Gypstop - colloidal silica for protective coating of porous building materials: practical experience at the Wawel Castle, Cracow, Poland

P. Stepien, R. Kozlowski, M. Tokarz

a PKZ SA, 30082 Cracow, Poland
b RK Developments, 30015 Cracow, Poland
c Eka Nobel AB, 445 80 Bohus, Sweden

ABSTRACT

The GypStop process involves the impregnation of porous building materials with water based silica materials to produce a protective layer of silica inside the pore system of the treated material. During the last two years the method has been employed in practical conservation projects on porous limestone and plaster at the Wawel Castle, Cracow, Poland. Our observations have shown that GypStop is very effective in protecting carbonatic porous materials against corrosion from acidic air pollutants. It also considerably reduces deposition of dirt and dust. The GypStop products were also successfully used to produce thin semi-transparent coatings on the surface of the stone or plaster. The GypStop treatment was effectively combined with other conservation procedures such as consolidation, impregnation with water repellent solutions, etc.

INTRODUCTION

Application of protective surface layers to stone and other building materials has been discussed frequently among conservators. Since the nineteenth century, a tendency to expose clean, "natural" stone surfaces has gradually prevailed. With the new possibilities offered by synthetic resins, a concept of transparent protective layers, which do not alter the appearance of the materials, was generally accepted in the sixties and seventies, Torraca (1). However, later studies on monuments, among which investigations of great ancient marble monuments of Rome should be mentioned, in particular, Allesandrini et al. (2), revealed that since ancient times non-transparent, or semi-transparent, protective layers have frequently been applied to stone in the past. In most cases these were based on lime-wash, to which organic components such as milk, casein, and egg white were added. Slow ageing of the coatings, which must have involved the decomposition of organic material and its interactions with calcium carbonate, has led, in a long term process, to the formation of layers resistant to
corrosion and thus protect the stone well. The formation of calcium oxalate documented for the ancient marbles may be mentioned as one possible mechanism of the lime-wash transformation, Gratziu (3). The lime-washes were not only used as protective coating, but also, when mixed with pigments, as colour layers. The colour of a layer was not necessarily different from that of the stone; it could be similar or identical.

At the Wawel Castle - Cracow, Poland, lime-washes very similar in colour to the underlying stone, were also identified during conservation of the Renaissance stonework. Historical sources confirm that the stonework was originally painted "colore lapideo" (in the colour of the stone). A combined protective and aesthetic function of this kind of the layers is obvious, according to Stepien (4). Parallel to the research on historic non-transparent, or semi-transparent protective layers, the idea of re-using them in the present-day conservation has emerged. The "lime-method" used in the conservation of the Wells Cathedral, Ashurst (5), and works in Rome - Stadium of Diocletian, Demitry (6), Collonna di Foca at the Forum Romanum, Stepien (7), are well-known examples.

If the re-use of the lime coatings has already been accepted by conservators, one should bear in mind that the method can perform well in relatively clean environments. In polluted, aggressive environment, lime coatings are quickly destroyed by acid corrosion before their slow natural ageing process can take place. The function of the lime layer is thus to be consumed gradually by the corrosion process retarding, for a limited period of time, the decay of the protected material. As a modification of the lime protective coating, a much more resistant silica enriched layer, which could serve also as a colour layer, was investigated.

MATERIALS

Special silica products, developed by Eka Nobel of Sweden under the brand name GypStop were used for the purpose. Two specific products, GypStop P (alkaline with a pH of 9.5) and GypStop S (slightly acidic with a pH just below 6), containing 40 wt-% and 20 wt-% silica in water respectively, have been used. Both products consist of minute colloidal particles dispersed in water and on contact with a porous material, they produce a dense silica layer.

GypStop P is capable of penetrating relatively deep into the pore system. The porous material acts as a sieve which stops the silica particles in the bottle-neck areas that separate the larger voids. When the critical concentration of the particles is exceeded, a silica gel grows and fills the pore space inside the treated material (Fig. 1).

The depth of the sol penetration is usually several millimetres, and depends on pore size and sol concentration/dilution. The artificial weathering in a humid atmosphere containing SO₂ indicated that the silica layer thus formed very effectively reduces the rate of stone decay (Fig. 2).

The GypStop S product also consists of colloidal silica particles, but comprises a layer of aluminum on the surface. This sol is stable only at slightly acidic pH.
Fig. 1. Cross-section of porous limestone during GypStop treatment.

On contact with any alkaline, e.g. carbonatic, material it flocculates very rapidly, which results in the formation of a thin, but relatively dense, surface coating of a thickness in the range of a fraction of a millimetre. The corrosion studies revealed that such a thin layer of GypStop S alone cannot sufficiently well protect the underlying stone against the corrosive action of SO₂, but combined with GypStop P treatment protect the surface very efficiently. (Fig. 2.)

Further details concerning the characteristics of the GypStop products and their evaluation as protective treatment for porous limestone have been described in a previous paper, Kozlowski et al. (8).

Fig. 2. Sulphur distribution in limestone samples artificially weathered.
Left: untreated. Right: GypStop treated.
PRACTICAL EXPERIENCES AT THE WAWEL CASTLE

Field tests of the described products were carried out in 1991 during conservation of the sixteenth century Konarski Chapel at the Royal Cathedral of Wawel. The chapel has a large window, a dividing cornice and a socle made of several varieties of porous limestone from Pinczow, Poland on its exterior wall (Fig. 3). Depending on the exposure to rain water, some areas of the stone work were covered with dense black crusts, others were washed - not only free from any corrosion product overlayers, but eroded and rough. After removal of the crusts, a variety of textures and colour tones appeared, owing to different modifications of stone, relics of colour layers and repairs from 1895 - 1910 (including cement joints).

From a conservator’s point of view, this variety had to be rendered more uniform to bring back the unity of composition, while at the same time respecting the varying original textures and colours of the materials. Repairs made with lime mortar fillings during the present conservation also had to be integrated with the old materials. An appropriate response to these needs was found in applying a semi-transparent layer of silica, produced from a mixture of GypStop S and pigments. Parallel to the protective function of the layer, the required uniform colour and texture were obtained, still with a natural character of stone rather than that of a painted surface. The settling of the silica layer on the stonework consolidated previously with Wacker Consolidant OH was the same as on untreated parts. The whole window frame was finally treated with Wacker 290 (oligomeric siloxane) to obtain water repellency - Fig. 4.

The parapet of the window and the dividing cornice, which showed very eroded surfaces, were first impregnated with the diluted GypStop P for deep penetration and filling the pores, and next treated in the same way as the window frame. The amount of water repellent solution absorbed by silica treated stone was not diminished by the GypStop treatment. On the socle, because of a danger of rising damp and salt crystallization several applications of GypStop P (in order to obtain considerable depth of penetration) were followed by the treatment with GypStop S mixed with pigments - Fig. 4.

The lime plaster, covering most of the wall surface, also needed its colour unified, microcracks filled and surfaces protected. In this case, a one-step treatment was chosen. Fast flocculating GypStop S was applied together with pigments and a small addition of silicone emulsion in water (Wacker BSR50) (Fig. 5). The pigments were the same as used for the stone conservation. Porous lime plaster absorbed the mixture well. Microcracks of the plaster were filled with silica, and a semi-transparent coating was produced on the surface. A more uniform colour of the chapel’s façade and a reduction of differences due to ageing have been obtained. However, the original appearance of the plaster has been retained.

Observations over the course of one year after conservation have confirmed that the effect is stable and the layer performs well as a protection against acid corrosion and dirt deposition (owing to smoothing of the surface). Figures 6 and 7 show a test area on the dividing cornice, of which the furthest right part was left unprotected, the middle part was treated only with a water repellent and the remaining part was
Fig. 3. Materials - stonework and plasters at the façade of the Konarski Chapel.

Fig. 4. Surface treatments executed at the façade of the Konarski Chapel.
Fig. 5. Semi-transparent coatings, consisting of GypStop S, inorganic pigments and silicone emulsion in water were tested on plaster.

An attempt has also been made to cover and mask with the silica layer the compact cement repairs in the lower part of the wall. The test proved negative. The dense "fatty" surfaces gave rise to poor adhesion of the silica layer, which then was partly washed away by rain-water.

The GypStop treatments were also applied in the chambers of the Royal Castle of Wawel. On several door frames of porous Pinczow limestone, dating from...
Fig. 6. Test areas on dividing cornice: right - untreated; middle - treated with Wacker 290; left - treated with GypStop P + GypStop S + Wacker 290.

Fig. 7. The same test areas on dividing cornice as shown on Fig. 6 but after 10 month after completion of conservation.
Renaissance times, or reconstructed in the nineteenth century, GypStop S with pigment was used for colour elaboration before final water repellent treatment with Wacker 290.

The conservators found the GypStop treatment more convenient than traditional elaboration with pigmented lime-wash. In contrast to the lime-wash, which changes the colour greatly during settling and drying, the colour of the layer based on GypStop S can be controlled much more easily as is only slightly lighter after drying. Settling of the coatings on the limestone and lime mortars was excellent; but proved less effective on some dense gypsum.

CONCLUSIONS

The tests of the GypStop silica products in practical conservation of several porous limestone sculptures, as well as historic plaster, proved generally positive.

Both deeply penetrating GypStop P and fast-gelling GypStop S have been used to provide protection against corrosion and desirable semi-transparent coatings coloured with pigments.

The conservators found the preparations easy and safe to use. Application can be combined with consolidating and water repellent impregnations.

The use of the products is particularly effective for porous materials, while the adhesion of silica layers to more dense, compact substrates proved weaker.

REFERENCES

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