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Stone Surface Protection by Fluoropolymers from Decay Caused by Mural Writings

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ABSTRACT: A copolymer based on perfluoropolyether (PFPE) blocks and containing carboxylate functional groups has been studied in water microemulsion. It is able to interact with polyfunctional reactive molecules, e.g. polyaziridines, giving chain extension and crosslinking. The reaction takes place "in situ" and allow the PFPE derivative to be modified directly on the stone surface. The application of this material on different stone samples improves not only the substrate hydrophobicity (as expected for a perfluoropolyether derivative) but also the resistance to the dirtying which could be caused by mural writings (e.g. by inks). The treatment generates a protecting layer which resists on the stone surface even after several repeated staining/cleaning cycles, giving rise to a permanent "antigraffiti" effect.

1 INTRODUCTION

In recent years monuments and buildings have been subject to decay caused not only by atmospheric components (e.g. water vapour and carbon dioxide) and pollutants (e.g. nitrogen and sulphur oxides) but also by a novel form of defacement induced by mural writings or "graffiti".

In fact, paints applied on the surface of natural or artificial stones by brush, spray or felt-tip pen usually contain binders which strongly adhere to the substrates. The resulting damage can be considered irreversible since, after drawing, the stone surface can be only partially restored by repainting in the original colour, by abrasion of the defaced particles (e.g. by sandblasting) or by cleaning with solvents. The final result of these treatments is always a modification of the substrate surface which is particularly undesirable for the monumental heritage.

Application of specific protecting agents which allow an easy removal of graffiti from the stone surface represents the most interesting alternative to the above mentioned "post-graffiti" treatments.

Some commercially available polymeric materials such as silicones and polyacrylates which have been proposed in the last years as anti-graffiti agents have given only a partial solution to the problem represented by mural writings. Organic polymers commonly used in the fields of protection and consolidation of stones display some performance limits: (i) they may modify the aesthetic appearance of a treated stone (e.g. chromatic variations); (ii) their degradation caused by atmospheric agents (e.g. oxygen, sunlight) induce a loss of protection ability and an optical defacement (Biscontin et al. 1987, Whitmore and Colaluca 1987); (iii) they may be sensitive to some components (e.g. solvents) of the paints used to draw graffiti.

Among recently developed protecting materials of synthetic origin, remarkable interest is accorded to fluorinated polymers. For instance, perfluoropolyethers (PFPE), owing to their chemical inertness and their enhanced hydrorepellency (Sianesi et al. 1994) were proposed and applied to protect natural and artificial stones from water penetration (Piacenti et al. 1981), while fluoroelastomers gave good results in protection and surface consolidation of decayed and very porous stones (Piacenti et al. 1988) as well as mortar and concrete (Moggi and Ingoglia 1990).

The peculiar surface properties of perfluoropolyethers suggested their use also to prevent the effect of stone decay caused by mural writings (Moggi et al. 1988, Piacenti et al. 1990). Early results were satisfactory only operating with high quantities of applied polymer (e.g. more than 100 g/m^2 of PFPE applied to a medium porosity sandstone) and in the presence of chlorofluorocarbon solvents (CFC) which are no longer usable for environmental reasons.

These considerations prompted us to carry out new studies in this field, in order to develop a PFPE derivative displaying a good "antigraffiti" effect at low applied quantities and, if possible, in the absence of hazardous solvents.

This work reports the results of a preliminary study on the "antigraffiti" performance displayed by polymeric compounds in which perfluoropolyether (PFPE) sequences are interrupted by urethane blocks as outlined in Fig. 1. Moreover, the macromolecular backbone contains carboxylic side groups which could allow curing, if requested, by reacting with specific reagents.

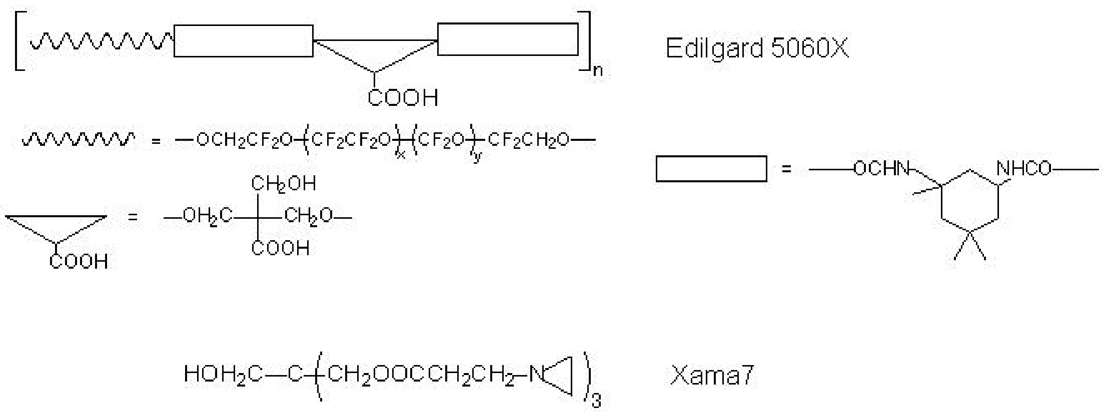

Figure 1 : Molecular structures of perfluoropolymer Edilgard 5060X and curing agent Xama 7

2 EXPERIMENTAL

2.1 Materials

Experiments have been performed on a set of three reference lithotypes which have been selected according to their petrophysical properties.

The three selected lithotypes are very widespread dimension stones and range from very compact to very porous material.

Slabs of white Carrara Marble, quarried from the Apuane Unit, have been used. This building material has a compact granoblastic polygonal structure and a very low porosity never exceeding 0.2%.

Pietra Serena sandstone, a quartz arenite belonging to the Marnoso-Arenacea Formation cropping out near Firenzuola (Northern Italy), is also used with a mean porosity of 3%.

The third lithotype is Pietra di Lecce, a highly porous fossiliferous bio-calcarenite quarried near Lecce (Southern Italy) with a mean open porosity of more then 30%.

Specimens of 20 × 10 × 2 cm were cut and divided into five equivalent areas of 4 × 10 cm, labelled from A to E.

Edilgard® 5060X**,** a water microdispersion of an anionic fluorinated polyurethane based on PFPE, with a solid content of 26% w/w and M_w of about 10^4 (see molecular structure sketched in Fig. 1) is a product of Syremont S.p.A. (Italy).

Remover® AC, a mixture of γ-butyrolactone (49%), dipropyleneglycol monomethylether (49%) and Triton® X100 (2%), has been supplied by Syremont S.p.A. (Italy) as cleaning agent.

Xama 7 (pentaerythrytol tris [3-(1-aziridinyl)propionate]) is produced by Flevo Chemie (The Netherlands).

2.2 Application of protecting material on the stone surface

Prior to use, stone samples have been conditioned in oven at 50°C until they reached a constant weight.

In a typical experiment, the fluorinated polymer *Edilgard 5060X* (19.4 g 26% w/w of water emulsion, 3.17 meq of carboxylate function considering an equivalent weight of 1592) and the curing agent Xama 7 (0.451g, 3.17 meq of aziridine function) were mixed for 0.5 h under magnetic stirring and the resulting mixture applied by a small brush on the surface of the stone samples. Increasing amounts of the polymeric mixture were applied to the areas labelled from B to D on the stone surface (area A was not treated and used as the reference surface). Owing to porosity differences the amounts applied on the surfaces of the three considered stones were not the same. The final applied quantities of protecting material for each stone are summarized in Table 1.

Table 1 : Protective quantities applied to the different lithotypes

Stone	Applied quantities on sample surface areas (g/m^2)				
	A	B	C	D	E
Carrara Marble	0	10	15	25	35
Pietra Serena	0	15	30	45	60
Pietra di Lecce	0	20	40	60	90

2.3 Study of surface properties

The tests performed on the stone samples in order to evaluate the surface properties and the anti-graffiti effectiveness have been carried out one week after the protective application.

Stone colour changes were measured on each sample area (after the polymer application as well as after the staining/cleaning process) by a Miniscan Hunter Lab 40004 spectrophotometer, determining the L*a*b* coordinates of the CIELAB space (Biscontin et al. 1986, Alessandrini and Pasetti 2004) and expressed as global chromatic variations ΔE^*.

Static contact angle measurements on the treated surfaces were performed by a Lorentzen & Wettre instrument according to the method adopted by UNI-NorMaL Commission (Alessandrini and Pasetti 2004).

2.4 Study of anti-writing effectiveness

Stone surface was stained by a BIC Permanent Marker (black ink) in all A-E areas. Cleaning was performed after 2 h after the staining by using Remover AC, a brush and a cotton wad. The surface properties were studied again after the complete evaporation of the cleaning solvent.

On a marble sample the staining/cleaning procedure was repeated five times and the measurements repeated at the end of each cycle.

2.5 Artificial ageing

The described procedures were repeated after artificial ageing of the samples under a 300W tungsten Osram Ultra-Vitalux© lamp which simulates the solar radiation.

Samples have been exposed for 1000 h at a distance of 30cm from the bulb, the mean measured temperature at the sample surface was 40±5 °C.

The properties of the treated samples and the anti-writing efficiencies were measured after 300, 500, 750 and 1000 h.

3 RESULTS AND DISCUSSION

The stone materials considered in the present study, Carrara Marble (CM), Pietra Serena (PS) and Pietra di Lecce (PL), are significant examples of materials frequently used in the past by architects and sculptors in monumental buildings or to create precious carvings. They are characterized by different petrophysical, physico-chemical and mechanical properties. In particular they have extremely different degrees of porosity.

The protecting material, commercially known as Edilgard 5060X, is a PFPE-based urethane copolymer containing the carboxylate side groups (see structure in Fig. 1). PFPE-based commercial compounds are manifactured by Solvay-Solexis (Spinetta Marengo, Italy) by photooxidation of tetrafluoroethylene; PFPE derivatives were patented and developed with the trade name of Fomblin Z by Montedison group since the sixties (Sianesi et al. 1994).

The curing agent used in this study is a tris-aziridine. The reaction involving carboxylate and aziridine groups is well known (Fanta 1964, Padwa and Woolhouse 1984) and already exploited as curing process of polymers (Roark and McKusick 1985).

The two components are homogeneously mixed just before application in order to let the curing reaction take place on the stone surface. The study of the surface properties are carried out after one week, when the water is completely evaporated and the curing reaction completed, even if preliminary results suggest that the curing reaction is completed in 3 days after application (Marzolla 2006).

The results obtained from the investigations carried out on the stone samples after the application of the protecting material are discussed in the following paragraphs.

3.1 Surface properties of treated stone samples

The variations in the stone surface properties induced by the application of the protecting material have been preliminarly studied in terms of chromatic changes and hydrorepellency. The variations of stone colours (expressed as ΔE*) and contact angle values determined for the treated samples are shown in Tables 2-3 and graphically summarized in Fig. 2.

Table 2 : Colour changes evaluated as global chromatic variation (ΔE*) after the application of the protecting material (treated) on the stone surface and after the staining/cleaning procedure (cleaned).

Carrara Marble			Pietra Serena			Pietra di Lecce		
Appl. quantity (g/m^2)	treated	cleaned	Appl quantity (g/m^2)	treated	cleaned	Appl. quantity (g/m^2)	treated	cleaned
10	0.3	0.9	15	2.8	1.8	20	8.4	3.3
15	0.6	1.1	30	3.7	1.8	40	8.4	5.0
25	0.6	1.5	45	3.5	0.9	60	9.3	3.4
35	0.5	2.0	60	4.1	1.1	90	7.5	6.1

Table 3 : Contact angle values (standard deviation in parenthesis) measured after the application of the protecting material (treated) on the stone surface and after the staining/cleaning procedure (cleaned).

Carrara Marble			Pietra Serena			Pietra di Lecce		
Appl.quantity (g/m^2)	treated (°)	cleaned (°)	Appl quantity (g/m^2)	treated (°)	cleaned (°)	Appl.quantity (g/m^2)	treated (°)	cleaned (°)
10	102 (3)	100 (1)	15	106 (6)	96 (4)	20	114 (4)	105 (6)
15	103 (2)	98 (7)	30	103 (3)	99 (4)	40	108 (5)	98 (6)
25	103 (5)	92 (2)	45	105 (6)	96 (10)	60	113 (1)	107 (6)
35	96 (3)	91 (5)	60	105 (6)	99 (5)	90	110 (4)	105 (4)

The application of the fluorinated polymer induces chromatic variations which are unimportant in the case of Carrara Marble and Pietra Serena: in fact ΔE* values lower than 5 correspond to colour changes which cannot be detected by naked eye (Vigliano 2000). Pietra di Lecce undergoes a more considerable chromatic change since ΔE* values are higher than 5 at any application rate. These results are in agreement with a general behaviour observed for stone materials treated with polymeric stuff: lithotypes displaying low porosity degree, homogeneous composition and clear colour generally undergo less pronounced chromatic variations (Biscontin et al.1986). In fact in the case of Carrara Marble (which has low porosity and homogeneous white colour) almost undetectable chromatic variation are observed.

After the curing of Edilgard 5060X on the surface of stone samples a considerable water-repellency is obtained. In fact contact angle values higher than 90° are observed in all cases, even with the lower applied quantities. In particular, contact angles close to 110° have been determined for the treated PL samples, showing a remarkable decrease of wettability owing to the application of protecting material.

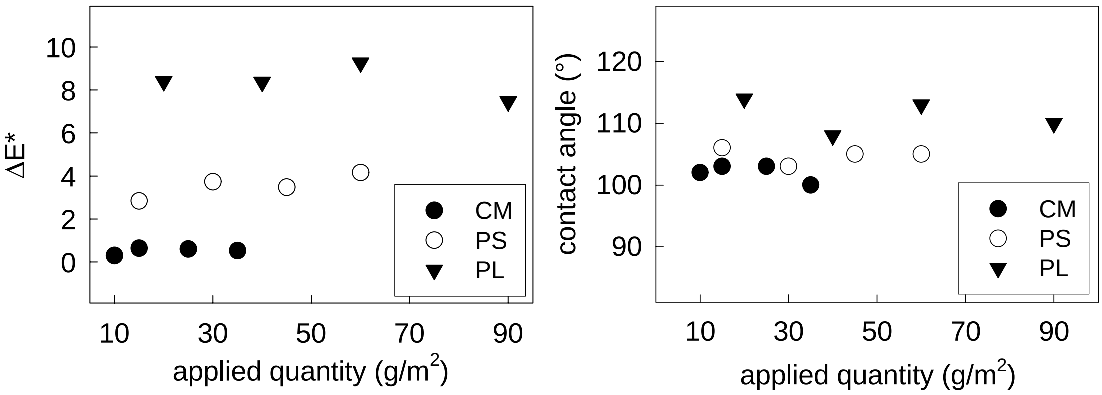

Figure 2 : Chromatic variations (left) and contact angle values (right) determined after the application of increasing quantities of the protecting material on the surface of the considered stone samples (CM = Carrara Marble; PS = Pietra Serena; PL = Pietra di Lecce).

3.2 Evaluation of anti-writing effectiveness

In order to evaluate the effectiveness of the cured Edilgard 5060X as protecting material from mural writings, the surface of treated stone samples have been stained by using a common permanent marker pen, then the ink removed with a specific solvent mixture (Remover® AC).

Afterwards, each sample has been examined by naked eye and by a microscope to verify if the removal of ink has been satisfactory from a qualitative point of view. Moreover, the surface properties have been studied again and the results compared with those obtained before the staining/cleaning cycle, in order to evaluate the efficiency of the protecting action.

The dirty seems to be efficiently removed from the surface of treated CM and PS samples. Pictures of a CM sample taken after staining and after cleaning steps are reported in Fig.3. Ink stains are disappeared from the treated areas B-E, while cannot be completely removed by area A on which no protective has been applied. That indicates a good protecting action of the cured Edilgard 5060X (even with the rather low applied quantity of 15 g/m^2) which prevents the penetration of ink into the stone porosity. The results are less satisfactory for Pietra di Lecce, since small traces of the dark ink remain on the surface after the cleaning step. Such a different behaviour could be ascribed to the rough stone surface rather than to a penetration of the ink. In fact, as shown by a microscope examination the dark traces are concentrated in the surface imperfections (e.g. small holes) where it is difficult to operate an exhaustive cleaning by the conventional laboratory method (see Experimental).

Chromatic variations observed after the staining/cleaning cycle performed on the stone samples are listed in Table 2. ΔE* values reported for the "cleaned" stones indicate the eventual colour modification of the treated surface due to traces of residual ink. Therefore such values are directly correlated to the efficiency of dirty removing as well as the efficiency of the protecting action. These results confirm what anticipated by the optical analysis of the samples: ΔE* is very low in the case of CM and PS according to a satisfactory if not complete removing of the ink stains at any of the considered applied quantities. The measurements performed on PL samples give ΔE* values ranging between 3 and 6 suggesting that traces of dirty remain on the surface after the cleaning procedure, as already indicated by a simple naked-eye examination.

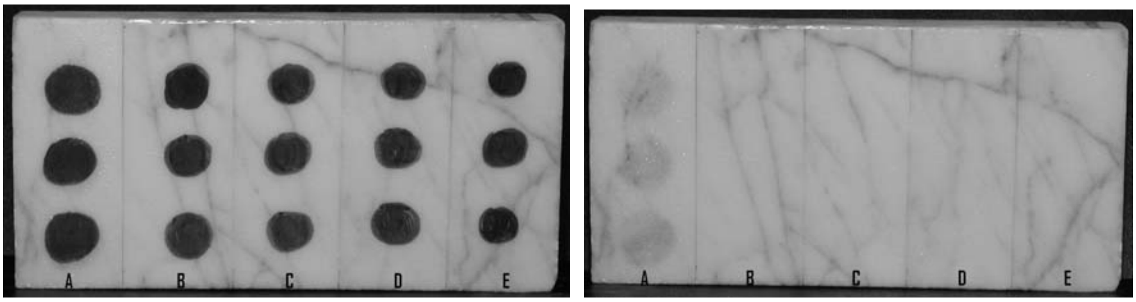

Figure 3 : Pictures of a Carrara Marble sample taken after the staining (left) and cleaning step (right). The ink stains are completely removed from areas B-D which have been treated with protecting material, while they are still present on the untreated area A.

After the cleaning step, the surfaces of the three stones still display a good hydrorepellency, even if the contact-angle values are lightly lower if compared to those measured on treated stone surfaces before the staining/cleaning cycle. These results, which are summarizes in Table 3, clearly indicate that the polymeric protecting material is quite unaltered on the stone surface after the cleaning. At any rate, the modest decreases of contact angle values observed for CM, PS and PL (2-10, 3-9 and 4-9 %, respectively) should suggest that a small amount of the protecting material is removed with the ink, maybe owing to the mechanical action rather than the solvent action in the cleaning step.

A specific experiment has been performed in order to evaluate the protecting ability of the applied material after several cleaning actions. A CM sample was treated with the protecting material (15 g/m^2) and the surface properties measured as already described. Then it has been stained and cleaned for five consecutive times (the ink stains were made always in the same part of the surface), determining contact angle and ΔE* values after each step. The results are graphically summarized in Fig. 4. Although the contact angle value seems to undergo a small decrease after each cleaning action, at the end of five staining/cleaning cycles the marble surface displays a still satisfactory hydrofobicity, (contact angle is distinctly higher then 90°) suggesting that a minimal part of the protecting material has been removed. The optical examination of the sample surface indicates a very light colour change after the fourth and fifth cycles, indicating the presence of residual ink traces. The colorimetric variations, as expected, increases with the number of the staining actions: ΔE* values are higher than 5 after the last two cycles, but it should be noted that values close to 7 do not correspond to intense colour variations, in agreement to what observed by naked-eye.

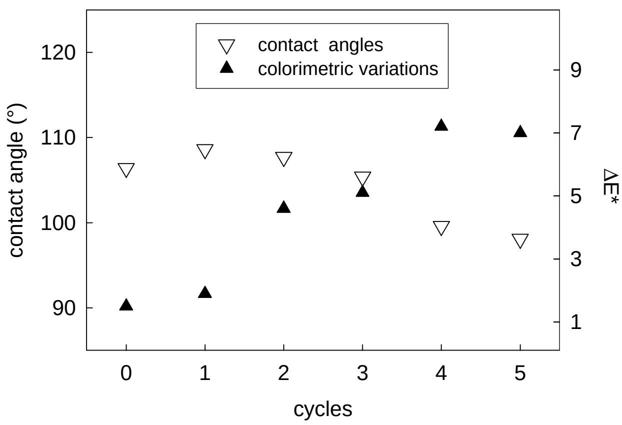

Figure 4 : Variation of Carrara Marble surface properties induced by repeated staining/cleaning cycles: chromatic variations, ΔE* (left) and contact angles (right).

3.3 Artificial ageing of treated stone samples

The effects of the accelerated ageing on the applied protecting material have been determined by irradiating treated marble samples (15g/m^2) with a solar spectrum lamp. The surface properties have been evaluated at about 300, 500, 750 and 1000h. The colorimetric variations determined during the laboratory ageing are very low ($\Delta E^* \leq 2$) indicating a good durability of the polymeric material. Such result is confirmed by the wettability measurements: contact angle values close to 105° were determined at any stage of the ageing. Moreover, staining/cleaning cycles have been performed on the stone samples during the artificial ageing in order to test the anti-writing efficiency of the aged protective too. The results are resumed in Fig. 5.

The colorimetric variations evaluated after removing the ink stains are very low ($\Delta E^* \leq 2.5$) at any ageing step and comparable to that determined for the un-aged marble sample. Moreover the surface wettability is almost unchanged since the contact angle values measured on the cleaned sample after all the considered ageing periods are distinctly higher than 90°. These results not only confirm the durability of the fluorinated polymer, but also indicate that the protecting material, even if aged, satisfactorily plays its anti-writing action.

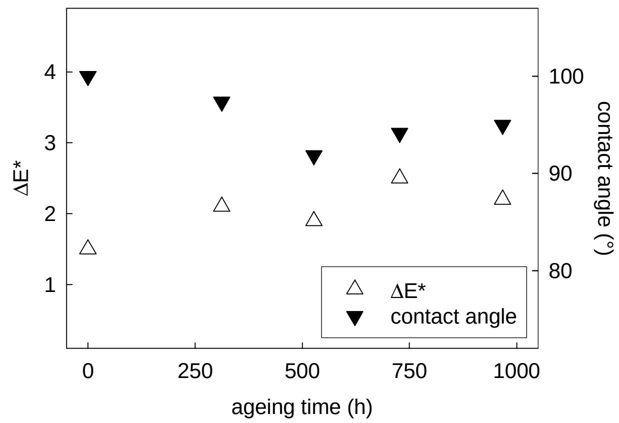

Figure 5 : Variation of Carrara Marble surface properties induced by staining/cleaning operations carried out onto artificially aged samples.

4 CONCLUSIONS

A fluorinated urethane copolymer containing carboxylate functions as side groups has been applied as water microdispersion on the surface of three different lithotypes in the presence of a polyaziridine curing agent. The reaction involving carboxylate groups and aziridine rings afford a durable material on the stone surface. The surfaces of the considered stone samples (Carrara Marble, Pietra Serena and Pietra di Lecce) display a good hydrorepellency and undergo sensible (for PL) or almost undetectable (CM and PS) colorimetric variations. These surface properties are almost unaltered after an artificial laboratory ageing performed on marble samples, confirming the well known resistance of PFPE derivatives to degradation.

Studies performed on treated stone samples which have been stained by a common permanent marker show that the considered polymeric material behaves as anti-writing protecting agent. In fact, ink stains are not adsorbed on the treated stone surface and can be exhaustively removed by a standard cleaning procedure. The results are particularly good for Carrara Marble and Pietra Serena, while in the case of the more porous Pietra di Lecce, the rough surface prevents an accurate removal of the stains and some traces of ink persist after the cleaning cycle. Since the polymeric material is not removed from the surface during the cleaning action, the treated stone surface can undergo repeated staining/cleaning cycles with no evident damage. Therefore, the fluorinated urethane copolymer studied in the present work can be considered an example of protecting material displaying a permanent “anti-graffiti” effect.

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