Transactions on the Built Environment vol 4, © 1993 WIT Press, www.witpress.com, ISSN 1743-3509

Protective coating for marble and stones using n-semiconductors as pigments

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ABSTRACT

In previous works we have proved that the mechanism of sulfation of marble or calcerous stones of ancient monuments is similar to the mechanism of the uniform corrosion of metals (galvanic cell model). Thus we have successfully protected marbles by anticorrosive paints so far for the protection of Steel, such as Coal Tar Epoxy (C.T.E.) and Chlorinated Rubber (C.R.). C.T.E. is black and can be used only to protect black marbles; C.R. changes color by UV light. Therefore we have used our new type of pigments that we have applied for the protection of Steel, i.e. n-semiconductors such as Al_2O_3, Fe_2O_3 (imitates the red patina) with epoxy or acrylic vehicle. In the present work we used the above n-semiconductor (Fe_2O_3) doped with 1% MgO in acrylic vehicle (Paraloid B 72) and the protective properties increased. Thus the quantity of the pigment in the vehicle can be less than 2% without changing at all the appearance of the marbles and stones.

INTRODUCTION

By successive publications and communications, Skoulikidis et al. [1-10], we proved that the galvanic cell model is valid in the sulfation of marbles, just as in the uniform corrosion of metals: rate determining step the diffusion of Ca^{2+}. One interesting consequence of this mechanism is, as we have also proved, that details of the statues and ornaments are preserved on the surface of gypsum films, which have been totally eliminated from the interface gypsum-marble. Thus we must consolidate the gypsum film and not destroy it. We do this by inversion of $CaSO_4.2H_2O$ into $CaCO_3$ back using K_2CO_3 solution, Skoulikidis et al.[11]. One severe consequence of the mechanism is that, according to the fast solid state diffusion of calcium

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ions from the active centers (including high reliefs) of the marble surfaces through the "protective coatings", cavities are formed in the interface gypsum-marble (this is the cause of the details destruction) and due to the fact that the atmospheric pressure is higher than the pressure in the cavities all types of organic (polymers) or inorganic coatings crack and accelerate the sulfation (Fig.1). In all commercial products measurements (% weight gain) of their sulfation were taken. In all cases gypsum was found (EPMA)on or/and in the "protective" coatings and the coatings were cracked after different time intervals, Skoulikidis [6,8,9,13,14](See also deterioration of coatings in Bell and Coulthard [12]).

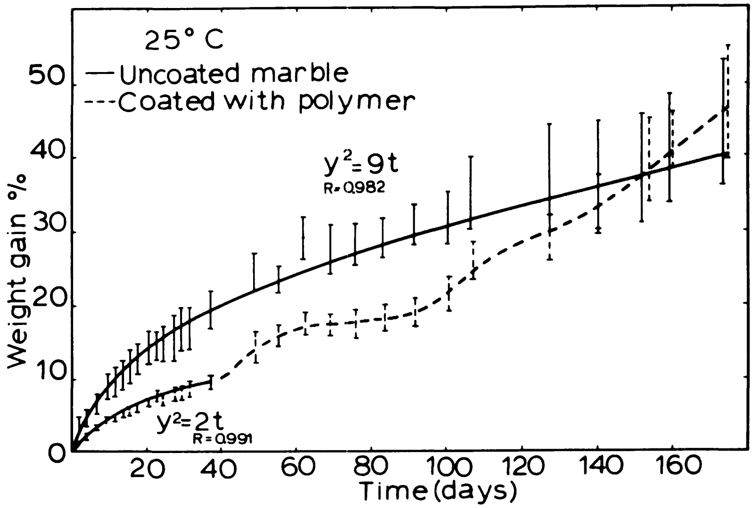

Figure 1: Sulfation: Weight gain % vs time for uncoated (-) and polymer coated (---) marble samples (Skoulikidis et al. [6,8]).

Similar results were taken with dilute sulfuric acid at 25°C. With dilute nitric acid at 25°C the coatings were immediately destroyed,e.g.Skoulikidis et al. [8,13]. On the contrary when we used Coal Tar Epoxy (C.T.E.) or Chlorinated Rubber (C.R.), Skoulikidis [6], known anticorrosive paints for steel, the results under the same conditions as for the diagram of Fig.1 are satisfactory (Fig. 2), Skoulikidis et al.[9,13,14]. But C.T.E. is black and can be used only for black marbles and C.R. changes colour under UV radiation.

In previous works of ours, Skoulikidis et al. [15,16], we used with success for the first time polymeric Epoxy or Acrylic vehicles with 30% Al_2O_3 or 5% Fe_2O_3 as pigments, especially prepared to have pronounced n-semiconductor properties, that intervened to the mechanism of corrosion of metals and retarded it. We employed the same systems for the protection of marbles. In Figures 3 and 4, we see that the epoxy+Al_2O_3 and

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epoxy+Fe_2O_3 protect satisfactorily the marbles and the coating does not crack as it is the case for the plain epoxy (Fig.2). The optimum percentage of the Al_2O_3 for both vehicles (epoxy and acrylic) is 30% for Al_2O_3 and 5% for Fe_2O_3.Al_2O_3 is a white powder and its proportion to the vehicles does not change appreciably the appearance of the marble. The Fe_2O_3 pigment is also possible to be used at 5%, matching the colour that marble acquires after some time of exposure in the environment (red patina) and to produce artificial patina on new marbles introduced during restoration. It must also be emphasized that both pigments act as anti-UV agents.

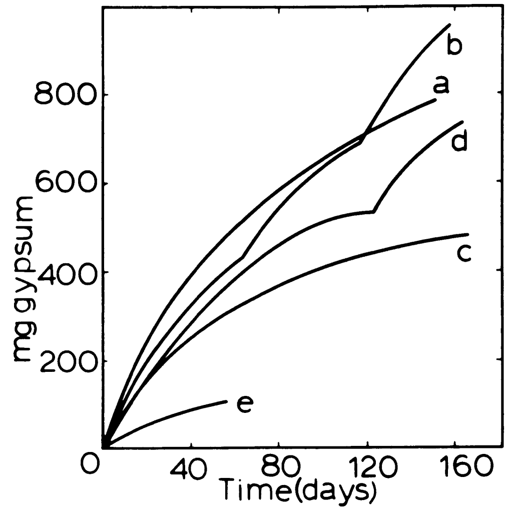

Figure 2: Quantity of gypsum formed on marble samples: a: uncoated marble, b: acrylic coated, c: coal tar epoxy, d: epoxy coated, e: chlorinated rubber, Skoulikidis et al. [9,13,14].

In spite of the fact that this pigment slightly changed the appearance of the white marble, it was used dopted in acrylic polymer to minimise the percentage of the pigment and consequently the color change.

EXPERIMENTAL

Materials

The following materials were used:
Marble specimens 3x5x0.5cm from the same quarry that the Acropolis Monuments were built; glass plates; distilled water, toluene, acetone; Paraloid B72 (P); Fe_2O_3, MgO, 4% Fe_2O_3.1% MgO (doped).

Procedure

The marble specimens were polished to 400 grit, washed with distilled water, dried at 40°C to constant weight and degreased with acetone. Nine of them were coated by paint brush with a toluene solution of plain P; nine with 5% (w/w) Fe_2O_3(vs solid P) pigmented (P) solution; nine with 10% MgO pigmented (P) solution and nine with 4% Fe_2O_3.1%MgO (doped) pigmented (P) solution. All specimens were dried at 40°C to a constant weight (total evaporation of the toluene). The final thickness of all coatings was 50 μm. With the same coatings glass plates were coated and dried at 40°C to a constant weight. This was done in order to measure a probable action of SO_2 on the pigments. All specimens, the nine uncoated ones included, were left in an environment of 50% SO_2 and 50% air saturated with water vapour at 25°C.

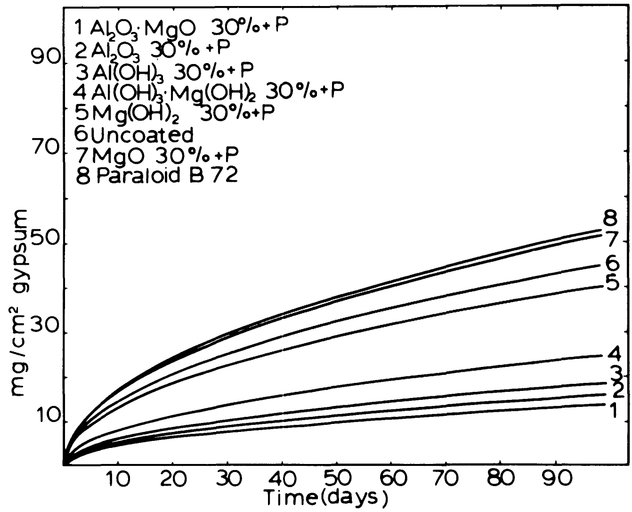

Figure 3: Weight gain of uncoated marble, epoxy coated and epoxy Al_2O_3 coated, Skoulikidis et al. [13].

Concerning the very high concentration of SO_2 compared to the concentration in the atmosphere (<200μg/m^3) we have proved that the simulation gives comparable results when the intensification of the conditions does not change the mechanism of the reactions[17]; the mechanism of sulfation remains the same (no change of activation energy) between a concentration of 150 μg/m^3 and 80% of SO_2, Skoulikidis [3,6]. Every 6, 11, 16, 25, 40, 80 days three specimens of each type were removed from the SO_2 environment and dried at 40°C to a constant weight. Thus the weight gain was measured. The weight gain was transformed to mg/cm^2 gypsum for each specimen.

From these weight gains of each specimen the mean value of the weight gain (mg/cm^2) of the corresponding (pigmented) coated glass specimen for the same time interval was substracted. [The weight gain of all pigmented coatings on glass plates are approximately in the reproducibility error limit

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of the weight gain of the coated marbles. In spite of this the results were calculated taking into account these values]. The results are shown in Fig.4.

DISCUSSION

From Fig.4 it follows that the plain Paraloid does not protect marbles from SO_2 as it was found and reported in other works, e.g. Skoulikidis et al. [9,13,14]. In addition to this the coatings crack, Skoulikidis et al. [9,13,14], and accelerate the attack of SO_2 to the marble. The MgO pigmented (P) retards to some degree the rate of sulfation. The Fe_2O_3 pigmented (P) protects satisfactorily marbles as it is also found and reported in works, Skoulikidis et al. [9,13,14]. The 4% Fe_2O_3.1%MgO pigmented (P) further retards the sulfation than the retarding of the sulfation by MgO and Fe_2O_3 used separately and thus protects the marbles more satisfactorily than the Paraloid pigmented with plain Fe_2O_3. This is an evidence that the preparation method of this pigment resulted to the formation of a doped semiconductor.

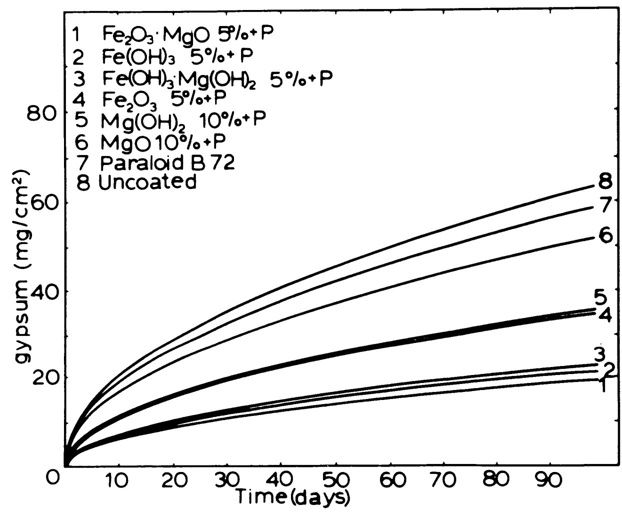

Figure 4: Weight gain vs time. 1.Uncoated marble; 2.Coated with vehicle (P); 3.Coated with 5% Fe_2O_3 pigmented (P); 4.Coated with 10% MgO pigmented (P); 5.Coated with 4% Fe_2O_3.1%MgO (doped Fe_2O_3).

Taking into account all values, the percentage of Fe_2O_3.MgO pigmented (P) that causes the same weight gain as the 5% Fe_2O_3 pigmented (P) is found to be 2%, i.e. 1.6% Fe_2O_3.0.4% MgO pigmented (P) can replace 5% Fe_2O_3 pigmented (P). Therefore the appearance of the white marble and its colour are not affected and the system can be used to protect white marble and stones.

CONCLUSIONS

From the above mentioned it follows:

1. The plain Paraloid B 72 (P) as coating does not protect marbles as it has been already reported in previous works.
2. The protection acquired by 5% w/w Fe_2O_3 pigmented (P) is once more verified.
3. The doping of Fe_2O_3 with MgO (Fe_2O_3.MgO 4:1) increases the protective properties of plain Fe_2O_3 pigmented (P) for the same content in (P).
4. The 2% Fe_2O_3.MgO 4:1 doped pigment in (P) can replace the 5% Fe_2O_3 pigmented one with the same protective results. Thus the appearance and the colour of marbles with or without red patina are not affected.

Experimental collaboration with Senior Chem. Eng. Student D. Koulouridis.

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