Progress in Organic Coatings 120 (2018) 132–142

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

A new preventive coating for building stones mixing a water repellent and an eco-friendly biocide

Stéphanie Eyssautier-Chuine[a,*], Ivan Calandra[b], Nathalie Vaillant-Gaveau[c], Gilles Fronteau[a], Céline Thomachot-Schneider[a], Julien Hubert[a], Jessica Pleck[d], Maxime Gommeaux[a]

[a] Groupe d'Étude sur les Géomatériaux et les Environnements Naturels Anthropiques et Archéologiques EA 3795 (GEGENAA) – SFR Condorcet FR CNRS 3417 – Université de Reims Champagne-Ardenne, Reims, France

[b] TraCEr, MONREPOS Archaeological Research Centre and Museum for Human Behavioural Evolution, RGZM, Neuwied, Germany

[c] Unité de Recherche Vignes et Vins de Champagne URVVC EA 4707, Laboratoire de Stress, Défense et Reproduction des Plantes – SFR Condorcet FR CNRS 3417 – Université de Reims Champagne-Ardenne, Reims, France

[d] Centre de Ressources Technologiques en Chimie (CERTECH), Seneffe, Belgium

ARTICLE INFO

Keywords:
Coating
Biocide
Hydrophobic
Chitosan
Silane/siloxane
Cultural Heritage

ABSTRACT

The durability of stone monuments is a constant problem as their decay through weathering is irremediable and endless. Fortunately, coatings are becoming more and more efficient and tailored to specific alterations of the stone material. This study aimed at developing an eco-friendly coating with both hydrophobic and biocide properties based on a silane/siloxane emulsion as a water repellent combined with chitosan and silver nitrate as biocides. Chitosan was first added at different concentrations to the water repellent and its efficacy was tested in laboratory conditions by the inoculation of axenic suspension of the green algae *Chlorella vulgaris* on a building porous limestone. Chlorophyll *a* fluorescence analysis displayed the chitosan acted on the photosystem of algae and limited their development but its effect was not optimal and higher dose modified the aspect of the stone. Low concentration of silver nitrate achieved a good performance thanks to the combination with the chitosan and the water repellent. The properties of coated stones and the efficacy of the formulation were assessed at two different doses of coating. The results showed that the lowest dose gathered all requirements to both preserve the stone monument with a weak colour change over time and to reach optimal biocide effect and a good hydrophobicity.

1. Introduction

For centuries, stone has been considered to be the perfect building material thanks to its durability. It imparted nobility and demonstrated the power and wealth of the building owners. The choice of stones was often dictated more by their aesthetics and availability rather than by their physical and mechanical properties. Now, the historical and cultural significance of many monuments calls to their preservation. The first effects of weathering are aesthetic but eventually lead to disintegration. Preserving stone in Cultural Heritage is a more effective way to assist in conservation than operating on altered stones by consolidation and substitution, processes that are more expensive and difficult since many quarries are now closed.

Weathering is mainly caused by climatic and anthropic conditions modulated by the intrinsic properties of stone linked to the fabric elements [1,2]. Water is the main natural factor of weathering which penetrates inside the stone directly by rainfall or by capillary rise. It causes damage through its chemistry laden with salts or pollutants and its mechanical stress induced by the changing states with temperature variations [3–5]. Protective layers, in the form of natural coatings, have been applied for a long time to prevent stone alteration. Some of them are still under study like oxalate salts for the protection of marble and limestone against chemical weathering [6]. Nevertheless, the development of water repellents based on synthetic inorganic and organic polymers substantially increased their efficiency and durability [7]. Hybrid coatings developed since the 1980s are mixed organic and inorganic components in mild synthetic conditions such as sol-gel process using metallo-organic precursors [8–10]. They have a good hydrophobic function that can still be improved to reach a superhydrophobicity with the silica nanoparticles embedded at various concentrations [11–13]. Avoiding the ingress of water could be the key to stop all the deleterious effects that alter stone monuments, but environmental factors like wall orientation, stone position and shape could favour biological degradation despite the application of a water

* Corresponding author at: GEGENAA – Université de Reims Champagne-Ardenne, CREA, 2 Esplanade R. Garros, 51100 Reims, France.
E-mail address: stephanie.eyssautier@univ-reims.fr (S. Eyssautier-Chuine).

https://doi.org/10.1016/j.porgcoat.2018.03.022
Received 19 February 2018; Received in revised form 14 March 2018; Accepted 20 March 2018
0300-9440/

repellent [14]. The intrinsic properties of building materials such as roughness, porosity and mineral composition also provide an appropriate environment for biological adhesion [15–17], thus compromising the efficiency of water repellents [18]. Furthermore, biocides used to remove biofouling inhibit the efficiency of water repellent if applied later [19]. Nowadays biocides are specifically developed for a preventive effect. Thanks to sol-gel process, many hybrid coatings are easily functionalised by the incorporation of metals as Ag, Cu, Zn, widespread for their antimicrobial properties and used in many fields for a long time [20]. In Cultural Heritage, they are still being investigated thanks to the emergence of nanoparticles (NPs – CuNPS, CuONPs, AgNPs, ZnONPs…), whose the performance has been assessed [21–24]. For many years, great interest has been devoted to the photocatalytic activity of the TiO_2, but many drawbacks persisted, e.g. its dependence on the wall exposition to sunlight, on the formation of soluble salts, on the dissolution of TiO_2 by rainfall and on its superhydrophilicity [25]. The best solution to reduce the penetration of water into the stone whilst keeping a biocide effect seemed to mix a water repellent and a biocidal or self-cleaning coating. Many studies demonstrated the effectiveness and the interaction of different components [13,26–28].

The present study aims at developing a new protective coating combining hydrophobic and biocide effects. Because many biocides have been banned due to their negative impact on the environment and human health, this research looked for an eco-friendly alternative. The chitosan, a polysaccharide derived from the chitin of crustaceans, exhibits an antibacterial activity despite its low toxicity towards mammalian cells [29,30].

In a previous study [31], the biocide effects of coatings based on tetraethoxysilane functionalised with hydrophobic silica as the water repellent were tested through chlorophyll *a* fluorescence with different $AgNO_3$ concentrations as the biocide. The lowest concentration of $AgNO_3$, when combined with chitosan and hydrophobic silica achieved an optimal biocide impact. Therefore, the addition of chitosan allowed reducing the use of $AgNO_3$, which is environmentally desirable. Moreover, the previous study used hydrophobic silica as the water repellent, which dispersed heterogeneously on the stone. The hydrophobic effect was also improved in the present study by the use of a hybrid silane/siloxane polymer. So the present study aimed at finding the best coating with chitosan as the only biocide or the best mixing of chitosan, silver nitrate and water repellent. It was designed to first validate the biocide effect with a biofouling test in laboratory conditions using the green alga *Chlorella vulgaris*. In a second step, coatings whose biocide impact was validated were further assessed for their influence on the aspect and microstructural properties of the stone. Finally, the hydrophobic performance and the durability were evaluated by artificial ageing procedure simulating sunlight and rainfall.

2. Material and methods

2.1. Substrate: Dom stone

Experiments were performed on a stone used in buildings and monuments in northern France and southern Belgium [32]. It is a limestone called the Dom stone dated from the Bajocian (180 Ma). For this study, fresh stone blocks were collected from the underground quarry located in the Dom-le-Mesnil village of the French Ardennes.

Dom stone is a russet bioclastic stone including iron oxide content (0.5%) and made of calcitic debris (85%): numerous echinoderm ossicles (25%) in a syntaxic cement (35%), shell fragments (10%), micritic grains (10%) and with only few quartz grains (5%) scattered in the rock [33]. It was chosen for its interesting petrophysical properties. Mercury (Hg) porosity value is about at 21.4%. The pore-size distribution is bimodal with a major pore access radius at 1.8 µm and a second one at 0.25 µm. More precisely, 51.6% of pore access radii are larger than 1 µm, 41% are between 1 and 0.1 µm and 7.4% are between 0.1 and 0.01 µm. The capillary coefficient C_1 relative to the weight increase per surface and per square root of time unit is $146\,g\,m^{-2}\,s^{-1/2}$ [34] and implies good connectivity in the intergranular macroporosity. Such characteristics make the stone particularly sensitive to weathering like heterogeneous disintegration [35] and mainly favour a bioreceptivity that results in a significant greening of the stone [36].

2.2. Composition and application of coatings

The protective coatings presented in this study have as a basis a formulation named Tegosivin® HE 328 developed by Evonik Industries AG. It is an emulsion concentrate based on organo-modified siloxanes and alkoxy-functional silanes. The polymerisation of this material is achieved at room temperature through a sol-gel process. This chemistry involves the evolution of nanoparticles in colloidal solution in a polymer network by gelation using Silicon as a precursor. Tegosivin® HE 328 was designed for the impregnation of building materials such as brick, stone and concrete, and is often used as a protective coating for porous stones in monuments [37,38]. It is diluted in water whereas many hybrid nanocomposite materials are diluted in organic solvents that promote the penetration of the treatment [39,40] but are less environmental friendly and pose health problem to the person applying the treatment. Moreover, Tegosivin® HE 328 was used here both as the precursor for the polymerisation of coatings and for its hydrophobic property.

Dom stone blocks were cut in prismatic slabs (5 × 5 × 1 cm) dried at 70 °C in a forced-air oven. They were weighed every day until the weight was stable. Products were sprayed on stone at a distance of about 20 cm in a single-step application with an airbrush tool which provides an air pressure of 8 bar and 25 L/min. Many procedures of coating application were investigated and the spraying procedure was used to match with the use of restoration workers and to limit the loss of product. They were applied on triplicate stone slabs. Table 1 gives an overview of the seven coatings investigated with their respective concentrations, their consumption and dry weight on samples. All tested coatings were based on 97 g/L of Tegosivin® HE 328 diluted in distilled water. Two biocide agents, commercially acquired from Sigma-Aldrich, were added. Chitosan is a poly-glucosamine polymer commonly obtained by de-acetylating chitin from crustacean waste. It is currently

Table 1
Coating names with the test used for their efficacy, their function, the applied product quantity, the equivalent dry weight and the concentration of components (Tegosivin® HE 328 concentration is not mentioned as it is 97 g/L in all coatings).

Coating name	Test	Function	Applied product quantity ($L\,m^{-2}$)	Equivalent dry weight ($g\,m^{-2}$)	Chitosan (g/L)	Silver nitrate (g/L)
TC-7	Biofouling	WR + biocide	0.2	7	1.5	
TC^{+}-7	Biofouling	WR + biocide	0.2	7	10.1	
TC^{++}-7	Biofouling	WR + biocide	0.2	7	13.6	
TCAg-7	Ageing + biofouling	WR + biocide	0.2	7	1.5	0.9
TCAg-14	Ageing + biofouling	WR + biocide	0.4	14	1.5	0.9
T-7	Ageing	WR	0.2	7		
T-14	Ageing	WR	0.4	14		
		WR: Water Repellent				