

# Nanostructured coatings for the protection of textiles and paper

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**Abstract:** Conservation environment with high humidity content or exposure to liquid water are directly linked to degradation of cellulosic materials, such as paper and fabrics. This research had as main objective the development of formulations based on two water-repellent products commercially available: a fluoroacrylic co-polymer and a polydimethylsiloxane. The purpose was to test their applicability to paper and textiles, both ancient and modern. Different analytical techniques have been used: FTIR-ATR spectroscopy, colorimetric analysis, observations by SEM-EDX and light microscopy, contact angle measurement and mechanical strength. Applications were carried out by spray and immersion achieving a systematization of the method and the choice of non-toxic solvents. Two of the four formulations tested were prepared with the addition also of silica nanoparticles. The results highlighted the compatibility and effectiveness of fluoroacrylic polymer with low nanosilica percentages applied by immersion.

**Key words:** textiles, paper, water repellence, protectives, coatings.

## Revestimientos nanoestructurados para la protección de tejidos y papel

**Resumen:** Altos porcentajes de humedad o el contacto con el agua son las mayores causas de deterioro de los materiales celulósicos, como papel y tejidos. El objetivo principal de esta investigación es el desarrollo de film protectores en función de dos productos comerciales hidrófugos: un fluoruro de copolímero acrílico y un polidimetilsiloxano con la adición de nano-sílice. La finalidad es verificar la aplicabilidad sobre papeles y tejidos tanto antiguos como contemporáneos. Se han utilizado distintas técnicas analíticas: espectrofotómetro de infrarrojo FTIR con ATR, análisis colorimétrico, observación con microscopía óptica y electrónica, medida del ángulo de contacto y de la resistencia mecánica. Los productos se han aplicado por medio de spray o inmersión con adecuada sistematización del método y elección de disolventes a bajatotoxicidad. Los resultados demuestran una buena compatibilidad y eficiencia de los productos fluoroacrilicos a bajo porcentaje de nano-sílice de inmersión.

**Palabras clave:** tejidos, papel, hidrorrepelencia, protectores, recubrimientos.

## Introduction

High humidity or direct contact with water are the principal causes of degradation for cellulosic materials, as textiles and paper. Acid and basic hydrolysis are, in fact, promoted in presence of water, involving the breakage of the glycosidic bonds and resulting in deterioration of cellulose. Fibres swelling is another consequence of water exposure, which causes internal tensions. In addition, high relative humidity environments may promote also the development of microorganisms such as mildew and bacteria (Eastop and Timar-Balazsi 1998; Roberts 2006).

According to literature, many hydrophobic coatings have been proposed to protect textiles and paper from

the action of water and several researches have been undertaken to find effective formulations. Carboxylate-alumoxanes sol-gel (Kiuberis and Tautkus 2005), titanium dioxide nanoparticles (Daoud et al 2005), modified copolymer lattices (Samyn et al. 2010) are only few examples among the many products proposed for the conservation of historical cellulosic materials.

In this research, four encouraging formulations based on water-repellent products present on the market were tested. The purpose was to examine their applicability for the conservation of specific cellulose substrates (paper and textiles) taking into consideration that in the field of Cultural Heritage conservation some necessary requirements have to be met, such as physico-chemical

and aesthetical compatibility of the treatments with the substrates (Pertegato 1993; Lorusso 1996). Four formulations have been investigated. Three of them were made of fluoroacrylic co-polymer diluted in ethanol, eventually added with hydrophobic silica nanoparticles; the fourth was based on a polydimethylsiloxane diluted in ethyl-acetate.

## Methods & methodology

Cellulosic samples used during the experimentation were three types of paper and four textiles. They are described in detail in [table 1].

Four distinct formulations were developed to be applied on the samples; they are also illustrated in [table 1]. Considering environmental impact and consumers' health, two solvents were chosen for their low toxicity: ethanol and ethyl-acetate.

Aiming at comparing well-founded methods used so soon for textile and book preservation, both spray and immersion were performed to apply the formulations (Mazzon et al. , in press). A constant volume of 8ml of each formulation was sprayed with an airbrush on a set of 3 replicates of each substrate (5x5cm<sup>2</sup>), 4ml on one side and the rest on the other side. T4 and T5 specimens were sprayed only on the side which did not present the preparation layer. Immersion treatment implied the dipping of each sample for 30 seconds; the solution was replaced every six samples. Both the application methods foresaw a two-hour-curing phase at 60°C.

Aging tests were carried out to check the formulation stability. After being treated, a selection of specimens underwent artificial ageing. The test was performed by using solar lamps (500 hours at circa 8500 lux, 280-400nm) to monitor eventual polymer degradation.

To estimate the treatments' efficacy, specimens were examined by visual observation, optical and electron microscopy (DINO-Light Digital microscope; SEM JEOL JSM-6490LA), colorimetric analysis (Konika Minolta CM-2600d) (Feller 2001) and spectroscopic analysis (Thermo Nicolet FTIR with ATR Nicolet Nexus Smart Orbit, 4cm<sup>-1</sup> resolution, 64 scans, 4000-400cm<sup>-1</sup>). Physical properties' changes were estimated by wettability measurements (static contact angle by a Dataphysics Contact Angle System OCA15EC) and tensile strength assessment (Maximum Load and Young's Modulus values by uniaxial tensile tests on dog bone-shaped samples of 25mm length with an Instron3365 dual column extensimeter). In particular, the determination of the Maximum Load provides a measure of the force necessary to break the specimens. Young's Modulus measures, instead, the specimens' deformation, providing information on stiffness or flexibility: higher Young's Moduli correspond to higher stiffness. Hygroscoy behaviour was studied (NORMAL ISO 12571:2013) to analyse the moist retention capability of the fibres in different humidity conditions (RH 60% and 80%), while water vapour permeability (DIN52615, 1987) helped to establish whether permeability of samples was altered by treatments and whether a continuous moist-blocking film was present on the surfaces of treated samples.

**Table 1.-** Presentation of samples and formulations used during the research. Brief description and details are also reported.

Sample name	Description	Details
C1	Printed book paper "Del diritto internazionale. Lezioni"	Year: 1876 Bulk: 84.56gsm
C2	Printed book paper "Commentario del Codice e delle leggi di procedura civile"	Year: 1923 Bulk: 93.6gsm
C3	Common white printing paper	Year: 2015 Bulk: 76.12gsm
T3	Cellulosic row canvas	Threads/cm: 9
T4	Painting canvas covered with red handmade preparation layer	Threads/cm: 9
T5	Painting canvas covered with white industrial preparation layer	Threads/cm: 21
T7	Blue Cotton textile	Threads/cm: 27
Formulation name	Description	
F1	Fluoroacrylic co-polymer at 5.00%w in ethanol	
F2	Fluoroacrylic co-polymer at 4.87% <sub>w</sub> mixed with 0.13% <sub>w</sub> of hydrophobic fumed silica nanoparticles (Aerosil® R812 – BET surface area: 260 ± 30m <sup>2</sup> /g), in ethanol	
F3	Fluoroacrylic co-polymer at 4.87%w mixed with 0.13% <sub>w</sub> of hydrophobic fumed silica nanoparticles (Aerosil® R812 – BET surface area: 260 ± 30m <sup>2</sup> /g), in ethanol	
F4	Polydimethylsiloxane (PDMS – Sylgard® 184 Silicone Elastomer) at 5.00%w in ethyl-acetate	

**Table 2.-** Colour change  $\Delta E^*$ , product applied  $\Delta M\%$ , Contact angle  $[\circ]$ , Vapour permeability  $[g/(s \cdot m^2)]$ , Young's Modulus  $[MPa]$ , Maximum Load  $[N]$ , Hygroscopy at 60% and 80% RH values recorded for (U) untreated samples, samples treated by (S) spray and samples treated by (I) immersion. Here are reported the data of T3, T4, T5 and T7 textiles and C1, C2 and C3 papers, treated with F1, F2, F3 and F4 formulations.

Samples	$\Delta E^*$		$\Delta M$ [%]		Contact angle $[\circ]$			Vapour permeability $[g/(s \cdot m^2)]$			Young's Modulus $[MPa]$			Maximum Load $[N]$			Hygroscopy 60% RH $[\Delta M\%]$			Hygroscopy 80% RH $[\Delta M\%]$			
	S	I	S	I	U	S	I	U	S	I	U	S	I	U	S	I	U	S	I	U	S	I	
T3	F1	2.6	5.9	10	8	0 $\pm 0$	143 $\pm 9$	143 $\pm 5$	582 $\pm 50$	522 $\pm 9$	606 $\pm 24$	464 $\pm 58$	397 $\pm 91$	371 $\pm 13$	107 $\pm 22$	94 $\pm 15$	111 $\pm 16$	1.2	0.7	1.5	4.9	4.5	5.3
	F2	2.6	5.0	7	12		140 $\pm 4$	140 $\pm 7$		481 $\pm 6$	566 $\pm 9$		377 $\pm 66$	324 $\pm 18$		92 $\pm 13$	105 $\pm 6$		0.6	0.5		4.0	4.3
	F3	3.8	7.0	15	13		139 $\pm 6$	140 $\pm 5$		478 $\pm 5$	558 $\pm 8$		356 $\pm 80$	339 $\pm 54$		96 $\pm 19$	111 $\pm 16$		0.6	1.0		4.5	5.1
	F4	5.7	3.9	5	6		136 $\pm 6$	142 $\pm 6$		503 $\pm 31$	577 $\pm 19$		230 $\pm 48$	255 $\pm 54$		25 $\pm 9$	43 $\pm 8$		0.9	1.2		4.8	4.7
T4	F1	2.8	4.0	2	2	131 $\pm 8$	132 $\pm 5$	134 $\pm 6$	341 $\pm 59$	279 $\pm 22$	238 $\pm 29$	188 $\pm 10$	195 $\pm 18$	113 $\pm 21$	34 $\pm 4$	29 $\pm 2$	44 $\pm 3$	0.3	0.3	0.5	2.0	2.0	2.2
	F2	3.5	2.0	2	2		133 $\pm 7$	131 $\pm 8$		284 $\pm 15$	244 $\pm 21$		136 $\pm 22$	216 $\pm 34$		36 $\pm 6$	37 $\pm 4$		0.1	0.5		1.8	2.2
	F3	9.4	8.8	5	2		122 $\pm 5$	124 $\pm 5$		268 $\pm 6$	229 $\pm 7$		140 $\pm 24$	134 $\pm 22$		37 $\pm 9$	33 $\pm 6$		0.2	0.5		2.1	2.5
	F4	8.7	9.5	1	1		129 $\pm 7$	137 $\pm 6$		307 $\pm 32$	283 $\pm 44$		120 $\pm 27$	179 $\pm 64$		32 $\pm 4$	33 $\pm 4$		0.6	0.3		2.1	1.9
T5	F1	1.0	1.4	7	5	129 $\pm 5$	143 $\pm 5$	136 $\pm 3$	288 $\pm 29$	253 $\pm 5$	261 $\pm 16$	196 $\pm 25$	161 $\pm 16$	173 $\pm 9$	41 $\pm 1$	45 $\pm 3$	47 $\pm 3$	1.1	0.5	1.2	4.2	3.5	4.2
	F2	2.1	1.5	9	6		136 $\pm 5$	140 $\pm 3$		261 $\pm 5$	236 $\pm 16$		157 $\pm 11$	151 $\pm 16$		41 $\pm 0$	41 $\pm 3$		0.6	0.2		3.8	3.1
	F3	3.9	1.3	17	5		132 $\pm 6$	140 $\pm 4$		254 $\pm 2$	223 $\pm 6$		167 $\pm 6$	174 $\pm 8$		45 $\pm 2$	45 $\pm 3$		0.4	1.2		3.6	4.4
	F4	2.9	2.4	9	2		143 $\pm 4$	147 $\pm 4$		241 $\pm 23$	306 $\pm 20$		191 $\pm 10$	173 $\pm 32$		39 $\pm 1$	39 $\pm 7$		0.6	0.9		3.8	4.2
T7	F1	2.5	10.7	16	10	0 $\pm 0$	127 $\pm 8$	130 $\pm 8$	600 $\pm 48$	543 $\pm 9$	519 $\pm 36$	564 $\pm 34$	389 $\pm 55$	429 $\pm 61$	39 $\pm 6$	43 $\pm 5$	43 $\pm 3$	1.3	0.5	1.2	6.1	4.4	4.9
	F2	3.6	3.3	24	11		131 $\pm 8$	137 $\pm 6$		529 $\pm 5$	489 $\pm 7$		418 $\pm 85$	388 $\pm 50$		45 $\pm 5$	44 $\pm 5$		0.5	0.5		3.7	4.1
	F3	9.4	8.9	35	12		133 $\pm 10$	140 $\pm 7$		523 $\pm 5$	483 $\pm 11$		363 $\pm 28$	420 $\pm 50$		42 $\pm 4$	46 $\pm 3$		0.4	1.4		4.3	5.2
	F4	24.0	8.0	14	7		138 $\pm 7$	138 $\pm 6$		533 $\pm 15$	510 $\pm 32$		362 $\pm 37$	466 $\pm 32$		29 $\pm 4$	36 $\pm 2$		0.8	1.2		4.5	5.0
C1	F1	4.8	1.3	30	11	129 $\pm 6$	126 $\pm 2$	126 $\pm 6$	578 $\pm 17$	284 $\pm 19$	403 $\pm 37$	713 $\pm 83$	1679 $\pm 236$	1378 $\pm 74$	2.0 $\pm 0.1$	7 $\pm 2$	5 $\pm 3$	0.7	0.5	0.5	2.8	3.0	3.2
	F2	0.9	3.2	39	10		122 $\pm 5$	128 $\pm 3$		315 $\pm 48$	482 $\pm 24$		5701 $\pm 69$	87 $\pm 0.2$		3 $\pm 1$	1 $\pm 1$		0.6	0.9		3.1	3.5
	F3	2.1	2.3	45	12		133 $\pm 5$	137 $\pm 6$		488 $\pm 39$	492 $\pm 49$		389 $\pm 23$	527 $\pm 44$		3 $\pm 0.1$	3 $\pm 1$		0.7	0.5		3.2	3.0
	F4	13.1	5.9	22	6		138 $\pm 2$	138 $\pm 2$		358 $\pm 32$	504 $\pm 13$		704 $\pm 62$	1082 $\pm 254$		4 $\pm 0.1$	5 $\pm 1$		0.2	0.6		2.3	2.5
C2	F1	3.4	1.6	24	7	122 $\pm 4$	117 $\pm 2$	123 $\pm 9$	496 $\pm 30$	229 $\pm 6$	318 $\pm 19$	1452 $\pm 97$	1146 $\pm 134$	1490 $\pm 99$	4 $\pm 1$	4 $\pm 1$	6 $\pm 1$	0.6	0.7	0.6	2.9	3.5	3.3
	F2	1.7	1.1	27	7		122 $\pm 2$	119 $\pm 2$		256 $\pm 17$	352 $\pm 7$		1280 $\pm 162$	1228 $\pm 90$		8 $\pm 1$	7 $\pm 0.1$		0.8	1.0		3.4	3.8
	F3	1.6	0.9	30	8		132 $\pm 4$	127 $\pm 7$		406 $\pm 21$	370 $\pm 10$		1359 $\pm 199$	1067 $\pm 23$		9 $\pm 3$	6 $\pm 0.1$		0.7	0.5		3.1	3.3
	F4	15.8	3.1	23	4		129 $\pm 2$	132 $\pm 2$		212 $\pm 19$	441 $\pm 3$		2949 $\pm 238$	1509 $\pm 89$		14 $\pm 0.1$	6 $\pm 0.1$		0.3	0.7		2.5	3.2
C3	F1	1.5	0.7	31	11	83 $\pm 12$	119 $\pm 3$	128 $\pm 3$	552 $\pm 15$	302 $\pm 1$	423 $\pm 19$	808 $\pm 156$	987 $\pm 155$	2531 $\pm 192$	5.0 $\pm 0.1$	6.0 $\pm 0.1$	14.0 $\pm 0.1$	0.9	0.9	0.5	4.6	4.8	4.2
	F2	1.2	0.6	32	10		122 $\pm 3$	126 $\pm 4$		408 $\pm 17$	437 $\pm 17$		669 $\pm 35$	2030 $\pm 85$		6.0 $\pm 0.1$	15 $\pm 2$		0.7	1.0		4.0	4.3
	F3	1.5	0.5	35	11		136 $\pm 3$	135 $\pm 6$		471 $\pm 23$	463 $\pm 22$		596 $\pm 91$	1952 $\pm 331$		5.0 $\pm 0.1$	13 $\pm 2$		0.8	0.6		4.2	4.1
	F4	4.8	1.6	29	6		133 $\pm 2$	135 $\pm 2$		383 $\pm 23$	520 $\pm 16$		1102 $\pm 113$	3318 $\pm 229$		5.0 $\pm 0.1$	15 $\pm 1$		0.4	0.9		3.6	4.7

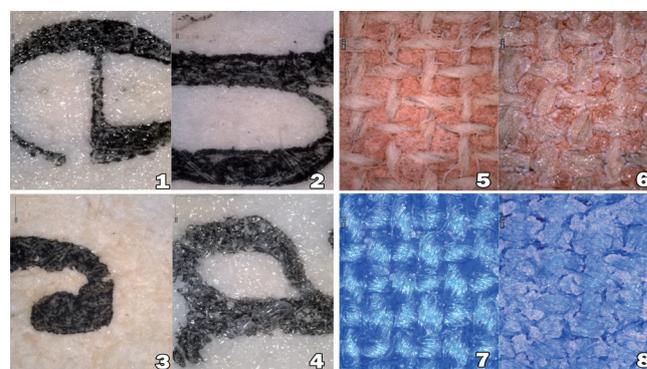
**Results & discussion**

A selection of data is reported in [table 2], in order to easily compare the results obtained.

The overall percentage mass variation due to the products deposition range between  $1\% < \Delta m < 45\%$ . Despite the use of formulation at similar concentrations and preliminary trials conducted to ensure a similar deposition of products on the systems, spray and immersion methods did not reach the same quantity of products deposited. In particular, spray application often entailed slightly higher weight variations than immersion; this could be due to a partial evaporation/ loss of solvent during spraying and the deposition of a more concentrated product.

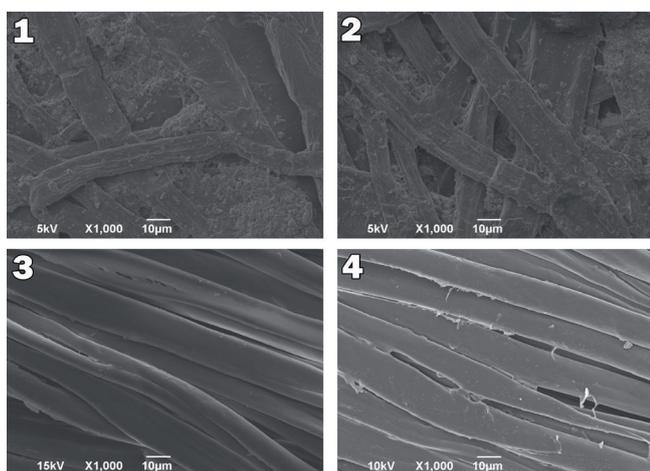
Generally, all the formulations caused an alteration to the appearance and colour variation of the surfaces, both when applied by spray and by immersion. Especially formulations F2 and F3, admixed respectively with  $0.13\%_w$  and  $0.25\%_w$  of nanosilica, caused white depositions; this phenomenon is clearly visible through digital microscope observations [figure 1]. The whitening observed when using F1, F2 or F3 is proportional to the quantity of nanosilica present in the

formulation. This was evident in particular for the treatment F3, with a larger quantity of nanosilica, while F1 formulation always resulted in lower  $\Delta E$  variation. Generally, a substantial  $\Delta E$  variation resulted from F4 treatments, applied both by spray and immersion, primarily due to changes in colour lightness ( $-15.41 < \Delta L < -0.41$ ).



**Figure 1.-** Dino-Light microscope investigation of C2 substrates treated by spray with (1) F1 and (2) F2 formulations. C1 substrates treated with F3 formulation by (3) immersion and by (4) spray. T4 substrates treated by spray with (5) F2 and (6) F3 formulations. T7 substrates treated with F3 formulation by (7) immersion and by (8) spray.

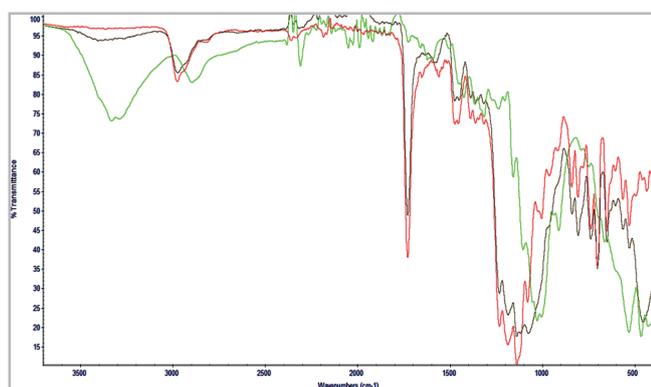
SEM analysis of white paper (C3) and all textiles treated with formulation F3 highlighted that nanoparticles sprayed on the surface formed a fragile film, which tended to crack, possibly due to a partial lack of solvent (loss during spraying) and deposition of agglomerated polymer particle. Immersion application, instead, allowed to obtain treated samples with a morphology similar to the untreated ones [figure 2] by homogeneously covering each fibre.



**Figure 2.-** SEM images of (1) untreated C3 paper, (2) the same C3 substrate treated by immersion with F1 formulation; (3) untreated textile T7 substrate, (4) the same T7 substrate treated by immersion with F1 formulation, Photographer: Simone Lauciello, IIT institute.

FTIR-ATR analysis was performed in order to evaluate possible reaction between substrates and products. The spectra showed the superimposition of characteristic absorption peaks of the cellulose specimens and of the formulations, without the presence of any extra-peak attributable to chemical reaction between substrates and products [figure 3].

Furthermore, the high contact angle values (between 115° and 147°), measured in order to test wettability, proved that each product contribute to reach excellent water-repellent



**Figure 3.-** FTIR-ATR spectra of (red) F1 formulation, (green) cellulosic substrate, (grey) cellulosic substrate treated with F1.

properties and decrease surface wettability; besides, the addition of nanosilica enhanced the water-repellence of the samples, especially on paper substrates. Treated samples probably present a nano-roughness causing the "lotus effect": the water drops tended to become spherical and to roll off even at low inclinations.

The Water Vapour Permeability (WVP) was not particularly affected by the application method chosen to treat textile samples, while immersion treatment lent paper samples a WVP closer to the untreated specimens in comparison to spray. Moderate WVP variations (around 15-20% for textiles and 20-30% for papers) were observed with the exception of spraying F1, F2 and F3 on specimen C2: WVP reductions between 30% and 60% were measured. WVP values close to the original ones suggested a homogeneous distribution of the products on each fibre with the formation of a thin and flexible coating structure without obstructing the natural pores between fibres and threads.

Hygroscopic tests, conducted at 60% or 80% RH, showed no significant weight growth of cellulose treated samples in comparison to the untreated samples, maintaining similar water retention properties and guaranteeing products compatibility. Treatments did not modify the process of samples to get into equilibrium with water vapour and this is a positive result, since the substrate was free to absorb and, most important, to release water vapour. A slight decrease in water vapour absorption may be an advantage to limit biological degradation and deterioration linked to hydrolysis.

As for paper specimens, mechanical tests demonstrated that treated samples generally gave analogous results for all formulations: higher values of Young's Modulus and slightly higher Maximum Load values indicating the formation of resistant but stiffer materials. It is important, however, to underline the high variability of Maximum Load values obtained for formulation F4, depending on the type of treated paper.

Instead, the textiles, after each treatment, always presented Young's Modulus decrease resulting in lower stiffness and probably a more flexible substrate; the Maximum Load remains similar. High standard deviations were measured probably due to intrinsic structural differences of the substrates.

After artificial ageing (500 hours at circa 8500 lux), the treated samples did not show any significant variation in wettability and chemical composition, as testified by contact angles and FTIR-ATR analysis. In fact, no new FT-IR peak related to functional groups were detected, even though signals already present before ageing seemed to show minimal intensity variations. This could be possibly due to minor breakage or the formation of new bonds, not easily quantifiable with this technique. After the exposure under UV light, colour measurements of treated surfaces were carried out together with measurements on untreated ones (used as reference). In [table 3] the mere contribution of UV radiation can be observed by comparing colour changes ( $\Delta E^*$ ), calculated with data collected before and after ageing,

of both untreated and treated specimens. As visible in [table 3], both yellowing of the treated and untreated specimens occurred, pointing out similar or even higher colour variation for the untreated ones. Due to their transparency, coating films did not entirely stop the UV radiations, resulting in a partial yellowing of the substrate. However, the yellowing observed on untreated specimens resulted slightly higher than on treated ones, thus suggesting the stability of the coatings under lamps radiation and a slight protection effect of the polymeric films with regards to UV radiation.

Positive results have been registered for contact angle on treated surfaces even after artificial ageing [table 3]. All values were higher than 90°, proving that UV radiations did not affect the water-repellence of the treatments. Slight decreases were generally observed for all the specimens, but water-repellence was definitely maintained.

## Conclusions

Restoration products must follow precise requirements of chemical and physical compatibility with Cultural Heritage objects. This could be assessed by measuring, after the application, differences in colour, WVP, hygroscopicity, mechanical strength and through ageing test.

All formulations tested, applied both by spray and immersion, lead to water-repellent papers and textiles.

Among them, F1 and F2 reached a good compromise between effectiveness and compatibility requisites stated above. F3 also guaranteed positive values of WVP, mechanical strength and wettability, but the surface whitening of the samples, due to the high quantity of nanosilica, was not aesthetically acceptable, especially when applied by spray. Among all, it can be said that formulation F4 was the least effective because of the wide colour variation and a negative effect on WVP.

Structure or physico-chemical properties of the substrates did not affect the treatments application and their performances, encouraging their potential use for the conservation of paper and textile. However, a preliminary study of the artefacts and the development of *ad hoc* products is always fundamental.

Both spray and immersion application methods generally gave good results, even if spray left some small nanoparticles' agglomerates. It is suggested to immersion application whenever possible, while spray would be desirable in presence of canvas with a preparation layer or for breakable papers.

Some perspectives for future researches should be focus on: 1) improvement of the application methods to homogenize weight variations, focusing for example on the solvent concentration for spray application and verifying how much product is lost during the application phase; 2) bending tests of the treated samples, providing more information on the behaviour of the polymeric films; 3) testing the stability and the behaviour of these four formulations in presence of biological agents of deterioration; 4) further investigations of the coating microstructure, e.g. by SEM-EDX; 5) application on actual Cultural Heritage artworks, to verify whether the results are confirmed and to understand if new issues arise.

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Samples		Colour change $\Delta E^*$				Contact angle [°]	
		Untr	S	Untr	I	S	I
T3	F1	4.8	4.7	6.2	8.8	137 ± 8	144 ± 8
	F2	5.0	4.2	5.1	6.7	133 ± 9	134 ± 6
	F3	3.1	5.5	7.5	7.3	139 ± 8	137 ± 8
	F4	5.5	4.3	7.5	6.3	143 ± 4	131 ± 10
T4	F1	6.2	5.6	14.1	9.7	131 ± 7	135 ± 4
	F2	10.1	6.2	9.2	7.5	129 ± 8	131 ± 6
	F3	6.2	4.1	11.0	8.6	123 ± 4	131 ± 6
	F4	10.2	7.0	8.7	8.3	134 ± 6	133 ± 7
T5	F1	8.5	7.5	7.7	8.9	124 ± 5	144 ± 4
	F2	8.0	6.9	10.8	12.0	132 ± 7	138 ± 4
	F3	9.6	7.8	11.5	10.1	135 ± 8	140 ± 4
	F4	10.4	9.7	12.3	13.8	145 ± 5	141 ± 4
T7	F1	5.0	3.2	4.6	4.6	135 ± 6	144 ± 5
	F2	4.2	2.2	4.6	4.2	139 ± 5	143 ± 5
	F3	4.2	2.5	4.8	4.0	139 ± 7	136 ± 5
	F4	4.7	5.3	6.3	7.1	147 ± 6	145 ± 5
C1	F1	1.4	1.1	0.9	0.9	114 ± 5	137 ± 3
	F2	2.7	1.8	2.1	3.8	117 ± 4	128 ± 3
	F3	3.2	3.4	7.6	10.1	121 ± 2	138 ± 3
	F4	1.2	6.9	4.8	7.3	129 ± 4	136 ± 3
C2	F1	1.4	0.9	2.0	0.9	112 ± 2	123 ± 3
	F2	0.7	1.7	1.0	1.0	117 ± 2	122 ± 5
	F3	0.7	0.7	1.0	0.5	137 ± 6	122 ± 2
	F4	1.8	2.8	0.5	0.8	124 ± 2	127 ± 5
C3	F1	16.0	16.1	16.9	17.9	108 ± 6	120 ± 4
	F2	16.0	16.0	15.7	17.7	117 ± 6	124 ± 4
	F3	17.1	16.1	16.4	18.2	123 ± 9	126 ± 6
	F4	17.4	22.2	17.2	19.2	127 ± 2	131 ± 3

**Table 3.-** Colour change [ $\Delta E^*$ ] recorded after ageing (500 hours) for untreated and treated samples. Contact angle [°] recorded after ageing (500 hours) for treated samples both by (S) spray and (I) immersion. The data regarding T3, T4, T5 and T7 textiles and C1, C2 and C3 papers treated with F1, F2, F3 and F4 formulations are reported.

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She graduated in 2014 in Technologies for Conservation and Restoration at Ca' Foscari University of Venice, in Italy, with a thesis on the conservation state of the wall paintings of "Ossario del Monte Pasubio" War Memorial. In 2015 she took part to Erasmus mobility program to study conservation science at University of Malta. In 2016 she got the Master degree in "Chemical Sciences for Conservation and Restoration" at Ca' Foscari University of Venice in 2016 submitting the thesis: "A Study of Coatings for the protection of Textiles". The thesis was developed in collaboration with Istituto Italiano di Tecnologia, of Genova, Italy. In 2016 she successfully got qualified at the Italian State Exam of the Chemical Register. She did an internship in CMR S.r.l. ACCREDIA chemistry laboratory for building materials and restoration; internship in analytical laboratory EcamRicert S.r.l.; teaching-integrative activities during laboratories of Analytical Chemistry and Archaeometry at Ca' Foscari University of Venice; working experience in R&D of F.lli Mazzon S.p.A. In 2017 she was selected for an internship at Deutsches Bergbau-Museum in Bochum, Germany. She has been working with natural and synthetic polymers, nanoparticles, water-repellent treatments, artificial and natural aged materials.



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Irene Zanocco is a conservation scientist and an assistant conservator with Master Degree (2016) in "Chemical Science for Conservation and Restoration" at Ca' Foscari University of Venice. Her thesis concerned the study of polymeric coatings for the protection of paper and the project was developed collaborating with the Istituto Italiano di Tecnologia (IIT) of Genova, Italy. She worked in 2014 as an intern at the Laboratorio di Analisi dei Materiali Antichi (LAMA) of the IUAV University of Venice. In 2017 she won a scholarship for a researcher internship at the Instituto Universitario de Ciencia de los Materiales (ICMUV) of the University of Valencia, Spain.

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2010- Graduated in “Chemical Sciences for the Conservation and Restoration” at the Ca’ Foscari University of Venice with the thesis “Chemical-physical study of consolidants based on water-borne acrylic emulsions and colloidal silica emulsions for historical mortars”. 2010-2011, Internship and working experience in the research product departments of the San Marco Group S.p.A., Volteco S.p.A, VENETO NANOTECH S.C.p.A. 2012, internship at the Federal Institute for Materials Research and Testing (BAM, Berlin), 2013 science teaching at the secondary school. 2013 Ph. Doctorate in “Chemical Science” at Ca’ Foscari with the topic “Study of Water-Repellent Systems for the Protection and Maintenance of Mortars”. Since 2014, fellow researcher at Ca’ Foscari University of Venice in the “Chemistry for the Conservation of Cultural heritage Group”. She has been working for the characterization of acrylic emulsion, colloidal silica, and epoxy resins suitable as consolidants for stone materials. Her actual research topics includes the study of architectural surfaces in Venice area also in relation with the environment and the climate changes, development of techniques and products for the protection of historic masonries.



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Muhammad Zahid was born in Pakistan, 1988. He received his Bachelor’s degree from Pakistan in 2009. From 2009 to 2011, he worked in a textile manufacturing industry as an assistant manager. In 2013, he received Master’s degree in Textile Engineering from Politecnico di Torino, Italy. He was selected for an Erasmus mobility program for his final year thesis. With the collaboration of “University of Ghent, Belgium”, he completed his master research thesis on “Biocompatible electrospun nanofibers for wound dressings”. Currently he is a PhD researcher at Istituto Italiano di Tecnologia, Genova. He has good experience in multifunctional materials and their characterization techniques. Polymers, nanofillers and nanocomposites are also one of his core competences.



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Athanassia Athanassiou since January 2011 has an appointment as Senior Researcher, responsible for the Smart Materials Group, in the Nanophysics Department of the Istituto Italiano di Tecnologia in Genoa. In September 2014 she became Tenured Scientist. She has graduated in 1996 in Physics at the University of Ioannina in Greece. In 1997 she got the Master of Science (MSc) in Laser Photonics and Modern Optics from the University of Manchester, Laser Photonics Group, Manchester, UK, submitting a thesis on "Determination of Third Order Non Linear Optic Susceptibilities for Thin Films by Third Harmonic Generation". In 2000 she became Doctor of Philosophy (PhD) at the University of Salford, Laser Photonics and Non-Linear Optics Group, Manchester, UK, in collaboration with the Foundation of Research and Technology-Hellas (FORTH), Institute of Electronic Structure and Laser (IESL), Crete, Greece, after submitting a thesis on the "Physical Effects in the UV-Laser Ablation of Polymeric Materials: Implications for the Laser Cleaning of Easel Paintings". Immediately after the completion of her PhD she got a Postdoctoral Fellowship at the Institute of Electronic Structure and Laser (I.E.S.L.), Foundation for Research and Technology-Hellas (FO.R.T.H.) in Heraklion, Crete, Greece, where she became associated researcher from January 2003 till the end of 2005. From January 2006 to December 2011 she was a Senior Researcher at NNL-National Nanotechnology Laboratory, CNR-Istituto di Nanoscienze in Lecce, Italy responsible for the Nanocomposite and Responsive Materials Division. In June 2006 she got a part time appointment at the Istituto Italiano di Tecnologia in Genova, Italy, as a scientist responsible for the development and initiation of the Optical Spectroscopy-Microscopy and Material Science lab-facility. From September 2009 to September 2012 she was also coordinating the Smart Materials Platform at the Center for Biomolecular Nanotechnologies of IIT@UniLe, Lecce.