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ASSESSMENT OF XIX-XX CENTURIES CONSERVATION INTERVENTIONS IN VENETIAN STONE MONUMENTS WITH ARTIFICIAL PRODUCTS: STATE OF THE ART AND PERSPECTIVES

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Abstract

Since ancient times, several products have been used to prevent the deterioration of building surfaces due to the adverse environmental factors in Venice. Natural products, mainly oxalate bearing solutions, waxes and other mixtures of vegetal and animal derivatives, were primarily used in the past to strengthen the stone surface and to prevent the effect of marine aerosols. In XIX century new products were introduced in the field thanks to the strong improvement of chemistry, which brought to several recipes for stone treatment. Most employed in Venice at that time were the silicate and fluosilicate treatments according to the Fuchs (1818), Kulmann (1854), Ransome (1856-60) and Kessler (1883) patents. Notwithstanding the innovations, the use of natural products was not abandoned until the middle of XX century, when polymers were introduced in the market and suddenly took the place of most traditional products, also in the occasion of the deleterious flood in 1966, that made clear the worst state of conservation of the city monuments. From that point, acrylic and vinyl polymers,epoxy resins alkylalkoxysilane, acrylic silicone blends were extensively used either as consolidant and water repellent, sometimes without a satisfactory preliminary assessment of the polymer performance.

The paper deals with the use of these materials on Venetian monuments and also reports the studies started in 2000 regarding the evaluation of the medium, long-term performance of treatments in the XIX-XX centuries in different monuments, i.e. Saint Mark's Basilica, Doge's palace, Acritani Pillars, etc., reporting benefits and unexpected drawbacks obtained before and, in some cases, after the surface re-treatment. Furthermore the perspectives of the employment of innovative materials for conservation (TiO_2 coating, organic and inorganic dispersions/solutions) are also discussed as the wide market offers are quickly displacing the "traditional" polymeric products, notwithstanding the performance evaluation of new materials on ancient ones is made only rarely and barely documented.

Keywords: Venice's restorations, polymeric treatments, inorganic treatments, Titania coatings

1. The research on stone materials conservation of XIX and XX centuries in Venice:

In the second half of the nineteenth century, the strong technological development, consequent upon the industrialization, opened new horizons also in the field of restoration. Therefore, the debate between the proponents of the traditional techniques, materials and products, and the supporters of the new ones was very lively. In favor of tradition, some generally opposed the innovation as an attitude to change rejection, but also many appreciate the behavior reliability of traditional materials over time, and their well-known physical and chemical compatibility with ancient ones. In favor of innovation, the majority supported generic instances of progress, but many were consciously confident that new discoveries could enhance the conservation efficiency. Among them, some intended to distinguish the new from the existent, in the operations of integration, especially in the use of materials, consistently with the change of the restoration culture, which began in the late nineteenth century.

Far from the treacherous arguments that oppose tradition and innovation and assuming a scientific approach to conservation, that considers each available material and product as an opportunity for operators of the restoration, it is clear that reliability, in the meaning of knowledge of material behavior, and compatibility, between new and existing materials, are essential issues in the choice of intervention methodologies. Also process reversibility have to be considered, although in recent years re-treatability of stone surfaces has gradually increased its relevance, especially when the restoration products penetrate in the material, and is more difficult to remove them.

The latter has become a new subject of debate.

For example it is difficult to establish a deadline for the evaluation of the efficiency of conservation materials and methodologies: even fifty years - often indicated as the minimum lapse of time needed to evaluate a product performance - , may be inadequate, particularly if considered an advice to future generations about the durability of conservation treatments for ancient materials. The assessment of the reliability of the processing cannot be expressed only in function of their durability and efficiency over time, but also in relation to the issues of compatibility, reversibility and re-treatability, previously mentioned.

Actually the need to develop specific research programs aimed at evaluating the behaviour of restoration products over time assumes a great relevance. In particular, it is essential to extend the study, as far as possible, to the materials used in past centuries, since the second half of the nineteenth century, when treatments with artificial products became part of the restoration practice. It must be taken into consideration that, more and more often in restoration practice, it happens to deal with materials subjected to multiple rounds of applications, each one entailing specific physical and chemical interactions between the ancient materials and the conservative products.

Within the mentioned issues, a research program, between the Institute for Inorganic Chemistry and Surfaces of National Research Council and the Superintendency for Architectural Heritage and Landscape of Venice and Lagoon, started more than ten years ago aimed at the study of artificial treatments used in the restoration of stone, from the late nineteenth century to nowadays. The research was carried out both by studies in historical archives and by an extensive program of scientific investigation and analysis on the main relevant monuments in Venice.

Below a summary of the current state of research and a hint to the possibilities for future developments are reported.

2. New materials for stone treatment used in Venice in the XIX century

The great development of chemistry in the 19th century, together with the need to prevent deterioration on monuments by applications of efficient consolidants, gave rise to the birth of many patents in Northern Europe (Spinosa 2007; Lewin 1966). Venice became an experimentation laboratory for these new methods of treatment due to the great number of monuments to be restored. The Venetian architect Giacomo Boni brought to Italy the methods of soluble silicates , the so called *wasser glass* (water glass), invented by Fuchs in 1818. Boni used a modification of the method (Ransome, 1856) where the alkaline silicate was used with the addition of calcium chloride (or barite or aluminium sulphate), to reduce the solubility and to prevent the negative effects of Na/K ions. He applied this mixture to the main entrance of Doge's Palace, Porta della Carta (1883) (Calabretta and Guidobaldi 1986). The presence of this treatment, confirmed by analysis made during the restoration of 1979 (Lazzarini and Fassina 1979), is well documented in a number of papers.

Since the beginning, this method was considered controversial (Piacenti 1993; Tomaselli 2005) and, again, Venice was the first Italian city where the modification of the silicate method was experimented. In fact, the engineer Pietro Saccardo treated the marbles of the façade of S. Mark's basilica with the fluosilicates (Kessler 1883), a mixture of silicic acid, fluoridric acid and a metal (Al, Cr, Mg, Pb, Cu, Zn). Nothwistanding the advice of caution expressed by the experts of the Italian Ministery, the method diffused, not only in Venice but also on other historical cities. (Tomaselli, 2005; Spinosa 2007)

In fact, it was used in many Venetian monuments: Acritani pillars (Fassina et al. 1993; Bassotto et al. 2010), Procuratie (Sgobbi 2010), Ca'Rezzonico (Sgobbi 2010), Marciana library (Basso et al. 1999), Doge's Palace, Ca' d'Oro (1967, application of fluosilicates under vacuum by Sanpaolesi) (Fassina et al., 1993, Spinosa 2007), façade of Scuola Grande di S. Marco (70's). (Fumo 2007)

The use of soluble silicates, and their mixture, even with fluosilicates together with waxes or fats, diffused very fast and their evidences were found in many Venetian monuments, according to the scientific survey firstly performed by the labs of Venice Superintendency of Fine Arts (Fassina 1994, 1995).

3. Venetian stone conservation with XX century new materials

A great enthusiasm welcomed in Italy new products synthetized by plastic industries in the middle of the 20th century. Many of them were quickly patented and sometimes tested, turning out to be useful products for the treatment of stone. A large variety of polymers became available (acrylics, epoxy, silicones) and researches on their application spread, because of the new needs induced by the increasing pollution of the city and of the new sensibility, generated also by the disastrous floods in Florence and Venice in 1966 (Alessandrini and Laurenzi Tabasso 1993; Ghigonetto 1985). Right in Venice, Marchesini experimented for the first time in 1966 the use of methylphenylpolysiloxane under-vacuum, for the consolidation of the marble statue of S. Alvise, located in the façade of S. Alvise Church (Amoroso and Fassina 1983). Analysis

on this monument showed, after more than 20 years, a controversial behavior of the application: where the polymer penetrated deeper and homogenously, it prevented further deterioration of the artifact, while it failed where the resin remained superficial (Fassina et al. 2001). The same product was also applied on marbles sculptures of central fastigium in Saint Mark's Basilica (Badan et al. 1979) and in S. Martino di Castello church.

As regards the acrylics, they were used for the first time in 1972 in the lunette of S. Marco in the Frari Church, while in the lunette of the portal of Scuola Grande di S. Marco in the following year (Fumo 1997).

The acrylic-silicone resin mixture, the well-known Bologna cocktail, used in many Italian and European monuments, was applied during the long restoration intervention of Saint Mark's Basilica (1982-2008). A very detailed survey of the first treatments on the central Arch and on S. Clemente Arch run more than 30 years later evidenced that the molecular alteration of the siliconic and acrylic polymers caused yellowing, reduced efficiency and also affect removability of the treatment. (Favaro et al. 2006, 2007a.). To address the removability issues, an extended study was carried out during the conservation intervention (2007-2011) on the marble columns of the gallery of the Renaissance courtyard facade of Doge's palace, extensively treated in the late 80's with the Bologna cocktail.(Abbate et al. 2010)

Epoxy resins were also used for stone conservation in Venice: relevant examples are the marble Statue of the Virgin and the Child in the church of Santa Maria dei Miracoli, different lithotypes in the loggetta del Sansovino (1972-1973) and the marble statues in the Doge's palace façade, facing on the Saint Mark's basin (Moncrieff 1976, Moncrieff and Hempel 1977). The restorers used also a siliconic resin (methyltrimethoxysilane) but for the Loggetta this was chosen only for the marbles, while an epoxy resin was used for other lythotypes. In 1995 a monitoring of the state of conservation of the Loggetta Sansoviniana, found evident chromatic alteration of the epoxy resin, scarce penetration and shrinkage, while the silicon resin appeared glossy, greyish and shrunk, showing also a limited superficial penetration. The decay of both lithotypes was even worsened by salt efflorescences and detachments. (Fassina et al. 1999) The resulting evaluation about this intervention underlined its inadequacy. Taking into account these controversial drawbacks of treatment with epoxy polymers, their use in conservation field was mainly restricted to re-adhesion of detached parts rather than consolidation.

Another interesting and complex application of resins was made during the restoration (1976-1979) of Porta della carta, the main entrance to Palazzo Ducale, where different treatment solutions were adopted according to the typology of stone and artifactsA mixture of acrylic siliconic resin, a silicon resin (by brush or under vacuum), a two-components silicon resin, an acrylic resin, were used for different parts according to the lithotype and the deterioration. (Antonelli 1979) The state of preservation of the marble sculptures, assessed 25 years after the treatment, was worse than that of the monument's other stone materials: the methyl-siloxane polymer has become tough and brittle, acting more as a filler rather than a consolidant (Favaro et al. 2005a).

As far as inorganic treatments concern, ethyl silicate has become one of the most used treatments for stone, particularly in the 80's. It is particularly useful in the treatment of silicate-based stone, while its applicability to calcareous stone has been

debated. Notwithstanding the fact that typical Venetian lithotypes are the calcareous Pietra d'Istria and the Verona limestone, ethyl silicate was widely used, especially in the treatment of bricks. The first documentation of its use regards the façade of San Salvador church (1985), but other examples can be found in many monuments: the bricks of the Cripta of San Marco, the lateritious surfaces of the south façade of Palazzo Ducale (Vio 1993), the statue of San Giovanni Nepomuceno, carved on Vicenza stone, a porous limestone with clay impurities. More disputable seems the consolidation with ethylsilicate of the façade of Dolfin Manin Palace, that is mainly composed by Pietra d'Istria. As a matter of fact, after a short time, the façade turned yellow in consequence of this and a further treatment was made, using also alkylalkoxysilane. (Ethyl silicates)

As far as another common inorganic treatment concerns, barium hydroxide was firstly applied only in the 60's, despite Church patent was developed one century before. An interesting example is the consolidation of the Lunette of Scuola Grande of San Giovanni Evangelista with the Lewin method (barium hydroxide, urea and glycerin) (Lewin 1971; Lewin and Baer 1974). During the investigation carried out in 1997 almost no trace of the barium treatment was detected in the polychrome plaque, leading to the assumption that this treatment has been barely effective as stone consolidation (Favaro et al. 2000).

4. Innovative materials for stone conservation: first experiences in Venice

The performance of synthetic polymers in preventing further deterioration has recently been drastically reconsidered as they frequently undergo chemical modifications induced by both environmental conditions and interaction with the substrate. This causes loss of efficiency and irreversibility of the treatment. Traditional and innovative inorganic materials (TEOS, micro- and nano-alcoholic suspensions of $Ca(OH)_2$ and titania) are supposed to be more suitable because of their chemical affinity with the building material itself.

Example of two different approaches can be found in some Venetian yard experimentation: the first is the "creative" re-use of old treatments, especially mortars, or the improvement of them, the second is the application of completely new products. Both treatments rely on the use of inorganic materials, reconsidered because more compatible with the substrates.

Two examples of the first approach are (figure 1):

- the restoration of the thin spires towering over the roof frame of the Doge's Palace in Venice, enveloped by a sheath of thin stainless steel mesh and consolidated only by lime mortar. (Menichelli et al. 2010)
- The restoration of the façade of San Geremia Church (1998) deeply damaged by an arson, that dramatically modified the architectural structure of the building and substantially changed the chemical and mechanical properties of the Istrian stone. For this reason, an application of inorganic mortars was preferred to the use of an epoxy resin, which at the beginning was used (cycloaliphatic epoxy resin) (figure 1.) Mortars with different characteristic of resistance, adhesion and fluidity were used in different parts and moments of restoration. The US data show a very good consolidation, at least in the 57% of the investigated areas (Bassotto et al. 2007)

Regarding the application of innovative chemicals, a completely new approach was firstly successfully tested in lab and then applied for marble consolidation also in Venice:

a isopropanol solution of a calcium alkoxide applied on stone gives rise to crystals of calcium carbonate within the pore network, which aims to restore the cohesion of calcareous stone (Favaro et al. 2008). An application on the columns of the balustrade of the Doge's Palace seems to give encouraging results (Abbate et al. 2010).

Another very interesting application of a new product was made in the restoration of the façade of the Camera di Commercio in Venice. The relevance of this conservation treatment relies in the first use of titania (TiO_2) nanoparticles for a Venetian monument. Titanium dioxide is actually claimed to be one of the most used self-cleaning materials in the field of construction and building materials (Chen and Poon 2009) and its behaviour on stone substrates has been recently explored by different authors mainly with lab experiments using UV light to ascertain the photocatalytic activity and self-cleaning efficiency (Licciulli et al. 2011; Quagliarini et al. 2012a, 2012b).

In this restoration, titania was also added by nanostructured silicon dioxide, to synergically enhance the hydrophilicity. Upon the results of a preliminary experimentation, the final application implied the use of a primer (a water solution of the copolymer styrene-maleic anhydride ammonium salt and colloidal silica) to improve adhesion of the TiO_2 nanoparticles (Noè R 2010). A careful monitoring of the treated surface has to be planned in order to evaluate the effects of these products, considered a new entry in the field of built heritage conservation with no extensive studies performed in outdoor for ancient materials.

a b

Figure 1. Consolidation with fluid inorganic mortars on the thin spires of the roof of the Doge's palace (a) epoxidic treatment in San Geremia Church (b).

5. Evaluation of conservation interventions

Diagnostic techniques as well as physico-chemical analyses play a crucial role in providing a means for assessing the outcome of interventions over the long term. Investigations should be focused not only on the weathering processes, but also on the conservation materials used as consolidative and protective agents, and their ageing behavior. Quantitative measurements of specific physico-mechanical properties, before and after restoration, preferably with non-destructive techniques, provide a useful reference framework for monitoring the effectiveness and durability of conservation treatments. Ideally, restoration reports should be supported by quantitative data, and archived together with samples of the products applied. The evaluation of the medium-

and long-term effect of restoration interventions is a complex and still relatively undeveloped field. (Favaro et al. 2005)

With these premises, the already mentioned project between Superintendency for Architectural Heritage of Venice and CNR-ICIS has been developed to identify an evaluation methodology of the behaviour of conservative polymeric treatments. The availability of a data base of the restorations made under the control of Superintendency and the chance to exploit some of the most modern analytical techniques allows to write down a detailed investigation protocol to evaluate the conservation state of the treated artefacts that includes both physical and molecular studies to test the efficiency, durability and drawbacks of applied products (Favaro et al. 2005b, 2006, 2007a, 2007b, 2007c). This fruitful cooperation among different expertnesses determined also a constant multidisciplinary approach to new restoration treatments (or better re-treatments). Two interesting examples are the new restoration of the Balustrade of Doge's Palace, treated in the 80's with Bologna cocktail and where, before the new intervention, an experimentation on cleaning and consolidating methods together with analytical investigations was carried out (Abbate et al. 2010), and the massive intervention in San Geremia Church, deeply damaged by a fire. Because of the characteristic of the artifact and of the damage, a continuous discussion in each phase was necessary, with a step-by-step verification of strategies, materials and methodologies (Bassotto et al. 2007).

Another good example of this fruitful discussion is the restoration of the thin spires towering over the roof frame of the Doge's Palace, where the use of polymers in a complex situation (sun and heat exposure, mechanical stress) was discarded in favor of more safe mechanical devices to ensure stone cohesion. (Menichelli et al. 2010)

6. Conclusions

Venice has always been a site where the most innovative materials have been used in order to ensure a long term durability of its stone monuments. Starting from the early debates on conservation issues, traditional and new products have been used and the response of time gave useful information on which are the most efficient one for conservative purposes. In the perspective to avoid the use of inadequate products and to evaluate the performance, compatibility, durability and the re-treatability of the already applied ones, a close collaboration between Research institutions, such as the National Research Council, and Cultural Heritage Venetian Offices has been set up since many years. The analytical techniques offer the chance to increase the knowledge on old and new materials, and, when necessary, to foreseen the possible drawbacks of new products.

The strict cooperation and continuous discussion among architects, scientists and curators and the sharing of knowledge on new and old materials, history and significance of the monuments, allow to perform sustainable interventions. This approach, including a wider concept of compatibility, encompasses all the history of the artefact, including all the treatments and becomes an example of good restoration practice.

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