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# ASSESSMENT OF SILOXANE-BASED POLYMERIC MATRICES AS WATER REPELLENT COATINGS FOR STONE MONUMENTS

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## Abstract

The effectiveness of four polymeric water repellent coatings used for the protection of two monumental limestones, commonly used as building materials in Spain and Romania, has been evaluated. The selected coatings include three commercially available siloxane-based water repellent products and a new hybrid nanocomposite with silsesquioxane units synthesized *via* sol-gel technique. The water repellents were applied onto the limestones, and the coating protective efficiency was determined by measuring the surface contact angles, water vapour permeability and water absorption by capillarity. The optical properties of the applied coatings were also investigated and ranked in consideration with their optical characteristics.

*Keywords:* polymer coating, siloxane-based water repellent, limestone

## 1. Introduction

The monumental stone buildings are usually deteriorating under environmental conditions. Water infiltration is one of the main causes of damage and degradation of porous stones, water acting as a transporting agent for aggressive pollutants that often cause corrosion. In addition, freezing/thawing cycles of water may lead to fractures inside stones structure. To prevent or reduce liquid water intrusion, water repellent treatments are applied on architectural stone surfaces in order to create an impermeable barrier to water, without limiting water vapour permeability of the material, thus allowing the passage of water vapour through the stone out of the walls [1]. The application of these protective/conservation treatments slows down the weathering process and increases the durability of the monumental stones, while the coating process can be repeated from time to time if necessary. The expected coating properties should ensure optimal and cost-effective water protection, avoiding on the other hand any physical or aesthetic stone alteration. In addition to impermeability to

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liquid water (water repellency), such surface modifications should also have a good permeability for water vapours, a reasonable chemical and photochemical stability and good optical properties in order to preserve, as much as possible, the initial stone colour.

For the present study, two types of limestones, from Spain and Romania, were selected, considering their regional significance, abundance and level of usage as construction materials of monumental buildings (churches, monasteries, cathedrals, etc.) with significant historic and artistic importance from the cultural heritage point of view. The first selected rock is a bright white micritic dolomitic stone, typical for the Spanish region of Asturias, called Laspra. This rock could be widely found in Asturias, especially in Oviedo area, being used, for example, as the main building material of San Salvador Cathedral of Oviedo (Figure 1a). This cathedral is one of the most representative buildings of the late gothic architectural style in the province of Asturias and presents a significant interest. Three types of stones were used for the construction of the cathedral, i.e., Laspra, Piedramuelle and Tinana, the first one being found, as building material, in more than 60 % of the cathedral. Laspra was used to build all the interiors (the church and Sala Capitular) and an important part of the exterior (Claustro and Portico), its period of usage having the roots in the $18^{th}$ century (until the first half of the $16^{th}$ century). The three types of ornamental stones can be easily distinguished just looking at the monument, Laspra being recognized by its bright white aspect. Small inner parts of two preromanic churches, from the $9^{th}$ century, outside Oviedo, namely Santa Maria del Naranco (Figure 1b) and San Miguel de Lillo (Figure 1c) were also built using Laspra as building material. These last two churches are included in UNESCO's Heritage List since 1985.

The second selected stone, named Repedea, comes from Romania and can be described as a bioclastic oolitic limestone. This type of stone can be found in the eastern part of Romania, along the Moldavian Platform, an oolitic limestone slate covering a surface of approximately 3000 $km^2$. Repedea was the main building material in the construction of many significant churches and monasteries, since antiquity until the present time, the most representative churches existing in the area being built, in many cases, only from this stone.

An important monastery, from both historic and cultural point of view, situated in the northeastern part of Romania is the Dobrovat Monastery (Figure 1d), the whole architectural assembly being built (1503–1504) using Repedea limestone. The choice of the place for building the monastery was not by chance, as confirmed by $15^{th}$ century documents. The Romanian voevods of that time choose the Dobrovat valley for building the monastery, being influenced by the ancient monastic life in that area. The monastic assembly, the way it looks today, contains many constructions like The Descending of the Holy Spirit on the Disciples Church – the only church from that period preserved intact in the Moldavian county, the chapel, the entrance tower with the enclosure wall (partially battered) build in the $18^{th}$ century, the ruins of some constructions from the $18^{th}$ century, the cell assembly with administrative places from the $20^{th}$ century. The Descending of the Holy Spirit on the Disciples Church is the most important sight from the enclosure and the most valuable one, architecturally and artistically speaking. The entire assembly is plastered by a thin layer through which one can see the construction materials, quarry and matched stones, set by the ridges. The great wall assembly from Dobrovat prefigures many iconographic trends of the wall painting in Moldavia of the 16th century.

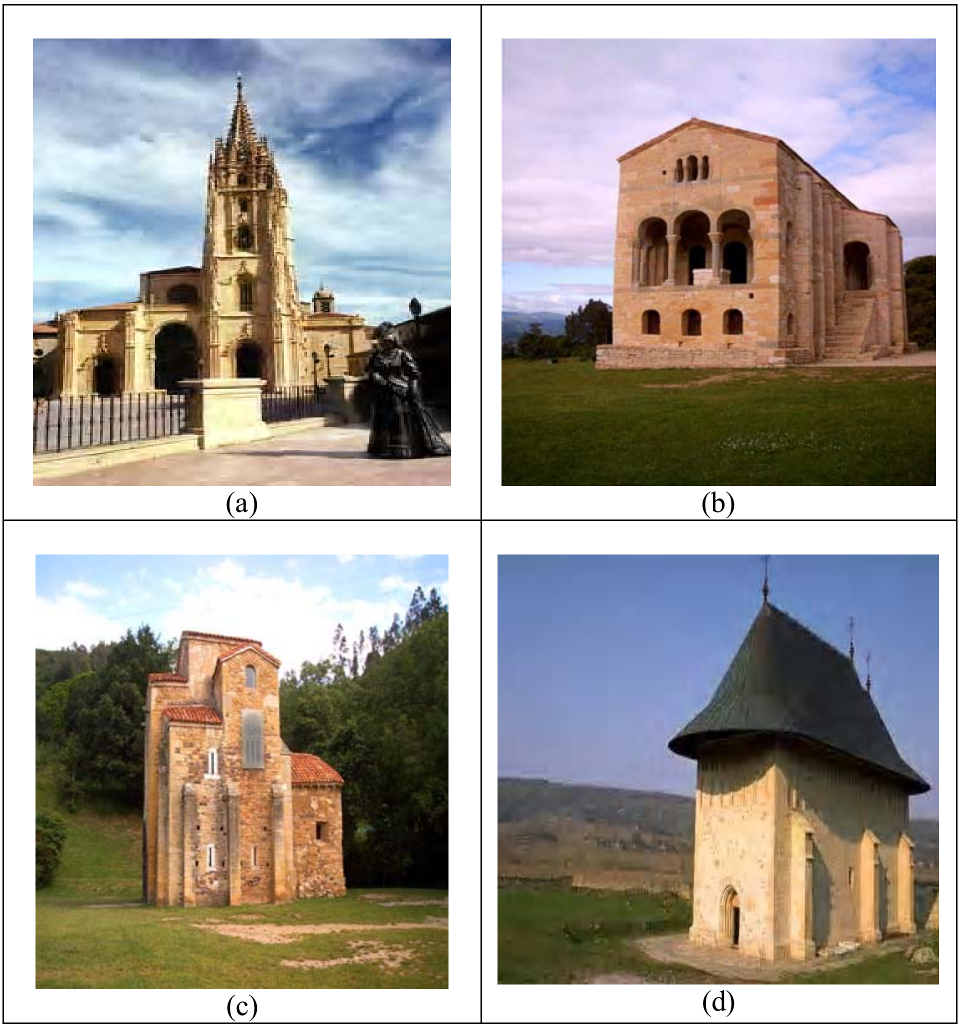


**Figure 1.** (a) San Salvador Cathedral (origin: 9th century, period: 16th century, style: gothic); (b) Santa María del Naranco (period: 9th century, style: pre-romanesque, UNESCO's world heritage site since 1985); (c) San Miguel de Lillo (period: 9th century, style: pre-romanesque, UNESCO's world heritage site since 1985); (d) Dobrovat Monastery (period: 16th century, style: medieval Moldavian).

A customary procedure in the protection of monumental buildings is the conservation/consolidation of the stonewalls by applying commercial products obtained through the sol-gel reaction, recognized as an excellent technological approach for protective coatings and able to impart new properties to the treated stones, such as water repellency, particularly if siloxane polymers are involved [2]. These products polymerize within the structure of the stone, thus significantly protecting the material. The advantages of sol-gel obtained products are well known to professional conservators/restorers:

- they are low viscosity products, which facilitates a deep and homogeneous penetration into stones substrates;
- the humidity present within the monumental stones is enough to produce the spontaneous crosslinking of the product;
- the polymer forms oxygen-silicon bonds similar to the ones existing in certain rock minerals.

The present study is aimed to investigate the stone protection efficiency of different polymeric coatings. Three of the applied coatings are commercially available siloxane-based oligomers and polymers and one is a new hybrid nanocomposite with silsesquioxane units, synthesized *via* sol-gel technique [3] in order to be used for the same purpose as the commercial ones.

## 2. Experimental

### *2.1. Materials*

The selected commercially available siloxane-based chemical products are (1) Lotexan-N (Keim), a siloxane prepolymer substituted with methoxy, methyl and alkyl groups, dissolved in a mixture of aromatic/aliphatic hydrocarbon solvents, (2) Silres BS 290 (Wacker), a mixture of silanes and siloxanes, to be applied using white spirit as solvent, and (3) Tegosivin HL 100 (Goldschmidt-Degussa), a typical siloxane resin having ethoxy and methyl substituents attached to the silicone atoms, mixed with white spirit as solvent. The hybrid nanocomposite with silsesquioxane units (TMSPMA) was obtained combining the sol-gel technique and the radical polymerization of an alkoxysilane sol-gel precursor, namely 3-(trimethoxysilyl)propyl methacrylate, in the presence of a primary amine surfactant [3]. The limestone substrates (Laspra, Repedea) were characterized in terms of chemical composition, texture and porosity through X-ray diffraction (XRD) (D8 Advance Bruker AXS) and polarized light microscopy (POL) (Leica DM 4500 P). The stones petrographic characteristics were determined by POL, and their porous system by mercury intrusion porosimetry tests (Fisons Porosimeter 2000).

### *2.2. Coating application and evaluation tests*

The stone samples were cut in blocks (5x5x1 cm) and stored in desiccators at 25° C and 50% relative humidity (RH) for at least 24 h prior to coating application. The products were applied by brushing the stone surfaces with polymer solution. After coating application, the stone samples were kept in desiccators at room temperature and a controlled value of 50% RH. Solvent evaporation was monitored gravimetrically until the treated stone specimens reached a steady weight. The contact angles were measured using a Kruss Easydrop Standard Goniometer (DSA 100 Soft). Capillary water absorption measurements were performed using the gravimetric sorption technique [4, 5]: the weighted stone blocks were placed for 24 h on a filter paper pad partially immersed in distilled water and then weighted again to determine the amount of water absorbed by capillary forces. The degree of protection against water absorption by capillarity, PC, was calculated for 24 h of samples exposure to water [6] with the relation:

$$PC = (A_1 - A_2)/A_1 \qquad (1)$$

where $A_1$ is the mass of water absorbed by the uncoated substrate and $A_2$ is the mass of water absorbed by the treated substrate [7]. Both $A_1$ and $A_2$ were determined by gravimetric measurements.

For water vapour permeability measurements, the sample blocks were fixed on the top of identical cylindrical poly(vinyl chloride) containers partially filled with distilled water. The containers were afterwards placed in a desiccator, kept at a value of 25% RH and at constant temperature (20° C). The containers were weighted every 24 h, for 7 days. It was assumed that the vapour flow through the stone had reached a constant value when the difference between two consecutive daily weight variations was less than 5%. The permeability coefficients (Kv) were calculated according to:

$$Kv = -(\Delta M/S)/t \ (g/m^2 \cdot 24h) \qquad (2)$$

where

$$(\Delta M/S) = -(Mt - Mo)/S \ (g/m^2) \qquad (3)$$

$M_0$ being the initial container mass at t = 0 (g), and $M_t$ the container mass at $\Delta t$ = 24 h; for t = 0, $M_t = M_o$, (g); S = 0.00159 $m^2$ (standard value).

The optical characteristics were evaluated through colour alteration measurements taken on homogeneous spot areas using a portable MiniScan XE Plus (HunterLab Associates Inc., USA) reflectance spectrophotometer and were determined by the use of L*, a* and b* coordinates of the CIE 1976 scale [8]. Colour measurements are expressed using CIE L* a* b* and CIE L* C* h systems, where L* is the variable lightness, which can vary from 0 (black) to 100 (white), a* and b* are the chromatic coordinates, i.e., +a is red, –a is green, +b is yellow and –b is blue. The attributes of chroma are C* – saturation or colour purity, and hue h – colour wheel. The global colour variation (ΔE) was evaluated using the formula:

$$\Delta E^* = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2} \qquad (4)$$

## 3. Results and discussion

The crystallographic structure of the stone samples was studied by X-ray diffraction. The XRD peaks of Laspra indicate the presence of ankerite, calcite, dolomite and quartz, while the ones corresponding to Repedea show the appearance of calcite, magnesian calcite, quartz and aragonite. Table 1 lists the chemical composition of stone samples investigated by XRD diffraction, as well as their structure and texture characteristics given by POL microscopy. From the porosity point of view, Laspra is a microporous stone, having a *moldica* porosity and the mercury intrusion porosimetry test revealed its open porosity of 30.3 %. Repedea's texture can be described as a *granuda oolitica*, with an open porosity of 13.7 %.

**Table 1**. Chemical composition and petrological properties of the stone substrates.

| **Substrate composition (%)** | **Laspra** | **Repedea** |
|---|---|---|
| Calcite ($CaCO_3$) | 7 | 85 |
| Ankerite ($Ca(Fe,Mg)(CO_3)_2$) | 90 | - |
| Quartz ($SiO_2$) | 3 | 10 |
| Calcite, magnesian ($(Ca,Mg)CO_3$) | - | 5 |
| Apparent density ($g/cm^3$) | 1.92 | 2.32 |
| Open porosity (%) | 30.29 | 13.67 |

**Table 2.** Protective efficiency tests for the selected stone substrates and treatments.

| | $Q_{c, degree}$ | PC | $-K_v$ (25°) ($g/m^2$x24 h) | ΔE* |
|---|---|---|---|---|
| Laspra | | | 292.14 | |
| Lotexan-N | 147 | 0.57 | 87.56 | 1.14 |
| Silres BS 290 | 149 | 0.53 | 66.13 | 1.91 |
| Tegosivin HL 100 | 146 | 0.93 | 108.11 | 0.75 |
| TMSPMA | 122 | 0.65 | 135.82 | 2.12 |
| Repedea | | | 161.89 | |
| Lotexan-N | 141 | 0.85 | 114.96 | 10.38 |
| Silres BS 290 | 122 | 0.95 | 80.7 | 12.18 |
| Tegosivin HL 100 | 103 | 0.75 | 54.83 | 11.92 |
| TMSPMA | 106 | 0.50 | 120.49 | 12.09 |

Table 2 presents the effect of the protective coatings applied onto the limestones in terms of static contact angle ($Q_c$), protection against water absorption by capillarity (PC), permeability coefficient ($K_v$) and global colour variation (ΔE). Contact angle measurements are a significant index of the treated stone surface water repellency. For stone protection, the minimum acceptable value for $Q_C$ is 90° [2] and, as can be seen from the experimental data given in Table 2, a good surface hydrophobicity was attained for all investigated coating/substrate combinations. An interesting conclusion can be drawn, i.e., the degree of hydrophobicity, expressed by the measured contact angles, is different for the same polymeric coating applied on different stone substrates. This behaviour is expected since Young's equation is valid only for passive, atomically flat and chemically homogeneous surfaces.

The petrophysical variations of the limestones after the application of water repellents (water–stone contact angle, water–vapour permeability and colour) allow the assessing of the performance of the tested treatments. Considering the water–stone contact angle results (Table 2), before and after impregnation, one can establish the following hierarchy:

- 100°-120°: Tegosivin HL 100 and TMSPMA applied on Repedea;
- 120°-140°: Silres BS 290 and TMSPMA cast on Repedea and Laspra, respectively;
- >140°: Lotexan-N, Silres BS 290 and Tegosivin HL 100 applied on Repedea and Laspra, respectively.

In contrast to the instant water repellency represented by the contact angle measurements, the long-term water resistance is represented by the differences in water absorption by capillarity for untreated and coated stone substrates. As expected, the polymer coatings are decreasing, to a higher or lower extent, the amount of absorbed water by the stone sample. Similar measurements were performed for all investigated coating/substrate combinations and the results are summarized in Table 2. The higher is the PC value, the higher protection against water absorption by capillarity is achieved. The impermeability of polymeric coating film to water vapour can lead to water condensation just underneath the film. In time, this can determine the loss of film adhesion and, eventually, film detachment [9].

The reduction in water vapour permeability is inevitable, as a consequence of the water repellent properties of the polymeric film, but the lowest possible decrease is pursued [5]. The less the reduction in water vapour permeability as compared to the untreated stone, the higher is the efficiency of the chemical treatment. The permeability coefficients registered for all investigated water repellents cast onto Laspra and Repedea are listed in Table 2. The water vapor permeability values of the specimens impregnated with the treatments yield to the following conclusions:

- reduction < 30 %: Lotexan-N and TMSPMA applied on Repedea;
- reduction ranging between 30 and 70 %: Silres BS 290 and Tegosivin HL 100 applied on Repedea and Tegosivin HL 100 and TMSPMA applied on Laspra;

- reduction > 70%: Silres BS 290 and Lotexan-N cast on Laspra.

The optical changes determined by the coatings are usually attributed to the degree of oxidation of the chromophore in the chromogen minerals, as well as to their concentration [7, 128; 10]. The chromatic parameters of the limestones before and after treatment (Table 2) were determined to analyze the effect of the protective coating on optical stone properties: the smaller the differences between the measured values before and after coating, the better the obtained results.

Finally, further categories can be established in accordance with the chromatic variations induced by the applied treatments, considering parameter $\Delta E^*$:

- $\Delta E^* < 1$: Tegosivin HL100 applied on Laspra;
- $1 < \Delta E^* < 10$: Lotexan-N, Silres BS 290 and TMSPMA applied on Laspra;
- $\Delta E^* > 10$: Lotexan-N, Silres BS 290, Tegosivin HL 100 and TMSPMA on Repedea.

It is to be mentioned that the acceptable chromatic variation is considered to be $\Delta E^* < 5$, but some monumental stones are not fitting in these limits no matter the applied treatment.

## 4. Conclusions

The efficiency of different siloxane-based coatings in the protection of stone monuments such as the Oviedo Cathedral (Spain) and the Dobrovat Monastery (Romania) was investigated. The advantages of coatings obtained from siloxane-containing polymer matrices are the consequence of their ability to crosslink *in situ* after substrate treatment. The best option of the siloxane-based water repellents used for the protection of the selected limestones should yield the best results in terms of water/stone contact angle, water absorption by capillarity, water vapour permeability and optical properties (colour alteration). For the assessment of siloxane-based water repellent coatings, one has to take into consideration the highest attained liquid water-repellency values – as evidenced by an increase in water–stone contact angle, the lowest induced decrease in water-vapour permeability, the lowest water absorption by capillarity and the smallest induced chromatic variations. From the obtained results, it can be pointed out that the same siloxane-based polymeric treatment yields different results and performances when applied to distinct carbonate stones.

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