Chapter 9.3

THE CHALLENGE OF PROTECTING OUTDOOR EXPOSED MONUMENTS FROM ATMOSPHERIC ATTACK: EXPERIENCE AND STRATEGY

Tommaso Poli and Lucia Toniolo
CNR – ICVBC Sezione di Milano "Gino Bozza", P.za L. da Vinci 32, 20133 Milano, Italy

Abstract: Natural and synthetic waxes, acrylic and siloxane resins, perfluoropolyethers, fluorinated polyolefin and fluoroelastomers are some of the most used commercial products employed as protective coatings for stone materials. The application of these products is aimed to prevent the attack of the environmental pollutants and the penetration of water, with the connected risks of freezing and thawing cycles and the crystallization of salt solutions, in order to slow the stone degradation processes. The common and easiest way to pursue this goal is through the deposition, on the stone surface, and possibly deeper beyond the surface, of a coating layer able to modify the interaction of the stone with water, turning the partial hydrophilic character of the stone surface into a high hydrophobic interface. This modification should be achieved by affecting only the thermodynamic superficial potentials, but leaving unaltered, as long as possible, the superficial aspect, morphology, open porosity and roughness. Hence the challenge is avoiding the change of the substrate colour, the natural water vapour permeability and do not react with the stone material in order to respect its natural chemistry.The use of polymers, as protective coatings for stone materials, started in the sixties as a consequence of the expansion of macromolecular chemistry and the successful diffusion of synthetic resins in many different market fields but in most cases of conservation they have been applied without adequate knowledge of the properties of the polymer/stone system and, moreover, without a satisfactory optimization of the molecular structures for protection purposes. It is necessary to point out that the various commercial products rarely have been studied and developed expressly for applications in this field, but they have been merely transferred from different technological applications with higher economic advantages. The way these products are working, the reasons of some failures and the most common problems that can occur, have been reported here. For instance, the influence of the substrates' nature (open porosity, superficial roughness) on the protective performances and the behaviour of water dispersed systems for the

S.K. Kourkoulis (ed.), Fracture and Failure of Natural Building Stones, 553–563.
© 2006 *Springer.*

stone conservation have been investigated and reported. Stability and resistance to the photoxidative and thermal ageing of the different polymeric classes are other crucial problems: often a long term chemical integrity does not correspond to a similar protection efficacy. When a polymer is applied on a stone surface, physical rearrangements could occur to the protective layer, reducing the shielding efficacy but leaving the chemical structure unaltered. In a similar way the reversibility, even when assessed for a polymer in laboratory conditions, is practically lost when the protective is applied on a stone material with high open porosity and the product can penetrate deeply in the bulk of the system. This paper aims at being a short but complete overview of the issues that have to be considered and the problems that have to be faced when the protection of an outdoor exposed stone material is concerned.

Key words: stone protection; stone conservation.

1. INTRODUCTION

The last phase of a modern conservative intervention on an outdoor exposed building, monument or artifact is the important decision about the opportunity of a protective treatment application. This choice is crucial and decisive because to protect a stone surface, as well as consolidate and clean it, means to alterate irreversibly the surface[1]. Indeed, applying a protective treatment on a degradated stone material means, not only to shield the “stone system” with a “polymeric system” but to create a new and more complex stone/polymer system having durability and resistance, in the favourable cases, higher than the damaged and untreated stone. The main tasks of a treatment for the stone protection are, as well known, to avoid or at least reduce the water penetration and to protect the surface from dangerous interactions with any aggressive and reactive substances that can be easily found in a polluted environment. The risks connected to an outdoor exposition are well assessed and, as predictable, strictly correlated to the interactions of water with stone material and other pollutants dispersed in the environment[2-4]:

- Water imbibition, with the weight increase of the material inducing micro-structural damages.
- Salt crystallization; the precipitation and the different hydration state passages of salts can generate tensions in the porosity of stone which are able to induce micro-fractures, scalings and detachments.
- Chemical threats; the reaction of water with anhydrides or simply the dissolution of aggressive substances dispersed in the polluted environment, leads to the formation of acids or other compounds able to chemically attack stone materials, mostly in the case of limestones and marbles.
- Freezing and thawing phenomena in wet condition; the crystallization of water into the porous structure of the material induces mechanical stresses with consequent formation of micro-fractures.

- Biological threats; high humidity content promotes the growth of micro-organisms like bacteria, moulds, fungi, algae and musks, which could alterate and damage the stone substrates.
- Erosion; mechanical action of water flow and particulate matter transported by water could induce loss of material, after damages and detachments of superficial crystals.

2. TREATMENT EFFICACY AND STONE PROPERTIES

The above mentioned phenomena could be avoided or, at least, slowed down by the application of protective and water repellent treatment[5]. The common and easiest way to pursue this goal is through the deposition, on the stone surface, and, possibly deeper beyond the surface, of a coating layer able to modify the interaction of the stone with water, turning the partial hydrophilic character of the stone surface into a high hydrophobic interface. This modification should be achieved by affecting only the thermodynamic superficial potentials but leaving unaltered, as long as possible, the superficial aspect, morphology, open porosity and roughness. This means, it should not alter the substrate colour, the natural water vapour permeability and not react with the stone material[6]. Nevertheless, some silicon based commercial protectives can establish some binding interactions with silicatic substrates[5,7].

It is clear that the success of treatments strictly depends on the nature of the substrate and the type of interaction with stone materials. In fact, it is well assessed that the efficacy and the water-repellency of a treatment is directly correlated to the chemical and physical properties of the substrate like composition, open porosity and superficial roughness. The main challenge in conservation is preventing deterioration of limestones and marbles; many historical architecture and monuments are built with precious marbles for their high aesthetical value.

Marble is a quite critical substrate to protect, due to many intrinsic reasons. Its chemical nature leaves the stone exposed to the attack of acid pollutants, starting from the discontinuities among grains of the crystalline structure and does not exploit linking capabilities with the silicon based products[5-7]. The very low open porosity does not allow the penetration of treatments in the bulk of the material, with many obvious disadvantages like the formation of a very thin water repellent layer (stone/polymer) and the accumulation of the coating on the stone surface, directly exposed to chemical (aggressive pollutants), thermal, photochemical (the UV range of the sunlight spectrum and the radical species) and mechanical (washing and vibrations) stresses[8,9]. An excessive amount of accumulated polymer on the surface favour the soot deposition and particulate sticking (usually these polymers show T_g temperatures - glass transition or softening temperature - around

50°C, lower than the temperature of sun exposed surfaces). Consequently, the physical characteristics of coatings can be modified by the presence and accumulation of pollutants, layered in thick films[10]. Moreover, on a thick superficial film, the formation of polymer/polymer and stone/polymer discontinuities, where the biological growth is favoured by the water and soot prolonged retaining, is more likely. Finally, a thick surface coating modifies the gloss properties inducing an important aesthetic damage: the film changes the natural aspect of the stone giving it the typical "wet" or "greased" aspect. The usual low surface roughness, typical of the marble artefacts, reduces the specific surface and, therefore, the adhesion of the coating to the substrate.

Usually static contact angle measurements are used to assess the water repellence of a treated surface[11]: the higher the measured angles, the higher the hydrophobic effect of the coating (note that water repellent surfaces should have angles higher than 90°). The static angle value is not only influenced by the chemical nature of the product but by the surface roughness as well: the lower the roughness, the lower the angles, which tend to the value of the coating itself[12-14]. The polymers applied to low porosity and smooth substrates tend to remain over the surface, favouring the polymer mobility when energy, as for example heating, is supplied to the system.

The shielding efficacy of a protective treatment is usually tested through the measurement of water absorption by capillarity which evaluate the amount of water absorbed by a stone specimen per surface unit (absorbed water/surface area in contact with water, mg/cm^2) vs. time ($t^{1/2}$), before and after a treatment[15]. The trend of the obtained capillary absorption curves, the final amount of absorbed water and the relative capillary index[15] (ICr, the ratio of the capillary curves integrals before and after treatment), are the numeric instruments for the study of the behaviour of stone coatings. These parameters allow the comparison among the efficacy of different considered products.

In particular, the protective efficacy would be better understood if one takes into account the nature of the considered stone, for example the fact that only a low amount of water absorption is involved in all the experiments with marble and even relatively minor effects become meaningful. It is evident that, in the case of low porosity stones, it is more difficult for a hydrophobic coating to fully display its capability of modifying the surface properties of the substrate as it happens in the case of porous stones. The capillary absorption tests show that a fully satisfactory protective treatment on a high porosity stone, like a calcarenite, is able to grant a 95% reduction of water uptake, while on a low porosity stone, like marble, the reduction is only about 40%; nevertheless, it is important to consider that a protected high porosity stone still keeps absorbing twice as much water (mg/cm^2) than an untreated low porosity one. The elevated surface roughness (see above) and the large amount of permeable pores, in the case of high porosity materials, allow the formation of a very thick and efficient protection layer with quite good water-repellency and shielding properties.

The problems that have to be faced when the protection of a high open porosity stone, like calcarenite, is considered are specific for this kind of substrate and sometimes completely different from those of the low porosity stones. The high porosity and the pore size distribution allow a large amount of product to penetrate into the bulk of the stone with many advantages for the shielding efficacy (a thicker hydrophobic stone/polymer layer) and for the durability of products (most of the polymer is inside the stone and not exposed to sunlight and environmental aggressive pollutants)[6,16].

Some drawbacks arise from the large amount of product inside the stone that increases the weight of the substrate surface layer and favours the formation of areas with high protective concentration that can create discontinuity in the mechanical properties of the stone (risk of micro-fractures and scaling). The uptake of large amount of product, reduces dramatically the natural water vapour permeability, or breathability, of the stone, i.e. the ability of the material to get the hygro-thermal equilibrium of the environment[17, 18]. Finally, the distribution of the polymer inside the stone excludes any reversibility of the treatment, making dramatically complicate any removing operation. The elevated superficial roughness, typical of high porosity stones, enhances apparently the contact angle values, deceiving about the real shielding efficacy and water-repellency of the protective treatment[12-14].

Considering the differences among the stone materials, it is clear that the same protective agent would not work equally well for low and high porosity substrates. It should be necessary to tune the characteristics of the coating according to the specific requirements of each stone material that has to be protected. Starting from the remark that commercial products have rarely been developed specifically for conservation applications, but they have been simply transferred from other technological fields with higher economic advantages, it is absolutely necessary before treating an artefact to perform a thorough study concerning the efficacy of the selected products. The aim of this preliminary approach is the selection of the most suitable protective treatment and, above all, the optimization of the application conditions like solvents, concentration, temperature and application methodology.

3. THE PROBLEM OF SOLVENT AND OF APPLICATION METHODS

Indeed the choice of the solvent is decisive for an effective and successful protection treatment of stone materials. The solvent, as well known, is the medium that “transforms” the treatment from solid to liquid, carries the product into the bulk of the stone and, evaporating, allows the transformation from liquid to solid. The solvating power and the volatility are therefore the characteristics that should be carefully controlled in order to enhance the effectiveness of a protection treatment[19]:

- Maximum solvating efficacy. The solvent must have the highest possible affinity with the polymer.
- No interaction with the substrate. Solvents with acid or basic characteristics should be avoided.
- No toxicity. The solvent should not cause risks for the operators' health or damages to the environment, according to the EU standard requirements.
- Minimum solvent viscosity; the dissolution of a polymer usually increases the viscosity of the organic liquid phase, therefore it is necessary to employ low viscosity solvents in order to favor the penetration of the solution into the stone material.
- Tuned volatility. The solvent must completely evaporate after the treatment, in order to prevent unwanted reactions induced or catalyzed by compounds present in the substrate. The lower the solvent's affinity with the polymer is, the easier it can evaporate; but it should be emphasized, that a fast evaporation induces the formation of an inhomogeneous solid phase and a poor penetration of the polymer into the substrate[19]. A compromise should be carefully reached, pursuing the most suitable solvent or solvents mixture.
- No chromatographic effect. No preferential adsorptions by polymer or solvent in the stone matrix should happen in order to prevent the formation of a gradient of treatment's concentration. When a polymeric solution penetrates in a stone substrate, this latter tends to behave like a static phase of a chromatographic column, working both in size exclusion (discriminating by size) and in adsorption (discriminating by affinity). It is easy to comprehend that the small molecules of the solvent move faster than the polymer through the pores, so that rarely the solvent front corresponds with that of the polymer[20]. This gives birth to areas with different polymer/solvent ratio that will behave differently in the formation of the solid phase and then in the shielding efficacy.
- Polymerisation favouring; in the case of reactive pre-polymeric treatment, the solvent should grant the polymerization process and, successively, favour the evaporation of by-products;
- No reversed migration. The solvent, inside the porous material, migrates towards the external surfaces, for evaporation purposes; during these processes, it tends to carry the polymer with it[20]. In order to minimize this effect, it is necessary to reduce the interaction solvent/polymer (using a thermodynamically "poor" solvent) and to slow the evaporation rate.

A solvent or a blend of solvents, showing all these characteristics cannot exist for the evident contradictions of the required chemical physical properties[21]. A "good" solvent, i.e. with a great solvating effect and polymer affinity, favours the penetration, reduces the chromatographic effect and does not interact with substrate, but only a "bad" solvent completely and quickly evaporates without any "reversed migration" effect. Moreover, it is important to consider the undesirable interactions between polymer and solvent, such as the formation of intermolecular complexes, clusters or physical gels that can occur in particular conditions of temperature and pressure. Only a suitable experimental work before the treatment, allows one to choose the appropriate solvent or solvent mixture, considering the characteristics of the stone material and of the polymeric coating. It is important to evaluate the correlation between the protection efficacy and the different solvent systems.

In the last years, in order to reduce the toxicity and the environmental impact of conservation treatments, new formulations of protective products have been developed in water dispersion, through the use of surfactants and other additives. These dispersions, nowadays, still show many limits and drawbacks[22,23], mainly due to the particles size (the radius of particles ranges from 100 to 1000 nm and from 10 to 100 nm for the classic emulsion and the so called micro-emulsion, respectively) and to the permanence of different additives in the formed solid phase. Initiators, primary and secondary surfactants, if not completely removed after the film formation, can favour dangerous reactions (oxidations, hydrolysis etc.) of the protection treatment and of the substrate; they can also alter the optical properties (the visual aspect: opalescence, whitening, yellowing, etc.) of the coating. The presence of plasticizers and of thickeners, often employed to enhance the film quality, can also produce undesired similar effects.

Finally two major drawbacks are correlated with the use of water: first, it is a high boiling solvent with a quite good chemical affinity with stone substrates and, therefore, evaporates very slowly; second, it is able to dissolve the residues of soluble salts (even if present in very low amount) increasing locally the ionic force and producing, sometimes, the collapse of the dispersion[24,25].

4. THE PROBLEM OF DURABILITY

The other crucial problems in the protection of outdoor exposed monuments are the prediction and the evaluation of stability and resistance to the photoxidative and thermal ageing of the applied treatments: often a long term chemical integrity, both in laboratory and in situ, does not correspond to a similar protection efficacy.

As far as it is verified that the chemical degradation of a polymeric treatment corresponds to a loss of the shielding efficacy, the contrary is not necessarily true. With the progress of natural or artificial ageing, a polymer applied on a stone surface could lose the protection effectiveness because of some physical rearrangements of the macromolecules, maintaining the chemical structure unaltered[8,26]. For example, SEM observation of different acrylic copolymers[10] showed a common pattern of microfractures on the coating surface after 1500 hours of UV artificial ageing, while, during the same ageing time, no such pronounced chemical decay was assessed[27]. It is evident that the chemical nature definitely influences the aging stability and, hence, the durability of the polymer. Concerning the polymers employed in conservation, the acrylics and siloxanes are the more studied and applied classes of products; similarly their degradation processes and protective features are well known. The introduction of fluorine into classical acrylic polymers, like Paraloid B72 and B67, resulted in a class of partially fluorinated acrylic copolymers[8,16,17] showing higher chemical stability, enhanced water repellency and reduced sensitiveness to photooxidation. Nevertheless, the durability and long term effectiveness of these polymers applied on stone substrates are not yet completely satisfactory.

In the case of silicon based water repellent treatments, the polymer resistance is intrinsically granted by the higher stability of Si-C and Si-O bonds; similarly, these favorable characteristics are unable to maintain a long term durability of the shielding efficacy. Actually, some authors[28] have studied a large number of sites treated with silicon based water repellents, after different aging periods, demonstrating that the shielding effectiveness decreases in about 5 years and dramatically drops in 10 years. After this period of time, the stone substrate shows an inverted gradient of protective efficacy, i.e. the outermost part of surface completely loses the water repellency while the inner is maintaining this property. This condition, favouring water retaining induces hygric dilation processes, frost events and biological attacks, which take place preferably in this thin un-protected superficial layer.

It is important to highlight that the available test to evaluate in situ effectiveness of treatments (low pressure water absorption measurement or Karsten pipe) is not completely reliable, especially when low porosity stones are considered.

5. THE “UTOPIA” OF REVERSIBILITY

The idea of the reversibility of conservation treatments[29], since their introduction, seemed crucial for a modern and correct approach to the restoration issues. The term “reversibility” usually means the possibility of completely remove an applied product from the treated surface, recovering it in the condition preceding the treatment, in order to allow a new and, possibly, more effective intervention.

In the case of consolidation treatment the concept of reversibility is not applicable; actually, most of the treatments with inorganic products (silicates, fluosilicates or barium hydroxide), for example, are intrinsically irreversible, considering that they work through the precipitation of compounds necessarily more stable than the matrix that has to be consolidated.

As far as the protection treatment is concerned, it is necessary to clarify a common misunderstanding connected to the term reversibility: often the product solubility is confused with the product/substrate reversibility. The solubility, and the long term solubility, of a polymeric material is not the only requirement that can assure its complete real reversibility. The penetration of the polymer inside the porous micro-structure of the stone[30], the adhesion to the crystalline material and the interaction of the polymer with the substrate are the crucial factors which, usually, do not enable the removal of the product[30,31].

Some organic products, like waxes[32] and many synthetic polymers, easily soluble in the suitable solvents and then theoretically reversible, once applied on a stone substrate lose their reversibility, for many reasons. First of all, once the product penetrates deeply in the porous matrix of the stone it cannot be easily reached by the solvent and extracted; moreover, the extraction could be complicated by preferential adsorptions, interactions with the stone matrix and cross-linking of the polymeric chains occurring over time. Large amounts of solvent and hazardous operation would be necessary to partially remove the polymer, without taking care of the safety regulations.

Some difficulties in removing the treatment from low porosity substrate are also verified; actually the polymeric films, exposed to the environmental aggression, lose their solubility properties after aging (photooxidation, crosslinking, chain degradation, etc). Then, the assessed impossibility of completely removing a treatment from a real surface leads to consider a new approach to the conservation intervention: the re-treatableness. A new generation coatings should be developed in order to permit the application of another material with the minimum interference.

ACKNOWLEDGMENTS

The Authors are gratefully thanking the CNR Target Project "Safeguard of Cultural Heritage" for the research support on stone protection and Dr. Antonio Sansonetti for his careful reading of the paper.

REFERENCES

1. J. M. Teutonico, A. E. Charola, E. De Witte, G. Grasseger, R. J Koestler, M. Laurenzi Tabasso, H. R. Sasse, R. Snethlage, Group report: how can we ensure the responsible and effective use of treatments (Cleaning, Consolidation, Protection)? in: *Saving Our Cultural Heritage*, 293-313 (Wiley and Sons, Bognor Regis UK, 1997).
2. E. M. Winkler, *Stone in architecture*, (Springer-Verlag, Berlin, 1994).
3. A.A.V.V., Natural stone, weathering phenomena, conservation strategies and case studies, Ed. S. Siegesmund, T. Weiss, A. Vollbrecht, Geological Society Special publication **205** (2002).
4. G. G. Amoroso, V. Fassina, *Stone decay and Conservation* (Elsevier, Amsterdam, 1983).
5. A. E. Charola. Water repellents and other "protective treatments": a critical review, *International Journal for Restoration of Buildings and Monuments* **9**(1), 3-22 (2003).

6. J. Delgado, E. Charola, *General report on water repellents, Science and Technology for Cultural Heritage* **5**(1), 93-101 (1996).
7. E. S. Goins, G. Wheeler, M. T. Wypyski, Alkoxysilane film formation on quartz and calcite crystal surfaces, in: *Proceedings of 8th Int. Cong. on Deterioration and Conservation of Stone*, Berlin, 1255-1264 (1996).
8. T. Poli, L. Toniolo, O. Chiantore, M. Lazzari, V. Castelvetro, A. Manariti, Tailoring new fluorinated acrylic copolymers as protective coatings for marble, *Journal of Cultural Heritage* **3**, 309-316 (2002).
9. O. Chiantore, C. Colombo, R. Peruzzi, T. Poli, L. Toniolo, Effect of fluorinated groups on photooxidative stability of polymeric protectives applied on marble *Annali di Chimica,* **91**, 741-748 (2001).
10. L. Toniolo, F. Casadio, C. Colombo, T. Poli, SEM observation of polymers applied to natural stones, *Actes du congrès "Art et Chimie, les polymères"* CNRS Editions, Paris, 163-167 (2003).
11. H. R. Sasse, R. Snethlage, Methods for the evaluation of stone conservation treatments in: *Saving Our Cultural Heritage*, 223-243 (Wiley and Sons, Bognor Regis UK, 1997).
12. C. Della Volpe, A. Penati, R. Peruzzi, S. Siboni, L. Toniolo, C. Colombo, The combined effect of roughness and heterogeneity on contact angles: the case of polymer coating for stone protection, *J. Adhesion Sci. Technol.*, **14**, 273-299 (2000).
13. T. Poli, L. Toniolo, R. Peruzzi, M. Brugnara, C. Della Volpe, Partially fluorinated acrylic copolymers as coatings for stone protection: characterization and surface properties *MRS Proceedings Volume 712 - Symposium II Materials Issues in Art and Archaeology VI*, Ed. by P. B. Vandiver, M. Goodway, J. L. Mass, Boston, **II3.3** (2002).
14. M. Brugnara, E. Degasperi, C. Della Volpe, D. Maniglio, A. Penati, S. Siboni, V. Castelvetro, T. Poli, L. Toniolo, S. Invernizzi, The application of the contact angle in monument protection: new materials and methods, *Colloids and Surfaces A*, **241**, 299-312 (2004).
15. R. Peruzzi, T. Poli, L. Toniolo, The experimental test for the evaluation of protective treatments: a critical survey of the Capillary Absorption Index, *Journal of Cultural Heritage*, **4**(3), 93-96 (2003).
16. G. Alessandrini, M. Aglietto, V. Castelvetro, F. Ciardelli, R. Peruzzi, L. Toniolo, Comparative evaluation of fluorinated and unfluorinated acrylic copolymers as water repellent coating materials for stone, *Journal of Applied Polymer Science*, **76**, 962-977 (2000).
17. G. Alessandrini, L. Toniolo, C. Colombo, Partially fluorinated acrylic copolymers as coatings for calcareous stone materials in: Preprints of the 18th IIC International Congress *Tradition and Innovation. Advances in Conservation*, Edited by A. Roy and P. Smith 1-6 (Melbourne, 2000).
18. C. M. Hansen, Water transport and condensation in fluoro-polymer films *Progress in Organic Coatings* **42**, 167-178 (2001).
19. C. V. Horie, *Materials for Conservation. Organic Consolidants, adhesives and coatings*, (Butterworths, London, 1987).
20. W. Domaslowski, The mechanism of polymer migration in porous stone, *Wiener berichte über Naturwisenschaft in der Kunst*, Doppelband 4/5, Vendl A., Pichler B., Weber J., Banik G., 402-425 (Wien, 1988).
21. D. Lopez, H. Reinecke, C. Mijangos, Some consequences of the polymer-solvent interaction, *Macromol. Symp.*, **166**, 25-33 (2001)
22. J. Snuparek, Principles and limits of polymer latex tailoring, *Prog. Org. Coatings,* **29**, 225-233 (1996).
23. A.A.V.V. *Emulsion polymer technologies*, Paint Research Association, **12**, 9, 2001.
24. K. Wanli, Interaction between alkali/surfactant/polymer and their effects on emulsion stability, *Coll. Surf.*, **175,** 243-247 (2000).

25. I. Fortelny, Coalescence in polymer blends: solved and open problems, *Macromol. Symp.* **158,** 137-147 (2000).
26. T. Poli, L. Toniolo, Protection efficacy of fluorinated acrylic copolymers applied on historical italian marbles, *Material Research Society, Materials Issues in Art and Archaeology*, in press (2005).
27. O. Chiantore, M. Lazzari, Photo-oxidative stability of Paraloid acrylic protective polymers, *Polymer* **42,** 17-27 (2001)
28. E. Wendler, New Materials and approaches for the conservation of stone in: *Saving Our Cultural Heritage*, 181-196 (Wiley and Sons, Bognor Regis UK, 1997).
29. G. Urbani, *Intorno al restauro*, a cura di B. Zanardi, (Skira, Milano, 2000).
30. L. Toniolo, F. Casadio, F. Cariati, A key factor in modern protection of historic buildings: the assessment of penetration of water repellent polymers into porous stone materials, *Annali di Chimica,* **91**, 823-832 (2001).
31. F. Casadio, L. Toniolo, Polymeric treatments for stone materials conservation: the problem of penetration depth, *J. American Institute for Conservation,* **43**, 1-19 (2004)
32. K. Raft, A preliminary report on the possibility of using bleached beeswax to improve the resolubility of picture varnishes based on polycyclohexanones, *Studies in conservation*, **30**, 143-144 (1985)