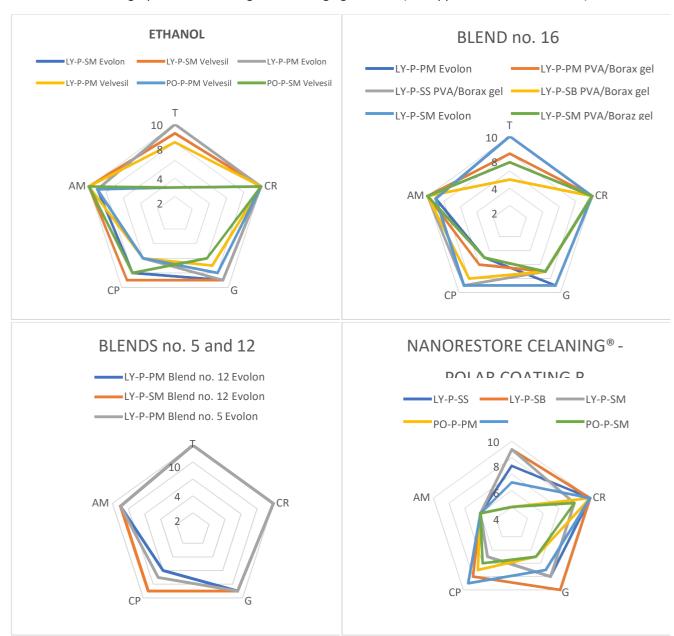
The method is also easily transferable on a real case on-situ.

⁴² It has to be precise that the following supporting agents have not been effective on the total four graffiti materials, but generally only on a half of them, depending on the type of graffiti, if it was filming or not.

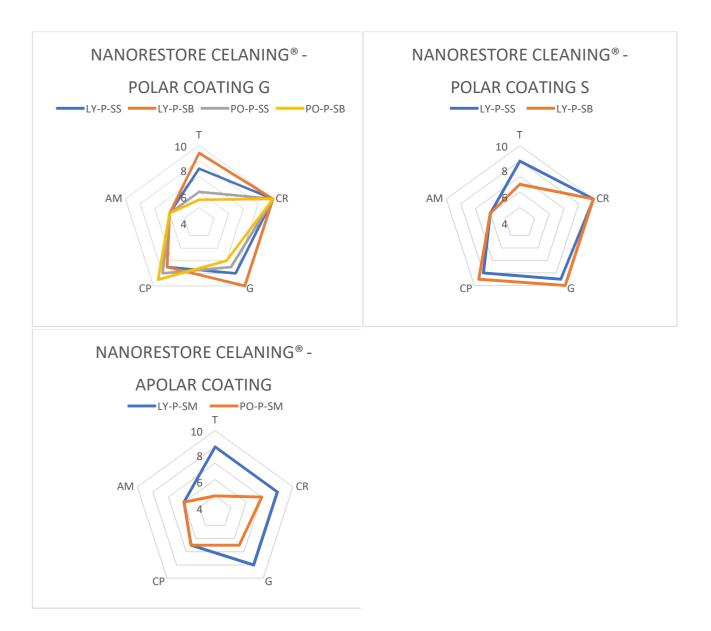
PVA/Borax gel: more effective to remove film-forming graffiti materials, which need to be swelled in order to remove them. Observing the cleaned areas with the naked eye this method seemed to be optimal, but when the same areas have been observed with the stereomicroscope, some abrasions, in particular on the more jutting zones have been noted, probably attributable to the necessary mechanical action performed after the gel application useful to remove the film-forming graffiti. This aspect consequently lowed the gel's score of the T and G parameters. The Cr parameter is excellent, in fact no residues have been noted on the cleaned areas; also the cleaning capability (Cp) is good, even if lots of the micro-pores have not been completely cleaned.

It is a method easily transferable on a real on-situ case: even if it is a little laborious to prepare, it is very cheap and its rheological characteristics and the fact that it is a non-Newtonian fluid, make it very versatile. The application times, from dozens minutes to hours, make it a high-controlled method too.

HWR gel: despite the low number of tests carried out with different cleaning agents than Nanorestore Cleaning[®] Coatings, it has reached satisfactory results only when charged/embedded with these last micro-emulsions. It has been more effective on the removal of thick film-forming graffiti (SS,SB). Observing the cleaned areas with the naked eye this method seemed optimal, but when the same areas have been observed with the stereomicroscope, some abrasions have been noted, probably attributable to the necessary mechanical action performed after the gel application useful to remove the film-forming graffiti material. Due to the method and type of graffiti that we had to remove during the research, the otherwise necessary (because of the presence of surfactants into gels and coatings) subsequent aqueous rinse have not been performed. The cleaning capability (Cr) was good, even if lots of the micro-pores have not been cleaned. About the applicability the method is not easily transferable on a real on-situ case, because it is difficult to apply on vertical surfaces.



Below the radar graphics, considering the cleaning agent used (see appendix for more details):



In order to assess the effectiveness of the above mentioned methods, further tests were carried out on the 2nd set of mock-up samples where the graffiti materials were two months ager than the 1st set.

The best product/methods for removing each graffiti materials, in particular on LY samples are the following:

SM and PM on LYBlend no.16 with Evolon, Ethanol with Evolon and Ethanol 20% in VelvesilSB and SS on LYNanorestore Cleaning® Polar Coating B, G and S in HWR gel, 10% of blend
no.16 into PVA/Borax gel 8%, 20% of blend no.16 into PVA/Borax gel 6%

These results are different from the ones collected on the 1st set of samples, in particular for what concerns the film forming graffiti materials SS and SB. In fact, the same method used in the same way (=% of solvent, =application time) gave total different results and some graffiti were hard to be removed.

For example the PVA/Borax 8% + 10% of blend no. 16 applied for 40' on LY-P-SB was completely ineffective on SB. Worse results than the one obtained on LY-P-SB of the 1st set were also registered

with PVA/Borax 6% + 20% of blend no. 16. The SB layer was only partially and heterogeneously removed, and in a totally unsafe way for the paint layer LY. Similar results were collected on LY-P-SS, and for the Nanorestore Gel HWR loaded with Nanorestore fluids (coatings B, G, S) on LY-P-SB. For what concerns Nanorestore Gel HWR + coatings B/G/S applied on LY-P-SS, no modifications of the application times were necessary in order to obtain similar results as the ones of the 1st set.

Probably the different aging of the graffiti materials of the 1^{st} and the 2^{nd} set is the reason that causes worse cleaning results in the 2^{nd} set tests.

2.2.4 Was it possible to transfer the methods/products on the objects on-site? If not, what has been different? Are there indications of a trend wether or not the behaviour of the product/method is the same on-site as under laboratory conditions? If not, what has been different?

The research did not foresee products application on-site but many applicative aspects has been taken into account, in particular the Am (method feasibility) parameter in the performance evaluation of the cleaning agents.

2.2.5 How is the monitoring of the objects planned on-site?

- 2.2.6 What were the benefits of the students and staff mobility?
- 2.2.7 Deviation of the work plan.

-

2.2.8 Problems encountered and implemented or proposed solutions.

During the research we have encountered some technical problems such as:

- the realization of standard dirt has resulted difficult and the standard recipe has been changed
- the preparation of samples cross-sections have failed maybe because of the high sensitivity of our fresh samples to the polyester resin. Other products are now being considered.
- The lack of information from suppliers regarding the composition of the paints and graffiti materials has been a problem because we could have started the research with more information useful for better optimizing the tests also in terms of time.

The research was carried out by 2 internal partners located in different cities and the work coordination has not been always easy.

2.2.9 Comments or short conclusion.

The present report provides a first set of results related to the cleaning of modern paints murals. It evaluates the performance of aqueous solutions, organic solvents blends and formulation in which organic solvents and water is combined (emulsions) applied to the paint surfaces with different methodologies. Products currently available on the market, including those of the latest generation and a green solvent never tested in the restoration field, were taken into account.

A common approach to cleaning and a shared evaluation criterion of the tests among the two working groups, although we have independently worked and we have carried out different tests valuated with different instruments, have allowed us to obtain some transferable results in terms of cleaning products and methods.

The data obtained from these tests can also be taken into account for other real case in which the paint film or the graffiti materials, that can be included among commonly used paints by artists and vandal writers, are similar materials to those studied are employed.

The common approach adopted could be applied in a simplified form on-site: starting from an indepth knowledge of the chemical composition, type (filming or penetrated layer, applied by spray or brush) and data on solubility (for example dedicated solubility tests with organic solvent blends and aqueous solutions) of paint layers and graffiti materials, already selected winner products and methods could be tested on-site.

Further tests of the winning products, of combined solvent-water chemicals and of green solvents are necessary to evaluate their action on a greater number of samples and better understand certain mechanisms of action.

However, cleaning is a challenge: to safeguard the integrity of the paint layer artwork with less risks, cleaning is intrinsically safer if a coating between the paint layer and soiling (see file 2) is present.

2.3 Acadamy of Fine Arts Warsaw (Poland)

NUMBER OF PARTNER	COUNTRY	NUMBER OF OBJECTS	NUMBER OF SAMPLES
Р7	Poland	Object 1	
		Object 2 (2d, 2g, 2m)	

2.3.1 Information on tested cleaning methods carried out on mock up samples within the companies/research centres and on-site based on the selected sculptures (output wp2 and wp3)

Describe your experimental setup, including details on sample preparation, instruments and experimental conditions used. Take into account to name the object number and sample identification.

All cleaning tests were carried out on two objects: *Szczudlarze* by Linas Domarackas on the tenement house at 37 Stalowa Street in Warsaw, and on a set of 24 murals by various authors on Mur Sztuki [Wall of Art] in Ogród Różany [Rose Garden] of the Warsaw Uprising Museum. The tests were carried out directly on the painting layer of the above-mentioned murals in situ. It was decided that it is best to carry out the tests on the objects and not on specially created samples under laboratory conditions. This gave us the opportunity to test the cleaning of paint layers made in various techniques. The cleaned facilities were naturally dirty – exposed to various external factors in an open urban space (e.g. dust, graffiti, traces of microbiological attacks). Purification tests were carried out on the following objects:

- Szczudlarze (Object 1): Plaster - lime mortar, lime and cement mortar with quartz filler; black charcoal Paint layer: acrylic and vinyl paints
- Wall of Art (Object 2): Plaster - lime mortar with quartz filler Paint layer: acrylic, polyester, phthalic, vinyl, and tempera paints List 3 murals from the Wall of Art in the Uprising Museum: 2d – mural by Stasys 2g – mural by Utz 2m – mural by Galeria Rusz

2.3.2 What were the results of the optical and analytical observation of the different cleaning methods on the ad hoc samples? (table) How did you get the results?

Object-	Sample-	Product-	Tests*	Analytical	Optical Results
number	number	number		Results	
Object 1	Not	CONTRAD	Cleaning with cotton	Not applicable	Very good 5/5
	applicable,	2000	wool tampons,		
	the tests		concentration 2% in		
	were		H ₂ O		
	carried out				
	on the				
	object				
	Not	Ethyl alcohol	Cleaning with cotton	Not applicable	Very good 5/5
	applicable,	-	wool tampons,		
	the tests		concentration 2-5% in		
	were		H ₂ O		
	carried out				
	on the				
	object				
	Not	Water	Cleaning with cotton	Not applicable	Good 4/5
	applicable,		wool tampons		
	the tests				
	were				
	carried out				
	on the				
	object				
	Not	Ammonia	Cleaning with cotton	Not applicable	Good 4/5
	applicable,	water	wool tampons,		, -
	the tests		concentration 1%		
	were				
	carried out				
	on the				
	object				
	Not	Bristle brushes		Not applicable	Very good for removing dust 5/5
	applicable,				
	the tests				
	were				
	carried out				
	on the				
	object				
Object 2d	Not	WISHAB sponge		Not applicable	not suitable for low-adhesion and
(Stasys)	applicable,				cohesion paint layers 2/5
())	the tests				
	were				
	carried out				
	on the				
	object				
	Not	Milano rubber		Not applicable	very good for removing tarnish
	applicable,	(synthetic)			from mold; not suitable for a paint
	the tests				layer with low adhesion and
	were				cohesion. It is necessary maintain
	carried out				caution when cleaning 4/5
	on the				
	object				
	Not	Melinex sponge		Not applicable	does not remove dirt 1/5
	applicable,				-
	the tests				
	were				
	carried out				
	on the				
	obiect				
Object 2g	object Not	WISHAB sponge		Not applicable	very good for removing dirt, 4/5

			[
	the tests				
	were				
	carried out				
	on the				
	object				
	Not	Milano rubber		Not applicable	very good for removing dirt, 5/5
	applicable,	(synthetic)		iter applicable	
		., ,			
	the tests				
	were				
	carried out				
	on the				
	object				
	Not	Melinex sponge		Not applicable	does not remove dirt 1/5
	applicable,				
	the tests				
	were				
	carried out				
	on the				
	object				
	Not	CONTRAD	Used for removing	Not applicable	very good for removing
	applicable,	2000	acrylic paint.		repaintings, 5/5
	the tests		Cleaning with cotton		
	were		wool tampons,		
	carried out		concentration 5-10%		
	on the		in H ₂ O		
	object				
	Not	Ethyl alcohol	Used for removing	Not applicable	very good for removing
	applicable,		acrylic paint.		repaintings, 5/5
	the tests		Cleaning with cotton		
	were		wool tampons,		
	carried out		concentration 60-		
	on the		90% in H₂O		
	object				
		Acatona	Used for removing	Notopolicable	too strong it domogoo the
	Not	Acetone	-	Not applicable	too strong, it damages the
	applicable,		acrylic paint.		original acrylic layer. The
	the tests		Cleaning with cotton		original paint layer can be
	were		wool tampons,		damaged 2/5
	carried out		concentration 20-		
	on the		50% in alcohol		
	object				
	Not	WISHAB sponge		Not applicable	not suitable for low-adhesion and
	applicable,			Not applicable	cohesion paint layers 2/5
	•••				,
•	the tests				
,	were				
	carried out				
	on the				
	object				
	Not	Milano rubber		Not applicable	very good for removing tarnish
	applicable,	(synthetic)			from mold; not suitable for a paint
	the tests				layer with low adhesion and
	were				cohesion 3/5, the object becomes
					powdered
	carriad out				
	carried out				
	on the				
	on the	Melinex sponge		Not applicable	does not remove dirt 1/5,
	on the object	Melinex sponge		Not applicable	but good for removing tarnish from
	on the object Not	Melinex sponge		Not applicable	
	on the object Not applicable, the tests	Melinex sponge		Not applicable	but good for removing tarnish from
	on the object Not applicable, the tests were	Melinex sponge		Not applicable	but good for removing tarnish from
	on the object Not applicable, the tests were carried out	Melinex sponge		Not applicable	but good for removing tarnish from
	on the object Not applicable, the tests were carried out on the	Melinex sponge		Not applicable	but good for removing tarnish from
	on the object Not applicable, the tests were carried out on the object				but good for removing tarnish from mold 4/5
	on the object Not applicable, the tests were carried out on the object Not	Melinex sponge		Not applicable Not applicable	but good for removing tarnish from mold 4/5 good for removing tarnish from
	on the object Not applicable, the tests were carried out on the object				but good for removing tarnish from mold 4/5

were			
carried out			
on the			
object			
Not applicable,	Leathercraft knife	Not applicable	good for removing tarnish from mold, 4/5
the tests were			
carried out			
on the object			
Not	Bristle brushes	Not applicable	Very good for removing dust 5/5
applicable,			
the tests			
were			
carried out			
on the			
object			
Not	Fiberglass	Not applicable	good for removing tarnish from
applicable,			mold, 3/5
the tests			
were			
carried out			
on the			
object			

* Please specify the work and tests you have done. The table is only a tool for organizing the results. Feel free to choose another form to present your results.

2.3.3 Which of the applied cleaning methods were most effective? (lowest impact on the surface, best cleaning result,...test winner) Why? What was your criteria for the evaluation?

The effects of cleaning by means of the above methods depended on the type of object (its condition and the technique used to create it). Each object can react differently to each of the above methods. On the paint layer characterized by lack of cohesion (with a tendency to become powdered), delicate dry mechanical methods – e.g. cleaning with different types of erasers – worked best. The following mechanical methods proved to be the best for removing mold marks: cleaning with a scalpel, leather knife, glass fiber and melinex sponge. Heavy dirt was removed well from the acrylic paint layer with the help of aqueous solutions – Contrad 2000, ammonia water and ethyl alcohol. As for acrylic repaints, they were removed effectively using concentrated Contradu 2000 solution and ethyl alcohol. In the case of removing traces of vandalism, the best method was the combination of chemical and mechanical methods consisting in softening graffiti paint and then mechanical removal (tests refer to an object with good cohesion of the paint layer). It was not possible to remove all traces of vandalism and mold marks.

2.3.4 Was it possible to transfer the methods/products on the objects on-site? If not, what has been different? Are there indications of a trend wether or not the behaviour of the product/method is the same on-site as **under laboratory conditions**? If not, what has been different?

All tests were carried out on site, on the object.

2.3.5 How is the monitoring of the objects planned on-site?

Photographic documentation was made before and after cleaning. The objects will be monitored this year.

2.3.6 What were the benefits of the students and staff mobility?

Students from Cologne could not come to Warsaw in 2019. An internship is planned in June 2020.

2.3.7 Deviation of the work plan.

Not applicable

2.3.8 Problems encountered and implemented or proposed solutions.

Difficulties associated with carrying out tests in the open air in summer: works were often carried out in very difficult conditions – murals were exposed to strong sunlight and high temperatures.

2.3.9 Comments or short conclusion.

Cleaning methods should be selected individually for each mural, according to the technique used to create the mural, its condition, and the external conditions in the area where it is located.

3 Report on the analytical evaluation of protecting treatments

3.1 CESMAR & ANTARES

NUMBER OF PARTNER	COUNTRY	NUMBER OF OBJECTS	NUMBER OF SAMPLES
P3-P4	ITALY		561

3.1.1 Information on tested protecting treatments carried out on mock up samples within the companies/research centres and on-site based on the selected sculptures (output wp2 and wp3) Describe your experimental setup, including details on sample preparation, instruments and experimental conditions used. Take into account to name the objectnumber and sample identification.

The performance of protecting products for murals was evaluated on mock up samples based on Reggio Emilia artworks (object n.3-6,8,16, Wp3 output):

- three supports (simple and layered)
- six paint colours among chromatically stable and unstable ones
- seven protecting products from different classes among varnishes and anti-graffiti coatings studied both alone than in layered systems (total 17 protecting treatments).

We have studied literature^{1,2}, assessed composition and availability on the market as well as way of usage and we selected products:

- ready to use
- waterbased
- designed for outdoor (painted and unpainted) surfaces
- sacrificial and permanent

in order to find better products/methods in terms of effectiveness and respect of the paint layers looking for green and transferable on-site products.

- In particular, experimental approach was focused on the study of the following key parameters:
 - a. chemical and physical stability of paint films and protecting products to aging
 - **b.** susceptibility of paint films and protecting products to microbiological attack
 - c. graffiti removal efficiency and applicative aspects
 - **d.** in addition, we are involved in the Capus collaborative work regarding the effectiveness of three coatings applied to low-medium resistance colours on concrete.

Several analytical and optical investigations were carried out before and after treatments and aging. Below the details of the experimental set up adopted for each of the above mentioned points and the results up to now collected.

¹Shank, W, 2015, Cambridge Scholars Publishing

² Macchia, A., 2019, Journal of Cultural Heritage

RESEARCH INTO CHEMICAL-PHYSICAL STABILITY OF PAINT FILMS AND PROTECTING PRODUCTS TO AGING

This research was performed in collaboration with Ca' Foscari University of Venice (MA Thesis).³ The aims of the research were:

- to study the chemical and physical stability of 5 selected commercial paint formulations comparable with some colours found in Reggio Emilia artworks
- to evaluate the performance of 5 different anti-graffiti coatings and 2 different UV stabilizers varnishes, in terms of chemical and physical stability and effectiveness in the protection of the underlying paint layers from vandalism (i.e. graffiti upon the mural artwork) and UV irradiation-induced damages

The experimental part of the present research was divided into 3 different steps:

- characterization of the starting materials (paints, UV varnishes, anti-graffiti coatings)
- coatings application on mock-ups: considerations and observations
- evaluation of the effects of accelerated ageing after 620 hours in a climate chamber

³See appendix for all the details regarding this research

Materials

Table 1 Product list with acronyms and information provided by manufacturers/dealers

Supports	Smoothing layer	Ground layer	Primer	Paint layers	Varnishes	Anti-graffiti coatings
Microscope slides V	Saint Gobain Webercem RS350 ⁴	Rival - Stella Oro- P03⁵	LECHLER Chrèon - Framaton Riveste Prof, white (Q107751) ⁶	Montana Colors MTN 94 FLUOR / Orange NF ⁷ Montana Colors MTN 94 Frame Gold (Marco) OM ¹⁰	Montana Cans Acrylic Varnish Gloss, T1000 AV1⁸	An.t.a.res s.r.l. Anti-Stain AS ⁹ Maflon s.p.a. Hexafor SA-6320 HX ¹¹
Bacchi Prontomalt Malta Bastarda Fibrata ¹²			Ρ	Montana Cans Montana Gold Pure Orange G2080 PO ¹³ Montana Colors MTN 94 RV 4010 / Magenta MA ¹⁶	Montana Colors MTN PRO Synthetic Varnish Gloss, MTN PRO SV1 ¹⁴	Pelicoat Italia s.r.l Pro-Stone PS ¹⁵ Guard Industrie s.a.s. Protect Guard TC matt PG ¹⁷
				LECHLER Chrèon - Framaton Riveste PROF Red 3060R FR¹⁸		Colorificio San Marco s.p.a Isograff IG ¹⁹

⁴ Saint Gobain - Webercem RS350: smoothing product composed of hydraulic lime, for finishing and leveling plasters, either indoor and outdoor.

⁵ Rival- Stella Oro – Idropittura traspirante opaca per interno: matt water paint for indoor use.

⁶ LECHLER – Chrèon - Framaton Riveste Prof: siloxane acrylic water white paint with quartz powder/flour with an additive to prevent mold and algae, for outdoor use

⁷ MTN 94 – Fluorescent alkyd spray paint. It contains Xylene (mixture of isomers), Ethyl Acetate, Ethylbenzene, n-Butyl Acetate, Acetone, Polyhydroxyalkylamides and 2-Butanone-Oxime.

⁸Montana-Cans- Acrylic Varnish gloss T1000: nitrocellulose-acrylic, acid-free, quick drying, with additive to guarantee UV

protection. No yellowing or de-saturation. For interior and exterior use. It contains: Dimetyl Ether, Acetone, Butane, Propane, Propylene Glycol monomethyl Ether Acetate, n-Butyl Acetate, Xylene, Nitrocellulose, Petroleum distillate, 1,2,4-Trimethylbenzene, Ethylbenzene, Cumene

⁹ Anti-stain - distribuited by An.T.A.Res: aqueous emulsion of waxes and organic fluoropolymers. Water and oil repellent, it

is a ready to use sacrificial anti-graffiti coating for porous surfaces like stones. It avoids the penetration of vandalism graffiti materials and at the same time it simplifies their removal from the surfaces where it is applied. It is also completely removable with hot water.

¹⁰ MTN 94 – Frame Gold/Oro Marco Alkyd spray paint containing Xylene (mixture of isomers), Ethyl Acetate, Ethylbenzene,

n-Butyl Acetate, Acetone, Polyhydroxyalkylamides and 2-Butanone-Oxime.

¹¹ Hexafor SA-6320 by Maflon: ready to use aqueous emulsion of perfluoro-alkyl siloxane cationic polymer that guarantees a durable and semi-transparent permanent (up to ten cleaning cycles) antigraffiti treatment on stone surfaces. It is both

water and oil repellent, and the treated surfaces are easily washable. PFOA free.

¹² Bacchi - Prontomalt - Malta Bastarda Fibrata: hydraulic mortar composed by Portland cement (10-13%) and quartz (70-90%).

¹³ Montana Gold – Pure Orange – G2080: Nitro-acrylic and solvent based spray paint containing DME, Ethyl Acetate,

Acetone, Propane, Butane, Naphta, Xylene, Isobutane, 2-Methoxy-1-Methylethyl Acetate, 2-Propanol, Ethylbenzene.

¹⁴ Montana Colors - MTN PRO - Synthetic Varnish, Gloss: Solvent based spray paint containing Xylene (mixture of isomers), Ethyl Acetate, Ethylbenzene, n-Butyl Acetate, Acetone, Polyhydroxyalkylamides, 2-Butanone-Oxime. very fast-drying,

alkydic, protective varnish to use on oil and acrylic media. It has high weather and UV-resistance properties, and once the film is completely polymerized, it is also resistant to abrasions.

¹⁵ Pro-stone by Pelicoat.: fluorinated acrylic copolymer in aqueous phase. Water and oil repellent and ready to use

permanent antigraffiti coating for stone surfaces (it persist 10 years). It penetrates by capillarity into the support, so it avoids water, fat, varnishes and felt pens penetration. It is totally reversible. pH 4.5-6

¹⁶ MTN 94 – Magenta – RV 4010 : Alkyd and solvent based spray paint containing Xylene (mixture of isomers), Ethyl Acetate,

Ethylbenzene, n-Butyl Acetate, Acetone, Polyhydroxyalkylamides, 2-Butanone-Oxime

¹⁷ Protect Guard by Guard Industrie.TC: acrylic emulsion in aqueous phase designed as a water and oil repellent permanent coating, specific for painted surfaces with acrylic colours. It is suited both for indoor and outdoor use.

¹⁸ Framaton Riveste PROF Red 3060R: acrylic resin and quartz

130 and 144 mock up samples were realized on microscope slides (**Table 2**) and on cement mortar (**Table 3**), respectively.

Samples were named according to the support and the products employed to create them and to the type of ageing they would have been exposed.

In general, the name was assigned as follows, using capital letters in each part: (*support*) – *type of* ageing – paints used – coatings upon paint (anti-graffiti follows by varnish, where both applied) – (primer)

130 mock up samples were realized on microscope slides V (**Table 2**) and subjected to natural (VN, 65 samples) and artificial aging (VA, 65 samples).

In particular,

4 sets of 24 slides each (96 samples) were sprayed with colours: NF, OM, PO, MA:

- 10 samples of each set were layered in twice (5+5) with layers of each anti-graffiti coating AS,
 HX, PS, PG, IG
- 2 samples of each set were treated with two layers of the varnish with the same brand of the colour, AV1 for Montana Cans color and SV1 for Montan colors
- 10 samples of each set were treated in twice (5+5) with a double layer; the first one made of the varnish with the same brand of the colour and the second one with each anti-graffiti coating
- 2 samples of each set were not treated (references)

2 sets of 2 slides each (4 samples) were layered in twice on each varnish AV1 and SV1.

5 sets of 6 slides each (30 samples) were coated in twice (1+1) with:

- each anti-graffiti coating (2 samples)
- each varnish with each anti-graffiti coating on the top (4 samples)

¹⁹ Isograff by San Marco. Code 7770002: polymer waxes in water dispersion. Ready to use sacrificial anti-graffiti used to protect mineral-based surfaces. It facilitates the removal of graffiti, simply through cleaning with hot water (80°C)

MISCOSCOPE SLIDES SAMPLES							
ID-SAMPLES		QUANTITY	ID-SAMPLES		QUANTITY		
VA-PO-AS	VA-PO-AS-AV1	2	VN-NF-HX	VN-NF-HX-SV1		2	
VA-PO-HX	VA-PO-HX-AV1	2	VN-NF-PS	VN-NF-PS-SV1		2	
VA-PO-PS	VA-PO-PS-AV1	2	VN-NF-PG	VN-NF-PG-SV1		2	
VA-PO-PG	VA-PO-PG-AV1	2	VN-NF-IG	VN-NF-IG-SV1		2	
VA-PO-IG	VA-PO-IG-AV1	2	VN-NF	VN-NF-SV1		2	
VA-PO	VA-PO-AV1	2	VA-OM-AS	VA-OM-AS-SV1		2	
VN-PO-AS	VN-PO-AS-AV1	2	VA-OM-HX	VA-OM-HX-SV1		2	
VN-PO-HX	VN-PO-HX-AV1	2	VA-OM-PS	VA-OM-PS-SV1		2	
VN-PO-PS	VN-PO-PS-AV1	2	VA-OM-PG	VA-OM-PG-SV1		2	
VN-PO-PG	VN-PO-PG-AV1	2	VA-OM-IG	VA-OM-IG-SV1		2	
VN-PO-IG	VN-PO-IG-AV1	2	VA-OM	VA-OM-SV1		2	
VN-PO	VN-PO-AV1	2	VN-OM-AS	VN-OM-AS-SV1		2	
VA-MA-AS	VA-MA-AS-SV1	2	VN-OM-HX	VN-OM-HX-SV1		2	
VA-MA-HX	VA-MA-HX-SV1	2	VN-OM-PS	VN-OM-PS-SV1		2	
VA-MA-PS	VA-MA-PS-SV1	2	VN-OM-PG	VN-OM-PG-SV1		2	
VA-MA-PG	VA-MA-PG-SV1	2	VN-OM-IG	VN-OM-IG-SV1		2	
VA-MA-IG	VA-MA-IG-SV1	2	VN-OM	VN-OM-SV1		2	
VA-MA	VA-MA-SV1	2	VA-AS	VA-AS-AV1	VA-AS-SV1	3	
VN-MA-AS	VN-MA-AS-SV1	2	VA-HX	VA-HX-AV1	VA-HX-SV1	3	
VN-MA-HX	VN-MA-HX-SV1	2	VA-PS	VA-PS-AV1	VA-PS-SV1	3	
VN-MA-PS	VN-MA-PS-SV1	2	VA-PG	VA-PG-AV1	VA-PG-SV1	3	
VN-MA-PG	VN-MA-PG-SV1	2	VA-IG	VA-IG-AV1	VA-IG-SV1	3	
VN-MA-IG	VN-MA-IG-SV1	2	VN-AS	VN-AS-AV1	VN-AS-SV1	3	
VN-MA	VN-MA-SV1	2	VN-HX	VN-HX-AV1	VN-HX-SV1	3	
VA-NF-AS	VA-NF-AS-SV1	2	VN-PS	VN-PS-AV1	VN-PS-SV1	3	
VA-NF-HX	VA-NF-HX-SV1	2	VN-PG	VN-PG-AV1	VN-PG-SV1	3	
VA-NF-PS	VA-NF-PS-SV1	2	VN-IG	VN-IG-AV1	VN-IG-SV1	3	
VA-NF-PG	VA-NF-PG-SV1	2	VA-AV1			1	
VA-NF-IG	VA-NF-IG-SV1	2	VN-AV1			1	
VA-NF	VA-NF-SV1	2	VA-SV1			1	
VN-NF-AS	VN-NF-AS-SV1	2	VN-SV1			1	
TOTAL	130						

Table 2 List of the microscope slides samples addressed to natural (VN) and artificial (VA) aging

144 mock up tiles were realized on a cement mortar support (4,5X4,5X1,5 h cm) (**Table 3**) (Figure 1 -3 – appendix) and subjected to natural (N, 72 samples) and artificial aging (A, 72 samples).

The support was prepared by pouring the mortar in a silicon mould then smoothed out with plastering trowels. After curing of at least 30 days, a smoothing layer then a coat of yellow ground layer were applied by trowels and roll, respectively.

3 sets of 24 samples each (72 samples) were painted with two layers of the primer P applied by roller simulating the object n.5,6.

3 sets of 24 samples each (72 samples) were not painted with the primer P simulating the object n.3

Two set of 24 samples with/without primer (48 samples) was painted using colours: PO, MA, FR. For PO and MA samples sets (24 samples each):

- 15 samples were treated by brush with each anti-graffiti coating AS²⁰, HX²¹, PS²², PG²³, IG²⁴, 5 samples for natural aging, 5 samples for artificial aging and 5 samples as references
- 5 samples of each set were treated with a double layer system (the first one made of the spray varnish with the same brand and chemical class of the colour and the second one with each anti-graffiti coating by brush) and addressed to artificial aging
- 1 sample set was treated with layers of the spray varnish with the same brand and chemical nature of the colour, AV1²⁵ for Montana Cans color and SV1²⁶ for Montana colors
- 3 samples were not treated (1 reference, 2 sample for aging (natural and artificial)

For FR sets (24 samples each):

20 samples were treated with layers (see notes below) of each anti-graffiti coating AS, HX, PS,
 PG, IG by brush, 5 samples for natural aging, 10 samples for artificial aging and 5 samples as references

- 4 samples were not treated (1 reference, 1 for natural aging and 2 for artificial aging) The manufacturer of FR colour does not indicate the use of a protective varnish.

²⁰ AS application: 2 coats, wet on wet, waiting 4-5 minutes in between (to repeat twice) . Try to get a homogeneous layer.

²¹ HX application: 1-3 coats, trying to get a homogeneous layer .

²² PS application; 2 coats, wet on wet, waiting 4-5 minutes in between (to repeat twice) . Try to get a homogeneous layer

²³ PG application: 2 coats, the second after the complete drying of the first coat.

²⁴ IG application: 3 times applied: two coats, wet on wet, trying to get a homogeneous layer and avoiding the formation of accumulations.

²⁵ AV1 was applied twice after shaking, waiting 5 minutes between the two coats

²⁶ Sv1 was applied twice after shaking, waiting 5 minutes between the two coats

	CEMENT SUPPORT SAMPLES							
ID	-SAMPLE	QUANTITY	ID	-SAMPLE	QUANTITY			
A-PO-AS	A-PO-AS-AV1	2	A-MA-AS-P	A-MA-AS-P-SV1	2			
A-PO-HX	A-PO-HX-AV1	2	A-MA-HX-P	A-MA-HX-P-SV1	2			
A-PO-PS	A-PO-PS-AV1	2	A-MA-PS-P	A-MA-PS-P-SV1	2			
A-PO-PG	A-PO-PG-AV1	2	A-MA-PG-P	A-MA-PG-P-SV1	2			
A-PO-IG	A-PO-IG-AV1	2	A-MA-IG-P	A-MA-IG-P-SV1	2			
A-PO	A-PO-AV1	2	A-MA-P	A-MA-P-SV1	2			
N-PO-AS		2	N-MA-AS-P		2			
N-PO-HX		2	N-MA-HX-P		2			
N-PO-PS		2	N-MA-PS-P		2			
N-PO-PG		2	N-MA-PG-P		2			
N-PO-IG		2	N-MA-IG-P		2			
N-PO		2	N-MA-P		2			
A-PO-AS-P	A-PO-AS-P-AV1	2	A-FR-AS		2			
А-РО-НХ-Р	A-PO-HX-P-AV1	2	A-FR-HX		2			
A-PO-PS-P	A-PO-PS-P-AV1	2	A-FR-PS		2			
A-PO-PG-P	A-PO-PG-P-AV1	2	A-FR-PG		2			
A-PO-IG-P	A-PO-IG-P-AV1	2	A-FR-IG		2			
A-PO-P	A-PO-P-AV1	2	A-FR		2			
N-PO-AS-P		2	N-FR-AS		2			
N-PO-HX-P		2	N-FR-HX		2			
N-PO-PS-P		2	N-FR-PS		2			
N-PO-PG-P		2	N-FR-PG		2			
N-PO-IG-P		2	N-FR-IG		2			
N-PO-P		2	N-FR		2			
A-MA-AS	A-MA-AS-SV1	2	A-FR-AS-P		2			
A-MA-HX	A-MA-HX-SV1	2	A-FR-HX-P		2			
A-MA-PS	A-MA-PS-SV1	2	A-FR-PS-P		2			
A-MA-PG	A-MA-PG-SV1	2	A-FR-PG-P		2			
A-MA-IG	A-MA-IG-SV1	2	A-FR-IG-P		2			
A-MA	A-MA-SV1	2	A-FR-P		2			
N-MA-AS		2	N-FR-AS-P		2			
N-MA-HX		2	N-FR-HX-P		2			
N-MA-PS		2	N-FR-PS-P		2			
N-MA-PG		2	N-FR-PG-P		2			
N-MA-IG		2	N-FR-IG-P		2			
N-MA		2	N-FR-P		2			
TOTAL	144							

Table 3 List of the samples on cement mortar addressed to natural (N) and artificial (A) aging

Characterization of the starting materials

Commercial paints, UV stabilizers varnishes and anti-graffiti protective products were characterized through FT-IR (ATR) and Raman spectroscopies in order to identify binding media, pigments and colorants, fillers, extenders and other additives in the formulations. Identification of the products was carried out comparing samples spectra with databases and data found in literature^{27,28,29,30,31,32} (**Table 4**).

Sample Name	Declared Composition	FT-IR (ATR) results	Raman results
NF	Modified alkyd resins	Alkyd resin	not determined (high fluorescence)
ОМ	Modified alkyd resins	Acrylic and alkyd resins, oxides as additives (probably titanium dioxide)	not determined (surface too much reflective)
PO	Nitrocellulose - Acrylic lacquer base PO43 PY74 PY83	Acrylic resin Nitrocellulose Styrene (either added for improving the rheological behaviour or linked to acrylic monomer-s)	РО67, РҮ74
MA	Modified alkyd resins	Alkyd resin	PR48
FR	Acrylic resin and quartz	Acrylic resin Calcium carbonate Silicates	PR 168, Calcite
AS	Aqueous emulsion of fluoropolymers	Alkyd resin Synthetic wax Fluorinated polymers	/
ΗХ	Perflouro-alkyl siloxane cationic polymer	Fluorinated polymers (siloxanes, Alkyd/ Acrylic)	/
PS	Fluorinated acrylic copolymer in aqueous phase	Fluorinated acrylic polymers	/
PG	Acrylic emulsion in aqueous phase	Acrylic resin	/
IG	Polymer waxes in water dispersion	Synthetic wax	/
AV1	Nitrocellulose-Acrylic	Acrylic resin	/
SV1	Alkyd resin	Alkyd resin	/

Table 4 Summary of FT-IR and RAMAN results

²⁷Germinario, 2016, Microchemical Journal, 124, 929-39

²⁸ Bosi, 2020, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 225, 117474

²⁹ Zięba-Palus, J., Kowalski, R., 2018, Vibrational Spectroscopy, 95, 57-61

³⁰ Papliaka, Z. E., 2010, Journal of Cultural Heritage, 11(4), 381-391

³¹ Pintus, V., 2016, Microchemical Journal, 124, 949-961

³² Ploeger, R., 2008, Journal of Cultural Heritage, 9(4), 412-419

Methods and instrumental conditions

Optical observations

Cross sections of the treated tile samples³³ were observed with an Olympus stereomicroscope under different magnifications for evaluating the thickness of the coatings and monitoring of changes induced during the ageing. Images were taken with an Olympus Camedia C-5050 camera.

The details of the samples surface (glass slides and tiles) was observed with a Dino-Lite Digital portable microscope equipped with Vis and UV light-sources and a camera.

Contact angle measurements

One drop of water was deposited on the sample surface and a picture of it was taken through fixed a portable microscope positioned perpendicularly to the surface. θ angle³⁴ evaluation was carried out with DinoCapture2.0 version 1.3.7.A software. The value reported is the average of three replicas.

Colorimetric measurements

Chromatic variations (in the CIE L*a*b* space) after the coating application and during ageing was studied using a Konica Minolta CM 2600d spectrophotometer (8-degree viewing angle geometry, Xenon lamp diffusion light and a high-resolution monolithic polychromator, 3 mm diameter circular area). The measurements were performed in SCI (Specular Component Included) modality. The obtained result is the average of three consecutive measurements on the same point. The recorded data were elaborated by Spectra Magic NX software.

Raman spectroscopy

BRAVO Handheld Raman spectrometer (Bruker) equipped with two excitation laser sources (Duo LASER[™] excitation system) in the range between 700 and 1100 nm was used for the identification of pigments of the commercial formulations. Raman spectra were recorded in the 3200÷300 cm⁻¹ range and were successively elaborated with Opus (version 8.2.28).

Fourier Transform Infrared (FT-IR) spectroscopy

Portable Bruker ALPHA spectrometer equipped with Attenuated Total Reflection (ATR) modulus based on a single-bounce diamond ATR crystal and a reflectance modulus was used acquiring 32 scans for sample in the spectral range 4000÷400 cm⁻¹. Elaboration was carried out with Opus (version 8.2.28).

Natural ageing

Samples have been naturally aged by exposing them outdoor for 1000 hours during the winter season, partially protected from precipitation. Mock-ups were placed in plastic cages.

Accelerated ageing

Accelerated ageing was carried out with a Q-Sun Xe-3 test chamber (Q-Lab) for 1240 hours, moving mock-ups every 256 hours in the four quarters of the samples plate in order to avoid possible exposition differences under the three lamps, simulating sun irradiation. The ageing followed a two steps cycle, repeated 10 times: 100 hours with radiant energy set at 68W/m2, 35°C and environment relative humidity (RH, approximately 30%) and 24 hours of dark, at 45°C and 95% of RH. Artificial ageing was performed using specific and deliberately extreme conditions in order to speed up the possible degradation processes.

Chemical-induced changes were evaluated after 620 hours.

³³ Small fragments were embedded in polyester resin C95 resin catalysed by methyl-ethyl-ketone peroxide produced by G. Angeloni and polished

³⁴ angle formed between the surface of the sample and the lowest part of the drop, when contact between the

objects is established

SUSCEPTIBILITY OF PAINT FILMS AND PROTECTING PRODUCTS TO MICROBIOLOGICAL ATTACK

This research was performed by CESMAR7 and ANTARES.

The aim of the research was:

- to assess the resistance of coatings/varnish to microbial attack after 1 year of exterior exposure.

The experiment was set up according to ASTM D 3456 (Standard Practice for Determining by Exterior Exposure Tests the Susceptibility of Paint Films to Microbiological Attack), ASTM D 3274 and ASTM D1006/D1006M.

Materials

Support	Paint layer	Varnish	Protective coating	Anti-graffiti coatings
Cement mortar support ³⁵	Montana Colors MTN 94 – Light Yellow – RV 1021 ³⁶ LY	Montana Colors MTN PRO Synthetic Varnish Gloss, MTN PRO ¹⁴ SV1	Idrosil Pronto + Algochene ³⁷ I A	An.t.a.res s.r.l. Anti-Stain ⁹ AS Maflon s.p.a. Hexafor SA-6320 ¹¹ HX Pelicoat Italia s.r.l Pro-Ston ¹⁵ PS Guard Industrie s.a.s. Protect Guard TC ¹⁷ matt PG Colorificio San
				Marco s.p.a Isograff ¹⁹

Table 5 Product list with acronyms and information provided by manufacturers/dealers

5 anti-graffiti coating, 1 protective coating (being the positive control) and 1 varnish (**Table 5**) were compared applying them side by side on the same cement panel (30x80x4h cm), uniformly colored with a light yellow (LY) spray.

The kind of support and stratigraphy was the same found in the artwork n.8, the only one where a biological attack has been occurred (see Wp3 report). The light colour was chosen in order to better perform the monitoring.

³⁵ ad hoc samples realized by Lo Dico Leonardo srl Bologna IT

 ³⁶ MTN 94 – Light Yellow – RV 1021: Alkyd and solvent based spray paint containing Xylene (mixture of isomers), Ethyl Acetate, Ethylbenzene, n-Butyl Acetate, Acetone, Polyhydroxyalkylamides, 2-Butanone-Oxime.
 ³⁷ Idrosil Pronto + Algochene by Antares: blend of about 7% of polysiloxane alkyl polymer with BBIT in White

Spirit. Ready to use water-repellent containing an antimicrobial at broad spectrum for stone supports and plasters

Test area for each coating/varnish measures 300 cm² (10x30 cm). Blank Control area is the colored support without any coating.

Each coating in the systems was applied as follow: one coat (wet on wet for IG and AS) for each coating except for PG that was applied twice, waiting 2 hour in between.

Each single panel used for the trial measures 30x80 cm and consists of 8 test areas. Each panel presents 2 metal hooks immersed in the thickness of the long side of the panel in order to hang it on the exposure rack.

Table 6 coated panels identification

E1 A D	E1 B D	E2 A D	E2 B D
E1 A W	E1 B W	E2 A W	E2 B W

E1=exposition in protective/shady condition E2= exposition in exposed condition A,B=replicates D= dry panel W= weathered panel

Coatings and varnish were applied on cement panels in two different conditions: on dry panel (just prepared and never exposed) and on weathered panel (exposed to the weather for 2 days).

Furthermore, coated cement panels are exposed in two different conditions: in protective/shady condition and in exposed condition.

Two replicates for each coated panel are considered.

In total 8 cement panels were set up (Figure
et up (Figure 4-7 - appo
- appendix) v
pendix) with a total of 64 test areas (sam
mples).

E2A D – LY -SV1		E1 A D – LY -SV1	
E2 A D – LY-AS		E1 A D – LY-AS	
E2 A D – LY-HY		E1 A D – LY-HY	
E2 A D – LY -PS	E2	E1 A D – LY -PS	Ē
F2 A D – LY –PG	A D	E1 A D – LY –PG	A D
E2 A D – LY –IG	Ű	E1 A D – LY –IG	Ŭ
E2 A D – LY		E1 A D – LY	
E2 A D – LY -IA		E1 A D – LY -IA	
E2B D – LY -SV1		E1 B D – LY -SV1	<u> </u>
E2 B D – LY-AS		E1 BD – LY-AS	
E2 B D – LY-HY		E1 B D – LY-HY	
E2B D – LY -PS	E2	E1 B D – LY -PS	E
E2 BD – LY –PG	вD	E1 B D – LY –PG	вD
E2 B D – LY –IG	Ŭ	E1B D – LY –IG	Ŭ
E2 B D – LY		E1 B D – LY	
E2 B D – LY -IA		E1 B D – LY -IA	
			L
E2 A W– LYSV1		E1 A W– LY- SV1	
E2 A W – LY-AS		E1 A W – LY-AS	
E2 A W – LY-HY		E1 A W – LY-HY	
	.	$E1 \wedge W = IV DS$	m

Table 7 mock up samples identification

E2 A W– LYSV1		E1 A W- LY- SV1	
E2 A W – LY-AS		E1 A W – LY-AS	E1
E2 A W – LY-HY		E1 A W – LY-HY	
E2 A W – LY -PS	E2	E1 A W – LY -PS	
E2 A W – LY –PG	A X	E1 A W – LY –PG	A∀
E2 A W – LY –IG		E1 A W – LY –IG	
E2A W – LY		E1 A W – LY	
E2 A W – LY -IA		E1 A W – LY -IA	
E2 B W– LY -SV1		E1 B W– LY- SV1	
E2 B W – LY-AS		E1 B W – LY-AS	
E2 B W – LY-HY		E1 B W – LY-HY	
E2 B W – LY -PS	5	E1 BW – LY -PS	
E2 BW – LY –PG	B ≶	E1 B W – LY –PG	B ≶
E2 B W – LY –IG	1	E1B W – LY –IG	
E2 B W – LY		E1 B W – LY	
E2 B W – LY -IA		E1 B W – LY -IA	

EPAL³⁸ wooden pallets (120X80X14,5h cm) were accurately polished and varnished³⁹ then chosen as racks for panels exposition in exterior in order to avoid wood contamination during the trial. Racks for shady/protective exposition were built fixing an eave on the upper edge of the rack overhanging it for about 35 cm.

Racks were leaned against the wall of the Cesmar7 in Reggio Emilia building with an inclination of about 5% and coated panels were mounted hanging the two metal hooks on the axis of the pallet. Each rack mounts two coated panels (the pairs of replicas, A and B), one above the other.

Exposed racks are placed on the south side, shady/protective racks were placed on the west side in a shaded area.

Panels were exposed outside on 27th of November 2019.

Methods and instrumental conditions

The first "in field" microbiological attack assessment was made the 8th of January 2020 by macro visual observations, following the rating scale for surface disfigurement proposed by ASTM D 3274. Rating is based on the percentage coverage of fungal / algal contamination on test areas. In the standard pictorial references provide a numerical basis for rating the degree of fungal or algal growth on paint films.

The trial will run till November 2020. Next visual observations will be on March, June and November 2020.

A biocide challenge test will be performed on test area affected by microbial attack at the end of the trial. Comparison will be among the following products: Bio 104⁴⁰, BAC⁴¹, enzymes and essential oils. Biocide effectiveness will be determined by cultural and biochemical (ATP assay) analysis.

³⁸ treated in accordance to ISPM 15 FAO

³⁹ Leroy Merlin

⁴⁰ Bio 104 by Antares: antimicrobial blend of octylisothiazolone and quaternary ammonium compound, effective against fungi and algae, to be diluited prior to use

⁴¹ BAC by Antares: antimicrobial product based on benzalkonium chloride at 50%, effective against against fungi and algae, to be diluited prior to use

GRAFFITI REMOVAL TESTS ON COATED PAINT LAYERS AND APPLICATIVE ASPECTS

This research was performed by ANTARES.

The aims of the research were:

- to provide useful information related to the application of selected 5 anti-graffiti coatings and 2 UV stabilizers varnishes
- to evaluate the cleaning performance in terms of removal of graffiti materials of 17 protective treatments composed of selected anti-graffiti coatings and varnishes (layered and non layered)

Materials

Table 8 Product list with acron	vms and information	provided by	manufacturers/dealers
	,	provided a	, manalaeta eta, acaleio

Supports	Finishing support layer	Ground layer	Primer	Paint layers	Varnishes	Anti-graffiti coatings	Graffiti materials
Bacchi - Prontomalt - Malta Bastarda Fibrata ¹² , on bricks	Saint Gobain - Webercem RS350 ⁴	Rival - Stella Oro- P03 ⁵	LECHLER - Chrèon - Framaton Riveste Prof, white (Q107751) ⁶ P	Montana Colors MTN 94 Light Yellow RV 1021 ³⁶ LY	Montana Colors Synthetic Varnish Gloss, MTN PRO ¹⁴ SV	An.t.a.res s.r.l. Anti-Stain ⁹ AS Maflon s.p.a. Hexafor SA-6320 ¹¹ HX	Montana Colors MTN 94 Matt Black R 9011 ⁴² SB Montana Cans Montana Gold Silverchrome M1000 ⁴³ SS
					Montana Cans Acrylic Varnish Gloss, T10008	Pelicoat Italia s.r.l Pro-Stone ¹⁵ PS	Pentel - Pen Permanent Marker N60 ⁴⁴ PM
				Montana Cans Montana Gold Pure Orange G2080 ¹³ PO	AV	Guard Industrie s.a.s. Protect Guard TC (matt) ¹⁷ PG Colorificio	Grog - Squeezer Mini 10 FMP-Diving Blue ⁴⁵ SM
				ru		San Marco s.p.a Isograff ¹⁹ IG	

⁴² MTN 94 – Matt Black – R 9011: Alkyd and solvent based spray paint containing Xylene (mixture of isomers), Ethyl Acetate, Ethylbenzene, n-Butyl Acetate, Acetone, Polyhydroxyalkylamides, 2-Butanone-Oxime.

⁴³ Montana Gold – Silverchrome – M1000: solvent based, Nitro-acrylic professional spray paint containing

aluminium powder (stabilised) and Acetone, aliphatic and aromatic hydrocarbons, Buthyl Acetate, Ethyl Acetate, DME, Propane, Butane, Naphta, 2-Propanol, Xylene, Isobutane, 2-Methoxy-1-Methylethylacetate.

⁴⁴ Pentel Pen – Permanent Marker N60, Black: oil based permanent marker, with synthetic chisel tip.

⁴⁵ Grog – Squeezer Mini 10 FMP – Diving Blue: Alcohol based paint marker. It contains: Ethanol, Methoxy-2-Propanol, 1-Methyl-2-Metoxyethyl Acetate.

168 mock-up samples were realized on 68 brick tiles (dimension 7,5x7,5x2 cm) (**Table 9**). Two sets for each anti-graffiti coating and varnish plus anti-graffiti coating treatment have been necessary to perform adequate cleaning tests.

A 2 cm thick layer of cement mortar was applied and smoothed out by plastering trowels on 68 tiles. After curing of at least 30 days, a thin layer of the finishing support then a layer of yellow ground were applied by trowels and paint roller, respectively. After three days, the samples were coated by roller with two layers of primer simulating the object n.3, and, the day after, one half of the mocksup were painted with nitro-acrylic spray-paint PO while the other half with alkyd spray-paint LY.

The first set of 88 samples (on 48 tiles) was realized at the end of October 2019. Among PO set:

- 8 days after paint layer application, 20 samples (on 10 tiles) were treated by brush with each anti-graffiti coating AS, HX, PS, PG, IG and, after a week, completely soiled with the four graffiti materials PM, SS, SB, SM (two kind of these materials for each tile)
- 7 days after paint layer application, 20 samples (on 10 tiles) were treated with Acrylic varnish spray AV and, the day after, with the 5 selected anti-graffiti coatings and, after a week, completely soiled with the four graffiti materials
- 7 days after paint layer application, 4 samples (on 4 tiles) were treated with Acrylic varnish spray AV and, the day after, completely soiled with the four graffiti materials

Among LY set:

- 8 days after paint layer application, 20 samples (on 10 tiles) were directly treated by brush with each anti-graffiti coatings and, after a week, completely soiled with the four graffiti materials
- 7 days after paint layer application, 20 samples (on 10 tiles) were treated by spray with Synthetic varnish SV and, the day after, with the 5 selected anti-graffiti coatings and, after a week ,completely soiled with the four graffiti materials.
- 7 days after paint layer application, 4 samples (on 4 tiles) were treated with Synthetic varnish spray SV and, the day after, soiled with the four graffiti materials

The second set of 80 samples (on 20 tiles) was realized in mid-December 2019.

Among PO set:

- a month and a half after paint layer application, 20 samples (on 5 tiles) were treated by brush with each anti-graffiti coatings and, after 5 days, soiled with the four graffiti materials
- a month and a half after paint layer application, 20 samples (on 5 tiles) were treated with Acrylic varnish spray AV, and, the day after, with the 5 selected anti-graffiti coatings and, after 5 days, completely soiled with the four graffiti materials

Among LY set:

- a month and a half after paint layer application, 20 samples (on 5 tiles) were treated by brush with each anti-graffiti coatings and and, after 5 days, completely soiled with the four graffiti materials
- a month and a half after paint layer application, 20 samples (on 5 tiles) were treated with Synthetic varnish spray SV, and, the day after, with the 5 selected anti-graffiti coatings and, after 5 days, completely soiled with the four graffiti materials

The selection of LY and PO colours, with different chemical composition, was justified by

- their light colour useful for checking the performance of cleaning
- their likely use in the realization of the object n. 3

See Table 1 – appendix for photos.

Another set of 7 samples was realized on microscope slides (Thermo scientific, smooth type, dimension 7,5x2,5 cm): using a pipette, each slides were coated with a layer of each protective products selected (5 anti-graffiti coatings and 2 varnishes).

ID-SAMPLES (with coatings)	QUANTITY	ID-SAMPLES (with varnish+coatings)	QUANTITY
PO-AS-P-PM	2	PO-AS-P-AV-PM	2
PO-AS-P-SS	2	PO-AS-P-AV-SS	2
PO-AS-P-SB	2	PO-AS-P-AV-SB	2
PO-AS-P-SM	2	PO-AS-P-AV-SM	2
РО-НХ-Р-РМ	2	PO-HX-P-AV-PM	2
PO-HX-P-SS	2	PO-HX-P-AV-SS	2
PO-HX-P-SB	2	PO-HX-P-AV-SB	2
PO-HX-P-SM	2	PO-HX-P-AV-SM	2
PO-PS-P-PM	2	PO-PS-P-AV-PM	2
PO-PS-P-SS	2	PO-PS-P-AV-SS	2
PO-PS-P-SB	2	PO-PS-P-AV-SB	2
PO-PS-P-SM	2	PO-PS-P-AV-SM	2
PO-PG-P-PM	2	PO-PG-P-AV-SW	2
	2		2
PO-PG-P-SS		PO-PG-P-AV-SS	
PO-PG-P-SB	2	PO-PG-P-AV-SB	2
PO-PG-P-SM		PO-PG-P-AV-SM	
PO-IG-P-PM	2	PO-IG-P-AV-PM	2
PO-IG-P-SS	2	PO-IG-P-AV-SS	2
PO-IG-P-SB	2	PO-IG-P-AV-SB	2
PO-IG-P-SM	2	PO-IG-P-AV-SM	2
PO-P-AV-PM	1	PO-P-AV-SS	1
PO-P-AV-SB	1	PO-P-AV-SM	1
LY-AS-P-PM	2	LY-AS-P-SV-PM	2
LY-AS-P-SS	2	LY-AS-P-SV-SS	2
LY-AS-P-SB LY-AS-P-SM	2	LY-AS-P-SV-SB LY-AS-P-SV-SM	2
LY-HX-P-PM	2	LY-HX-P-SV-PM	2
LY-HX-P-SS	2	LY-HX-P-SV-SS	2
LY-HX-P-SB	2	LY-HX-P-SV-SB	2
LY-HX-P-SM	2	LY-HX-P-SV-SM	2
LY-PS-P-PM	2	LY-PS-P-SV-PM	2
LY-PS-P-SS	2	LY-PS-P-SV-SS	2
LY-PS-P-SB	2	LY-PS-P-SV-SB	2
LY-PS-P-SM	2	LY-PS-P-SV-SM	2
LY-PG-P-PM	2	LY-PG-P-SV-PM	2
LY-PG-P-SS	2	LY-PG-P-SV-SS	2
LY-PG-P-SB	2	LY-PG-P-SV-SB	2
LY-PG-P-SM LY-IG-P-PM	2	LY-PG-P-SV-SM LY-IG-P-SV-PM	2
LY-IG-P-SS	2	LY-IG-P-SV-SS	2
LY-IG-P-SB	2	LY-IG-P-SV-SB	2
LY-IG-P-SM	2	LY-IG-P-SV-SM	2
LY-P-SV-PM	1	LY-P-SV-SS	1
LY-P-SV-SB	1	LY-P-SV-SM	1
TOTAL	168		

Table 9 List of the mock up samples soiled with graffiti materials

Methods

Before and after application of protective products, all the sample surfaces were observed with the naked eye and by using stereomicroscope. Practical aspects were also considered. Three weeks after soiling, cleaning tests were carried out.

The first set of samples was cleaned according to the products/methods suggested by the coatings' manufactures (

Table 10), Ligroin and Ethanol.

Product-number	Cleaning Methods	
Anti-Stain	high pressure hot water at 80/90°C and at 20/40 bar or steam ⁴⁶	
Hexafor SA-6320	Mapei - Wallguard Remover Gel ⁴⁷ + high pressure hot water at > 100 bar ⁴⁶	
Pro-Stone	Guard-Industrie - Graffi-Guard 2030 Ecological ⁴⁸ + high pressure hot water rinse ⁴⁹	
Protect Guard TC	Guard-Industrie - Graffi-Guard 2030 Ecological ⁵⁰ + high pressure hot water rinse ⁴⁹	
Isograff	high pressure hot water at 80°C or steam at low pressure	

As you can see below, the majority of these methods have resulted too aggressive or ineffective. Subsequent cleaning tests have been necessary in order to preserve the paint layers and, if possible, the overlying coatings and/or the varnishes too.

Two organic solvents were selected:

- Ligroin was chosen for its safety on both paint layers
- Ethanol was chosen for its cleaning effectiveness on the four different graffiti materials and for its relative safety on the paint LY.

The second set of samples was cleaned using the most effective products/methods found for removal the same graffiti materials tested on uncoated samples (see Wp4 Report – part 1 – point 3 Antares) (

 Table 11) because Ligroin and Ethanol have not optimal performed.

Table 11 Cleaning methods selected for the second set of samples	
--	--

Samples	Cleaning Methods
Samples soiled with non	Velvesil Plus with 20% of Ethanol
film forming graffiti	Evolon soaked with Ethanol
materials (SM, PM)	Evolon soaked with blend n.16 ⁵¹

⁴⁶ We used an Ariete Vapori jet equipment at very low hot water pressure

⁴⁷ Wallguard Remover Gel: thixotropic detergent gel for cleaning stone and unpainted plaster surfaces damaged by graffiti. It contains dipropyleneglycol methyl ether (≥75 -<100%); propylene carbonate (≥5-<10%);

(z)-octadec-9-enylamine, ethoxylated (\geq 2.5 - <5%); Isotridecanol, ethoxylated (\geq 1 - <2.5%); 1-methoxy-2-propanol; monopropylene glycol methyl ether (\geq 0.05 - <0.1%)

⁴⁸ Graffi-Guard 2030 Ecological: graffiti remover designed for non-painted stone surfaces, containing a mixture

of organic solvents, but not products hazardous to humans, the environment or the ozone layer. Containing formic acid $1 \le x \% \le 2.5$

⁴⁹ We used hot water rinse using cotton swabs

⁵⁰ Not written communication of the supplier

⁵¹ 40% DBE (Di-Basic Esther), 35% Loxanol MI 6470, 25% PC (Propylene Carbonate)

Samples soiled with film	PVA/Borax hydrogel 6% with 20% of blend n.16
forming graffiti materials (SB, SS)	Nanorestore gel HWR loaded with Nanorestore coatings B, G and S

The following solubility tests were carried out rolling cotton swabs for 10 sec on the glass slides samples:

- LA-LE blends
- Blend n.16

in order to study:

- coatings/varnishes sensitivity in terms of organic solvents polarity
- coatings/varnishes resistance to the selected cleaning methods.

Instrumentation

The performance of the cleaning tests on mock up samples was evaluated with the naked eye observing surfaces (already protected) and pigment pick up.

The documentation of cleaning tests was carried out by using digital camera Nikon - D3100 under Visible (two vtlamp6 by Velleman, 6500 K), Tiffen colour separation guide and gray scale (small) and UV light (portable Wood's lamp - model 31200).

Only the better tests were documented and evaluated under stereomicroscope (Optech) equipped with Digital camera ISDV5003 and led ring light at different magnifications (7x, 20x, 45x), comparing the uncoated surfaces (LY, PO) with the ones covered with varnishes, coatings, varnishes+coatings, graffiti soil and the final ones resulting after the cleaning tests.

3.1.2 What are the results from the application of different types of coatings on the ad hoc samples? (table) how did you get the results?

RESEARCH INTO CHEMICAL-PHYSICAL STABILITY OF PAINT FILMS AND PROTECTING PRODUCTS TO AGING ³

Coatings application on mock-ups

Applicative considerations

In general, the application of the anti-graffiti coatings by brush was not very handy: right after product application we noticed separation of phases and/or formation of a film with areas differing in thickness.

Appearance of the protective products films

Optical Results

Product

AS	Fairly homogeneous film with medium islands scattered on the surface
HX	Homogeneous film, sporadic islands
PS	Fairly homogeneous film
PG	Homogeneous and covering film

- IG Homogeneous film with different thicknesses on the surface.
- AV1 After the application the surface appears shiny, but less sticky than the surface treated with SV1. Homogeneous layer
- SV1 After the application the surface appears shinier and stickier. Homogeneous layer

Colour variation due to the application of the anti-graffiti coatings

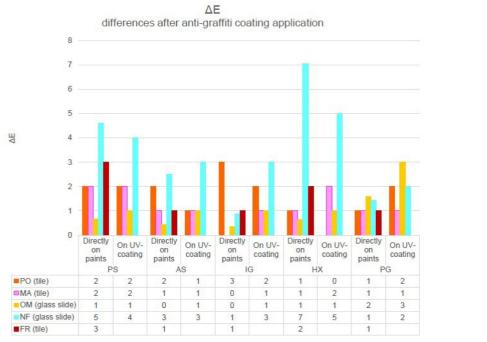


Figure 1

ΔE values calculated for samples and mock-ups based on colorimetric data recorded before and

after the application of the antigraffiti products

The application of all protective coatings does not modify the aesthetical appearance of the paint

layers in a significant way. The variation in terms of L*, a*, b* resulted, in first approximation, lower or at least next to human discrimination ability, as highlighted in **Figure 1**, where values of the ΔE are mostly in the range 1÷3. The exception is associated with the fluorescent orange **NF** spray paint, whose appearance is especially affected by the application of **PS** and **HX**, independently the antigraffiti product was applied directly on the painted layer or on the UV-coating.

Wettability changes due to the application of the anti-graffiti coatings

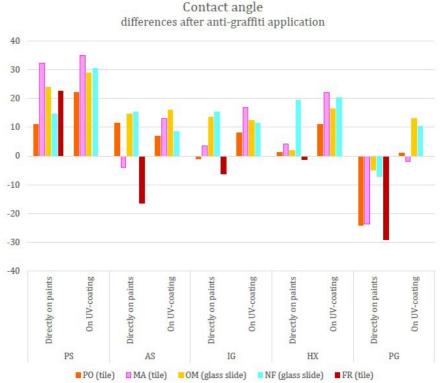


Figure 2 data reported showed the difference of contact angle values and the relative change in wettability between pre and post application, according to the layer on top of which the coating was spread (i.e. paint layer or UV-coating)

Modern spray paints are generally designed to be used outdoor: for this reason, they are mainly formulated having a certain hydrophobicity.

The contact angle values recorded in this study highlight this characteristic, showing an average value of the measured angles of 87 degrees. It has to be said that these measurements are subjected to a considerable variability depending on the homogeneity of the roughness of the surface and to the roughness of the substrate itself. Furthermore, it was ascertained that the application of a UV stabilizer product increased the wettability of the surface, without significant differences between the products used. **PG** is the only anti-graffiti formulation which does not contain any waxes or siloxanes, but mainly acrylic-based polymers. Thus, the formation of a proper film, more adherent to the surface, is promoted and the low viscosity of the formulation might favour, at the same time, limited roughness, which could explain why the application on specimens on glass slides resulted more effective.

The relative high ratio of inorganic fillers in the red paint (**FR**) can be at the base of the opposite behaviour of the parameter here considered when most of the anti-graffiti coatings are applied.

According to the datasheets of the selected anti-graffiti coatings, all products contain water-repellent components in the formulation, therefore an increase of the contact angle was expected after their application. Nevertheless, in two particular cases, this value decreased: it occurred when products beside **PS** were applied on red (**FR**) paint and for almost all application of **PG** directly on the paint layer, independently of the chemical nature of the binder, but with significant differences related to the specimen support (i.e. glass or mortar). An increase of the contact angle value for this product was observed only when the application was on glass slides (exception for tiles made with orange (**PO**) paint, but the increment is very low and within the experimental error).

Performance evaluation

In order to combine practical and experimental observations related to the application of the antigraffiti coating, five different parameters

- 1. ease of application
- 2. film homogeneity
- 3. morphological changes
- 4. colorimetric variation
- 5. contact angle variation

have been used to create the following performance charts(Figure 3).

Each parameter has a scale with a maximum value of 5 and a minimum value of 0, corresponding to the best and worst performance, respectively.

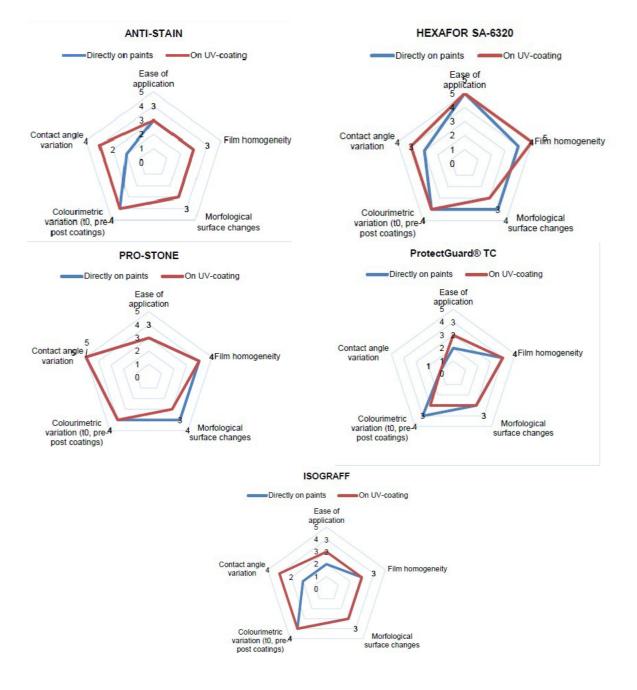


Figure 3 performance charts of protective products tested

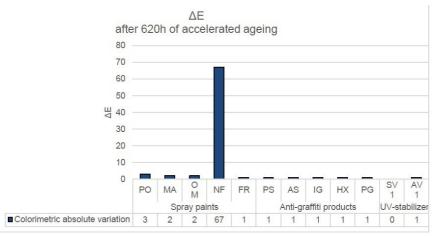
The values attributed to the **ease of application**, **film homogeneity** and **morphological changes** were processed considering the average performance of the individual coatings on all spray paints under study, with or without the interposition of UV stabilizer coatings.

As regards the values of the **color variations**, the average of the ΔE (pre-post coating application) was considered for each anti-graffiti coating.

The score attributed to the products related to the **change of the wettability** of the surface, (based on the difference pre-post application in the value of the contact angle), considered a relative comparison among the tested formulations. The best score was given to **PS** that showed the maximum increase in this parameter.

The best coating is the one that presents a performance chart with a larger area. According to these parameters, **HX** seems to be the coating with better performances among the others, followed by **PS**. Similar performances were reached using **AS** and **IS**, whereas **PG** seems to be the worst-performing coating, in this context.

Evaluation of the effects of accelerated ageing after 620 hours in a climate chamber



Color variation induced by accelerated ageing on raw materials

Figure 4 colorimetric absolute variation (ΔE) calculated for all starting materials

Colorimetric analyses (**Figure 4**) have highlighted how the fluorescent orange (NF) formulation was the most sensitive to the ageing parameters, with a final ΔE of 67. For all the other products the variations are within the experimental range and not significant aesthetical changes occurred.

Chemical changes induced by accelerated ageing on raw materials

STARTING MATERIALS	FT-IR OBSERVATIONS	NOTES
PO	No significant changes induced by test parameters	
MA	Shift of the hydroxyl band towards lower spectral region, decrease of the total spectrum intensity	Possible thinning of the film in some areas on the base of the lower intensity of the recorded spectra
OM	Slight increase of hydroxyl groups band (around 3300 cm-1)	
NF	Increase of the hydroxyl band at around 3300 cm-1 and increase in the lower wavenumber range (<800 cm-1), slight decrease of signals probably ascribable to the fluorescent pigment (not identified)	Changes clue of oxidation and hydrolysis phenomena
FR	Changes in the relative intensities between the two main inorganic compounds, changes in the ration and changes between inorganic and organic signals intensity	
PS	Slight increase of the hydroxyl band at 3350 cm-1	Hydrolysis
AS	Changes in the intensity and in the shape of the characteristic signals of the alkyd component. Broadening between 1060 and 750 cm-1	Weak degradation of the alkyd component, the presence of the synthetic wax makes the product less prompt to degradation. Presence of oxidized products
IG	Contribute of the glass slide in the spectrum. Raise of 1577/1541 doublet, increased	Possible thinning of the film in some areas, possible formation of carboxylates or

	absorption in the lower spectral range	presence of a phthalic-based compound whose signals increased with the ageing, evidence of the presence of oxidized products
НХ	Changes of signals ascribable to the alkyd- based component	Hydrolysis, possible thinning of the film in some areas
PG	Increase of the hydroxyl groups signals (bands at 3370, 1650, 1560 cm-1), broadening of the band at 1130 cm-1, increased absorption in the lower spectral range	Hydrolysis and oxidation degradation processes
SV1	Band at 3475 cm-1 shifted towards lower wavenumbers, the doublet at 1605/1580 cm-1 apparently did not appear after ageing, decrease of the carbonyl peak and of signals at 1460 and 1380 cm-1	Degradation occurred mainly on the lipidic fraction of the polymer (Difficulties in the acquisition of the spectrum after ageing)
AV1	No significant changes induced by test parameters	

Only in two cases spectra resulting from the acquisition before and after the ageing test did not show any meaningful degradation phenomena (namely orange paint (PO) and acrylic varnish UV stabilizer (AV1)).

In the remaining cases, and in particular where a lipidic component was present in the formulation (i.e. alkyd-based products), products derived from hydrolysis phenomenon were observed and/or the formation of carboxylates was registered. This is the case, for instance, of the magenta (MA), gold (OM), and fluorescent orange (NF) spray paints, ANTI-STAIN (AS), HEXAFOR (HX) and ProtectGuard (PG) anti-graffiti products. Acquisition of the curve of the UV stabilizer MTN PRO Synthetic Varnish (SV1) after ageing was not easy and the result was affected by a poor S/N ratio, which might hide some of the most characteristic functional groups absorptions.

Acrylic-based products and those containing synthetic wax/wax-like compounds showed greater stability.

These observations led the hypothesis that UV stabilizers are added to most of the selected formulations although not easily detectable by FT-IR measurements due to the detection limits of the instrument (ca 5% w/w).

The fluorescent orange (NF) spray paint, as previously introduced by colorimetric analysis, is the most unstable sample in the analyzed sets. The infrared spectrum registered a decrease of signals attributable to the organic fluorescent compound.

Further interpretation of the minor peaks is still needed to better understand the possible ongoing degradation processes and results will be provided in the final report.

Optical observations on mock-ups after 620 hours of accelerated ageing

For the evaluation of the stability and the efficacy of the products after the ageing, the comparison was carried out taking into consideration only the data taken after the application of the whole stratigraphy of coatings, thus without considering values obtain on the samples before protective coatings were spread anymore. Observations with a portable microscope were carried out and the following table (Table 15 and Table 16) report a brief observation for each case.

Coating on			
mortar tiles	Anti-graffiti coating 0h	620h accelerated ageing	
PS	Formation of an homogeneous film, with thicker areas only on FR- SET1 with primer, PO- SET 2 no primer (fairly homogeneous with irregularities in thickness- rounded areas)and FR- SET2 no primer and with primer (non homogeneous, even distribution of thicker areas)	possible thickness variation on PO-SET1 no primer, presence of small white spots and thickness variation for PO SET1 with primer and only white spots for MA SET2 no primer/with primer. More homogeneous in PO-SET2 no primer	
AS	PO SET1 and SET2 (primer/no primer)fairly/rather homogeneous layer with irregularities in thickness (rounded areas) or homogeneous with thicker areas (MA SET1 primer/no primer and FR SET1 no primer); for MA SET2 no primer and FR SET2 with primer formation of a whitish layer. Homogeneous layer in all other cases	in PO SET 1 with primer, MA SET1 no primer/with primer film more homogeneous after ageing, in PO SET2 no primer possible thickness variation	
IG	Homogeneous film formation on PO SET1 no primer and FR SET1 with primer, homogeneous with white spots in PO SET1 with primer, non homogeneous with coating accumulations for MA SET1 with/without primer, whitish film for MA SET1 no primer. In PO SET2 with/without primer fairly homogeneous layer with irregularities in thickness (rounded areas); in MA SET2 with/without primer uneven distribution on the surface and irregular thickness. Formation of an homogeneous whitish layer for FR SET2 with/without primer	possible thickness variation in PO SET1 no primer, in MA SET1 with primer film became more homogeneous after ageing	
нх	in SET1 formation of an homogeneous film (whitish for PO SET1 with primer and with small shite spots in FR SET1 no primer); in SET2 fairly homogeneous layer with irregularities in thickness (rounded areas) in PO with primer. Non homogeneous film in FR SEt2 no primer (uneven distribution of thicker areas). Formation of an homogeneous layer in MA SET2 with primer and FR SET2 with primer	possible thickness variation in PO SET1 without primer	
PG	in PO SET1 without primer formation of a rather homogeneous film; where the sample surface was rougher, small accumulation of the protective coating (whitish dots in the picture), for PO SET1, MA SET1 without primer with primer, uneven distribution due to the rough surface of the sample; for MA SET1 with primer formation of an homogeneous layer with small white spots. Formation of whitish layer for FR SET1 with/without primer and all SET2 samples	possible thickness variation in PO SET1 without primer, in PO SET1 with primer, film more homogeneous after ageing	

Table 15 optical observation on mock ups (tiles) after the first step of the accelerated ageing

Table 16 optical observation on glass slide samples after the first step of the accelerated ageing

Coating on glass slides	Anti-graffiti coating Oh	620h accelerated ageing
PS	homogeneous film	On OM SET 1 Presence of black dots, due to migration of the ink of the pen used for naming the sample. Homogeneity of the film was lost, with formation of clumps of the protective product, on NF SET1 and SET2 Colour-induced change; non homogeneous protective film after ageing (more evident under UV-light), possible phase separation or thinning of the protective coating.
AS	homogeneous film	On OM SET 1 Presence of black dots, due to migration of the ink of the pen used for naming the sample. on NF SET1 and SET2 Colour-

		induced change; non homogeneous protective film after ageing (more evident under UV-light), possible phase separation or thinning of the protective coating. in OM SET1 Formation of darker areas, possible separation of phases or redistribution of the product on the surface;on NF SET1 and SET2 colour-induced change; non homogeneous protective
IG	homogeneous film	film after ageing (more evident under UV-light), possible phase separation or thinning of the protective coating (also for OM-SET2) Homogeneity of the film was lost, with formation of clumps of the protective product. (Presence of black dots, due to migration of the ink of the pen used
нх	homogeneous film	for naming the sample) Possible separation of phases or redistribution of the product on the surface for OM SET1; for NF SET1 Colour-induced change; non homogeneous protective film after ageing (more evident under UV- light), possible phase separation or thinning of the protective coating. in SET2, fro OM film became more homogeneous after ageing
PG	homogeneous film, whitish for NF SET1, OM SET2. Quite homogeneous for NF SET2	for NF SET1, non homogeneous protective film after ageing, possible phase separation or thinning of the protective coating. For NF SET 2 Colour-induced change; non homogeneous protective film after ageing (more evident under UV-light), possible phase separation or thinning of the protective coating. in SET2, fro OM film became more homogeneous after ageing

Several morphological changes of the surface layer occurred, mostly well detectable under UV-light observation and mostly related to the thickness of the protective coating. Sometimes the coating was thicker in some areas, either because of the formation of clumps of materials or because of a separation of phases.

The former hypothesis might find three reasons:

1) heating specimens during the first step of the ageing cycle let the synthetic wax rearranged its shape above the surface;

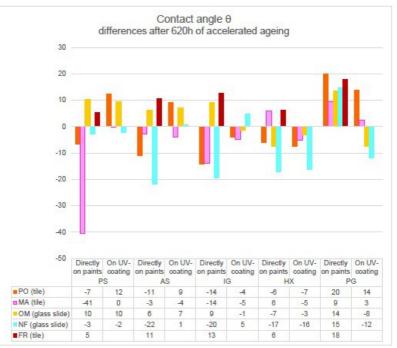
2) part of the coating might be washed away during the dark step of the ageing cycle;

3) induced chemical changes caused variations in the wettability at the interface, thus inducing a rearrangement of the coating under heating condition, when mobility of the molecular chains are favourable. The latter hypothesis instead takes into consideration the possibility that wax might migrate at the surface upon heating.

Variations seemed mostly independent from the substrate the coating was applied on and of a different entity, even though some differences could be found.

ANTI_STAIN (AS) tended to form a more homogeneous layer after ageing, whereas films of the other commercial formulations often showed different thickness at the end of the test and a non-homogeneous appearance.

Coatings applied on the fluorescent orange (NF) paint showed the greatest changes, especially when the anti-graffiti products were applied on UV stabilizers. It is worth to notice that observations under UV-light of these samples might be falsified due to the presence of the fluorescent colouring compound; nevertheless, interesting differences are visible between the two sets made with this paint.



Wettability changes induced by accelerated ageing on treated samples

Figure 5 variation of contact angle values before and after the first step of the accelerated ageing

Coatings applied on the fluorescent orange (NF) paint layers increased their wettability, on the contrary, the surface of mock-ups with red (FR) paint showed a decrease of this property. Almost in all cases where Protect-Guard was applied, contact angle values recorded increased. The most dramatic change occurred on the mock-up where Pro-Stone anti-graffiti formulation was applied directly on top of a magenta (MA) paint layer: in this case, the recorded variation meant having at the end a surface which is not considerable any more hydro repellent. Nevertheless, the reached value of this specimen after ageing is close to those registered for some specimens before the test (specimens where ProtectGuard anti-graffiti coating is present).

If wettability after the application of the protective coating is mostly affected by the roughness of the substrate, after ageing it is mainly dependent by chemical changes occurred at the different compounds in formulation, especially hydrolysis. Since commercial formulations are very complex mixtures, the phenomenon and its kinetics will be more carefully investigate at the end of the second ageing step, together with results of the natural ageing test.

Color variation induced by accelerated ageing on painted samples

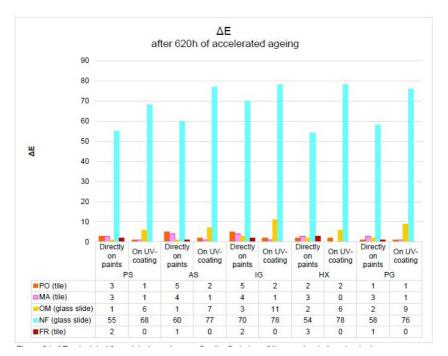


Figure 6 ΔE calculated for painted specimens after the first step of the accelerated ageing test

As expected, the most important colorimetric variations were recorded on specimens where the fluorescent orange (NF) spray paint was present. Another paint formulation that registered significant ΔE is the gold (OM) one, which, in most cases exceed the limit value of 3. Besides a specific colour variation, there is probably the influence of the variation of the morphological aspect. Tiles painted with red paint (FR) showed the lowest variation and in general the remaining specimens registered limited changes, even though sometimes above sensitivity of the human eye.

Sample - IDCoating typeTestsSurface microbial disfigurementfading fading painting layernoteE1 A D - L'Y-SVSynthetic Varnish Glossvisual inspection100000000E1 A D - L'Y-SXAnti-Stainvisual inspection10000000000E1 A D - L'Y-SXPro-StoneVisual inspection1000000000000E1 A D - L'Y-SKPro-StoneVisual inspection100 <t< th=""><th></th><th></th><th></th><th>Optica</th><th></th></t<>				Optica			
E1 A D - LY-AS E1 A D - LY-HX H xafor SA-6320visual inspection10000000E1 A D - LY-HX E1 A D - LY-HS Pro-Stonevisual inspection100000000E1 A D - LY-HG E1 A D - LY-HSProtect Guard TC visual inspection1004000000E1 A D - LY-HG E1 A D - LY-HSNone visual inspection100000000E1 A D - LY E1 A D - LY-HANone visual inspection100000000E1 A D - LY E1 B D - LY-SV1Synthetic Varnish Gloss visual inspection100000060 % witrificationE1 B D - LY-SV1Synthetic Varnish Gloss visual inspection100000060 % witrificationE1 B D - LY-SV1Synthetic Varnish Gloss visual inspection100000000E1 B D - LY-SV1Synthetic Varnish Gloss visual inspection100000000E1 B D - LY-SV1Synthetic Varnish Gloss visual inspection100000000E1 B D - LY-SV1Nonevisual inspection100000000E2 A D - LY-S4Anti-Stainvisual inspection100000000E2 A D - LY-S4Anti-Stainvisual ins	Sample - ID	Coating type	Tests	microbial		of the painting layer	note
E1 A D - LY-HX Hexafor SA-6320 visual inspection 10 0 0 0 E1 A D - LY -PS Pro-Stone visual inspection 10 40 0 0 E1 A D - LY -PS Pro-Stone visual inspection 10 40 0 0 E1 A D - LY -MG Rogerff visual inspection 10 0 0 0 E1 A D - LY -M Idrosit Pronto + Algochem visual inspection 10 0 0 0 E1 B D - LY -MA Idrosit Pronto + Algochem visual inspection 10 0 0 0 E1 B D - LY -MA Hexafor SA-6320 visual inspection 10 0 0 0 E1 B D - LY -MA Frostone visual inspection 10 0 0 0 0 E1 B D - LY -MA Isograff visual inspection 10 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 <t< td=""><td>E1 A D – LY -SV1</td><td></td><td>visual inspection</td><td>10</td><td>0</td><td>0</td><td></td></t<>	E1 A D – LY -SV1		visual inspection	10	0	0	
E1 A D - LY -PS Pro-Stone visual inspection 10 40 00 E1 A D - LY -PG Protect Guard TC visual inspection 10 40 00 E1 A D - LY -PG Protect Guard TC visual inspection 10 00 00 E1 A D - LY -NA Infosi Pronto + Algochene visual inspection 100 00 60% vitrification E1 B D - LY -NA Anti-Stain visual inspection 100 00 60% vitrification E1 B D - LY -NA Anti-Stain visual inspection 100 00 00 E1 B D - LY -NS Protect Guard TC visual inspection 100 00 00 E1 B D - LY -NG Protect Guard TC visual inspection 100 00 00 E1 B D - LY -NG Incore fill fronto + Algochene visual inspection 100 00 0 E1 B D - LY -NA Idrosi Pronto + Algochene visual inspection 100 10 10 E2 A D - LY -NA Idrosi Stone visual inspection 100 0 0	E1 A D – LY-AS	Anti-Stain	visual inspection	10	0	0	
E1 A D - LY -FGProtect Guard TCvisual inspection104000Protect Guard TCE1 A D - LY -FGIsograffvisual inspection10010000E1 A D - LY -FMNonevisual inspection100000060% vitrificationE1 A D - LY -FMIdrosil Pronto + Algochenevisual inspection1000060% vitrificationE1 B D - LY -SAAnti-Stainvisual inspection1000060% vitrificationE1 B D - LY -SPPro-Stonevisual inspection100000060% vitrificationE1 B D - LY -SPPro-Stonevisual inspection10010100100E2 A D - LY -SPPro-Stonevisual inspection1001010100E2 A D - LY -SPPro-Stonevisual inspection100000100E2 A D - LY -SPPro-Stonevisual inspection100000100E2 A D - LY -SPPro-Stonevisual insp	E1 A D – LY-HX	Hexafor SA-6320	visual inspection	10	0	0	
E1 A D - LY -IG Isograff visual inspection 10 10 0 0 E1 A D - LY None visual inspection 10 0 0 0 E1 A D - LY Al idrosil Pronto + Algochene visual inspection 10 0 0 60 % vitrification E1 B D - LY-AS Anti-Stain visual inspection 100 0 0 60 % vitrification E1 B D - LY-AS Anti-Stain visual inspection 100 0 0 0 E1 B D - LY-AS Pro-Stone visual inspection 100 0 0 0 E1 B D - LY-AS Procett Guard TC visual inspection 100 0 0 0 E1 B D - LY-AS None visual inspection 100 0 0 0 0 E2 A D - LY-AS Anti-Stain visual inspection 100 10 10 0 0 E2 A D - LY-AS Anti-Stain visual inspection 100 0 0 0 E2 A D -	E1 A D – LY -PS	Pro-Stone	visual inspection	10	0	0	
E1 A D - LYNonevisual inspection10000E1 A D - LY - IAIdrosil Pronto + Algochenevisual inspection1000060% vitrificationE1 B D - LY -NSSynthetic Varnish Glossvisual inspection100000060% vitrificationE1 B D - LY -NSAnti-Stainvisual inspection100000060% vitrificationE1 B D - LY -NSProstonevisual inspection100000060%E1 B D - LY -PSProstonevisual inspection100000060%E1 B D - LY -PSProstonevisual inspection100000060%E1 B D - LY -PSProstonevisual inspection100000060%E1 B D - LY -NSNonevisual inspection100000060%E1 B D - LY -NSNonevisual inspection100000060%E2 A D - LY -SSNonti-Stainvisual inspection10010010060%E2 A D - LY -SSProstonevisual inspection100000060%E2 A D - LY -SSProstonevisual inspection1005060%60%E2 A D - LY -SSPr	E1 A D – LY –PG	Protect Guard TC	visual inspection	10	40	0	
E1 A D - LY - MIdrosil Pronto + Algochenevisual inspection10000000E1 B D - LY - S0Anti-Stainvisual inspection100000000E1 B D - LY - S0Hexafor SA-6320visual inspection100000000E1 B D - LY - SPPro-Stonevisual inspection100000000E1 B D - LY - SNSynthetic Varnish Glosvisual inspection100000000E2 A D - LY - SN1Synthetic Varnish Glosvisual inspection100100100100E2 A D - LY - SN1Synthetic Varnish Glosvisual inspection100100100100E2 A D - LY - SPPro-Stonevisual inspection1000000100E2 A D - LY - SPPro-Stonevisual inspection1000000100E2 A D - LY - SPPro-Stonevisual inspection1000000100E2 A D - LY - SPPro-Stonevisual inspection1001005100E2 A D - LY - SPNother Sacosavisual inspection1001005100E2 A D - LY - SPNother Sacosavisual inspection1001001	E1 A D – LY –IG	Isograff	visual inspection	10	10	0	
E1 B D - LY-SVSynthetic Varnish Glossvisual inspection100060 % vitrificationE1 B D - LY-ASAnti-StainVisual inspection100000000100 </td <td>E1 A D – LY</td> <td>None</td> <td>visual inspection</td> <td>10</td> <td>0</td> <td>0</td> <td></td>	E1 A D – LY	None	visual inspection	10	0	0	
E1 B D - LY-ASAnti-Stainvisual inspection1000000E1 B D - LY-HXHexafor SA-6320Visual inspection1000000E1 B D - LY-PGProtect Guard TCVisual inspection1000000E1 B D - LY-PGProtect Guard TCVisual inspection1000000E1 B D - LYNoneVisual inspection1000000E1 B D - LYNoneVisual inspection1000000E2 A D - LY-SVSynthetic Varnish GloSVisual inspection100100100E2 A D - LY-SPPro-StoneVisual inspection100100100E2 A D - LY-PGProtect Guard TCVisual inspection1000000E2 A D - LY-PGProtect Guard TCVisual inspection10010050E2 A D - LY-SPRosteneeVisual inspection10010050E2 A D - LY-SPPro-StoneVisual inspection10010050E2 A D - LY-SPPro-StoneVisual inspection1005000E2 A D - LY-SPPro-StoneVisual inspection1005000E2 A D - LY-SPPro-StoneVisual inspection100 <t< td=""><td>E1 A D – LY - IA</td><td>Idrosil Pronto + Algochene</td><td>visual inspection</td><td>10</td><td>0</td><td>0</td><td></td></t<>	E1 A D – LY - IA	Idrosil Pronto + Algochene	visual inspection	10	0	0	
E1 B D - LY-HX E1 B D - LY-PS Pro-StoneVisual inspection1000E1 B D - LY-PS E1 B D - LY-PG B Protect Guard TCvisual inspection1000E1 B D - LY-PG E1 B D - LY-PGIsograffvisual inspection1000E1 B D - LY-PG E1 B D - LY-NANonevisual inspection10000E1 B D - LY-NAIdrosil Pronto + Algochenevisual inspection10000E2 A D - LY-SVSynthetic Varnish Glossvisual inspection10101010E2 A D - LY-ASAnti-Stainvisual inspection10000E2 A D - LY-PSPro-Stonevisual inspection10000E2 A D - LY-PSPro-Stonevisual inspection10000E2 A D - LY-PSPro-Stonevisual inspection10000E2 A D - LY-PGProtect Guard TCvisual inspection10000E2 A D - LY-PGProtect Guard TCvisual inspection10000E2 A D - LY-PGNonevisual inspection100000E2 A D - LY-PGProtect Guard TCvisual inspection10000E2 A D - LY-HSAnti-Stainvisual inspection101050E2 A D - LY-SYSynthetic Varnish Glossvisual inspection10500E2 B D - LY-SYPro-Stone <td< td=""><td>E1 B D – LY -SV1</td><td>Synthetic Varnish Gloss</td><td>visual inspection</td><td>10</td><td>0</td><td>0</td><td>60 % vitrification</td></td<>	E1 B D – LY -SV1	Synthetic Varnish Gloss	visual inspection	10	0	0	60 % vitrification
E1 B D - LY -PS E1 B D - LY -PGPro-Stonevisual inspection10000E1 B D - LY -PG E1 B D - LY -PGProtect Guard TCvisual inspection100000E1 B D - LY -IG E1 B D - LY -IAIsograffvisual inspection100000E1 B D - LY -IAIdrosil Pronto + Algochenevisual inspection100000E1 B D - LY -IAIdrosil Pronto + Algochenevisual inspection100255E2 A D - LY -SAAnti-Stainvisual inspection10010100100E2 A D - LY -KSAnti-Stainvisual inspection100000E2 A D - LY -KSPro-Stonevisual inspection100000E2 A D - LY -PGProtect Guard TCvisual inspection100000E2 A D - LY -PGProtect Guard TCvisual inspection100000E2 A D - LY -IAIdrosil Pronto + Algochenevisual inspection100000E2 A D - LYNonevisual inspection1000000E2 A D - LYNonevisual inspection1000000E2 A D - LYNonevisual inspection1005000E2 A D - LYSynthetic Varnish Glossvisual inspection1005000E2 B D - LY -SSPro-Stonevisual inspection10000 <td>E1 B D – LY-AS</td> <td>Anti-Stain</td> <td>visual inspection</td> <td>10</td> <td>0</td> <td>0</td> <td></td>	E1 B D – LY-AS	Anti-Stain	visual inspection	10	0	0	
E1 B D - LY -PGProtect Guard TCvisual inspection10000E1 B D - LY -IGIsograffvisual inspection100000E1 B D - LY -IAIdrosil Pronto + Algochenevisual inspection100000E2 A D - LY -SVSynthetic Varnish Glossvisual inspection10010100E2 A D - LY -SVSynthetic Varnish Glossvisual inspection100101010E2 A D - LY -SYPro-Stonevisual inspection100000E2 A D - LY -PSPro-Stonevisual inspection100000E2 A D - LY -PGProtect Guard TCvisual inspection100000E2 A D - LY -PGProtect Guard TCvisual inspection100000E2 A D - LY -PGProtect Guard TCvisual inspection100000E2 A D - LY -HGIsograffvisual inspection100000E2 A D - LY -S1Synthetic Varnish Glossvisual inspection1001050E2 B D - LY -S4Anti-Stainvisual inspection1003040010E2 B D - LY -S4Prostonevisual inspection10056010E2 B D - LY -S4Prostonevisual inspection10056010E2 B D - LY -S4Prostonevisual inspection1000020% VitrificationE2 B D - LY -S	E1 B D – LY-HX	Hexafor SA-6320		10	0	0	
E1 B D - LY -IGIsograffvisual inspection10000E1 B D - LYNonevisual inspection10000E1 B D - LY -IAIdrosil Pronto + Algochenevisual inspection10000E2 A D - LY -SVSynthetic Varnish Glossvisual inspection10500E2 A D - LY -SAAnti-Stainvisual inspection10101010E2 A D - LY -PSPro-Stonevisual inspection10000E2 A D - LY -PGProtect Guard TCvisual inspection10000E2 A D - LY -PGProtect Guard TCvisual inspection10000E2 A D - LY -IGIsograffvisual inspection10000E2 A D - LY -IGIsograffvisual inspection101050E2 A D - LY -IAIdrosil Pronto + Algochenevisual inspection101050E2 B D - LY -SAAnti-Stainvisual inspection103040-E2 B D - LY -SAAnti-Stainvisual inspection105010E2 B D - LY -SAAnti-Stainvisual inspection10580-E2 B D - LY -SAPro-Stonevisual inspection10580-E2 B D - LY -SAAnti-Stainvisual inspection10580-E2 B D - LY -SASynthetic Varnish Glossvisual inspection </td <td>E1 B D – LY -PS</td> <td>Pro-Stone</td> <td>visual inspection</td> <td>10</td> <td>0</td> <td>0</td> <td></td>	E1 B D – LY -PS	Pro-Stone	visual inspection	10	0	0	
E1 B D - LYNonevisual inspection10000E1 B D - LY - IAIdrosil Pronto + Algochenevisual inspection100000E2 A D - LY -SYSynthetic Varnish Glossvisual inspection100101010E2 A D - LY -SAAnti-Stainvisual inspection100101010E2 A D - LY -PSPro-Stonevisual inspection100000E2 A D - LY -PGProtect Guard TCvisual inspection100000E2 A D - LY -PGProtect Guard TCvisual inspection100000E2 A D - LY -PGProtect Guard TCvisual inspection100000E2 A D - LY -IAIdrosil Pronto + Algochenevisual inspection1001050E2 A D - LY -IAIdrosil Pronto + Algochenevisual inspection1001050E2 A D - LY -SYSynthetic Varnish Glossvisual inspection1001050E2 B D - LY -ASAnti-Stainvisual inspection1003040010E2 B D - LY -SPPro-Stonevisual inspection1005010E2 B D - LY -BIdrosil Pronto + Algochenevisual inspection10056010E2 B D - LY -SPPro-Stonevisual inspection10056010E2 B D - LY -SPNonevisual inspection1000000 <t< td=""><td>E1 B D – LY –PG</td><td>Protect Guard TC</td><td>visual inspection</td><td>10</td><td>0</td><td>0</td><td></td></t<>	E1 B D – LY –PG	Protect Guard TC	visual inspection	10	0	0	
E1 B D - LY - IAIdrosil Pronto + Algochenevisual inspection10000E2 A D - LY -SV1Synthetic Varnish Glossvisual inspection10255E2 A D - LY -SV1Anti-Stainvisual inspection10500E2 A D - LY -SVHexafor SA-6320visual inspection10000E2 A D - LY -PSPro-Stonevisual inspection10000E2 A D - LY -PGProtect Guard TCvisual inspection10000E2 A D - LY -IGIsograffvisual inspection10000E2 A D - LY -IGIsograffvisual inspection10000E2 A D - LY -IGIsograffvisual inspection10000E2 A D - LY -IAIdrosil Pronto + Algochenevisual inspection10000E2 B D - LY -SYSynthetic Varnish Glossvisual inspection10200E2 B D - LY -SYProtect Guard TCvisual inspection10500E2 B D - LY -SPProtect Guard TCvisual inspection1058000E2 B D - LY -SPProtect Guard TCvisual inspection1056000E2 B D - LY -SPProtect Guard TCvisual inspection10000E2 B D - LY -AGIsograffvisual inspection100020% virtificationE2 B D - LY -AG <td>E1 B D – LY –IG</td> <td>Isograff</td> <td>visual inspection</td> <td>10</td> <td>0</td> <td>0</td> <td></td>	E1 B D – LY –IG	Isograff	visual inspection	10	0	0	
E2 A D - LY -SV1Synthetic Varnish Glossvisual inspection102510E2 A D - LY -ASAnti-Stainvisual inspection10101010E2 A D - LY -HXHexafor SA-6320visual inspection10000E2 A D - LY -PSPro-Stonevisual inspection10000E2 A D - LY -PGFrotect Guard TCvisual inspection10000E2 A D - LY -PGIsograffvisual inspection10000E2 A D - LY -BGNonevisual inspection10050E2 A D - LY -BGNonevisual inspection10050E2 A D - LY -BIdrosil Pronto + Algochenevisual inspection10200E2 B D - LY -SVSynthetic Varnish Glossvisual inspection1030400-E2 B D - LY -SVAnti-Stainvisual inspection1050-E2 B D - LY -BGProtect Guard TCvisual inspection10560-E2 B D - LY -BGProtect Guard TCvisual inspection10560-E2 B D - LY -BGProtect Guard TCvisual inspection10560-E2 B D - LY -BGIsograffvisual inspection10000-E2 B D - LY -BGIsograffvisual inspection10000-E2 B D - LY -BGIsograffvis	E1 B D – LY	None	visual inspection	10	0	0	
E2 A D - LY-ASAnti-Stainvisual inspection1050E2 A D - LY-HXHexafor SA-6320visual inspection101010E2 A D - LY -PSPro-Stonevisual inspection1000E2 A D - LY -PGProtect Guard TCvisual inspection10000E2 A D - LY -PGProtect Guard TCvisual inspection100000E2 A D - LY -PGProtect Guard TCvisual inspection100000E2 A D - LY -PGNonevisual inspection100050E2 A D - LY -IAIdrosil Pronto + Algochenevisual inspection1001050E2 B D - LY -SV1Synthetic Varnish Glossvisual inspection10030400-E2 B D - LY -PGProtect Guard TCvisual inspection10050-E2 B D - LY -PGProtect Guard TCvisual inspection1005800-E2 B D - LY -PGProtect Guard TCvisual inspection1005800-E2 B D - LY -PGNonevisual inspection1005600-E2 B D - LY -PGNonevisual inspection100000E2 B D - LY -PGNonevisual inspection1000020% virtificationE2 B D - LY -PGNonevisual inspection100000E2 B D - LY -PGNonevisual inspection1000 </td <td>E1 B D – LY - IA</td> <td>Idrosil Pronto + Algochene</td> <td>visual inspection</td> <td>10</td> <td>0</td> <td>0</td> <td></td>	E1 B D – LY - IA	Idrosil Pronto + Algochene	visual inspection	10	0	0	
E2 A D - LY HXHexafor SA-6320visual inspection10101010E2 A D - LY -PSPro-Stonevisual inspection10000E2 A D - LY -PGProtect Guard TCvisual inspection10000E2 A D - LY -PGIsograffvisual inspection10000E2 A D - LY -IGIsograffvisual inspection10050E2 A D - LY -IGKorsil Pronto + Algochenevisual inspection101050E2 A D - LY -IAIdrosil Pronto + Algochenevisual inspection10304000E2 B D - LY -SV1Synthetic Varnish Glossvisual inspection10500E2 B D - LY -HXHexafor SA-6320visual inspection10500E2 B D - LY -PSPro-Stonevisual inspection105800E2 B D - LY -PGProtect Guard TCvisual inspection105800E2 B D - LY -PGProtect Guard TCvisual inspection105800E2 B D - LY -PSProtect Guard TCvisual inspection100000E2 B D - LY -IAIdrosil Pronto + Algochenevisual inspection100000E2 B D - LY -IAIdrosil Pronto + Algochenevisual inspection100000E1 A W - LY -SVSynthetic Varnish Glossvisual inspection100 <t< td=""><td>E2 A D – LY -SV1</td><td>Synthetic Varnish Gloss</td><td>visual inspection</td><td>10</td><td>2</td><td>5</td><td></td></t<>	E2 A D – LY -SV1	Synthetic Varnish Gloss	visual inspection	10	2	5	
E2 A D - LY -PSPro-Stonevisual inspection10000E2 A D - LY -PGProtect Guard TCvisual inspection10000E2 A D - LY -PGIsograffvisual inspection10000E2 A D - LYNonevisual inspection10050E2 A D - LY -IAIdrosil Pronto + Algochenevisual inspection101050E2 B D - LY -SVSynthetic Varnish Glossvisual inspection100304000E2 B D - LY -SVSynthetic Varnish Glossvisual inspection100500E2 B D - LY -SVPro-Stonevisual inspection100500E2 B D - LY -SVPro-Stonevisual inspection10050010E2 B D - LY -PGProtect Guard TCvisual inspection100580010E2 B D - LY -PGProtect Guard TCvisual inspection100560010E2 B D - LYNonevisual inspection100560010E2 B D - LYIdrosil Pronto + Algochenevisual inspection1000020% vitrificationE1 A W - LY - IAIdrosil Pronto + Algochenevisual inspection1000020% vitrificationE1 A W - LY - IAIdrosil Pronto + Algochenevisual inspection1000020% vitrificationE1 A W - LY - IAHexafor SA-6320visual inspection1000 <td>E2 A D – LY-AS</td> <td>Anti-Stain</td> <td>visual inspection</td> <td>10</td> <td>5</td> <td>0</td> <td></td>	E2 A D – LY-AS	Anti-Stain	visual inspection	10	5	0	
E2 A D - LY -PGProtect Guard TCvisual inspection10000E2 A D - LY -IGIsograffvisual inspection10000E2 A D - LYNonevisual inspection10050E2 A D - LY - IAIdrosil Pronto + Algochenevisual inspection101050E2 B D - LY -SV1Synthetic Varnish Glossvisual inspection10200E2 B D - LY -SV1Synthetic Varnish Glossvisual inspection1030400E2 B D - LY -SV1Synthetic Varnish Glossvisual inspection10500E2 B D - LY -SV1Synthetic Varnish Glossvisual inspection10500E2 B D - LY -SV1Pro-Stonevisual inspection10500E2 B D - LY -PGProtect Guard TCvisual inspection105800E2 B D - LY -GIsograffvisual inspection105600E2 B D - LYNonevisual inspection100020% vitrificationE2 B D - LYIdrosil Pronto + Algochenevisual inspection100020% vitrificationE1 A W - LY -SAAnti-Stainvisual inspection100000E1 A W - LY -SAAnti-Stainvisual inspection100000E1 A W - LY -SAPro-Stonevisual inspection1000some bubbles	E2 A D – LY-HX	Hexafor SA-6320	visual inspection	10	10	10	
E2 A D - LY -IGIsograffvisual inspection10000E2 A D - LYNonevisual inspection100510E2 A D - LY -IAIdrosil Pronto + Algochenevisual inspection1010510E2 B D - LY -SV1Synthetic Varnish Glossvisual inspection102010E2 B D - LY -SVSynthetic Varnish Glossvisual inspection10304010E2 B D - LY -SVAnti-Stainvisual inspection105010E2 B D - LY -PSPro-Stonevisual inspection105010E2 B D - LY -PGProtect Guard TCvisual inspection1056010E2 B D - LY -PGProtect Guard TCvisual inspection1000010E2 B D - LY -IAIdrosil Pronto + Algochenevisual inspection1056010E2 B D - LY -IAIdrosil Pronto + Algochenevisual inspection100020% vitrificationE1 A W - LY -SVSynthetic Varnish Glossvisual inspection100020% vitrificationE1 A W - LY -SVSynthetic Varnish Glossvisual inspection10000E1 A W - LY -SVSynthetic Varnish Glossvisual inspection10000E1 A W - LY -SVPro-Stonevisual inspection10000E1 A W - LY -SVPro-Stonevisual inspection10 <t< td=""><td>E2 A D – LY -PS</td><td>Pro-Stone</td><td>visual inspection</td><td>10</td><td>0</td><td>0</td><td></td></t<>	E2 A D – LY -PS	Pro-Stone	visual inspection	10	0	0	
E2 A D - LYNonevisual inspection1005AdditionalE2 A D - LY - IAIdrosil Pronto + Algochenevisual inspection10105AdditionalE2 B D - LY -SV1Synthetic Varnish Glossvisual inspection1020AdditionalE2 B D - LY -SV1Anti-Stainvisual inspection103040AdditionalE2 B D - LY -RSAnti-Stainvisual inspection1050AdditionalE2 B D - LY -PSPro-Stonevisual inspection1050Ightly paleE2 B D - LY -PGProtect Guard TCvisual inspection10580Ightly paleE2 B D - LY -PGProtect Guard TCvisual inspection10560Ightly paleE2 B D - LY -PGIsograffvisual inspection10560Ightly paleE2 B D - LY -IAIdrosil Pronto + Algochenevisual inspection1000some bubblesE1 A W - LY -SV1Synthetic Varnish Glossvisual inspection100020% vitrificationE1 A W - LY -SV1Synthetic Varnish Glossvisual inspection1000Ightly paleE1 A W - LY -SV1Synthetic Varnish Glossvisual inspection1000Ightly paleE1 A W - LY -SV1Synthetic Varnish Glossvisual inspection1000Ightly paleE1 A W - LY -SV1Pro-Stonevisual inspection1000Ightly pale </td <td>E2 A D – LY –PG</td> <td>Protect Guard TC</td> <td>visual inspection</td> <td>10</td> <td>0</td> <td>0</td> <td></td>	E2 A D – LY –PG	Protect Guard TC	visual inspection	10	0	0	
E2 A D - LY - IAIdrosil Pronto + Algochenevisual inspection10105InstanceE2 B D - LY - SV1Synthetic Varnish Glossvisual inspection10200E2 B D - LY - ASAnti-Stainvisual inspection10304040E2 B D - LY - HXHexafor SA-6320visual inspection105010E2 B D - LY - PSPro-Stonevisual inspection105010E2 B D - LY - PGProtect Guard TCvisual inspection1058010E2 B D - LY - PGIsograffvisual inspection1056010E2 B D - LY - IAIdrosil Pronto + Algochenevisual inspection1056010E2 B D - LY - IAIdrosil Pronto + Algochenevisual inspection100020% vitrificationE1 A W - LY - SVSynthetic Varnish Glossvisual inspection100020% vitrificationE1 A W - LY - SVSynthetic Varnish Glossvisual inspection100020% vitrificationE1 A W - LY - SVSynthetic Varnish Glossvisual inspection10000E1 A W - LY - SVProtect Guard TCvisual inspection10000E1 A W - LY - SVProtect Guard TCvisual inspection10000E1 A W - LY - HSProtect Guard TCvisual inspection1000some bubblesE1 A W - LY - HS	E2 A D – LY –IG	Isograff	visual inspection	10	0	0	
E2 B D - LY - SV1Synthetic Varnish Glossvisual inspection10200E2 B D - LY-ASAnti-Stainvisual inspection1030400400E2 B D - LY-HXHexafor SA-6320visual inspection1050600E2 B D - LY-PSPro-Stonevisual inspection1050100E2 B D - LY -PGProtect Guard TCvisual inspection10001ghtly paleE2 B D - LY -PGProtect Guard TCvisual inspection105800600E2 B D - LYIsograffvisual inspection105600600E2 B D - LYNonevisual inspection100020% vitrificationE2 B D - LYIdrosil Pronto + Algochenevisual inspection100020% vitrificationE1 A W - LY -SV1Synthetic Varnish Glossvisual inspection100020% vitrificationE1 A W - LY -SV3Synthetic Varnish Glossvisual inspection100000E1 A W - LY -PGPro-Stonevisual inspection100000E1 A W - LY -PGProtect Guard TCvisual inspection100000E1 A W - LY -PGProtect Guard TCvisual inspection10000some bubblesE1 A W - LY -PGProtect Guard TCvisual inspection1000some bubblesE1 A W - LY -PGProtect Guard TCvisual inspection100<	E2 A D – LY	None	visual inspection	10	0	5	
E2 B D - LY-ASAnti-Stainvisual inspection103040E2 B D - LY-HXHexafor SA-6320visual inspection1050E2 B D - LY -PSPro-Stonevisual inspection1050E2 B D - LY -PGProtect Guard TCvisual inspection1000lightly paleE2 B D - LY -PGIsograffvisual inspection105800E2 B D - LYIsograffvisual inspection105600E2 B D - LYNonevisual inspection1000some bubblesE2 B D - LYIdrosil Pronto + Algochenevisual inspection100020% vitrificationE1 A W - LY -SV1Synthetic Varnish Glossvisual inspection100020% vitrificationE1 A W - LY -SV3Synthetic Varnish Glossvisual inspection100020% vitrificationE1 A W - LY -SV3Pro-Stonevisual inspection10000E1 A W - LY -PGProctect Guard TCvisual inspection1000some bubblesE1 A W - LY -PGProtect Guard TCvisual inspection1000some bubblesE1 A W - LY -PGProtect Guard TCvisual inspection1000some bubblesE1 A W - LY -PGProtect Guard TCvisual inspection1000some bubblesE1 A W - LY -PGIsograffvisual inspection1000some	E2 A D – LY - IA	Idrosil Pronto + Algochene	visual inspection	10	10	5	
E2 B D - LY-HXHexafor SA-6320visual inspection1050E2 B D - LY -PSPro-Stonevisual inspection1050lightly paleE2 B D - LY -PGProtect Guard TCvisual inspection1000lightly paleE2 B D - LY -PGIsograffvisual inspection10580E2 B D - LY -IGIsograffvisual inspection10560E2 B D - LYNonevisual inspection10000some bubblesE2 B D - LY -IAIdrosil Pronto + Algochenevisual inspection100020% vitrificationE1 A W - LY -SV1Synthetic Varnish Glossvisual inspection100020% vitrificationE1 A W - LY -SVAnti-Stainvisual inspection1000020% vitrificationE1 A W - LY -PGProcett Guard TCvisual inspection1000020%E1 A W - LY -PGProtect Guard TCvisual inspection1000020%E1 A W - LY -PGProtect Guard TCvisual inspection1000some bubblesE1 A W - LY -HGIsograffvisual inspection1000some bubblesE1 A W - LY -PGProtect Guard TCvisual inspection1000some bubblesE1 A W - LY -HGIsograffvisual inspection1000some bubblesE1 A W - LY -HGIsograff	E2 B D – LY -SV1	Synthetic Varnish Gloss	visual inspection	10	2	0	
E2 B D - LY -PSPro-Stonevisual inspection1050Identify paleE2 B D - LY -PGProtect Guard TCvisual inspection1000lightly paleE2 B D - LY -IGIsograffvisual inspection105800E2 B D - LYNonevisual inspection105600E2 B D - LYNonevisual inspection1000some bubblesE2 B D - LY - IAIdrosil Pronto + Algochenevisual inspection100020% vitrificationE1 A W - LY -SV1Synthetic Varnish Glossvisual inspection100020% vitrificationE1 A W - LY -SXAnti-Stainvisual inspection100020% vitrificationE1 A W - LY -FSPro-Stonevisual inspection100020% vitrificationE1 A W - LY -FSPro-Stonevisual inspection100020% vitrificationE1 A W - LY -FSPro-Stonevisual inspection100020% vitrificationE1 A W - LY -FGProtect Guard TCvisual inspection1000some bubblesE1 A W - LY -FGIsograffvisual inspection1000some bubblesE1 A W - LY -FGIsograffvisual inspection1000some bubblesE1 A W - LYNonevisual inspection1000some bubblesE1 A W - LY -KIIdrosil Pronto + Algochenevisual	E2 B D – LY-AS	Anti-Stain	visual inspection	10	30	40	
E2 B D - LY - PGProtect Guard TCvisual inspection1000lightly paleE2 B D - LY - IGIsograffvisual inspection10580E2 B D - LYNonevisual inspection10560E2 B D - LY - IAIdrosil Pronto + Algochenevisual inspection1000some bubblesE1 A W - LY - SV1Synthetic Varnish Glossvisual inspection100020% vitrificationE1 A W - LY - SV1Synthetic Varnish Glossvisual inspection100020% vitrificationE1 A W - LY - SV1Synthetic Varnish Glossvisual inspection100020% vitrificationE1 A W - LY - SV1Hexafor SA-6320visual inspection10000E1 A W - LY - PSPro-Stonevisual inspection10000E1 A W - LY - PGProtect Guard TCvisual inspection1000some bubblesE1 A W - LY - PGProtect Guard TCvisual inspection1000some bubblesE1 A W - LY - HXIdrosil Pronto + Algochenevisual inspection1000some bubblesE1 A W - LY - HXIdrosil Pronto + Algochenevisual inspection1000some bubblesE1 A W - LY - HXIdrosil Pronto + Algochenevisual inspection1000some bubblesE1 A W - LY - SSynthetic Varnish Glossvisual inspection1000	E2 B D – LY-HX	Hexafor SA-6320	visual inspection	10	5	0	
E2 B D - LYIsograffvisual inspection10580E2 B D - LYNonevisual inspection10560E2 B D - LY - IAIdrosil Pronto + Algochenevisual inspection1000some bubblesE1 A W - LY - SV1Synthetic Varnish Glossvisual inspection100020% vitrificationE1 A W - LY - SV1Synthetic Varnish Glossvisual inspection100020% vitrificationE1 A W - LY - SV1Synthetic Varnish Glossvisual inspection100020% vitrificationE1 A W - LY - SV1Hexafor SA-6320visual inspection10000E1 A W - LY -PSPro-Stonevisual inspection10000E1 A W - LY -PGProtect Guard TCvisual inspection1000some bubblesE1 A W - LY -PGProtect Guard TCvisual inspection1000some bubblesE1 A W - LYNonevisual inspection1000some bubblesE1 A W - LY - JAIdrosil Pronto + Algochenevisual inspection1000	E2 B D – LY -PS	Pro-Stone	visual inspection	10	5	0	
E2 B D - LYNonevisual inspection105600Indextextextextextextextextextextextextexte	E2 B D – LY –PG	Protect Guard TC	visual inspection	10	0	0	lightly pale
E2 B D - LYNonevisual inspection105600Indextextextextextextextextextextextextexte	E2 B D – LY –IG	Isograff	visual inspection	10	5	80	
E1 A W- LY- SV1Synthetic Varnish Glossvisual inspection100020% vitrificationE1 A W - LY-ASAnti-Stainvisual inspection100000E1 A W - LY-HXHexafor SA-6320visual inspection100000E1 A W - LY-PSPro-Stonevisual inspection100000E1 A W - LY -PGProtect Guard TCvisual inspection10000some bubblesE1 A W - LY -PGProtect Guard TCvisual inspection1000some bubblesE1 A W - LY -PGIsograffvisual inspection1000some bubblesE1 A W - LY -PAIdrosil Pronto + Algochenevisual inspection1000light vitrificationE1 B W - LY -SVSynthetic Varnish Glossvisual inspection1000Ilight vitrificationE1 B W - LY -ASAnti-Stainvisual inspection1000Ilight vitrificationE1 B W - LY -HXHexafor SA-6320visual inspection1000Ilight vitrificationE1 B W - LY -PSPro-Stonevisual inspection1000Ilight vitrifica	E2 B D – LY	None	visual inspection	10	5	60	
E1 A W - LY-ASAnti-Stainvisual inspection10000E1 A W - LY-HXHexafor SA-6320visual inspection10000E1 A W - LY -PSPro-Stonevisual inspection10000E1 A W - LY -PGProtect Guard TCvisual inspection10000E1 A W - LY -PGProtect Guard TCvisual inspection1000some bubblesE1 A W - LY -HGIsograffvisual inspection1000some bubblesE1 A W - LYNonevisual inspection1000some bubblesE1 A W - LYIdrosil Pronto + Algochenevisual inspection1000some bubblesE1 B W - LY -SVSynthetic Varnish Glossvisual inspection1000light vitrificationE1 B W - LY-ASAnti-Stainvisual inspection1000Ilght vitrificationE1 B W - LY-HXHexafor SA-6320visual inspection1000Ilght vitrificationE1 B W - LY -PSPro-Stonevisual inspection1000Ilght vitrification	E2 B D – LY - IA	Idrosil Pronto + Algochene	visual inspection	10	0	0	some bubbles
E1 A W - LY-HXHexafor SA-6320visual inspection10000E1 A W - LY -PSPro-Stonevisual inspection100000E1 A W - LY -PGProtect Guard TCvisual inspection1000some bubblesE1 A W - LY -PGIsograffvisual inspection1000some bubblesE1 A W - LY -IGIsograffvisual inspection1000some bubblesE1 A W - LYNonevisual inspection1000some bubblesE1 A W - LY -IAIdrosil Pronto + Algochenevisual inspection1000some bubblesE1 B W - LY -SVSynthetic Varnish Glossvisual inspection1000light vitrificationE1 B W - LY -ASAnti-Stainvisual inspection10000E1 B W - LY -HXHexafor SA-6320visual inspection10000E1 B W - LY -PSPro-Stonevisual inspection10000	E1 A W- LY- SV1	Synthetic Varnish Gloss	visual inspection	10	0	0	20% vitrification
E1 A W - LY -PSPro-Stonevisual inspection10000E1 A W - LY -PGProtect Guard TCvisual inspection1000some bubblesE1 A W - LY -PGIsograffvisual inspection1000some bubblesE1 A W - LYNonevisual inspection1000some bubblesE1 A W - LYIdrosil Pronto + Algochenevisual inspection1000some bubblesE1 A W - LY - JAIdrosil Pronto + Algochenevisual inspection1000light vitrificationE1 B W - LY - SV1Synthetic Varnish Glossvisual inspection1000light vitrificationE1 B W - LY - ASAnti-Stainvisual inspection1000Image: Comparison of the compariso	E1 A W – LY-AS	Anti-Stain	visual inspection	10	0	0	
E1 A W - LY -PSPro-Stonevisual inspection10000E1 A W - LY -PGProtect Guard TCvisual inspection1000some bubblesE1 A W - LY -PGIsograffvisual inspection1000some bubblesE1 A W - LYNonevisual inspection1000some bubblesE1 A W - LYIdrosil Pronto + Algochenevisual inspection1000some bubblesE1 A W - LY - JAIdrosil Pronto + Algochenevisual inspection1000light vitrificationE1 B W - LY - SV1Synthetic Varnish Glossvisual inspection1000light vitrificationE1 B W - LY - ASAnti-Stainvisual inspection1000Image: Comparison of the compariso		Hexafor SA-6320	visual inspection	10	0	0	
E1 A W - LY -PGProtect Guard TCvisual inspection1000some bubblesE1 A W - LY -IGIsograffvisual inspection1000some bubblesE1 A W - LYNonevisual inspection1000some bubblesE1 A W - LY -IAIdrosil Pronto + Algochenevisual inspection1000some bubblesE1 B W - LY -SV1Synthetic Varnish Glossvisual inspection1000light vitrificationE1 B W - LY -ASAnti-Stainvisual inspection100010E1 B W - LY -HXHexafor SA-6320visual inspection10000E1 B W - LY -PSPro-Stonevisual inspection10000							
E1 A W - LY -IGIsograffvisual inspection1000some bubblesE1 A W - LYNonevisual inspection1000some bubblesE1 A W - LY -IAIdrosil Pronto + Algochenevisual inspection1000some bubblesE1 B W - LY -SV1Synthetic Varnish Glossvisual inspection1000light vitrificationE1 B W - LY-ASAnti-Stainvisual inspection1000010E1 B W - LY-HXHexafor SA-6320visual inspection1000010E1 B W - LY -PSPro-Stonevisual inspection1000010					0	0	some bubbles
E1 A W - LYNonevisual inspection1000some bubblesE1 A W - LY - IAIdrosil Pronto + Algochenevisual inspection1000some bubblesE1 B W - LY - SV1Synthetic Varnish Glossvisual inspection1000light vitrificationE1 B W - LY - ASAnti-Stainvisual inspection10000E1 B W - LY - HXHexafor SA-6320visual inspection10000E1 B W - LY - PSPro-Stonevisual inspection10000				10	0	0	some bubbles
E1 A W - LY -IAIdrosil Pronto + Algochenevisual inspection1000some bubblesE1 B W - LY - SV1Synthetic Varnish Glossvisual inspection1000light vitrificationE1 B W - LY - ASAnti-Stainvisual inspection1000010E1 B W - LY -HXHexafor SA-6320visual inspection1000010E1 B W - LY - PSPro-Stonevisual inspection1000010		None				0	some bubbles
E1 B W- LY- SV1Synthetic Varnish Glossvisual inspection1000light vitrificationE1 B W - LY-ASAnti-Stainvisual inspection10000E1 B W - LY-HXHexafor SA-6320visual inspection10000E1 B W - LY - PSPro-Stonevisual inspection10000	E1 A W – LY -IA	Idrosil Pronto + Algochene		10		0	some bubbles
E1 B W - LY-ASAnti-Stainvisual inspection1000E1 B W - LY-HXHexafor SA-6320visual inspection1000E1 B W - LY -PSPro-Stonevisual inspection1000	E1 B W-LY-SV1			10	0	0	light vitrification
E1 B W - LY-HXHexafor SA-6320visual inspection1000E1 B W - LY - PSPro-Stonevisual inspection1000					0	0	
E1 BW - LY -PS Pro-Stone visual inspection 10 0 0						0	
	E1 B W – LY –PG	Protect Guard TC	visual inspection	10	0	0	

Table 17 Optical results collected at the first monitoring (Figure 8-10 – appendix).

E1 B W – LY –IG	Isograff	visual inspection	10	0	0	
E1 B W – LY	None	visual inspection	10	0	0	
E1 B W – LY -IA	Idrosil Pronto + Algochene	visual inspection	10	0	0	
E2 A W-LYSV1	Synthetic Varnish Gloss	visual inspection	10	0	0	
E2 A W – LY-AS	Anti-Stain	visual inspection	10	0	0	
E2 A W – LY-HX	Hexafor SA-6320	visual inspection	10	0	1	
E2 A W – LY -PS	Pro-Stone	visual inspection	10	0	0	
E2 A W – LY –PG	Protect Guard TC	visual inspection	10	0	0	lightly pale
E2 A W – LY –IG	Isograff	visual inspection	10	0	0	
E2A W – LY	None	visual inspection	10	0	0	
E2 A W – LY -IA	Idrosil Pronto + Algochene	visual inspection	10	0	0	
E2 B W– LY -SV1	Synthetic Varnish Gloss	visual inspection	10	0	0	
E2 B W – LY-AS	Anti-Stain	visual inspection	10	0	0	
E2 B W – LY-HX	Hexafor SA-6320	visual inspection	10	0	0	
E2 B W – LY -PS	Pro-Stone	visual inspection	10	0	0	
E2 BW – LY –PG	Protect Guard TC	visual inspection	10	0	0	lightly pale
E2 B W – LY –IG	Isograff	visual inspection	10	0	0	
E2 B W – LY	None	visual inspection	10	0	0	
E2 B W – LY -IA	Idrosil Pronto + Algochene	visual inspection	10	0	0	

* Rating scale is 1 -10, being 10 the lowest surface microbial disfigurement (0%, no microbial growth) and 1 the highest (50%, complete coverage)

Coatings application on mock-ups and on microscope slide samples

Product-number	Sample	Application of the product	Optical result
Anti-Stain (AS)		Applied by brush: 2 coats wet on wet waiting 7 minutes in between. 2 more coats wet on wet after 2/3hours. Difficult to apply at first: it forms tiny drops. The second layer is easier to apply and allows to form a coherent film	The paint surfaces seem just slightly glossier than the uncoated ones. The coating seems to be a bit opalescent
	On slide	1,5 ml of product applied with a pipette	Thick, opaque and slightly yellowish layer, with some tiny opaque and whitish particles
Hexafor SA-6320 (HX)	On mock-up	Applied by brush: 1 coat (1 st set) 2 coats (2 nd set). Very easy to apply: it immediately forms a coherent and homogeneous film	The paint surfaces appear just slightly glossier than the uncoated ones. The coating seem to be completely transparent
	On slide	1,5 ml of product applied with a pipette	Thin colorless transparent layer. Some wrinkling parts visible on the surface
Pro-Stone (PS)		Applied by brush: 2 coats wet on dry waiting 2/3hours in between. Very difficult to apply: it forms big drops and does not allow to form a coherent and homogeneous film	The paint surfaces seem to be slightly glossier than the uncoated ones, but not in a homogeneous way, because of the big drops formed during application
		1,5 ml of product applied with a pipette	Very thin colorless and transparent layer
Protect Guard TC (PG)		Applied by brush: 2 coats wet on dry waiting 2/3hours in between. Easy to apply: it almost immediately forms a coherent film, but it tends to create accumulations of product	The paint surfaces appear much more matt than the uncoated ones. The coating seem to be partially opaque and whitish
	On slide	1,5 ml of product applied with a pipette	Very thick, white-yellowish and opaque layer. Thick accumulation of the white matt agent on one side of the slide
Isograff (IG)		Applied by brush. 2 coats wet on wet waiting 10/15 minutes in between Difficult to apply: it forms tiny drops. The second layer is a bit easier to apply and allows to form a coherent film	The paint surfaces appear slightly glossier than the uncoated ones. The coating is a bit opalescent and slightly soft
	On slide	1,5 ml of product applied with a pipette	Very thick, opaque and non homogeneous layer. Lots of whitish particles (wax?) visible inside the layer. Slightly soft layer.
Anti-Stain on Synthetic varnish (AS-SV)		Applied by brush: 2 coats wet on wet waiting 5 minutes in between.2 more coats wet on wet after 2/3hours. Very easy to apply: it immediately forms a coherent and homogeneous film	The paint surfaces appear more gloss than the uncoated ones. The coating dulls the glossy appearance of the underneath varnish

Table 18 List of applicative and optical considerations (see Table 2 – appendix)

Hexafor SA-6320 on Synthetic varnish (HX-SV)	On mock-up	Applied by brush: 1 coat. Very easy to apply: it immediately forms a coherent and homogeneous film	The paint surfaces appear much more gloss than the uncoated ones due to the underneath varnish
Pro-Stone on Synthetic varnish (PS-SV)	On mock-up	Applied by brush: 2 coats wet on dry waiting 2/3hours in between. Very difficult to apply: it forms tiny drops and does not allow to form a coherent and homogeneous film	The paint surfaces appear much more gloss than the uncoated ones due to the underneath varnish
Protect Guard TC on Synthetic varnish (PG-SV)	On mock-up	Applied by brush: 2 coats wet on dry waiting 2/3hours in between. Easy to apply: it almost immediately forms a coherent film, but it tends to create accumulations	The paint surfaces appear more matt than the uncoated ones. The coating seems to be whitish and non transparent. The matt appearance of the coating mitigates the gloss varnish
Isograff on Synthetic varnish (IG-SV)	On mock-up	Applied by brush: 2 coats wet on wet waiting 10/15 minutes in between. Difficult to apply: it forms tiny drops. The second layer is a bit easier to apply and allows to form a coherent film	The paint surfaces appear glossier than the uncoated ones. The coating dulls the glossy appearance of the underneath varnish
Anti-Stain on Acrylic varnish (AS- AV)	On mock-up	Applied by brush: 2 coats wet on wet waiting 7 minutes in between.2 more coats wet on wet after 2/3hours. Difficult to apply at first: it forms tiny drops. The second layer is easier to apply and allows to form a coherent and homogeneous film	The paint surfaces appear slightly glossier than the uncoated ones. The coating dulls the glossy appearance of the underneath varnish
Hexafor SA-6320 on Acrylic varnish (HX-AV)	On mock-up	Applied by brush: 1 coat. Very easy to apply: it immediately forms a coherent and homogeneous film	The paint surfaces appear glossier than the uncoated ones due to the underneath varnish
Pro-Stone on Acrylic varnish (PS- AV)	On mock-up	Applied by brush: 2 coats wet on dry waiting 2/3hours in between. Very difficult to apply: it forms tiny drops and does not allow to form a coherent and homogeneous film	The paint surfaces appear glossier than the uncoated ones due to the underneath varnish
Protect Guard TC on Acrylic varnish (PG-AV)	On mock-up	Applied by brush: 2 coats wet on dry waiting 2/3hours in between. Easy to apply: it almost immediately forms a coherent film, but it tends to create accumulation of materials	The paint surfaces appear more matt than the uncoated ones. The coating seems to be whitish. The matt appearance of the coating mitigates the gloss of the varnish
Isograff on Acrylic varnish (IG- AV)	On mock-up	Applied by brush: 2 coats wet on wet waiting 10/15 minutes in between. Difficult to apply: it forms tiny drops. The second layer is a bit easier to apply and allows to form a coherent film	The paint surfaces appear glossier than the uncoated ones The coating dulls the glossy appearance of the underneath varnish
Synthetic varnish (SV)	On mock-up	Spray. Easy to apply, accumulation of materials is visible	The paint surfaces appear much more gloss than the LY uncoated ones. Thick layer
	On slide		Thin transparent and slightly yellowish layer
Acrylic varnish (AV)	On mock-up	Spray. Easy to apply	The paint surfaces appear more gloss than the uncoated ones It slightly changes the original appearance of PO. Thin layer
	On slide		Thin colorless and clear layer

Graffiti removal tests

The performance of the cleaning tests on mock up samples was firstly evaluated with the naked eye observing the treated paint surfaces and the pigment pick up on cotton swabs.

Table 19,

Table 20, Table 21 and **Table 22** summarize the cleaning tests results performed on all the mock upsamples divided for cleaning product/method.

Each test has been evaluated with a colour and a symbol that mean:

not respectful cleaning for PO or LY paint layer not effective cleaning for graffiti materials (PM, SS, SB, SM) and paint layers (PO, LY) respectful cleaning for PO or LY paint layer
Total removal of graffiti material (PM, SS, SB, SM)
Partial removal of graffiti material (PM, SS, SB, SM) Test not performed

See the Table 3 and Table 4, Figure 11 and 12 – appendix all the details regarding tests: timing, application methods, cleaning efficacy and respect of the paint layers.

	REMOVAL METHODS					
SAMPLES	Wallguard remover Gel	Graffi-Guard 2030	Steam	Ligroin	Ethanol	
LY-AS-P-PM	-	-	/	/	Х	
LY-AS-P-SS	-	-	/	Х	Х	
LY-AS-P-SB	-	-	Х	-	-	
LY-AS-P-SM	-	-			Х	
PO-AS-P-PM	-	-	/	/	Х	
PO-AS-P-SS	-	-	/	Х	Х	
PO-AS-P-SB	-	-	Х	-	-	
PO-AS-P-SM	-	-	/		Х	
LY-HX-P-PM	Х	-	-	/	Х	
LY-HX-P-SS	Х	-	-	/	Х	
LY-HX-P-SB	1	-	-		/	
LY-HX-P-SM	Х	-	-		Х	
PO-HX-P-PM	Х	-	-	/	Х	
PO-HX-P-SS	Х	-	-	Х	/	
PO-HX-P-SB	1	-	-		/	
PO-HX-P-SM	Х	-	-		Х	
LY-PS-P-PM	-	Х	-		/	
LY-PS-P-SS	-	Х	-	Х	/	
LY-PS-P-SB	-	1	-		/	
LY-PS-P-SM	-	Х	-		Х	

PO-PS-P-PM	-	Х	-	/	/
PO-PS-P-SS	-	Х	-	Х	/
PO-PS-P-SB	-	1	-		/
PO-PS-P-SM	-	Х	-		Х
LY-PG-P-PM	-	Х	-		Х
LY-PG-P-SS	-	Х	-	Х	/
LY-PG-P-SB	-	Х	-		/
LY-PG-P-SM	-	Х	-		Х
PO-PG-P-PM	-	Х	-	1	/
PO-PG-P-SS	-	Х	-	Х	/
PO-PG-P-SB	-	Х	-		/
PO-PG-P-SM	-	Х	-		Х
LY-IG-P-PM	-	-	/	Х	Х
LY-IG-P-SS	-	-	Х	Х	Х
LY-IG-P-SB	-	-	Х		/
LY-IG-P-SM	-	-	/	1	Х
PO-IG-P-PM	-	-	1	Х	Х
PO-IG-P-SS	-	-	Х	Х	/
PO-IG-P-SB	-	-	Х		/
PO-IG-P-SM	-	-	1	1	Х

Table 20 Cleaning methods performed on the 1st set of samples protected with varnishes-coatings and
varnishes

	REMOVAL METHODS						
SAMPLES	Wallguard remover Gel	Graffi-Guard 2030	Steam	Ligroin	Ethanol		
LY-AS-P-SV1-PM	-	-	/	/	/		
LY-AS-P-SV1-SS	-	-		Х	Х		
LY-AS-P-SV1-SB	-	-	Х	-	-		
LY-AS-P-SV1-SM	-	-	/	/	Х		
PO-AS-P-AV1-PM	-	-	/	/	Х		
PO-AS-P-AV1-SS	-	-	Х	Х	Х		
PO-AS-P-AV1-SB	-	-	Х	-	-		
PO-AS-P-AV1-SM	-	-	1		Х		
LY-HX-P-SV1-PM	Х	-	-	1	Х		
LY-HX-P-SV1-SS	1	-	-	/	Х		
LY-HX-P-SV1-SB	1	-	-		/		
LY-HX-P-SV1-SM	1	-	-		Х		
PO-HX-P-AV1-PM	1	-	-	1	/		
PO-HX-P-AV1-SS	Х	-	-	/	/		
PO-HX-P-AV1-SB	1	-	-		/		
PO-HX-P-AV1-SM	1	-	-		Х		
LY-PS-P-SV1-PM	-	1	-	/	/		
LY-PS-P-SV1-SS	-	1	-	Х	/		
LY-PS-P-SV1-SB	-	/	-		/		

				1	V
LY-PS-P-SV1-SM	-	X	-	/	Х
PO-PS-P-AV1-PM	-	/	-	/	Х
PO-PS-P-AV1-SS	-	/	-	/	Х
PO-PS-P-AV1-SB	-	Х	-		/
PO-PS-P-AV1-SM	-	Х	-	/	Х
LY-PG-P-SV1-PM	-	1	-	1	/
LY-PG-P-SV1-SS	-	Х	-		Х
LY-PG-P-SV1-SB	-	1	-		/
LY-PG-P-SV1-SM	-	1	-		Х
PO-PG-P-AV1-PM	-	Х	-	/	Х
PO-PG-P-AV1-SS	-	/	-	1	Х
PO-PG-P-AV1-SB	-	1	-		/
PO-PG-P-AV1-SM	-	Х	-		Х
LY-IG-P-SV1-PM	-	-	1	Х	Х
LY-IG-P-SV1-SS	-	-	1	х	Х
LY-IG-P-SV1-SB	-	-	1		/
LY-IG-P-SV1-SM	-	-		1	Х
PO-IG-P-AV1-PM	-	-	/	Х	Х
PO-IG-P-AV1-SS	-	-	Х	Х	Х
PO-IG-P-AV1-SB	-	-	1		
PO-IG-P-AV1-SM	-	-		/	Х
LY-P-SV1-PM	-	-	-	1	/
LY-P-SV1-SS	-	-	-	/	Х
LY-P-SV1-SB	-	-	-		
LY-P-SV1-SM	-	-	-		х
PO-P-AV1-PM	-	-	-		/
PO-P-AV1-SS	-	-	-	1	Х
PO-P-AV1-SB	-	-	-		/
PO-P-AV1-SM	-	-	-		Х

Table 21 Cleaning methods performed on the 2nd set of mock-up samples protected only with coatings

SAMPLES	REMOVAL METHODS										
	Velvesil + E 20%	Evolon + E	Velvesil + Bl.16	PVA/B 6% + bl.16 20%	HWR + coating B	HWR + coating G	HWR + coating S				
LY-AS-P-PM	Х	Х	Х	-	-	-	-				
LY-AS-P-SS	-	-	-	Х	Х	Х	Х				
LY-AS-P-SB	-	-	-	1	Х	Х	Х				
LY-AS-P-SM	Х	Х	Х	-	-	-	-				
PO-AS-P-PM	Х	/	/	-	-	-	-				
PO-AS-P-SS	-	-	-	1	/	Х	Х				
PO-AS-P-SB	-	-	-	1	/	Х	/				
PO-AS-P-SM	Х	1	Х	-	-	-	-				
LY-HX-P-PM	Х	Х	Х	-	-	-	-				
LY-HX-P-SS	-	-	-	X	Х	Х	Х				

LY-HX-P-SB	-	-	-	1	/	/	Х
LY-HX-P-SM	х	х	х	-	-	-	-
PO-HX-P-PM	Х	Х	Х	-	-	-	-
PO-HX-P-SS	-	-	-	/	/	Х	/
PO-HX-P-SB	-	-	-	/		Х	X
PO-HX-P-SM	Х	1	/	-	-	-	-
LY-PS-P-PM	/		1	-	-	-	-
LY-PS-P-SS	-	-	-	1	-	-	-
LY-PS-P-SB	-	-	-		-	-	-
LY-PS-P-SM	Х	Х	Х	-	-	-	-
PO-PS-P-PM	/	1	/	-	-	-	-
PO-PS-P-SS	-	-	-	/	-	-	-
PO-PS-P-SB	-	-	-	/	-	-	-
PO-PS-P-SM	Х	1	Х	-	-	-	-
LY-PG-P-PM			Х	-	-	-	-
LY-PG-P-SS	-	-	-	Х	Х	Х	Х
LY-PG-P-SB	-	-	-	Х	Х	Х	Х
LY-PG-P-SM	Х		Х	-	-	-	-
PO-PG-P-PM	Х	/	/	-	-	-	-
PO-PG-P-SS	-	-	-	1	/	Х	/
PO-PG-P-SB	-	-	-	1	/	/	/
PO-PG-P-SM	Х	/	х	-	-	-	-
LY-IG-P-PM	Х			-	-	-	-
LY-IG-P-SS	-	-	-	Х	Х	Х	Х
LY-IG-P-SB	-	-	-	Х	Х	Х	Х
LY-IG-P-SM	Х	Х	Х	-	-	-	-
PO-IG-P-PM	Х	1	/	-	-	-	-
PO-IG-P-SS	-	-	-	Х	Х	Х	Х
PO-IG-P-SB	-	-	-	х	Х	Х	Х
PO-IG-P-SM	Х	Х	Х	-	-	-	-

Table 22 Cleaning methods performed on the 2nd set of samples protected with varnishes-coatings and
varnishes

				REMOVAL ME	THODS		
SAMPLES	Velvesil + E 20%	Evolon + E	Velvesil + bl.16	PVA/B 6% + bl.16 20%	HWR + coating B	HWR + coating G	HWR + coating S
LY-AS-P-SV1-PM	Х	Х	Х	-	-	-	-
LY-AS-P-SV1-SS	-	-	-		Х	Х	Х
LY-AS-P-SV1-SB	-	-	-	/	Х	Х	Х
LY-AS-P-SV1-SM	Х	Х	Х	-	-	-	-
PO-AS-P-AV1-PM	Х	/	Х	-	-	-	-
PO-AS-P-AV1-SS	-	-	-	/	Х	Х	Х
PO-AS-P-AV1-SB	-	-	-	/	Х	Х	
PO-AS-P-AV1-SM	Х		Х	-	-	-	-

LY-HX-P-SV1-PM	Х	Х	Х	-	-	-	-
LY-HX-P-SV1-SS	-	-	-	Х	Х	Х	Х
LY-HX-P-SV1-SB	-	-	-		Х	Х	Х
LY-HX-P-SV1-SM	Х	Х	Х	-	-	-	-
PO-HX-P-AV1-PM	Х	Х	Х	-	-	-	-
PO-HX-P-AV1-SS	-	-	-	1	/	Х	/
PO-HX-P-AV1-SB	-	-	-		/	Х	Х
PO-HX-P-AV1-SM	Х	Х	Х	-	-	-	-
LY-PS-P-SV1-PM	1	1	1	-	-	-	-
LY-PS-P-SV1-SS	-	-	-		-	-	-
LY-PS-P-SV1-SB	-	-	-		-	-	-
LY-PS-P-SV1-SM	Х	Х	Х	-	-	-	-
PO-PS-P-AV1-PM	Х	/	Х	-	-	-	-
PO-PS-P-AV1-SS	-	-	-	/	-	-	-
PO-PS-P-AV1-SB	-	-	-	/	-	-	-
PO-PS-P-AV1-SM	Х		Х	-	-	-	-
LY-PG-P-SV1-PM	Х		Х	-	-	-	-
LY-PG-P-SV1-SS	-	-	-	Х	Х	Х	Х
LY-PG-P-SV1-SB	-	-	-	/	Х	Х	Х
LY-PG-P-SV1-SM	Х		Х	-	-	-	-
PO-PG-P-AV1-PM	Х		1	-	-	-	-
PO-PG-P-AV1-SS	-	-	-	/	/	Х	/
PO-PG-P-AV1-SB	-	-	-	/		/	/
PO-PG-P-AV1-SM	Х	/	Х	-	-	-	-
LY-IG-P-SV1-PM	Х	Х	Х	-	-	-	-
LY-IG-P-SV1-SS	-	-	-	Х	Х	Х	Х
LY-IG-P-SV1-SB	-	-	-	Х	Х	Х	Х
LY-IG-P-SV1-SM	Х	Х	Х	-	-	-	-
PO-IG-P-AV1-PM	Х	1	/	-	-	-	-
PO-IG-P-AV1-SS	-	-	-	Х	Х	Х	Х
PO-IG-P-AV1-SB	-	-	-	х	Х	Х	Х
PO-IG-P-AV1-SM	Х	Х	Х	-	-	-	-
LY-P-SV1-PM	1	Х	Х	-	-	-	-
LY-P-SV1-SS	-	-	-	Х	Х	Х	Х
LY-P-SV1-SB	-	-	-	Х	Х	/	Х
LY-P-SV1-SM	Х	х	Х	-	-	-	-
PO-P-AV1-PM	Х	Х	Х	-	-	-	-
PO-P-AV1-SS	-	-	-	-	-	-	-
PO-P-AV1-SB	-	-	-	-	-	-	-
PO-P-AV1-SM	Х	Х	Х	-	-	-	-

ID SAMPLE				SC	DLUBILIT	Y TEST L	A BLEN	DS			
	LA1	LA2	LA3	LA4	LA5	LA6	LA7	LA8	LA9	А	bl.16
Anti-Stain											

Hexafor SA-6320											
Pro-Stone											
Protect Guard TC											
Isograff											
Synthetic Varnish											
Acrylic Varnish											
	L	LE1	LE2	LE3	LE4	LE5	LE6	LE7	LE8	LE9	E
Anti-Stain											
Hexafor SA-6320											
Pro-Stone											
Protect Guard TC											
Isograff											
Synthetic Varnish											
Acrylic Varnish											

summarizes the cleaning tests results performed on microscope slide samples.

Each test has been evaluated with a colour and a symbol that means:

Red	the coating or varnish is completely removed by the solvent/blend
Orange	the coating or varnish is partially removed by the solvent/blend
Green	the coating or varnish is not removed by the solvent/blend
	Table 23 Results of the cleaning tests on microscope slide samples

ID SAMPLE		SOLUBILITY TEST LA BLENDS										
	LA1	LA2	LA3	LA4	LA5	LA6	LA7	LA8	LA9	А	bl.16	
Anti-Stain												
Hexafor SA-6320												
Pro-Stone												
Protect Guard TC												
Isograff												
Synthetic Varnish												
Acrylic Varnish												
	L	LE1	LE2	LE3	LE4	LE5	LE6	LE7	LE8	LE9	E	
Anti-Stain												
Hexafor SA-6320												
Pro-Stone												
Protect Guard TC												
Isograff												
Synthetic Varnish												
Acrylic Varnish												

Data collected from the 17 protecting systems (5 anti-graffiti coatings, 5 synthetic varnish + anti-graffiti coatings, 5 acrylic varnish + anti-graffiti coatings, 1 synthetic varnish, 1 acrylic varnish) have

shown that their effectiveness depends, beyond their chemical-physical features, on the cleaning method applied and on the nature of the paint layer underneath.

An ideal coating on respect of the cleaning should guarantee a physical barrier (in terms of porosity, homogeneity, thickness, permeability etc.) in order to protect the underlying paint layer from the cleaning agent applied, selected among green products.

If the coating is permanent, the barrier should be also chemical: the coating should not be sensitive to the cleaning agent. On the contrary, the sacrificial coatings should be sensitive to the cleaning agent: it will be the removal of coating that allow to the subsequently removal of graffiti without damaging the underlying paint layer.

Below the observations collected, from best to worst cleaning performer coating.

Isograff (IG)

As per manufacturer's recommendation, the steam is effective but only for the removal of film forming graffiti like SS and SB. In general, the interposition of varnishes has not great improved the IG cleaning effectiveness, PM marker remains particularly difficult to remove in a safe way.

The other cleaning methods tested have generally well worked: at least one suitable method for each graffiti material was identified, except for PM marker on PO.

The coating is sensitive to all the tested solvents:

- the simple rolling of cotton swab soaked with Ligroin, one of the safest solvent for the underlying paint layers, was effective except for the removal of the thick SB.
- Ethanol, when applied with Evolon CR, caused the slightly swelling and temporarily dulling the coating surface: this effect is likely dealing with the partial evaporation of the solvent and disappeared by slightly rubbing the coating surface with a silicon brush.

Despite the good results obtained, IG does not form a "total" barrier: pigment pick-up was observed on some mock-ups even if the coating was still present on their surfaces; this is likely due to a certain porosity of this sacrificial coating.

In addition, IG coating is quite soft and it is easily removable by mild mechanical action even after drying.

In fact, after Nanorestoregels application on soiled mock-ups protected by IG, the cleaned areas were bigger than the areas effectively covered by the gels, in particular for SS graffito. This was also favoured by the long application times (dozens of minutes) and by the low evaporation rate of the gels (covered with plastic films during application) causing a partial swelling of the coating around the gels with the subsequent removal of coating and graffiti material even on these zones.

Anti-stain (AS)

As per manufacturer's recommendation, the steam is effective, in particular for the removal of film-forming graffiti like SB and SS.

Despite AS is classified as sacrificial anti-graffiti, the steam did not completely remove the coating leaving the surfaces partially protected.

In general, a suitable and effective cleaning method for removing each kind of graffiti material has been found, even if the PM marker on PO was only partially removed.

Some highly retentive gels for controlled and selective removal of graffito are among the non suitable methods then AS does not guarantee a "total barrier" able to protect the underlying paint layers from the cleaning agents, in particular for the more sensitive PO:

- AS has not shown a particular resistance to the tested solvents, even the more polar ones, likely due to its complex composition
- designed for stones, AS is not able to form a total physical barrier: in fact, it reduces the stones' permeability to water vapor by 20% and their water absorption by 60%, even if it is a good oil repellent.

At the same time, even the graffiti materials are not able to form total physical barriers: for example, SB, despite its highly thickness and homogeneity, it has an intrinsic porosity due to spray application, so during the cleaning can be bypassed by solvents gaining access to the paint layers.

In general, the layered system with synthetic varnish SV has improved the barrier effect, so the cleaning effectiveness. For example, Ethanol (applied by cotton swabs) was optimal to remove in a safe way the graffiti materials sensitive to it, even if the coating AS was partially removed. In fact, synthetic varnish SV forms a thick layer that is quite resistant to the tested solvents. On the contrary, the acrylic varnish AV is thin and particularly sensitive to solvents, so it did not always help to protect and clean the very delicate paint layer PO.

Protect Guard TC (PG)

Despite PG is a specific anti-stain product designed for acrylic mural painting and not an anti-graffiti coating, the supplier suggested to use a paint stripper that has been resulted too aggressive and not always effective for our aims.

In general, it was noticed that if the coating was partially swelled and a sufficient mechanical action was applied, the coating tended to slightly film during the removal.

An effective cleaning method has not been found on the mock-ups protected with the coating only: only SM, both on PO and LY, and SS on LY were removed in a safe way.

The interposition of the acrylic varnish AV has not helped the protection and cleaning of PO layer. On the contrary, synthetic varnish SV has improved both the protection and the cleaning of LY: in fact, an effective and safe method has been found to remove all the graffiti materials.

The PG coating alone is not able to form a total barrier on the paint layers: the solubility tests carried out on glass slides have shown a good chemical resistance of the coating but some pigment pick-up has been noticed during the tests carried out on mock-ups. The different supports and the different thickness of the films, very thick on the glass slides on respect to the mock-ups ones, could have caused this behavior.

Hexafor SA-6320 (HX)

An effective cleaning method to remove each graffiti material has not been found.

Both the paint stripper suggested by the manufacturer to clean the surfaces protected with HX and the other cleaning methods tested were way too aggressive or not effective.

SM, secondly SS and PM are the only graffiti removable in a safe way, but only when applied on LY paint layer.

The poor performance of HX concerning the cleaning is likely due to a physical matter: the coating is thin and it has low concentration of active matter (5%), unfortunately there is no information available about other main features.

However, HX imparts a permanent protection, as a matter of fact it is highly resistant to solvents⁵⁸ and it remained on the mock-up surfaces after the cleaning cycles (confirmed by stereomicroscope observations).

⁵⁸ That was confirmed by the manufacturer too. They asserted that the coating is poorly sensitive both to apolar and polar solvents. In particular it is resistant to DPM-based solvents (Dipropylenglycol Monomethylether), hydrocarbons, acetates, ethers, ketones, and alcohols but only for briefly applications.

The interposition of varnishes, in particular of SV, have slightly improved the cleaning performance, especially on the non film forming graffiti materials SM and PM, towards which the coating seems to be more specific. An explicative example could be the tests on mock-up LY-HX-P-SV-SB, where on the half protected with both the synthetic varnish and coating, the graffiti material SB was partially removed, while on the half protected with the coating only, SB was not removed.

Pro-stone (PS)

The paint stripper suggested by the manufacturer to clean the mock-ups protected with PS was way too aggressive. No cleaning method has been found to remove each graffiti material on the mock ups protected with the coating only. SS and SM on LY paint layer were the only graffiti materials resulted removable in a safe way.

The interposition of synthetic varnish SV improved the protection and cleaning effectiveness, in particular, it was possible to partially remove the PM marker in a safe way. On the contrary, the acrylic varnish AV did not improve the protection nor the cleaning of PO paint layer.

The product did not form a continuous and homogeneous film causing a poor performance of PS: the graffiti materials were partially removed only where the coating was present. This is particularly visible on the mock-ups soiled with SB and cleaned with PVA/Borax gel. On these cleaned areas the coating seemed partially o completely removed.

The tests on glass slides have confirmed the high sensitivity of PS to solvents: the coating is very thin and it has a low concentration of active matter (5%). Moreover, the manufacturer asserts the coating is micro-porous in order to let the stones breath by 100%.

After these observations we have decided to not perform all the cleaning tests carried out on the mockup samples protected with the other anti-graffiti coatings. Depending on the type of graffiti material, the cleaning methods have shown different efficacy:

- Velvesil with solvents and Evolon soaked with Ethanol have better performed for the removal of non-filming graffiti (PM, SM) and penetrating (PM) ones
- PVA/Borax gels and HWR gel loaded with Nanorestore coatings have better removed thick and filming graffiti materials (SB) and partially film forming graffiti (SS)
- Steam has better removed thick and film forming graffiti materials (SB) and partially film forming graffiti (SS) only on wax based coatings
- Ligroin has better performed on SS graffito

Among these methods, Velvesil Plus has obtained the best scores on non film forming graffiti materials: despite a slight mechanical action was necessary during the cleaning process, it did not seem to cause damages of the superficial morphology of paint layers, in particular of LY. In general, Velvesil Plus has obtained the best results for removing SM for two reasons:

- the high SM sensitivity to the solvent contained in the gel (20% of Ethanol)
- the high chemical inertia of the gel for removing a graffito partially penetrated inside the underneath layers.

The best method to remove the film forming graffiti materials was the HWR Nanorestore gel loaded with Nanorestore micro emulsions B, G, S. In general, these gels were able to swell the graffiti materials and/or the coatings underneath then a final mechanical action was necessary (applied by wet cotton swabs or silicon brush) to remove the graffiti films. The use of swab/brush has determined modifications on mock-up superficial morphology: slight on LY, evident and not acceptable on PO.

The only exception was for the Isograff IG, where the PVA/Borax gel (6% hydrogel containing 20% of blend no. 16) has resulted optimal in particular on SB without applying any mechanical action at the end of the cleaning process.

In general, it is necessary to highlight that the Nanorestore micro emulsions need an aqueous rinse after application and when confined in highly retentive Nanorestore Gel HWRt its use on vertical "real" surfaces are particularly difficult. About this aspect, the PVA/Borax gels tested resulted very suitable to be applied on vertical surfaces, because of their property to gently adhere without dripping and because they do not need rinse after application.

Graffiti materials SB and SS were particularly difficult to remove when applied on PO paint layers, independently of the anti-graffiti coating, with the only exception of Isograff IG. SB and SS in fact, were more resistant to solvents than PO.

Depending on the type of the paint layer, the cleaning methods have shown different efficacy:

- PO was very sensitive to solvents and was almost always removed by the cleaning methods tested, even if protected with the coatings or with the varnish and coatings.
- LY was more resistant to solvents than PO and the cleaning tests gave better results too.

The evident and wide pigment pick-up observed on a lot of mock-ups, both painted with PO and LY, suggest that none of the selected anti-graffiti coatings was able to form an isolating physical barrier. With the only exception of PG, the coatings used are developed for stones, where the not total closure of their porosity is fundamental in order to avoid internal stresses.

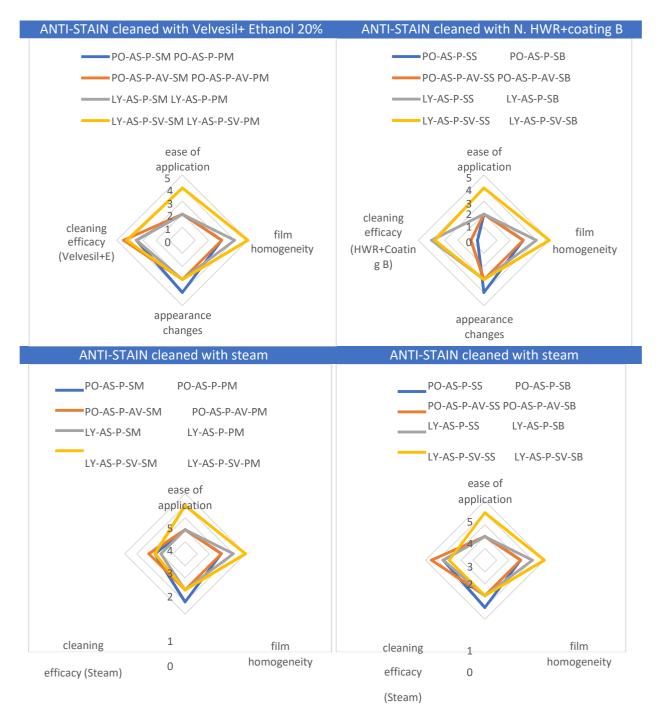
Performance evaluation

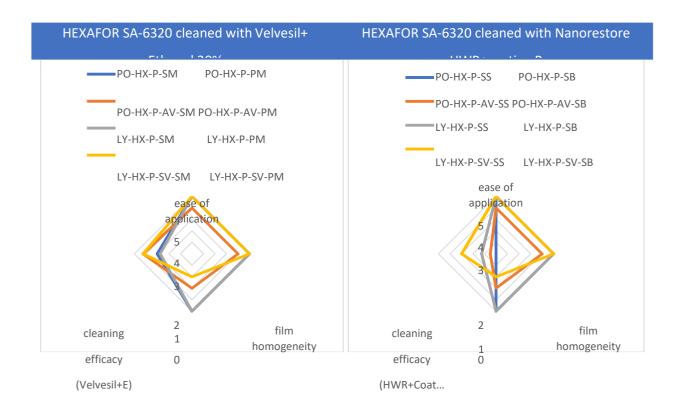
In order to combine practical observations related to the application of the anti-graffiti coating and the subsequent cleaning tests, four different parameters

- 1. ease of application
- 2. film homogeneity
- 3. appearance changes
- 4. cleaning efficacy (ease of graffiti removal in a safety way)

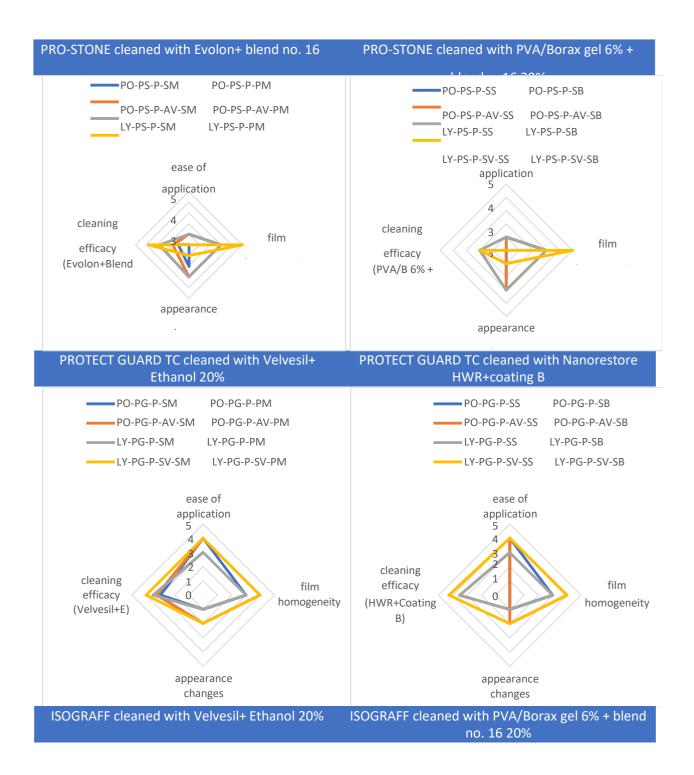
have been used to create the following performance radar graphics (**Figure 7 – Table 5- appendix**). Each parameter has a scale with a maximum value of 5 and a minimum value of 0, corresponding to the best and worst performance, respectively.

Only the cleaning tests with better results (see point 3) were observed and documented under stereomicroscope and assessed following the above mentioned evaluation criterion.





appearance changes appearance changes



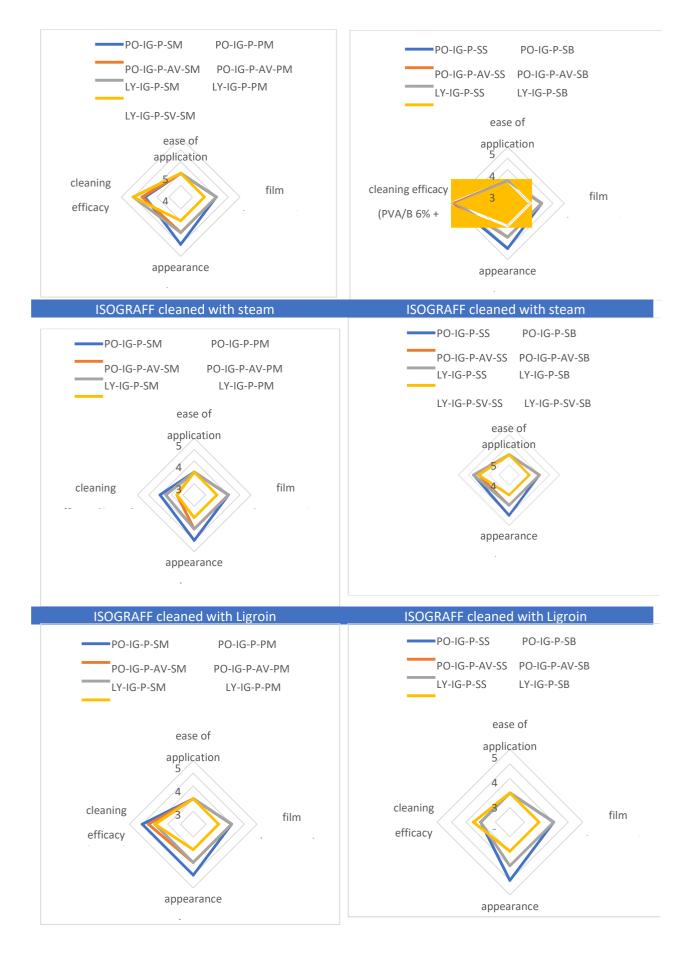


Figure 7 performance charts of anti-graffiti coatings

3.1.3 Which of the applied protection treatments were most effective? (in terms of surface changes and of inner properties of the coatings themselves) (best protection and best aesthetic appearance,... test winner) what was your criteria for the evaluation?

3a.3c. The performance of the selective protective products, both applied alone and in combination, was evaluated considering the following parameters:

- 1. easy of application
- 2. homogeneity of the film
- 3. morphological change compared to the untreated surfaces
- 4. appearance change compared to the untreated surfaces
- 5. colorimetric variation compared to the untreated surfaces
- 6. wettability changes compared to the untreated surfaces
- 7. cleaning efficacy

Scores (from 0 to 5) were assigned to the parameters; although samples to study were different, 1 and 2 parameters were taken into account by all working groups following a shared evaluation criterion.

Once all aging cycles will be finished, in detail evaluation of values change of the following parameters compared to before ageing will be also possible:

- 8. morphological change
- 9. colorimetric variation
- 10. wettability changes
- 11. chemical changes

This data will be collected for both raw materials and samples.

At this stage and for both working groups, which have independently worked, **Hexafor SA-6320 (HX)** has been the best product.

Easily to apply on modern paints, despite being designed for stone application (absorbent and hydrophilic surfaces), it has formed very homogeneous films used both alone than with varnishes. It has not substantially changed the morphology or the appearance of the surfaces, except when a varnish is present underneath.

It has not modified the aesthetical appearance of the paint layers in a significant way ($\Delta E \leq 2$) except for the fluorescent NF spray paint.

The wettability has remained roughly unchanged with respect to the painted surfaces and slightly increased as for all coatings with the varnish underneath.

It has poorly performed regarding the cleaning.

Better cleaning results have been obtained from waxy based sacrificial anti-graffiti such as IG followed by AS. In particular, the removal of film forming graffiti materials can be effectively carried out with steam. The method is safe and respectful of the underlying paint layers.

Their application has been difficult and laborious (a second coat has been generally necessary) therefore the films have appeared scarcely homogeneous except, for the AS only, which has improved with the SV varnish underneath. The SV varnish also improved its cleaning performance.

AS and IG has been less performing than HX due to morphological change and change in appearance, but wettability has not significantly changed.

The performance of the PS remains to be defined because a great discordance of results has been highlighted by the two working groups.

Aging: the first results have shown no significant changes from an aesthetic and chemical point of view. Acrylic-based (AV1) products and those containing synthetic wax/wax-like compounds (AS, IG) have shown greater stability while for alkyd-based products (AS, HX, PG) hydrolysis phenomenon has been observed and/or the formation of carboxylates have been registered.

Morphological variations after the first step of the accelerated ageing looked mostly independent from the substrate on which the coating was applied even though some differences could be found. ANTI_STAIN (AS) tended to form a more homogeneous layer after ageing, whereas films of the other commercial formulations often showed different thickness at the end of the test and a non-homogeneous appearance.

Wettability of the surfaces after the first step has shown an important variation and PG has been the better product for this point of view.

As expected, the most important colourimetric variations has been recorded on specimens where the fluorescent orange (NF) spray paint is present follow by gold (OM) one.

3b. Biological research: after one month of exposition, as expected, no microbial attack was observed. However, some physical decay was already observed on dry coated panels exposed to the weather. Until now no clear differences among the coating have been observed.

3d. None of the protective products tested on the four different paint layers has resulted optimal: all the coatings have changed the appearance of the not treated samples.

Despite this, some conclusions can be made.

- ACPU-Clearlaquer: since it forms a very thick and levelling film, it is able to slow down in a significant way the morphological changes caused by ageing. Despite this feature, the coating appears glossier than original painting surfaces and it is not able to protect all the colours from fading. It also does not completely avoid the thinning of the paint layers underneath and sometimes it causes cracks and subsequently lacunas of the paint layers. Yellowing and whitening of the coating have been observed after ageing. It does not seem highly stable.
- Multisurface AL: it forms a thick and homogeneous film that protects the paint surfaces from morphological change due to aging, even if a slight thinning of the layers has been noticed. Despite this characteristic, the coating appears way glossier than the painting surfaces and it is not able to protect all the colours from fading. Yellowing and strong whitening of the coating have been also observed after ageing. It does not seem highly stable.
- Anti-Stain: despite it does not create a very thick and homogeneous film on the sample surfaces, it better respects their original appearance (gloss, morphology) than the other two coatings. Compared to the other coatings, it most mitigates the fading of the unstable painting layer due to ageing. Anti-stain coating has the drawback to not protect the surfaces from morphological changes: after ageing the coated surfaces are quite similar to the uncoated ones after ageing. It seems to be slightly more stable than the other two: no significant whitening/yellowing or chromatically alterated areas have been noted.

3.1.4 Was it possible to transfer the methods/products on the objects on- site? If not, what has been different? Are there indications of a trend wether or not the behaviour of the product/method is the same on- site as under laboratory conditions? If not, what has been different?

The research, still ongoing, did not foresee products application on-site but many applicative aspects has been taken into account.

3.1.5 How is monitoring of the objects planned on-site?

3.1.6 What were the benefits of the students and staff mobility?

3.1.7 Deviation of the work plan.

-

In the initial cleaning working schedule, also based on literature, at least 10 graffiti removal cycles were planned in order to verify effectiveness and resistance of the films of coating. The manufacturer's removal methods, as explained above, were not suitable and therefore new solutions have been sought.

3.1.8 Problems encountered and implemented or proposed solutions.

The research under a) and b) were carried out by different partners (company, university and association) with different needs and located in different cities.

An important issue was to agree a common working plan acceptable for all parties: it resulted in a long and time consuming process.

Once started, we did not encountered major problems and in fact we gathered significant preliminary results.

3.1.9 Comments or short conclusion.

This report provides an insight into the composition and the chemical and physical stability of selected commercial spray paints commonly used by contemporary artists and writers and it evaluates the performance of seven commercial products employed as anti-graffiti coatings and varnishes providing new data on their chemical and physical stability and effectiveness in protecting the underlying spray paint layers and in cleaning treatments.

It also evaluates the optical appearance of two other type of protective products proposed by the other partners of Capus as a part of a deeper research.

The results have to be considered as preliminary.

Further research is needed to gain a deeper insight into the complexity of commercial spray paints and coatings formulations. Thus, gas chromatography coupled mass spectrometry with pyrolytic sampling technique (Py-GC-MS) will be carried out in order to better identify binders and possible additives, whereas X-ray Fluorescence spectroscopy (XRF) together with Thermogravimetry (TGA) will help in a

more detailed identification of inorganic fillers, extenders and other inorganic additives.

A deeper interpretation of the data just introduced within a complete overview of the degradation phenomena at the end of the two ageing tests (natural and accelerated) will be presented in the final report.

Biological research: the visual monitoring has just stared and will run till November 2020.

Common research: data obtained from optical observation of reference and aged samples will be shared with the other partners and compared to other investigations (such as colour measurements, chemical analyses) and other studies (developed within Capus and others) in order to define the most effective protection treatments and, at the same time, the requirements that a suitable coating for modern paints should have.

The cleaning tests have been useful to find suitable and safe methods to remove graffiti from coated paint layers: the presence of coatings or layered protective products allow to carrying out such delicate treatment otherwise difficult to perform.

When the aging tests and the biological tests will be finished we would be able to asses which of the 17 protective systems studied are the best from all points of view considered.

3.2 Acadamy of Fine Arts Warsaw (Poland)

NUMBER OF PARTNER	COUNTRY	NUMBER OF OBJECTS	NUMBER OF SAMPLES
P7	Poland	Object 1	
		Object 2 (2d, 2g, 2m)	

3.2.1 Information on tested protective methods carried out on mock up samples within the companies/research centres and on-site based on the selected sculptures (output wp2 and wp3)

Describe your experimental setup, including details on sample preparation, instruments and experimental conditions used. Take into account to name the object number and sample identification.

All protecting treatment tests were carried out on two objects: *Szczudlarze* by Linas Domarackas on the tenement house at 37 Stalowa Street in Warsaw, and on a set of 24 murals by various authors on Mur Sztuki [Wall of Art] in Ogród Różany [Rose Garden] of the Warsaw Uprising Museum.

The tests were carried out directly on the painting layer of the above-mentioned murals in situ. It was decided that it is best to carry out the tests on the objects and not on specially created samples under laboratory conditions. This gave us the opportunity to test methods of protecting paint layers made in various techniques. The objects were exposed to various external factors in the open urban space, which meant that the condition of the paint layer was varied.

Protecting treatment tests were performed on:

• Szczudlarze (Object 1):

Plaster - lime mortar, lime and cement mortar with quartz filler; black charcoal Paint layer: acrylic and vinyl paints

- Wall of Art (Object 2): Plaster - lime mortar with quartz filler Paint layer: acrylic, polyester, phthalic, vinyl, and tempera paints List 3 murals from the Wall of Art in the Uprising Museum: 2d – mural by Stasys
 - 2g mural by Utz
 - 2m mural by Galeria Rusz

3.2.2 What are the results from the application of different types of coatings on the ad hoc samples? (table) How did you get the results?

Object- number	Sample- number	Product- number	Tests*	Analytical Results	Optical Results
Object 1	Not applicable, the tests were carried out on the object	Paraloid B-72	concentration 2% in toluene by spraying method (procedure performed in special masks)	Not applicable	Very good effect, the paint layer was protected very well. Paraloid B-72 did not optically change the colour of the object.
	Not applicable, the tests were carried out on the object	Keim Lotexan- N	Located in the bottom part of the painting, a brush was used (procedure performed in special masks)	Not applicable	The substance has not been checked. There was a need for applying it due to the location of the object by a busy road and the construction of an apartment building not far from the object.
Object 2d (Stasys)	Not applicable, the tests were carried out on the object	Paraloid B-72	concentration 2% in toluene by spraying method (procedure performed in special masks)	Not applicable	Very good effect, the powdered white layer and the paint layer are now well preserved. Paraloid B-72 did not optically change the colour of the object. In addition, in the case of this object, it made the paint layer more vivid in places where the paint layer was washed and worn.
Object 2g (Utz)	Not applicable, the tests were carried out on the object	none	none	Not applicable	In the case of this mural, no attempts were made to preserve it because during the previous conservation works it was covered with a layer of Primal AC33, which could not be completely removed from the object.
Object 2m (Galeria Rusz)	Not applicable, the tests were carried out on the object	Paraloid B-72	concentration 2% in toluene by spraying method (procedure performed in special masks)	Not applicable	Very good effect, the powdered white layer and the paint layer are now well preserved. Paraloid B-72 did not optically change the colour of the object. In addition, in the case of this object, it made the paint layer more vivid in places where it was washed and worn.

* Please specify the work and tests you have done. The table is only a tool for organizing the results. Feel free to choose another form to present your results.

3.2.3 Which of the applied protection treatments were most effective? (in terms of surface changes and of inner properties of the coatings themselves) (best protection and best aesthetic appearance, ... test winner) What was your criteria for the evaluation?

The effects of protecting treatments by means of the above methods depended on the type of object (its condition and the technique used to create it). An appropriate method had to be developed individually for each mural. On the painting layer characterized by lack of cohesion (with a tendency to become powdered), Paraloid B-72 in toluene with a sprayer worked best.

The acrylic paint layer with good cohesion was protected with Paraloid B-72 in toluene because it is a proven agent, has a long tradition of use, does not adversely affect the paint layer, and it provides a reliable protective layer. In the case of the lower part of the mural *Szczudlarze*, which is exposed to very strong dirt, it was decided to use an unverified agent, because otherwise the lower part of the mural would be completely destroyed.

3.2.4 Was it possible to transfer the methods/products on the objects on-site? If not, what has been different? Are there indications of a trend wether or not the behaviour of the product/method is the same on-site as **under laboratory conditions**? If not, what has been different?

All tests were carried out on site, on the object.

3.2.5 How is monitoring of the objects planned on-site?

Photographic documentation was made before and after protecting treatments. The objects will be monitored this year.

3.2.6 What were the benefits of the students and staff mobility?

Students from Cologne could not come to Warsaw in 2019. An internship is planned in June 2020.

3.2.7 Deviation of the work plan.

Not applicable

3.2.8 Problems encountered and implemented or proposed solutions.

Difficulties associated with carrying out tests in the open air in the summer – the murals were exposed to strong sunlight, high temperatures, and wind during the application of the products.

3.2.9 Comments or short conclusion.

Protecting treatment methods should be selected individually for each mural, according to the technique used to create the mural, its condition, and the external conditions in the area where it is located.

3.3 CICS

NUMBER OF PARTNER	COUNTRY	NUMBER OF OBJECTS	NUMBER OF SAMPLES
P 5	Germany	1	50

3.3.1 Information on tested protection methods carried out on mock up samples within the companies/research centres and on-site based on the selected sculptures (output wp2 and wp3)

Describe your experimental setup, including details on sample preparation, instruments and experimental conditions used. Take into account to name the objectnumber and sample identification.

The lacquer tutoProm[®] bright is a transparent, ready-to-use coating solution to protect smooth, nonabsorbent surfaces from graffiti and soiling. It is used as a protective coating for Deutsche Bahn trains. It was first tested as a potential agent for the restoration of metal objects.

Preparation of the samples

According to DIN EN ISO 1513 and EN ISO 12944-6 we used test plates out of brass DIN A 5 size (148 mm x 210 mm) 3 mm thick with a smooth surface structure.

Pre-test

Pre-tests were made to get to know the conduct of the coating and to determine the right application method for the conservation of metal objects.

The technical data sheets recommend to apply the coating with roller, brush or airbrush. To compare different application materials we tested the following.

- "french polishing" (cotton thread in linen cloth)
- brush
- BlitzFix sponge
- PU sponge
- microfiber cloth "Reinraum" RTSM 711D
- PMMA cleaning cloth

The coating was applied at a temperature of 22 °C and a relative humidity of 44 % and it was performed in circling or straight motions depending on the material.

Under UV-light the coating showed a white-greenish fluorescence. This helped to monitor the traces of the application technique.

Microfibre cloth

The recommended application technique with microfibre cloths did not work. The cloths resorbed the coating, so when applying the coating it was not possible to glide smoothly over the surface. Under UV-light it shows little to no fluorescence.

French polishing

The coating could be easily applied. Though small residues of the cloth remained on the surface and merged with the coating. Under UV-light one sees clearly the traces of circular movements and the uneven distribution of the coating.

<u>brush</u>

The application with a brush leaves a rough structure of the surface. Dust particles are stucked in the coating.

PU sponge

The sponge absorbed the coating and made it easy to apply it on the surface. Under UV light the surface shows a denser layer than the surfaces of other application techniques.

<u>Blitz Fix</u>

Blitz Fix does not become soaked with the coating but produces a sealed surface. Under UV-light one sees clearly the stripes of the application technique.

PMMA cleaning cloth

The coating could be easily applied. There remained no residues on the surface. The UV light shows stripes and an uneven distribution.

In total the coating Tuto Prom©bright showed less fluorescence than Tuto Prom© matt HD. This is probably because of the different composition of the coatings. Another reason could be its lower layer thickness.

Test plates that showed a very low fluorescence were marked with a permanent marker to test the protective function of the coating. The lines had to be cleaned with aceton, so there was no protective function. Low or no fluorescence is an indicator of poor application and therefore little or no protection. Although Merck recommends applying the coating with microfibre wipers, there was no satisfactory outcome with using microfibre cloth.

A good and economical acceptable outcome was achieved with the PU sponge. However, no test plate had an even fluorescent surface, which indicates various layer thicknesses on one surface. But according to the manufacturer these uneven distributions of lacquer has no impact on the surface protection.

3.3.2 What are the results from the application of different types of coatings on the ad hoc samples? (table) How did you get the results?

We tested the products TutuProm[©] bright and TutuProm[©] matt HD. As these products were not developed for restoration purposes, a method of application had first to be found that would suit both the varnish and the object/sample.

Application

Before applying the coating on the test plates, they were cleaned with white spirit. After the solvent transpired with a pipette 1,5 ml of the coating were applied on the PU sponge. The best way of applying the coating on the plates was to put several layers wet in wet.

To avoid visible fine stripes on the surface after one to two minutes the coating was polished without pressure with a fine microfibre cloth, so that the nanostructure could be kept.

According to the manufacture small defect points are normal. Especially with Tuto Prom bright particles may be compounded in the coating, but not covered with it, because of the thin layer. Still the coating binds to the carrier material by covalent bonding. A potential corosion would only occur on the defect point. Also small variations of the film thickness are normal.

The following table shows the brass sample plates and their treatment.

[Hier eingeben]

Probetafel	0000	Name	Semester	Vorbereitung	Quelle Vorbereitun	Kategorie TRB	Rezeptnam e, Produkte	Quelle Überzug	Datierung	Ingredienzien	Auftragstechnik	Träger	Bernerkunge n	Schäden der Beschichtung
TRB-2019-	0754	CAPuS-Projekt, Waentig, Bresser, Kmiotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	g durXtreme	Fertigprodukt: Polysilazan	tutoProm matt HD		2019	organic polysilazane compound, n- Butylacetate, The following percentage of the mixture consists of ingredients with unknown hazards to the aquatic environment: 1, 535%	Ballenpolitur: Baumwollfäden in Leinentuch	Metall: Messing		
TRB-2019-	0755	CAPuS-Projekt, Vaentig, Bresser, Kmiotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm matt HD	6	2019	see above	Ballenpolitur: Baumwollfäden in Leinentuch	Metall: Messing		
TRB-2019-	0756	CAPuS-Projekt, Waentig, Bresser, Kmiotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm matt HD		2019	see above	Ballenpolitur: Baumwollfäden in Leinentuch	Metall: Messing		
TRB-2019-	0757	CAPuS-Projekt, Waentig, Bresser, Kmiotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm bright		2019	n-Butylacetate, organic polysilazane compound	Ballenpolitur: Baumwollfäden in Leinentuch	Metall: Messing		
TRB-2019-	0758	CAPuS-Projekt, Waentig, Bresser, Kmiotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm bright		2019	see above	Ballenpolitur: Baumwollfäden in Leinentuch	Metall: Messing		
rrb-2019-	0759	CAPuS-Projekt, Waentig, Bresser, Kmiotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm bright		2019	see above	Ballenpolitur: Baumwollfäden in Leinentuch	Metall: Messing		
"RB-2019-	0760	CAPuS-Projekt, Waentig, Bresser, Kmiotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm matt HD		2019	see above	Pinselauftrag	Metall: Messing		¢
rrb-2019-	0761	CAPuS-Projekt, Waentig, Bresser, Kmiotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm bright		2019	see above	BlitzFix	Metall: Messing		
(RB-2019-	0762	CAPuS-Projekt, Waentig, Bresser, Kmiotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm bright		2019	see above	PUSchwamm	Metall: Messing		
FRB-2019-	0763	CAPuS-Projekt, Waentig, Bresser, Kmiotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm matt HD		2019	see above	PUSchwamm	Metall: Messing		¢
TRB-2019-	0764	CAPuS-Projekt, Waentig, Bresser, Kmiotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm matt HD		2019	see above	PU Schwamm	Metall: Messing		

TRB-2019-	0765	CAPuS-Projekt, Waentig, Bresser, Kmiotek	2019	Beinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm bright	2019	see above	Vischtechnik: Mikrofasertuch "Reinraumtuch" RTSM 7110 (ein Tag später: 2. Reinigung mit Aceton, 2. Aufurag mit PU Schwamm)	Metall: Messing	
TRB-2019-	0766	CAPuS-Projekt, Vaentig, Bresser, Kmiotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm matt HD	2019	see above	Mikrofasertuch "Reinraumtuch" RTSM 711D	Metall: Messing	
TRB-2019-	0767	CAPuS-Projekt, Waentig, Bresser, Kmiotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm matt HD	2019	see above	Mikrofasertuch "Reinraumtuch" RTSM 711D	Metall: Messing	
TRB-2019-	0768	CAPuS-Projekt, Waentig, Bresser, Kmiotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm bright	2019	see above	Ballen: Baumwollfäden in feinem Leinentuch	Metall: Messing	
TRB-2019-	0769	CAPuS-Projekt, Waentig, Bresser, Kmiotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm bright	2019	see above	Ballen: Baumwollfäden in gröberem Leinentuch	Metall: Messing	
TRB-2019-	0770	CAPuS-Projekt, Waentig, Bresser, Kmiotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm bright	2019	see above	Vischtechnik: Mikrofasertuch "Reinraumtuch" RTSM 711D (ein Tag später: 2. Reinigung mit Aceton, 2. Auftrag mit PU Schwamm)	Metall: Messing	
TRB-2019-	0771	CAPuS-Projekt, Vaentig, Bresser, Kmiotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm bright	2019	see above	PUSchwamm	Metall: Messing	
TRB-2019-	0772	CAPuS-Projekt, Waentig, Bresser, Kmiotek	2020	Reinigung mit Siedegrenzbe nzin 100/141	durXtreme	Fertigprodukt: Polysilazan	tutoProm bright	2020	see above	Ballen: Baumwollfäden in Mikrofasertuch "Reinraumtuch" RTSM 711D	Metall: Messing	
TRB-2019-	0773	CAPuS-Projekt, Waentig, Bresser, Kmiotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm bright	2019	see above	Wischtechnik: PMMA Reinigungstuch	Metall: Messing	

TRB-2019-	0774	CAPuS-Projekt, Waentig, Bresser, Kmiotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm bright	2019	see above	Ballen: Baumwollfäden in PMMA Reinigungstuch	Metall: Messing	
TRB-2019-	0775	CAPuS-Projekt, Waentig, Bresser, Kmiotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm matt HD	2019	see above	PU Schwamm getränkt	Metall: Messing	
TRB-2019-	0776	CAPuS-Projekt, Waentig, Bresser, Kmiotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm matt HD	2019	see above	PU Schwamm getränkt	Metall: Messing	
TRB-2019-	0843	CAPuS-Projekt, Waentig, Bresser, Kmiotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm bright	2019	see above	Auftrag mit Mikrofasertuch "Reinraumtuch" RTSM 711D, 1-2min. Wartezeit, dann abpoliert mit feinem Mikrofasertuch	Metall: Messing	zur Alterung im Hof aufgestellt
TRB-2019-	0844	CAPuS-Projekt, Waentig, Bresser, Kmiotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm bright	2019	see above	Auftrag mit Mikrofasertuch "Rein aumtuch" RTSM 711D, 1-2min. Wartezeit, dann abpoliert mit feinem Mikrofasertuch	Metall: Messing	zur Alterung mit Seidenpapier umwickelt und in LSMSchrank gelagert, Proben unter REM betrachtet
rab-2019-	0845	CAPuS-Projekt, Waentig, Bresser, Kmiotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm bright	2019	see above	Auftrag mit Mikrofasertuch "Reinraumtuch" RTSM 711D, 1-2min. Wartezeit, dann abpoliert mit feinem Mikrofasertuch	Metall: Messing	zur Alterung 4Wochen im Alterungssch rank unter UV Bestrahlung
FRB-2019-	0846	CAPuS-Projekt, Waentig, Bresser, Kmiotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm matt HD	2019	see above	Auftrag mit Mikrofasertuch "Reinraumtuch" RTSM 711D, 1-2min. Wartezeit, dann abpoliert mit feinem Mikrofasertuch	Metall: Messing	zur Alterung mit Seidenpapier umwickelt und in LSMSchrank gelagert

TRB-2019-	0847	CAPuS-Projekt, Waentig, Bresser, Kmiotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm matt HD	2019	see above	Auftrag mit Mikrofasertuch "Reinraumtuch" RTSM 7110, 1-2min. Wartezeit, dann abpoliert mit feinem Mikrofasertuch	Metall: Messing	zur Alterung im Hof aufgestellt
TRB-2019-	0848	CAPuS-Projekt, Waentig, Bresser, Kmiotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm matt HD	2019	see above	Auftrag mit Mikrofasertuch "Reinraumtuch" RTSM 711D, 1-2min. Wartezeit, dann abpoliert mit feinem Mikrofasertuch	Metall: Messing	zur Alterung 4Wochen im Alterungssch rank unter UV Bestrahlung
TRB-2019-	0849	CAPuS-Projekt, Waentig, Bresser, Kmiotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm bright	2019	see above	Auftrag mit PU Sohwamm1-2min. Wartezeit, dann abpoliert mit feinem Mikrofasertuch	Metall: Messing	Testreihe Schäden mobility week CAPuS Übung mit polnischen Studierenden
TRB-2019-	0850	CAPuS-Projekt, Waentig, Bresser, Kmiotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm bright	2019	see above	Auftrag mit PU Schwamm1-2min. Wartezeit, dann abpoliert mit feinem Mikrofasertuch	Metall: Messing	Testreihe Schäden mobility week CAPuS Übung mit polnischen Studierenden
TRB-2019-	0851	CAPuS-Projekt, Waentig, Bresser, Kmiotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm bright	2019	see above	Auftrag mit PU Schwamm1-2min. Wartezeit, dann abpoliert mit feinem Mikrofasertuch	Metall: Messing	Testreihe Schäden mobility week CAPuS Übung mit polnischen Studierenden
TRB-2019-	0852	CAPuS-Projekt, Waentig, Bresser, Kmiotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm bright	2019	see above	Auftrag mit PU Schwamm1-2min. Wartezeit, dann abpoliert mit feinem Mikrofasertuch	Metall: Messing	Testreihe Schäden mobility week CAPuS Übung mit polnischen Studierenden
TRB-2019-	0853	CAPuS-Projekt, Waentig, Bresser, Kmiotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm bright	2019	see above	Auftrag mit PU Schwamm1-2min. Wartezeit, dann abpoliert mit feinem Mikrofasertuch	Metall: Messing	Testreihe Schäden mobility week CAPUS Übung mit polnischen Studierenden
TRB-2019-	0854	CAPuS-Projekt, Waentig, Bresser, Kmiotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm bright	2019	see above	Auftrag mit PU Schwamm1-2min. Wartezeit, dann abpoliert mit feinem Mikrofasertuch	Metall: Messing	Testreihe Schäden mobility week CAPuS Übung mit polnischen Studierenden
TRB-2019-	0855	CAPuS-Projekt, Waentig, Bresser, Kmiotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm bright	2019	see above	Auftrag mit PU Schwamm1-2min. Wartezeit, dann abpoliert mit feinem Mikrofasertuch	Metall: Messing	Testreihe Schäden mobility week CAPuS Übung mit polnischen Studierenden

TRB-2019-	0856	CAPuS-Projekt, Waentig, Bresser, Kmiotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm bright	2019	see above	Auftrag mit PU Schwamm1-2min. Wartezeit, dann abpoliert mit feinem Mikrofasertuch	Metall: Messing	Testreihe Schäden mobility week CAPuS	
TRB-2019-	0857	CAPuS-Projekt, Waentig, Bresser, Kmiotek	2019	Reinigung mit Siedegrenzbe nzin 100/140		Fertigprodukt: Polysilazan	tutoProm bright	2019	see above	Auftrag mit PU Schwamm1-2min. Wartezeit, dann abpoliert mit feinem Mikrofasertuch	Metall: Messing	Testreihe Schäden mobility week CAPuS	
TRB-2019-	0858	CAPuS-Projekt, Waentig, Bresser, Kmiotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm bright	2019	see above	Auftrag mit PU Schwamm1-2min. Wartezeit, dann abpoliert mit feinem Mikrofasertuch	Metall: Messing	Testreihe Schäden mobility week CAPuS	
TRB-2019-	0859	CAPuS-Projekt, Waentig, Bresser, Kmiotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm bright	2019	see above	Auftrag mit PU Schwamm1-2min. Wartezeit, dann abpoliert mit feinem Mikrofasertuch	Metall: Messing	Testreihe Schäden mobility week CAPuS	
TRB-2019-	0860	CAPuS-Projekt, Vaentig, Bresser, Kmiotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm bright	2019	see above	Auftrag mit PU Schwamm1-2min. Wartezeit, dann abpoliert mit feinem Mikrofasertuch	Metall: Messing	Testreihe Schäden mobility week CAPuS	•
TRB-2019-	0861	CAPuS-Projekt, Waentig, Bresser, Krniotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm bright	2019	see above	Auftrag mit PU Schwamm1-2min. Wartezeit, dann abpoliert mit feinem Mikrofasertuch	Metall: Messing	Testreihe Schäden mobility week CAPuS	
TRB-2019-	0862	CAPuS-Projekt, Vaentig, Bresser, Kmiotek	2019	Beinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm bright	2019	see above	Auftrag mit PU Schwamm1-2min. Wartezeit, dann abpoliert mit feinem Mikrofasertuch	Metall: Messing	Testreihe Schäden mobility week CAPuS	
TRB-2019-	0863	CAPuS-Projekt, Vaentig, Bresser, Krniotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm bright	2019	see above	Auftrag mit PU Schwamm1-2min. Wartezeit, dann abpoliert mit feinem Mikrofasertuch	Metall: Messing	Testreihe Schäden mobility week CAPuS	
TRB-2019-	0864	CAPuS-Projekt, Waentig, Bresser, Kmiotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm bright	2019	see above	Auftrag mit PU Schwamm1-2min. Wartezeit, dann abpoliert mit feinem Mikrofasertuch	Metall: Messing	Testreihe Schäden mobility week CAPuS zur Alterung im Hof aufgestellt	senk- u waagerechte Kratzer durch Gitterschnittprüfger ät, 6 Hammerschläge, Abrieb: Hammerkopf über Fläche gezogen
TRB-2019-	0865	CAPuS-Projekt, Waentig, Bresser, Kmiotek	2019	Beinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	utoProm bright	2019	see above	Auftrag mit PU Schwamm1-2min. Wartezeit, dann abpoliert mit feinem Mikrofasertuch	Metall: Messing	Testreihe Schäden mobility week CAPuS zur Alterung im Hof aufgestellt	senk- u waagerechte Kratzer durch Gitterschnittprüfger ät, 6 Hammerschläge, Abrieb: Hammerkopf über Fläche gezogen

TRB-2019-	0866	CAPuS-Projekt, Vaentig, Bresser, Kmiotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm bright	2019	see above	Auftrag mit PU Schwamm1-2min. Wartezeit, dann abpoliert mit feinem Mikrofasertuch	Metall: Messing	Testreihe Schäden mobility week CAPuS zur Alterung im Hof aufgestellt	senk- u waagerechte Kratzer durch Gitterschnittprüfger ät, 6 Hammerschläge, Abrieb: Hammerkopf über Fläche gezogen
TRB-2019-	0867	CAPuS-Projekt, Waentig, Bresser, Kmiotek	2019	Beinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm bright	2019	see above	Auftrag mit PU Schwamm1-2min. Wartezeit, dann abpoliert mit feinem Mikrofasertuch	Metall: Messing	Testreihe Schäden mobility week CAPuS zur Alterung im Hof aufgestellt	senk- u waagerechte Kratzer durch Gitterschnittprüfger ät, 6 Hammerschläge, Abrieb: Hammerkopf über Fläche gezogen
TRB-2019-	0868	CAPuS:Projekt, Waentig,Bresser, Kmiotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm bright	2019	see above	Auftrag mit PU Schwamm1-2min. Wartezeit, dann abpoliert mit feinem Mikrofasertuch	Metall: Messing	Testreihe Schäden mobility week CAPuS zur Alterung im Hof aufgestellt	senk- u waagerechte Kratzer durch Gitterschnittprüfger ät, 6 Hammerschläge, Abrieb: Hammerkopf über Fläche gezogen
TRB-2019-	0869	CAPuS-Projekt, Vaentig, Bresser, Kmiotek	2019	Reinigung mit Siedegrenzbe nzin 100/140	durXtreme	Fertigprodukt: Polysilazan	tutoProm bright	2019	see above	Auftrag mit PU Schwamm1-2min. Wartezeit, dann abpoliert mit feinem Mikrofasertuch	Metall: Messing	Testreihe Schäden mobility week CAPuS zur Alterung im Hof aufgestellt	senk- u waagerechte Kratzer durch Gitterschnittprüfger ät, 6 Hammerschläge, Abrieb: Hammerkopf über Fläche gezogen

Table 3: Treatment of brass sample plates

Object- number	Sample- number	Product- number	Tests*	Optical Results
	(1) sandblasted (medium grain) brushed- sulphur patina	4	weathering	-
	(2) sandblasted (medium grain) rubbed with stell wool - sulphur patina	4	weathering	-
	(3) sanded, grain size K 400 – polished	4	weathering	-
	(4) sanded, grain size K 400 - grinding fleece fine	4	weathering	-
	(5) sanded grain size K 400,blasted with glass pearls(round grain super fine)	4	weathering	-
	(6) sandblasted (rough grain)	4	weathering	first points of corrosion are formed (refer to fig. 7)
	(7) hammered sandblasted (medium grain), brushed - sulphur patina	4	weathering	first points of corrosion and oxidation are formed (refer to fig. 5,6)

In addition to the test plates we applied the coating on four bronze plates with 7 different surface structures.

Table 4: bronze sample plates with different surface structures

3.3.3 Which of the applied protection treatments were most effective? (in terms of surface changes and of inner properties of the coatings themselves) (best protection and best aesthetic appearance, ... test winner) What was your criteria for the evaluation?

After the coating has dried, the appearance of the surface of the brass plate hardly changes. But the cross-section shown below shows that the dried coating has a brittle structure due to the organic polysilazane and does not form an even surface. There are some cracks in the film which can lead to further damage (**Figure 1**).

After about 6 months of monitoring, first damages could be detected despite the protective coating. Punctual corrosion and an initial patina formation could be detected on two test plates. The plates on which corrosion and oxidation have formed do not have a smooth surface. One plate is roughened due to coarse sandblasting, the second plate has a hammered surface. The coating did not spread evenly on these rough surfaces due to its thin layer thickness. This is the reason for punctual damage. This means in reverse that the coating can only be applied to smooth surfaces, as it does not penetrate into depressions due to its low thickness and thus cannot form a continuous layer.

Furthermore images taken with a raster electron microscope show that after one year of weathering, the coating layer becomes brittle and detaches from the metal surface. (Figure 2)

The sample remaining in the darkroom in a constant climate, on the other hand, shows a thin coating that has not detached from the substrate (Figure 3).

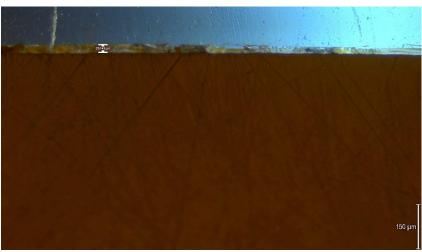


Figure 1: Cross section TutoProm[©] bright on brass

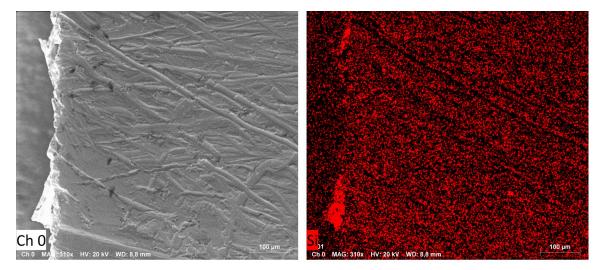
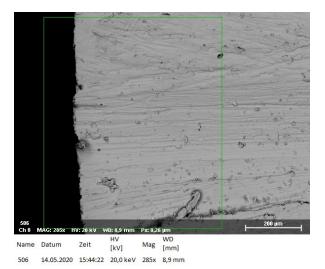


Figure 2: REM picture after one year of exposure. The coating separates from the support. The silicate compound of the coating is illustrated by the condensed red dots.



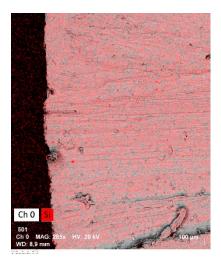


Figure 3: REM picture after 1 year in a dark chamber in constant climate.

[Hier eingeben]

3.3.4 Was it possible to transfer the methods/products on the objects on-site? If not, what has been different? Are there indications of a trend whether or not the behaviour of the product/method is the same on-site as under laboratory conditions? If not, what has been different?

No. Since the varnish was not developed for conservation purposes, the test plates should first be used to determine whether it is suitable for conservation practice. After observing it for a year, it can be said that the sculpture should not be treated with it. The company Schmincke has provided us with a further coating, which we will test on further test panels to see if it is better suited for the sculpture as graffiti protection.

3.3.5 How is monitoring of the objects planned on-site?

Since this coating was to be tested for its suitability for conservation, only test panels were treated with this coating. However, these were observed for one year and showed the first changes after only 6 months. The test plates were documented photographically every month.



Figure 4: Weathering station with brass and bronze test plates



Figure 5: corrosion on plate 7



Figure 6: oxidation on plate 7



Figure 7: corrosion on plate 6

3.3.6 What were the benefits of the students and staff mobility?

Students trained teamwork in an international team, problem solving in a short time, a high degree of initiative and independence, as well as social skills.

The mobility week enabled fruitful discussions and a professional exchange on an international level among both students and teachers.

3.3.7 Deviation of the work plan.

None.

3.3.8 Problems encountered and implemented or proposed solutions.

None.

3.3.9 Comments or short conclusion.

As far as we now know the TutuProm[©] bright and TutuProm[©] matt HD lacquers are rather not recommended for the restoration of metal objects. Deutsche Bahn uses these coatings to protect its trains from vandalism by graffiti and renews the coating after 5 years, as it wears out due to the weathering and regular washing of the trains: The previous tests showed that already after one year of weathering, the lacquers do not offer sufficient protection on structured surfaces due to their low layer thickness.

3.4 University of Vigo

NUMBER PARTNER	OF	COUNTRY	NUMBER OF OBJECTS	NUMBER OF SAMPLES

3.4.1 Information on tested protecting methods carried out on mock up samples within the companies'/research centres and on-site based on the selected sculptures (output wp2 and wp3). Describe your experimental setup, including details on sample preparation, instruments and experimental conditions used. Take into account to name the objectnumber and sample identification.

This research was addressed in

two ways: On-site control

For this, a specific artwork was selected, *A GUARDA ESCRITA NAS ESTRELAS* (object 26), in A Guarda, a mural 150 m long by 8 m highthat was created in september 2018. This mural is painted on a base painting blue (*MONTOKRIL plain S 554*0r90b) with *MONTANA* sprays (see Table 1) of six different colors (blue, brown, yellow, pink, orange and green).

Once the artwork was created, two color protectors were applied to individualized areas of each of the palettes in order to monitor their effectiveness during one year. The selected color protectors are products generally used by artists and commissioners consulted during WP2.

- P-PROA: PROA BV 000, satin water varnish
- P-EGA: EGA-352-M00-01-FT, CARLUS water varnish

The color of each of the paint palettes used in this artwork without and with protectors was recorded each 30 days until december 2019, with the aim of knowing the effectiveness of the protectors. The color was characterized by spectrophotometry using a Minolta CM-700d equipment. To assess the quantitative color change, the differences ΔL^* , Δa^* , Δb^* , ΔC^* ab, ΔH^* , and the global color change ΔE^* ab were calculated.

Ageing tests using mockups:

Mock ups were prepared with two different supports commonly used in urban art murals in the NW of the Iberian Peninsula: concrete and brick. The concrete was prepared with a silicated aggregate of granulometry 2-0,1mm and a cement CEM-II / BM (VL) 32.5 N. As for the brick, simple hollow bricks of 24 cm x 11 cm x 4 cm were selected. From each support, 3 cm x 3 cm x 2 cm (to use as a reference) and 7 cm x 7 cm x 2 cm specimens (to use for tests) were prepared. The specimens were painted with ten different paints (Table 2): four acrylic paints applied by brush (B-paints) and six sprays (S-paints). Acrylic paints were applied by brush, applying the number of layers necessary to completely cover the surface, as an artist would have done on the wall. The spray application was carried out at a distance of 30 cm from the surface of the sample and with an inclination angle of 45 ° and during a time necessary to completely and homogeneously cover the surface of the sample. To a batch of specimens, P-PROA and P-EGA protectors were applied.

The specimens were subjected to two tests:

1. Accelerated aging test by solar radiation

The surfaces of the painted samples were irradiated using four 300V OSRAM Ultra Vitalux bulbs. The samples were subjected to the test for a total of 4620 hours, which corresponds to 210 days, with 22 hours of exposure per day and 2 hours of darkness.

2. Alteration due to natural exposure to marine spray

A test piece of each paint / support / protector was exposed during 1 year to the environment in an exhibitor located 5 meters away from the sea, in NW orientation.

In both tests the color of the specimens is measured every certain time (15 days in the case of the solar test and 30 days in the case of exposure to the marine aerosol). Both trials were ended in December 2019. After both tests, the specimens were analyzed by x-ray diffraction, FTIR and SEM.

In addition to protectors, the durability of all paints has been assessed with the presence of a previous preparatory layer made of a chenical product manufactured by PROA named *PROA IP 000H Fijador abrillantador*.

Table 1: IN SITU PROTECTIVE EFFECTIVENESS MONITORING: List of the paints of urban art object 26 in which the evaluation of the protectors (P-PROA and P-EGA) was monitored during 1 year, indicating commercial name, manufacturer and methods for the evaluation of effectiveness (SEM -scanning electron microscopy; FTIR: Fourier Transform Infrared Spectroscopy; DRX: x ray diffraction).

		IN		IVE EFFECTIVE	NESS	
ID	TRADENAME	MANUFACTURER	COLOUR	OBJECT	PROTECTIVE	EFFECTIVENESS EVALUATION
				26	P-PROA	
SAZ	Freedom blue RV-151			26	P-EGA	
					P-PROA	Color monitoring each 30
SM	Safari brown RV-135			26	P-EGA	
			Vellow		P-PROA	days Optic microscopy
SY	RV 1021 Light Yellow	Montana Colors	Yellow	26	P-EGA	SEM
CD.			Diale	20	P-PROA	SEIVI
SP	RV 151 Tutti Frutti		Pink	26	P-EGA	FTIR
so	RV 2004 Orange		Orange	26	P-PROA	
30	NV 2004 Orange		Orange	20	P-EGA	DRX
			Green	20	P-PROA	
SG	RV 6018 Valley Green		Green	26	P-EGA	
	Blue base paint MONTOKRIL	μουτό	51	26	P-PROA	
В	S 5540r90b	MONTÓ	Blue	26	P-EGA	

Table 2: PROTECTIVE EVALUATION RESEARCH ON MOCK UPS - List of selected paints for the evaluation of the protectors (P-PROA and P-EGA), indicating commercial name, manufacturer, urban art object in which each paint has been used, type of ageing test performed and methods for the evaluation of effectiveness (SEM -scanning electron microscopy; FTIR: Fourier Transform Infrared Spectroscopy; DRX: x ray diffraction).

PROTECTIVE EVALUATION RESEARCH ON MOCK UPS								
ID	Tradename	Manufacturer	Colour	Object	Protective product	Ageing tests	EFFECTIVENESS EVALUATION	
						Solar (artificial)		
BY	P7-Reveproa Primary Yellow- outdoor	PROA	Yellow	16	P-PROA -	Natural marine aerosol		
ВТ					P-EGA	Solar (artificial)		
						Natural marine aerosol		
		EGA	Red	4	P-PROA -	Solar (artificial)		
BR	Teppisol Fire red mat					Natural marine aerosol		
ы					P-EGA	Solar (artificial)		
		FEUA	Natural marine aerosol					
					P-PROA	Solar (artificial)	Color monitoring each 15-	
BG	Green RAL 6024		Green	18	THNOA	Natural marine aerosol	30 days	
50				10	P-EGA	Solar (artificial)		
		KROMO				Natural marine aerosol	Optic	
	Pink RAL 4010		Pink	18	P-PROA P-EGA	Solar (artificial)		
BP						Natural marine aerosol	microscopy SEM	
Di						Solar (artificial)		
					I-LOA	Natural marine aerosol	FTIR	
					P-PROA	Solar (artificial)		
SY	RV 1021 Light Yellow		Yellow	26	TINOA	Natural marine aerosol	DRX	
01	IN 1021 Light renow			20	20	P-EGA	Solar (artificial)	
					1-107	Natural marine aerosol		
	RV 151 Tutti Frutti	Montana 151 Tutti Frutti Colors		nk 26 P-PROA P-EGA	Ρ-ΡΒΟΔ	Solar (artificial)		
SP			Pink 26			Natural marine aerosol	_	
					P-EGA	Solar (artificial)		
						Natural marine aerosol	_	
	RV 2004 Orange		Orange	26	P-PROA -	Solar (artificial)	_	
so						Natural marine aerosol	1	
					P-EGA	Solar (artificial)	<u> </u>	
						Natural marine aerosol		

					P-PROA	Solar (artificial)
SG	RV 6018 Valley Green	Gru	Green	26	FFRUA	Natural marine aerosol
50	NV 0010 Valley Green		cen	20	P-EGA	Solar (artificial)
					FLOA	Natural marine aerosol
					P-PROA	Solar (artificial)
SFO	FLUOR Orange		Fluor Orange	14	FFROA	Natural marine aerosol
510	1 LOOK Ordinge	Ora			P-EGA	Solar (artificial)
						Natural marine aerosol
SFG FLUOR Green				P-PROA	Solar (artificial)	
	FLUOR Green		Fluor	14, 7, 12	I -I NOA	Natural marine aerosol
5,0			een	±=,,,12	P-EGA	Solar (artificial)
					I -LUA	Natural marine aerosol

3.4.2 What are the results from the application of different types of coatings on the ad hoc samples? (table) How did you get the results?

The effectiveness of each protector was different depending on the color of the paint on which they are applied, depending on the support and depending on the alteration environment.

In Figure 1, it can be seen how the effectiveness of each protector, in the *on-site* control, is different depending on the paint (blue, pink). In the case of Blue Base paint (B), the P-EGA protector slows the color change of the paint more effectively than P-PROA protector. Conversely, in the Pink Montana spray, both protectors confer no significant improvement against color modification.

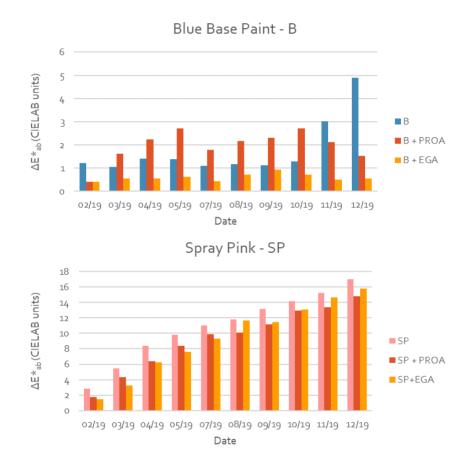


Figure 1: ΔE^*ab (CIELAB units) during time (one year) suffered by Blue Base paint on Object 26 (on site evaluation) without (bar of blue color) and with the two protectors (PROA and EGA).

Figure 2 depicts another interesting results of the ageing tests with mockups. During these test, it can be concluded that:

1) each paint shows a different durability depending on the ageing test (solar test or natural exposition to marine aerosol): compare, in Figure 1, ΔE^* ab suffered by yellow spray-paint on concrete during solar test and ΔE^* ab suffered by yellow spray-paint on concrete marine aerosol exposition. This paint suffered highest ΔE^* ab during marine aerosol exposition.

2) <u>each protector showed a different effectiveness depending of the support</u>: compare in Figure 1, ΔE^*ab of P-PROA and P-EGA applied on Yellow spray paint on concrete during solar test and ΔE^*ab of

P-PROA and P-EGA applied on yellow spray paint on brick. In the latter, both protectors increase the resistance of the paint to radiation even P-PROA which, in concrete samples, did not show any improvement against solar radiation degradation.

3) each protector has a different effectiveness depending on the paint on which is applied: compare in Figure 1, ΔE^*ab suffered by yellow spray-paint on concrete during solar test and ΔE^*ab suffered by green brush paint on concrete during solar test. On yellow paint, P-PROA did not exert any protection whereas, on green paint, the protection against solar radiation degradation is spectacular.

The analytical results (SEM, FTIR, DRX) are still unfinished, so the mechanisms through which these protectors act is still unknown.

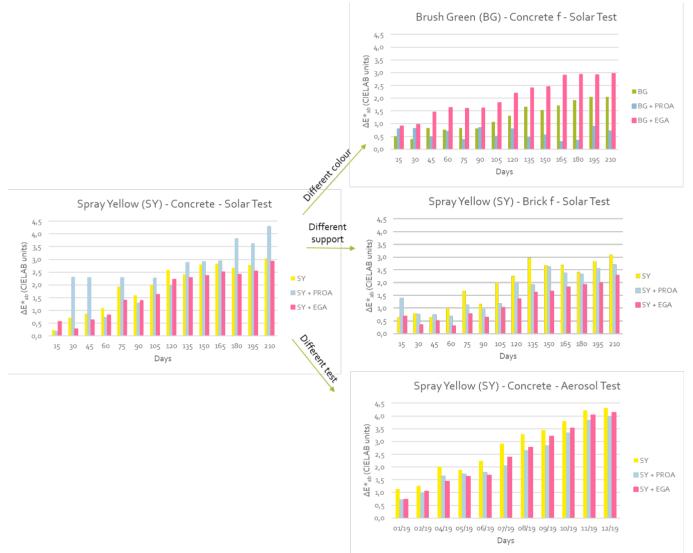


Figure 2: ΔE^*ab (CIELAB units) during time (one year) suffered by Yellow spray paint on concrete and on brick and green brush paint under concrete, with and without the protectors and during different alteration test.

3.4.3 Which of the applied protection treatments were most effective? (in terms of surface changes and of inner properties of the coatings themselves) (best protection and best aesthetic appearance,... test winner) What was your criteria for the evaluation?

It is impossible to identify the most effective protector since it depends on the support, the paint on which it is applied and the exposure environment.

What is unquestionable is that, at least in situ, the EGA protector proved more durable. The PROA protector applied to the brown and blue spray suffered intense yellowing and strong cracking after 2 months of being applied; In mock-ups, PROA cracked as soon as it was applied to the specimens.

3.4.4 Was it possible to tranfer the methods/products on the objects on-site? If not, what has been different? Are there indications of a trend wether or not the behaviour of the product/method is the same on-site as under laboratory conditions? If not, what has been different?

We are unable, before obtaining such disparate results, to define with certainty a clear recommendation towards the application of one protective product or another. In this uncertainty, between the two products evaluated, we would recommend P-EGA.

But, taking into account other data obtained in the documentation phase (interviews with artists, description of the pathologies of the artworks and analysis of the deterioration causes) we consider it important to point out that colour changes also occur for other reasons, in addition to the low resistance of this type of modern paintings to UVA radiation. In our environment (NW Spain), the action of other factors causes (such as water or biological colonization) much or more deterioration in colour than UVA radiation so, apart from recommending one or the other protector, most of the effort to slow down the deterioration should be aimed at avoiding the action of these other factors that endanger the integrity of the pictorial layer more quickly.

3.4.5 How is monitoring of the objects planned on-site?

The use of colour spectrophotometry is a very useful tool to control effectiveness of protectors since it allows to accurately monitor, in most cases, how the products slow down (or not) the colour degradation. It is important to carry out the measurements periodically and under the same environmental conditions. For example, in Galicia, where it rains between 1800-2000 mm per year, it is advisable to wait a few days after the rains to perform the measurements. The deterioration of the protectors (if these crackle and are detached or if they turn yellow) or the growth of cyanobacteria or algae on the paints can complicate the interpretation of the data but, in general terms, it is a good and reliable methodology.

3.4.6 What were the benefits of the students and staff mobility?

No students neither staff memnber have been received in mobility actions.

3.4.7 Comments or short conclusion.

The work was carried out as planned; The results allow us to draw interesting conclusions about the precautions to be applied in the process of monitoring color changes. Rapid deterioration is observed, especially in situ, due to extreme weather conditions and marine influence and under these conditions, the protectors are also greatly altered.

3.4.8 Deviation of the work plan.

None.

3.4.9 Problems encountered and implemented or proposed solutions.

None.

3.5 Collaborative work

At the third meeting of CAPUS partners in Milan (on 2019-06-11) it was decided to carry out a collaborative work between the partners A.N.T.A.R.E.S, CCR, UNITO, Montana, Vigo and Schmincke on protective coatings.

The aim was to test one protective coating product of each industrial partner (A.N.T.A.R.E.S, Montana and Schmincke) on concrete samples produced in four different colours. Very resistant and less resistant colours were used for the colour shades.

In parallel to the concrete samples, microscopy slices of the three coating products were also produced in a defined application thickness, which were also subjected to the tests.

Due to the pandemic with COVID-19 in 2020, not all results of the tests carried out by the individual partners are available at this time. It was therefore decided to publish all results of this collaborative work in a supplementary report at a later date with title: WP4: supplementary report - results of collaborative work.

4 Report on the analytical evaluation of consolidation methods

4.1 University of Turin (Italy) and Conservation and Restoration Centre "La Venaria Reale" (Italy)

NUMBER OF	COUNTRY	NUMBER OF OBJECTS	NUMBER OF SAMPLES
PARTNER			
P2	Italy	1	34

4.1.1 Information on tested consolidation methods carried out on mock-up samples within the companies/research centres and on-site based on the selected artworks (output wp2 and wp3).

Describe your experimental setup, including details on sample preparation, instruments and experimental conditions used. Take into account to name the object number and sample identification.

After the preliminary survey on the 14 selected artworks, flaking and scaling are found to be the most relevant decay phenomena of the 14 artworks in Turin, representing one of the most critical issues for the conservation of outdoor contemporary murals. Therefore, tests on mock-ups have been set up, to select the most effective product and methodology for painting consolidation.

Samples have been prepared with materials currently used for contemporary buildings: as confirmed by the analysis made on samples collected from two of the selected murals, background layers are often realised with concrete mortars, eventually covered with a primer and than painted with synthetic products, mainly belonging to acrylic, vinylic or alkyd resins.

Two different situations have been taken into account for mock-ups preparation:

- 1) Scales completely detached from the painted surface
- 2) Scales partially detached from the painted surface

Therefore readhesion tests have been made both with scales (with different thickness), prepared separately with different techniques (type 1), and with scales partially detached from the mocks-up surface after thermal stress (type 2).

In order to study the various possibilities, in term of the thickness of the detached scale and relating to the number of painting/background layers involved, tests have been realised with different combinations of painting layers and detached fragments, useful to replicate and observe:

- The adhesion of fragment of acrylic paint and concrete, on a cement, untreated, background;
- The adhesion of scales of acrylic painting layer on a cement, untreated, background;
- The readhesion of detached scales from a complex stratigraphy of cement background, acrylic first painting layers, overlaid by a second alkyd painting layer;
- The readhesion of detached scales from an alkyd painting layer on a cement background;
- The adhesion of acrylic scales on an alkyd painting layer, applied on two different concrete backgrounds.

MOCK-UPS PREPARATION

Mock-ups have been made on mobile support of fiber glass and aluminium honeycomb, called Aerolam[®], useful for further handling of the samples.

Background layers have been prepared following three recipes, varying the rate of both sand and cement in order to obtain layers with different chemical and physical properties:

- 1) Sand/cement rate 4:1
- 2) Sand/cement rate 3:1
- 3) Sand/cement rate 15:1

Due to the absence of a primer in the two fully investigated murals, the painting layers have been applied directly on the totally dried background layers, with both alkyd spray and acrylic paints. For mock-ups preparation the following materials have been used:

- Concrete
- Grey, fine, river sand
- Red acryl paint by Schmincke
- Blu Acryl Paint by Schmincke
- Red AlphaAcryl paint by Sikkens
- Red Alkyd-nitro Spray by Belton
- Red Alkyd Spray by Montana94

Once dried out, all the mock-ups have been exposed to outdoor weather condition for three days. Then, only "type 2" mock-ups have been subjected to a thermic shock by cyclic application of hot dried air (around 200°C) instantly followed by liquid nitrogen (around -195°C), in order to enhance the selective detachment of the painting layers.

SCALES PREPARATION

Two type of scales, to be used for adhesion tests on previously prepared mock-ups, have been realised:

- 1) CEMENT+ALKYD SCALES, useful to simulate the flaking of multilayer scales, have been realised applying a 2 mm layer of cement on a siliconat sheet and drying the surface with hot air from an hair dryer, until the surface started cracking. Then, a layer of alkyd paint has been sprayed on the surface and let dry. The cracking of the cement originates painted scales that have been used to adhesion tests.
- 2) ACRYLIC SCALES, useful to simulate a single painting layer scaling, have been realised applying single hand of acrylic red, blue or black paint on a siliconate sheet and leaving dry outdoor. The painting and very elastic layers have then been cut in little squares or slices and used for adhesion test on cement background and acrylic/alkyd painting layers both.

ADHESION TESTS AND EVALUTATION

Finally, adhesive properties of four products have been tested, evaluating both the effectiveness in consolidation of detached scales (partially detached or prepared separately from the background) and the absence of optical alteration of the painted surfaces. Products selected are all synthetic resin, each tested in three different rate of water or alcoholic-water solutions:

- Primal B60A, a water dispersion of acrylic resin. Percentage rate of the water solutions: 5%, 15% and 40% (V/V).
- Microacril, a microemulsion of acryl resin; in water solutions with 5%, 15% e 30% rate (V/V).
- E 411, a water dispersion of acrylic resin; in water solution with 3%, 15% e 25% rate (V/V).

- K52, microemulsion of acrylic resin; in ethanol-water solution (1:1), with 3%, 10% e 25% rate (V/V) (used only for preliminary consolidation of the surface when loss of cohesion is attested)

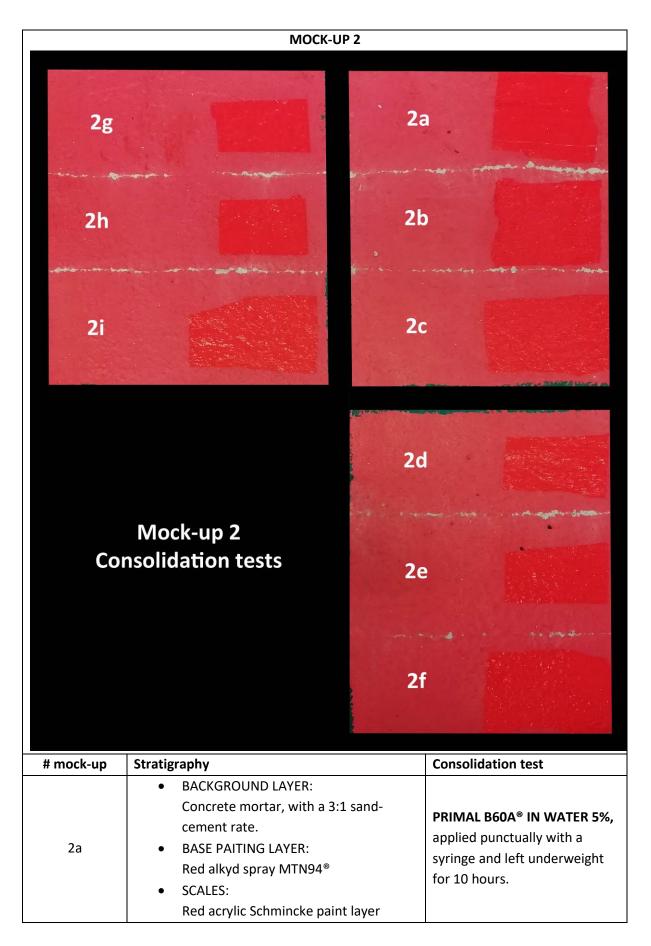
Adhesion tests have been evaluated optically. Tape test has not been selected for adhesion tests evaluation because of the significant difference in the shape, the thickness and the dimension of the scales in the different mock-ups: therefore, considering the heterogeneity of the samples, tape test would not be replicable and none comparison would have been made with the results obtained. Once realised a preliminary selection of the products, on the basis of the optical results, the eventual variation of the absorbing properties of the treated layers has been tested with "contact sponge test", using the standard procedure described in UNINORMAL 11432:2011.

The table below summarizes names and stratigraphy of all the mock-ups and the related consolidation tests:

	MOCK-UP 1	
1a 1j 1g 1p	1 th	<pre>1 f</pre>
# mock-up	Stratigraphy	Consolidation test
1a	 BACKGROUND LAYER: Concrete mortar, with a 4:1 sand- cement rate. SCALES: Cement + red alkyd MTN94[®] sprayed layer 	PRIMAL B60A[®] IN WATER 5%, applied punctually with a syringe and left underweight for 10 hours.
1b	 BACKGROUND LAYER: Concrete mortar, with a 4:1 sand- cement rate. SCALES: Cement + red alkyd MTN94[®] sprayed layer 	PRIMAL B60A® IN WATER 15%, applied punctually with a syringe and left underweight for 10 hours.
1c	 BACKGROUND LAYER: Concrete mortar, with a 4:1 sand- cement rate. 	PRIMAL B60A [®] IN WATER 40%, applied punctually with a

	SCALES:	syringe and left underweight
	Cement + red alkyd MTN94 [®] sprayed layer	for 10 hours.
1d	 BACKGROUND LAYER: Concrete mortar, with a 4:1 sand- cement rate. SCALES: Cement + red alkyd MTN94[®] sprayed layer 	E411[®] IN WATER 3%, applied punctually with a syringe and left underweight for 10 hours.
1e	 BACKGROUND LAYER: Concrete mortar, with a 4:1 sand- cement rate. SCALES: Cement + red alkyd MTN94[®] sprayed layer 	E411[®] IN WATER 15%, applied punctually with a syringe and left underweight for 10 hours.
1f	 BACKGROUND LAYER: Concrete mortar, with a 4:1 sand- cement rate. SCALES: Cement + red alkyd MTN94[®] sprayed layer 	E411 [®] IN WATER 25%, applied punctually with a syringe and left underweight for 10 hours.
1g	 BACKGROUND LAYER: Concrete mortar, with a 4:1 sand- cement rate. SCALES: Cement + red alkyd MTN94[®] sprayed layer 	MICROACRIL [®] IN WATER 5%, applied punctually with a syringe and left underweight for 10 hours.
1h	 BACKGROUND LAYER: Concrete mortar, with a 4:1 sand- cement rate. SCALES: Cement + red alkyd MTN94[®] sprayed layer 	MICROACRIL [®] IN WATER 15%, applied punctually with a syringe and left underweight for 10 hours.
1i	 BACKGROUND LAYER: Concrete mortar, with a 4:1 sand- cement rate. SCALES: Cement + red alkyd MTN94[®] sprayed layer 	MICROACRIL [®] IN WATER 30%, applied punctually with a syringe and left underweight for 10 hours.
1j	 BACKGROUND LAYER: Concrete mortar, with a 4:1 sand- cement rate. SCALES: Blue acrylic Schmincke paint layer 	PRIMAL B60A [®] IN WATER 5%, applied punctually with a syringe and left underweight for 10 hours.

	BACKGROUND LAYER:		
	Concrete mortar, with a 4:1 sand-	PRIMAL B60A [®] IN WATER 15%,	
1k	cement rate.	applied punctually with a	
	SCALES:	syringe and left underweight	
	Blue acrylic Schmincke paint layer	for 10 hours.	
	BACKGROUND LAYER:		
	Concrete mortar, with a 4:1 sand-	PRIMAL B60A [®] IN WATER 40%,	
11	cement rate.	applied punctually with a	
	SCALES:	syringe and left underweight	
	Blue acrylic Schmincke paint layer	for 10 hours.	
	BACKGROUND LAYER:		
	Concrete mortar, with a 4:1 sand-	E411 [®] IN WATER 3%, applied	
1m	cement rate.	punctually with a syringe and	
	• SCALES:	left underweight for 10 hours.	
	Blue acrylic Schmincke paint layer	-	
	BACKGROUND LAYER:		
	Concrete mortar, with a 4:1 sand-	E411 [®] IN WATER 15%, applied	
1n	cement rate.	punctually with a syringe and	
	• SCALES:	left underweight for 10 hours.	
	Blue acrylic Schmincke paint layer		
	BACKGROUND LAYER:	E411 [®] IN WATER 25%, applied	
	Concrete mortar, with a 4:1 sand-	punctually with a syringe and	
10	cement rate.	left underweight for 10 hours.	
	• SCALES:	left under weight for 10 hours.	
	Blue acrylic Schmincke paint layer		
	BACKGROUND LAYER:	MICROACRIL [®] IN WATER 5%,	
	Concrete mortar, with a 4:1 sand-	applied punctually with a	
1p	cement rate.	syringe and left underweight	
	• SCALES:	for 10 hours.	
	Blue acrylic Schmincke paint layer		
	BACKGROUND LAYER:	MICROACRIL [®] IN WATER 15%,	
	Concrete mortar, with a 4:1 sand-	applied punctually with a	
1q	cement rate.	syringe and left underweight	
	• SCALES:	for 10 hours.	
	Blue acrylic Schmincke paint layer		
	BACKGROUND LAYER:	MICROACRIL [®] IN WATER 30%,	
	Concrete mortar, with a 4:1 sand-	applied punctually with a	
1r	cement rate.	syringe and left underweight	
	• SCALES:	for 10 hours.	
	Blue acrylic Schmincke paint layer		



2b	 BACKGROUND LAYER: Concrete mortar, with a 3:1 sand- cement rate. BASE PAITING LAYER: Red alkyd spray MTN94[®] SCALES: Red acrylic Schmincke paint layer 	PRIMAL B60A® IN WATER 15%, applied punctually with a syringe and left underweight for 10 hours.
2c	 BACKGROUND LAYER: Concrete mortar, with a 3:1 sand- cement rate. BASE PAITING LAYER: Red alkyd spray MTN94[®] SCALES: Red acrylic Schmincke paint layer 	PRIMAL B60A® IN WATER 40%, applied punctually with a syringe and left underweight for 10 hours.
2d	 BACKGROUND LAYER: Concrete mortar, with a 3:1 sand- cement rate. BASE PAITING LAYER: Red alkyd spray MTN94[®] SCALES: Red acrylic Schminke paint layer 	E411[®] IN WATER 3%, applied punctually with a syringe and left underweight for 10 hours.
2e	 BACKGROUND LAYER: Concrete mortar, with a 3:1 sand- cement rate. BASE PAITING LAYER: Red alkyd spray MTN94[®] SCALES: Red acrylic Schmincke paint layer 	E411[®] IN WATER 15%, applied punctually with a syringe and left underweight for 10 hours.
2f	 BACKGROUND LAYER: Concrete mortar, with a 3:1 sand- cement rate. BASE PAITING LAYER: Red alkyd spray MTN94[®] SCALES: Red acrylic Schmincke paint layer 	E411[®] IN WATER 25%, applied punctually with a syringe and left underweight for 10 hours.
2g	 BACKGROUND LAYER: Concrete mortar, with a 3:1 sand- cement rate. BASE PAITING LAYER: Red alkyd spray MTN94[®] SCALES: Red acrylic Schmincke paint layer 	MICROACRIL® IN WATER 5%, applied punctually with a syringe and left underweight for 10 hours.

2h	 BACKGROUND LAYER: Concrete mortar, with a 3:1 sand- cement rate. BASE PAITING LAYER: Red alkyd spray MTN94[®] SCALES: Red acrylic Schmincke paint layer 	MICROACRIL [®] IN WATER 15%, applied punctually with a syringe and left underweight for 10 hours.
2i	 BACKGROUND LAYER: Concrete mortar, with a 3:1 sand- cement rate. BASE PAITING LAYER: Red alkyd spray MTN94[®] SCALES: Red acrylic Schmincke paint layer 	MICROACRIL [®] IN WATER 30%, applied punctually with a syringe and left underweight for 10 hours.

MOCK-UP 3		
	3c 3b 3a	
# mock-up	Stratigraphy	Consolidation test
За	 BACKGROUND LAYER: Concrete mortar, with a 15:1 sand- cement rate. FIRST PAITING LAYER: Blue acrylic Schmincke paint SECOND PAINTING LAYER: Red alkyd-nitrocellulose Belton spray 	PRIMAL B60A® IN WATER 40%, applied punctually with a syringe and left underweight for 10 hours.
3b	 BACKGROUND LAYER: Concrete mortar, with a 15:1 sand- cement rate. FIRST PAITING LAYER: Blue acrylic Schmincke paint SECOND PAINTING LAYER: Red alkyd-nitrocellulose Belton spray 	E411[®] IN WATER 25%, applied punctually with a syringe and left underweight for 10 hours.
3c	 BACKGROUND LAYER: Concrete mortar, with a 1:3 sand- cement rate. 	MICROACRIL [®] IN WATER 30%, applied punctually with a

BASE PAITING LAYER:	syringe and left underweight
Red alkyd spray MTN94 [®]	for 10 hours.
• SCALES:	
Red acrylic Schmincke paint layer	

	MOCK-UP 4	
	4a	4c
	4a 1 1 1 1 4b	4d
# mock-up	Stratigraphy	Consolidation test
4a	BACKGROUND LAYER: Concrete mortar, with a 15:1 sand- cement rate.	E411[®] in water 25%, applied by brush
4b	 BACKGROUND LAYER: Concrete mortar, with a 15:1 sand- cement rate. 	Preconsolidation with K52 [®] 3% in a alcohol/water solution (1/1) + E411 [®] in water 25%, applied by brush
4c	 BACKGROUND LAYER: Concrete mortar, with a 15:1 sand- cement rate. 	PRIMAL B60A [®] in water 40%, applied by brush
4d	 BACKGROUND LAYER: Concrete mortar, with a 15:1 sand- cement rate. 	Preconsolidation with K52 [®] 3% in a alcohol/water solution (1/1) + PRIMAL B60A [®] in water 40%, applied by brush

4.1.2 What were the results of the optical and analytical observation of the different consolidation methods on the *ad hoc* samples? How did you get the results?

Sample number	1a	
Aim	Adhesion of cement/alkyd scales on a concrete background.	
Cement+Alkyd scale Adhesive Concrete back-ground		
Consolidation test Optical results & general observations		Optical results & general observations
		Not effective. Probably because of the excessively irregular surface of the cement/alkyd scales, any adhesion has been obtained.

Sample number	1b	
Aim	Adhesion of cement/alkyd scales on a concrete background.	
Cement+Alkyd scale Adhesive Concrete back-ground		
Consolidation test	Optical results & general observations	
PRIMAL B60A [®] IN	PRIMAL B60A® IN WATER 15% Not effective. Probably because of the excessively irregular surface of the cement/alkyd scales, scarce adhesion has been obtained.	

Sample number	1c
Aim	Adhesion of cement/alkyd scales on a concrete background.
Cement+Alkyd scale Adhesive Concrete back-ground	
Consolidation test	Optical results & general observations
PRIMAL B60A [®] IN WATER 40% irregular surface of the cement/alkyd scales, littl adhesion has been obtained.	

Sample number	1d	
Aim	Adhesion of cement/alkyd scales on a concrete background.	
Cement+Alkyd scale Adhesive Concrete back-ground		
Consolidation test	Optical results & general observations	
E411 [®] IN WATER 3% irregular surface of the cement/alkyd scales, any ad has been obtained.		

Sample number	1e
Aim	Adhesion of cement/alkyd scales on a concrete background.
Cement+Alkyd scale Adhesive Concrete back-ground	
Consolidation test Optical results & general observations	
E411 [®] IN WATER 15% Not effective. Probably because of the excessive irregular surface of the cement/alkyd scales, any adh has been obtained.	

Sample number	1f
Aim	Adhesion of cement/alkyd scales on a concrete background.
Cement+Alkyd scale Adhesive Concrete back-ground	
Consolidation test	Optical results & general observations
E411® IN WA ⁻	Not effective. Probably because of the excessively irregular surface of the cement/alkyd scales, any adhesion has been obtained.

Sample number	1g	
Aim	Adhesion of cement/alkyd scales on a concrete background.	
Cement+Alkyd scale Adhesive Concrete back-ground		
Consolidation test	Consolidation test Optical results & general observations	
MICROACRIL® IN WATER 5% irregular surface of the cement/alkyd scales, any adh has been obtained.		

Sample number	1h	
Aim	Adhesion of cement/alkyd scales on a concrete background.	
Cement+Alkyd scale Adhesive Concrete back-ground		
Consolidation test	Optical results & general observations	
MICROACRIL® IN WATER 15% Not effective. Probably because of the excessively irregular surface of the cement/alkyd scales, any adhes has been obtained.		

Sample number	1i	
Aim	Adhesion of cement/alkyd scales on a concrete background.	
Cement+Alkyd scale Adhesive Concrete back-ground		
Consolidation test	Consolidation test Optical results & general observations	
MICROACRIL [®] IN	WATER 30% Not effective. Probably because of the excessively irregular surface of the cement/alkyd scales, any adhesic has been obtained.	

Sample number	1j	
Aim	Adhesion of acrylic scales on a concrete background.	
	Blue acrylic paint Adhesive	
Concrete back-ground		
Consolidation test		Optical results & general observations
PRIMAL B60A [®] IN WATER 5% Scarce adhesive power, no alterations in gloss or in t hue of the surface are visible.		Scarce adhesive power, no alterations in gloss or in the hue of the surface are visible.

Sample number	1k	
Aim	Adhesion of acrylic scales on a concrete background.	
	Blue acrylic paint Adhesive	
Concrete back-ground		ack-ground
Consolidation test		Optical results & general observations
PRIMAL B60A [®] IN WATER 15%		Good adhesive power, little alterations in gloss and in the hue of the surface are visible.

Sample number	11	
Aim	Adhesion of acrylic scales on a concrete background.	
Blue acrylic paint Adhesive		
Concrete back-ground		
Consolidation test Optical results & general observations		
PRIMAL B60A® IN	PRIMAL B60A [®] IN WATER 40% Strong adhesive power, alterations in gloss and in the h of the surface are visible.	

Sample number	1m	
Aim	Adhesion of acrylic scales on a concrete background.	
Blue acrylic paint Adhesive Concrete back-ground		
Consolidation test	Optical results & general observations	
E411 in WATER 3% Insufficient adhesive power, no alterations in g the hue of the surface are visible.		

Sample number	1n	
Aim	Adhesion of acrylic scales on a concrete background.	
Blue acrylic paint Adhesive Concrete back-ground		
Consolidation test Optical results & ger		Optical results & general observations
		Lousy adhesive power, no alterations in gloss or in the hue of the surface are visible.

Sample number	10	
Aim	Adhesion of acrylic scales on a concrete background.	
Blue acrylic paint Adhesive Concrete back-ground		
Consolidation test	Optical results & general observations	
E411 in WAT	ER 25% Good adhesive power, no alterations in gloss or in the hue of the surface are visible.	

Sample number	1p	
Aim	Adhesion of acrylic scales on a concrete background.	
Blue acrylic paint Adhesive Concrete back-ground		
Consolidation test Optical results & get		tical results & general observations
MICROACRIL in WATER 5%		sufficient adhesive power, no alterations in gloss or in the hue of the surface are visible.

Sample number	1q	
Aim	Adhesion of acrylic scales on a concrete background.	
Blue acrylic paint Adhesive Concrete back-ground		
Consolidation test Optical results & general observations		Optical results & general observations
MICROACRIL in WATER 15% Insufficient adhesive power, no alterations in gloss the hue of the surface are visible.		

Sample number	1r		
Aim	Adhesion of acryli	Adhesion of acrylic scales on a concrete background.	
Blue acrylic paint Adhesive Concrete back-ground			
Consolidation test Optical results & general observations		Optical results & general observations	
MICROACRIL in V	MICROACRIL in WATER 30% Scarce adhesive power, no alterations in gloss or hue of the surface are visible.		

Sample number	2a	
Aim	Adhesion of acrylic scales on an alkyd painted concrete background.	
Acrylic paint scale Adhesive Alkyd spray paint Concrete back-ground		
Consolidation test Optical results & general observations		
PRIMAL B60A in	WATER 5% Insufficient adhesive power, no alterations in gloss or in the hue of the surface are visible.	

Sample number	2b		
Aim	Adhesion of acryl	Adhesion of acrylic scales on an alkyd painted concrete background.	
Acrylic paint scale Adhesive Alkyd spray paint		esive	
Concrete back-ground		ack-ground	
Consolidation test		Optical results & general observations	
PRIMAL B60A in WATER 15%Good adhesive power, little alterations in glosshue of the surface are visible.		Good adhesive power, little alterations in gloss and in the hue of the surface are visible.	

Sample number	2c
Aim	Adhesion of acrylic scales on an alkyd painted concrete background.
Acrylic paint scale Adhesive Alkyd spray paint Concrete back-ground	
Consolidation test	Optical results & general observations
PRIMAL B60A in V	WATER 40% Strong adhesive power, little alterations in gloss and in the hue of the surface are visible.

Sample number	2d	
Aim	Adhesion of acrylic scales on an alkyd painted concrete background.	
Acrylic paint scale Adhesive Alkyd spray paint Concrete back-ground		
Consolidation test Optical results & general observations		
E411 in WA	Insufficient adhesive power, no alterations in gloss or in the hue of the surface are visible.	

Sample number	2e		
Aim	Adhesion of acrylic sc	Adhesion of acrylic scales on an alkyd painted concrete background.	
Acrylic paint scale Adhesive Alkyd spray paint Concrete back-ground			
Consolidation test	Consolidation test Optical results & ge		l observations
E411 in WATER 15% S		•	no alterations in gloss or in the surface are visible.

Sample number	2f		
Aim	Adhesion of acryl	Adhesion of acrylic scales on an alkyd painted concrete background.	
	Acrylic paint scale Adhesive Alkyd spray paint Concrete back-ground		
Consolidation test		Optical results & genera	lobservations
E411 in WATER 25%		-	alterations in gloss or in the hue face are visible.

Sample number	2g		
Aim	Adhesion of acryli	Adhesion of acrylic scales on an alkyd painted concrete background.	
Acrylic paint scale Adhesive Alkyd spray paint Concrete back-ground			
Consolidation test Optical results & general observations		l observations	
MICROACRIL in WATER 5%		concrete background. The	ne adhesive solution into the adhesive power is not sufficient ale adhesion.

Sample number	2h		
Aim	Adhesion of acryl	Adhesion of acrylic scales on a alkyd painted concrete background.	
Alkyd spra			
	Concrete back-ground		
Consolidation test		Optical results & genera	l observations
MICROACRIL in WATER 15%		concrete background. The	e adhesive solution into the adhesive power is not sufficient le adhesion.

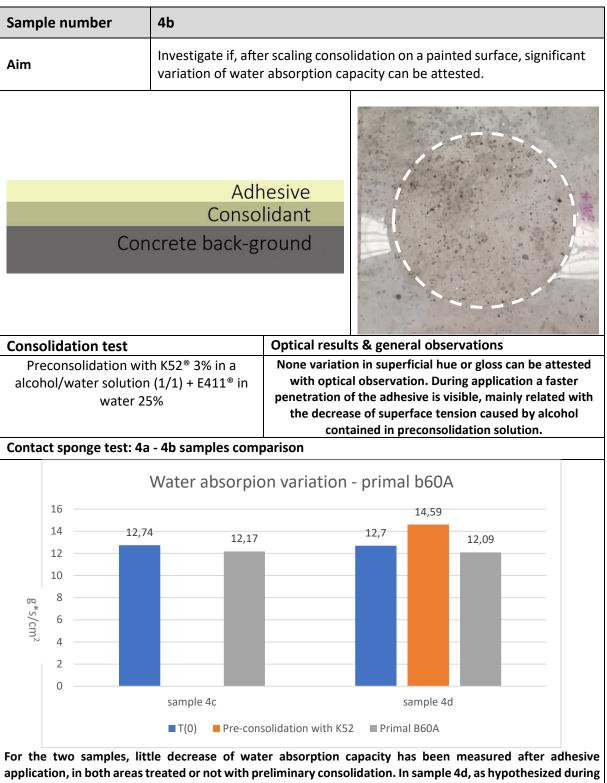
Sample number	2i	
Aim	Adhesion of acrylic scales on an alkyd painted concrete background.	
Acrylic paint scale Adhesive Alkyd spray paint Concrete back-ground		
Consolidation test	Optical results & general observations	
MICROACRIL in V	VATER 30% High penetration of the adhesive solution into the concrete background. The adhesive power is barely sufficient for scale adhesion.	

Sample number	3a	
Aim	Consolidation of painting layer affected by flaking decay.	
adhesive	Alkyd paint Acrylic paint ete back-ground	
Consolidation test	Optical results & general observations	
PRIMAL B60A in V	VATER 30% Good adhesive power (scales remain attached to the background after being treated); little alteration in the superficial gloss is visible.	

Sample number	3b		
Aim	Consolidation of painting layer affected by flaking decay.		
adhesive	Alkyd pain Acrylic paint ete back-groun		
Consolidation test	Optical results & general observations		
E411 in WAT	ER 25%	 Good adhesive power (scales remain attached to the background after being treated); no alterations in gloss or in the hue of the surface are visible. 	

Sample number	3c	
Aim	Consolidation of painting layer affected by flaking decay.	
adhesive Concr	Alkyd paint Acrylic paint ete back-ground	
Consolidation test	Optical results & general observations	
MICROACRIL in V	VATER 30% Low adhesive power but no alterations in gloss or in th hue of the surface are visible.	e

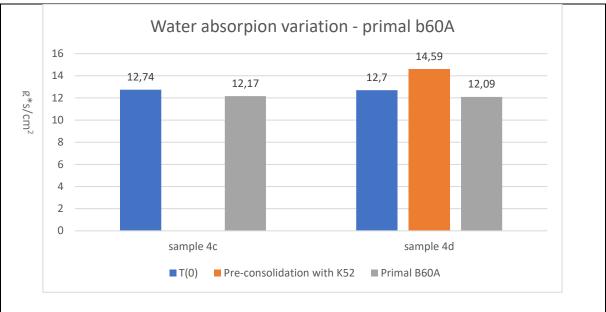
Sample number	4a	
Aim	Investigate if, after scaling consolidation on a painted surface, significant variation of water absorption capacity can be attested.	
	Adhesive	
Со	ncrete back-ground	
Consolidation test	Optical results & general observations	
E411 in wate	er 25% None variation in superficial hue or gloss can be attested with optical observation.	



application, in both areas treated or not with preliminary consolidation. In sample 4d, as hypothesized during application, the alcohol act as a carrier for water penetration in the concrete substrate, resulting in a temporary increase of water absorption.

Sample number	4c	
Aim	Investigate if, after scaling consolidation on a painted surface, significant variation of water absorption capacity can be attested.	
	Adhesive	e
Concrete back-ground		ground
Consolidation test	Optical results & general observations	
PRIMAL B60A® in	in water 40% None variation in superficial hue or gloss can be attes with optical observation.	

Sample number	4d			
Aim		Investigate if, after scaling consolidation on a painted surface, significant variation of water absorption capacity can be attested.		
Adhesive Consolidant Concrete back-ground				
Consolidation test		Optical results & general observations		
Preconsolidation with K52 [®] 3% in a alcohol/water solution (1/1) + PRIMAL B60A [®] in water 40%		None variation in superficial hue or gloss can be attested with optical observation. During application a faster penetration of the adhesive is visible, mainly related with the decrease of surface tension caused by alcohol contained in preconsolidation solution.		
Contact sponge test: 4c – 4d samples comparison				



For the two samples, little decrease of water absorption capacity has been measured after adhesive application, in both areas treated or not with preliminary consolidation. In sample 4d, as hypothesized during application, the alcohol act as a carrier for water penetration in the concrete substrate, resulting in a temporary increase of water absorption.

4.1.3 Which of the applied consoidation methods were most effective? Why? What was your criteria for the evaluation?

After optical observations of the different surfaces reproduced by the mock-ups, E411 in water (25% solution) and Primal B60A in water (40%) resulted to be the most effective products, relating to, totally and partially detached, scales readhesion. Nevertheless, tests with Primal B60A showed mild to moderate alterations in the hue and in superficial gloss, in relation with the absorption properties of the background. Conversely, E411, characterised by smaller polymers and specifically formulated for matt surfaces, showed no significant variation in the optical properties of the surfaces, even if a little lower adhesive power has been observed.

Relating to the variation of water absorption, both the adhesives tested resulted to be responsible for little decrease of hydrophily of unpainted concrete background; the preliminary consolidation seemed to temporarily increase water penetration, most likely because of the alcohol contained in the solution of the consolidantion product. In any case, this variation ceased after the application of the adhesive, which, as seen, always caused a reduction in the amount of water absorbed by the substrate.

4.1.4 Was it possible to transfer the methods/products on the objects on-site? If not, what has been different? Are there indications of a trend whether or not the behaviour of the product/method is the same on-site as under laboratory conditions? If not, what has been different?

Both primal B60 A in 30% water solution and E411 25% in water solution have been tested for scaling readhesion on Thyssen mural. The first, despite a stronger adhesive power, on site was found to be

[Hier eingeben]

responsible for localised increase of superficial glossy and hue saturation. Therefore, further application focussed on E411 solutions, found to be more respectful toward the painted surface; in these perspective, the main critical aspect was related with the low viscosity of the solution, often resulting in an excessive penetration into the concrete background. In order to mitigate this problem, a cellulose polymer (Klucel G) has been added to E411 solution with good results in term of adhesive capacity and solution lower penetration.



Fig. 1: Adhesion tests on site, showing the different behaviour of E411 and Primal B60A solutions.

4.1.5 How is the monitoring of the objects planned on-site?

No monitoring of the objects has been planned so far, except for close-up photographic documentation of all the consolidated areas. During summer 2020 internship activities, all the treated areas will be investigated in order to check whether, after one year time, superficial alterations or lacks in adhesion might be detected.

4.1.6 Comments or short conclusion.

On the basis of the preliminary survey on the artworks selected by UniTO-CCR team, scaling and flaking resulted to be among the most widespread and significant decay phenomena visible on outdoor contemporary urban murals. Therefore, specific tests have been set up to evaluate and compare different methodologies and products for on site intervention. Three adhesives and one consolidant have been tested on various substrate, specifically realised to simulate the different possibilities of

scaling and flaking showed by the artworks analysed. Preliminary results, based on optical observations of both adhesive power and lack of modification of the optical properties of the substrates, showed adequate effectiveness of two products, that have been therefore, used for further tests on Thyssen mural, showing good results. In particular, little differences in the absorption properties of the substrates has been showed in the case of study, resulting in a lower penetration of Primal B60A solution. This seemed to be the cause for significant variation in the saturation of the painted areas treated with Primal B60A solutions, that have been therefore excluded.

Conversely, E411 solution resulted to have a highest penetration rate into the mural background, causing a significant decrease of the adhesive power of the product. Consequently, addition of cellulose ethers to the E411 solution has been considered to reduce solution penetration and increase adhesive power with great results.

4.2 Acadamy of Fine Arts Warsaw (Poland)

NUMBER OF PARTNER	COUNTRY	NUMBER OF OBJECTS	NUMBER OF SAMPLES
P7	Poland	Object 1	
		Object 2 (2d, 2g, 2m)	

4.2.1 Information on tested consolidation methods carried out on mock up samples within the companies/research centres and on-site based on the selected sculptures (output wp2 and wp3)

Describe your experimental setup, including details on sample preparation, instruments and experimental conditions used. Take into account to name the object number and sample identification.

All consolidation tests were carried out on two objects: *Szczudlarze* by Linas Domarackas on the tenement house at 37 Stalowa Street in Warsaw, and on a set of 24 murals by various authors on Mur Sztuki [Wall of Art] in Ogród Różany [Rose Garden] of the Warsaw Uprising Museum.

The tests were carried out directly on the murals in situ. It was decided that it is best to carry out the tests on the objects and not on specially created samples under laboratory conditions. It gave us the opportunity to test methods of consolidation of different paint layers and plasters.

Consolidation treatment tests were performed on:

- Szczudlarze (Object 1): Plaster - lime mortar, lime and cement mortar with quartz filler; black charcoal Paint layer: acrylic and vinyl paints
- Wall of Art (Object 2): Plaster - lime mortar with quartz filler Paint layer: acrylic, polyester, phthalic, vinyl, and tempera paints List 3 murals from the Wall of Art in the Uprising Museum: 2d – mural by Stasys 2g – mural by Utz
 - 2m mural by Galeria Rusz

4.2.2 What are the results of the different consolidation methods / products on the ad hoc samples? (table) How did you get the results?

Object- number	Sample- number	Product- number	Tests*	Analytical Results	Optical Results
Object 1	Not applicable, the tests	Primal AC33	5% concentration in water with added alcohol	Not applicable	Good effect, properly adhered the paint layer to the plaster. In some

	were carried out on the object				cases the product turned out to be ineffective.
	Not applicable, the tests were carried out on the object	Ammonia casein	concentration 2-3% in H2O with the addition of alcohol	Not applicable	Very good effect, properly adhered the paint layer to the plaster. It worked in places where Primal AC33 failed.
	Not applicable, the tests were carried out on the object	Ledan (3 types of Kremer products)	concentration in water 1:1 Material introduction by injection	Not applicable	Very good effect. Good adhesion of the plaster layer to the brick substrate.
	Not applicable, the tests were carried out on the object	PLM-A with H2O	concentration in water 1:1 Material introduction by injection	Not applicable	Good effect. Good adhesion of the plaster layer to the brick substrate.
Object 2d (Stasys)	Not applicable, the tests were carried out on the object	none	none	Not applicable	none
Object 2g (Utz) a (Utz) t v c c	Not applicable, the tests were carried out on the object	Primal AC33	5% concentration in water with added alcohol	Not applicable	Good effect, properly adhered the paint layer to the plaster. In some cases the product turned out to be ineffective.
	Not applicable, the tests were carried out on the object	Ledan (3 types of Kremer products)	concentration in water 1:1 Material introduction by injection	Not applicable	Very good effect. Good adhesion of the plaster layer to the brick substrate.
	Not applicable, the tests were carried out on the object	PLM-A with H2O	concentration in water 1:1 Material introduction by injection	Not applicable	Good effect. Good adhesion of the plaster layer to the brick substrate.
Object 2m (Galeria Rusz)	Not applicable, the tests were carried out on the object	Primal AC33	5% concentration in water with added alcohol	Not applicable	Good effect, properly adhered the zinc white layer and paint layer to the plaster.

* Please specify the work and tests you have done. The table is only a tool for organizing the results. Feel free to choose another form to present your results.

4.2.3 Which of the applied consolidation methods/products were most effective? (best consolidation quality, best aesthetic appearance,...test winner) Why? What was your criteria for the evaluation?

The effects of consolidation by means of the above methods depended on the type of object (its condition and the technique used to create it). Each object can react differently to each of the above methods. Ledan gave good results of adhering plasters to the brick substrate. Slightly worse results were obtained with PLM-A. In the case of delamination of the paint layer from the substrate, good results were obtained by gluing with Primal AC33 and in the case of the Studel wall mural, ammoniacal casein, because these are proven products with a long tradition of use and do not adversely affect the paint layer. Ammonia casein proved to be especially effective in the case of the *Szczudlarze* mural, where the paint layer with the top layer of plaster was detached from the substrate.

4.2.4 Was it possible to transfer the methods/products on the objects on-site? If not, what has been different? Are there indications of a trend wether or not the behaviour of the product/method is the same on-site as **under laboratory conditions**? If not, what has been different?

All tests were carried out on site, on the object.

4.2.5 How is monitoring of the objects planned on-site?

Photographic documentation was made before and after consolidation. The objects will be monitored this year.

4.2.6 What were the benefits of the students and staff mobility?

Students from Cologne could not come to Warsaw in 2019. An internship is planned in June 2020.

4.2.7 Deviation of the work plan.

Not applicable

4.2.8 Problems encountered and implemented or proposed solutions.

Difficulties associated with carrying out tests in the open air in the summer – the murals were exposed to strong sunlight, high temperatures, and wind during the application of the products.

4.2.9 Comments or short conclusion.

Consolidation methods should be selected individually for each mural, according to the technique used to create the mural, its condition, and the external conditions in the area where it is located.