

Colour and Landscape

# Proceedings of the International Colour Association (AIC) Conference 2019

**Buenos Aires, Argentina** 14-17 October 2019 Universidad de Belgrano

**Organized by** Grupo Argentino del Color (GAC)

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grupo argentino del color international colour association





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The original website of the conference was http://aic2019.org.

The contents have been moved to a more permanent site: https://aic2019color.wordpress.com.

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Web: http://grupoargentinodelcolor.blogspot.com Mail: gac@fadu.uba.ar



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# Prevention of the color changes in waterborne antimicrobial coatings with nano-functionalized siliceous filler

### Leyanet Barberia-Roque<sup>a\*</sup>, Erasmo Gámez Espinosa<sup>a</sup>, Marisa Viera<sup>ab</sup>, Natalia Bellotti<sup>ac</sup>

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### ABSTRACT

Color fastness represents the capacity of a given paint to maintain its original color over the time when exposed to biotic and abiotic environmental factors. The aim of this work is to assess the color changes due to the addition of Ag nanoparticles in a natural siliceous based material in coatings. Analysis of the color data from 24 hours showed the effectiveness of the functionalized materials to decrease the color change. Paints with nanoparticles added directly presented color variation rated as very big, considering the colorimeter method by Teichmann, while with the addition of functionalized silica was barely evident. These results kept during the six months in which the study was conducted.

Keywords: silver nanoparticles nano-functionalized, color change, antimicrobial waterborne paint

### INTRODUCTION

In the decorative paints field, color fastness represents the capacity of a given paint to maintain its original color over the time when exposed to environmental conditions such as chemical attack, UV radiation and the organisms activities (Hare 1992). The color of coatings is generated by addition of pigments, which can selectively absorb light in the visible spectrum. Waterborne coatings are colloidal systems composed of mineral and organic particles of distinctive sizes and shapes, dispersed at different volume concentrations into a polymeric resin. They also include small quantities of specific chemical species, additives whose function is to enhance the paint properties such as foam control, flow, leveling and rheology (Mahltig 2017).

In environmental engineering, biodeterioration is defined as any detrimental change made by an organism on a surface (Morton and Surman 1994). These changes can be caused by the mere presence of the organism as well as the result of its metabolic activity and can affect both the appearance and the structure of the materials, as well as potentially damaging to human health. The potential of metals to inhibit the growth of bacteria and fungi is well known, the mechanistic

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background of metallic antimicrobial effects is still under discussion and not yet fully understood (Mahltig 2017).

In recent years, the use of metal nanoparticles has been intensely studied as a antimicrobial component to be applied in functional material (Saratale et al. 2018). Despite all the advantages of adding metal compounds to paints, some of their properties are affected given the reactivity of metal ions (Arreche et al. 2015). For this reason, the addition of functionalized components with nanoparticles in coating formulations is an increasingly contemplated option (Barberia-Roque et al. 2019). However, some characteristics of the coating are affected by the nanoparticles, the color is one of the most recurrent (Zheng et al. 2018).

Silver nanoparticles have been used for the functionalization of other materials, transferring their antimicrobial activity to them and decreasing incidence on the color (Arreche et al. 2019). In the present research a natural siliceous based material-functionalized with silver nanoparticles has been used as an antimicrobial additive for a paint formulation. The color changes and antimicrobial performance during six months of natural aging were measured.

#### MATERIALS AND METHODS

#### Obtaining of nano-functionalized siliceous filler

A powdered siliceous material (SM), extract from Río Negro, Argentina; was first activated with an alkaline solution of NaOH 2.2 M (Fernández and Bellotti 2017). Then, two strategies were used: the direct addition of AgNO<sub>3</sub> 10<sup>-2</sup>M solution (SMAg) and the addition of silver complexed with ammonium (SMAgC). Seven grams of activated SM was mixed with 100mL of the salt solution. The amount of adsorbed silver in the SM was determinated from measurements of silver in the supernatant by a Mohr method variation.

Silver ions were reduced using the aqueous plant extract of *Senna occidentalis*, following a green synthesis method (Barberia-Roque et al. 2019). The green synthesis of free nanoparticles (AgNps) was carried out using the same silver nitrate solution and the plant extract as a reducing agent.

### **Paint preparation**

The base paint composition was (% by mass): 48.6% of distilled water, 25.9% CaCO<sub>3</sub> (natural), 6.3% acrylic resin (1:1), 3.6% TiO<sub>2</sub>, 2.0% CaCO<sub>3</sub> (precipitated) and 3.6% of additives (antifoaming, cellulosic thickener, dispersants and surfactants). The three products (AgNPS, SMAg and SMAgC) previously obtained were incorporated into the waterborne acrylic paint considering a silver concentration of 25 mg / 100 g of total paint.

Three different paintings were obtained AgNPsP, SMAgP and SMAgCP, respectively. In addition, two control paints without biocides were used: the base paint formulation (CP) and the base paint formulation with SM (SMP). The paints were applied on glass slides and cured for fifteen days. Some glasses were aged for six months exposed to natural light from behind a window, in laboratory conditions.

#### **Color measurement**

Color was measured by the CIELAB system with a colorimeter By K Gardner. CIELAB gloss and color parameters were evaluated on cured paints during their sunlight exposure. The change of color ( $\Delta E$ )

was calculated as:  $\Delta E = [(a - a_0) 2 + (b - b_0) 2 + (L^* - L_0^*) 2]^{\frac{1}{2}}$ , being: "a" the variation between magenta blue and green, "b" the variation between yellow and green and "L\*"into black and white. The CIELAB parameters at t = 0 are referred as:  $a_0$ ,  $b_0$ , and  $L_0^*$  while a, b and L\*, correspond with the time elapsed. Visual appearance and  $\Delta E$  were related with the rating as follow: < 0. 2 No visible, 0.2– 0.5 Very slightly, 0.5–1.5 Slightly, 1.5–3.0 Evident, 3.0–6.0 Very evident, 6.0–12.0 Big, > 12.0 Very big (Arreche et al. 2019). An ANOVA parametric method was performed using the Tukey test for media comparison with 95% of confidence. SigmaPlot software was used in tabulation and graphing of all data.

### Normalized antimicrobial assay

The antifungal efficiency of the prepared paints was evaluated by an in vitro procedure similar at the ASTM D5590 specification. The painted glasses, after two weeks and six months of aging, were cut in  $2.5 \times 2.5$  cm and placed in minimum mineral media. The samples were inoculated with 50 µL of a spore suspension (10<sup>5</sup> spores/mL) of *Chaetomium globosum* KU 936228. The suspension was distributed homogeneously all over the painted surface. After four weeks of incubation at 28°C, fungal growth on the painted glasses was evaluated using a Leica magnifying glass at with an increase of 40 x.

#### **RESULTS AND DISCUTION**

#### Color change

The color assessment of the samples showed that, AgNPsP had the greatest change respect to the control whose initial values were used as a standard throughout the experiment like  $a_0$ ,  $b_0$  and  $L^*_0$ . Statistical analysis of the color data from 24 hours showed the effectiveness of the functionalized materials to decrease the color change, as it can be seen in Figure 1. However, in all paints containing nanoparticles,  $\Delta E$  changes were statistically significant, which translates to naked eye detectable color changes. No significant differences were observed between  $\Delta E_{30}$  and  $\Delta E_{180}$  (subscripts represent aging time), in all the paints.

The color variation in the control paints was rated as slight. In the alternative paints with SMAg and AgNps it was big and very big. However, with the addition of SMAgC, the color change was barely evident. The color variation over time highlighted the effectiveness of the SMAgC to prevent the color change by approximately six months of weathering. These results allowed determining that the functionalization of SM with AgNPs is not enough the color change. However, we could conclude that complexing silver with ammonium helps to preserve more efficiently the properties of the paints.

The parameter L\* had a higher incidence on the color change measured in each of the paintings. This phenomenon could be due to can be attributed to the composition initially and decomposition later of black compounds as those formed when silver reacts with sulfur compounds at the environmental pollution. Degradation of these compounds by the action of light or O<sub>3</sub> could explain that L\* was the most affected color parameter during the natural aging process (Arreche et al. 2019). There were no significant changes in the brightness of the paints obtained with respect to the CP even after the aging process. The overall average brightness was 2 approximately.



Figure 1: Graph of color change over time for six months (left). Paintings after 15 and 120 days of curing (right) (A: CP; B: SMAgCP; C: SMAgP and D: AgNpsP).

### Antifungal activity

All paints with AgNps showed a high degree of antifungal activity which can be seen in Figure 2. Control paint CP in Figure 2A, shows the development of the inoculated spores. In the rest of the samples (Figure 2B, C, D) can be observed how the inoculated spores were not even able to germinate. All the samples were rated as 0 according to the ASTM. However, samples with the functionalized fillers at t = 0 and those aged showed fungal growth around them while the paints without SM only presented fungal growth around the samples after six months, which could be related to loss of antifungal activity over time.



Figure 2: Antifungal assay against C. globosum (A: CP; B: SMAgCP; C: SMAgP and D: AgNpsP).

### CONCLUSIONS

In the present work we have found that the functionalization of SM with silver nanoparticles impart their antimicrobial activity to the coatings, therefore, functionalized SM can be used as biocide in waterborne coating formulations. The addition of nanoparticles, associated to SM positively affects the maintenance of the color of the tested waterborne paint, allowing the color to remain without significant alterations over time.

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