# Study of a Hydrophobic Coating of Paraffin Wax and Calcium Decanoate for Corrosion Protection of Silver Cultural Heritage Objects

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## RESUMO

RESUMO – Objetos artísticos e museológicos de ligas de prata sofrem corrosão eletroquímica em atmosferas com sulfetos e alta umidade relativa do ar gerando produtos coloridos de $Ag_2S$. Revestimentos hidrofóbicos podem inibir esta corrosão e sua eficiência pode ser aumentada com inibidores de corrosão. Neste trabalho, foi desenvolvido um revestimento hidrofóbico de cera de parafina com decanoato de cálcio como inibidor de corrosão. A hidrofobicidade foi medida por ângulo de contato estático e a eficiência contra corrosão por ensaio de corrosão artificial em atmosfera de $H_2S$ e medidas de espectrofotometria no espaço de cor CIELab*. Medidas de ângulo de contato indicaram a hidrofobicidade dos revestimentos em certas concentrações de cera e decanoato. Medidas de Variação de Cor ($\Delta E$) obtidas pela espectrofotometria, mostraram uma correlação entre os valores de ângulo de contato e eficiência de inibição de corrosão. Os revestimentos se mostraram promissores para inibir a corrosão de objetos culturais feitos de prata.

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*Palavras-chave: Corrosão, Prata, Bens Culturais, Revestimento Hidrofóbico*

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## Introduction

Artistic and museological objects, which constitute our cultural heritage, serve to illustrate the technologies and cultures of the past, through which it is possible to understand how the item was produced and used by a given society. Many of these objects are made of silver and copper alloys, which are prone to deterioration by electrochemical corrosion. Metallic silver initially oxidizes to AgO, and in an atmosphere containing sulfides ($H_2S$ or COS) and high relative humidity—which allows these gases to be absorbed by water—$Ag_2S$ forms, creating a tarnish that ranges in color from brown to black depending on its thickness (1). Water also facilitates the dissolution of metallic silver (2).

$$4Ag + O_2 \rightarrow 2Ag_2O$$
$$Ag_2O + H_2S \rightarrow Ag_2S + H_2O$$

One way to reduce or prevent this corrosion is through the use of hydrophobic coatings that act as a barrier, hindering contact between corrosive compounds and the water from atmospheric humidity. These coatings can be paraffin waxes, whose hydrophobic nature can be enhanced with the use of corrosion inhibitors. In this study, a hydrophobic coating of paraffin wax containing calcium decanoate was developed as a corrosion inhibitor. Calcium decanoate, $Ca(C_{10}H_{19}O_2)_2$, is a low-toxicity inhibitor and a possible substitute—according to Green Chemistry principles—for more toxic corrosion inhibitors.

## Experimental

### *Preparation of the Coatings*

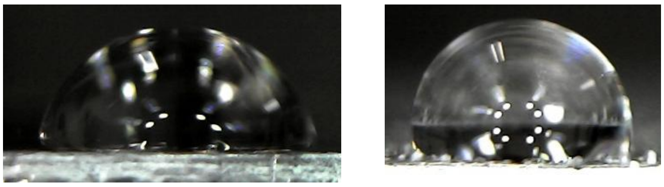
The hydrophobic coatings were obtained from solutions with varying concentrations of calcium decanoate (CaDec) and paraffin wax (P), referred to as the CaDec-P system, with compositions ranging from 0.175–0.70% to 0.200–0.80% (the first value corresponding to CaDec content and the second to paraffin wax). The solvent system for these compounds consisted of ethanol, isopropanol, turpentine, and 1,2-propylene glycol. These solutions formed coatings when sprayed at 10 psi pressure and dried at room temperature on plates and decommissioned coins made from two silver alloys: silver 500 (50% Ag, 50% Cu) and silver 900 (90% Ag, 10% Cu). The study was conducted on both silver alloys because the copper content affects their corrosion stability.

### *Characterization of Hydrophobicity and Corrosion Inhibition*

The hydrophobic character of the films was evaluated by measuring static contact angles using ImageJ software and the Low-Bond Axisymmetric Drop Shape Analysis (LBADSA) plugin. Corrosion inhibition was assessed through artificial corrosion tests involving 24-hour exposure to an $H_2S$ atmosphere generated by the reaction of $H_2SO_4$ and FeS. The corrosion tests were carried out in Schlenk flasks. The degree of corrosion was evaluated by spectrophotometry using the CIELab* color space and a Linshang Ls173 portable spectrophotometer.

## Results and Discussion

The measured static contact angles for the obtained coatings showed maximum values at concentrations of 0.100% and 0.125% CaDec for the silver 500 and silver 900 surfaces, respectively. These values were 107° and 104°, and since they are greater than 90°, they characterize the surfaces as hydrophobic (3). Figure 1 shows images of the contact angle variation on the silver 500 surface, with an increase of 30° from the uncoated surface (77°) to the coated surface (107°).



(a) (b)

**Figure 1.** Images of distilled water droplets on (a) silver 500 surface and (b) silver 500 surface with coating.

It was observed that the contact angles were higher on the silver 500 surface, which has a higher copper content (Figure 2), indicating a greater affinity of the coating with this metal. There is a tendency for the contact angle to decrease beyond certain concentration values, which was attributed to the increased viscosity of the solution. This higher viscosity favored the formation of imperfections in the coating due to reduced leveling during drying.

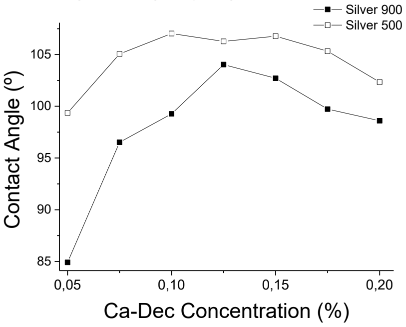


**Figure 2.** Diagrams of static contact angles as a function of CaDec concentration (%).

Regarding the artificial corrosion tests, the intensity of corrosion was measured by spectrophotometry using the CIELab* color space. The CIELab* color space uses a three-axis diagram with orthogonal axes: a vertical L axis ranging from 0 to 100, where 0 represents black and 100 represents white; a horizontal a axis ranging from 0 to 100 for red and 0 to -100 for green; and a horizontal b axis ranging from 0 to 100 for yellow and 0 to -100 for blue. These three coordinates define the color of the material, and any variation in position within this space indicates a color change.

Since the tarnish formed by $Ag_2S$ has a color that depends on its thickness and concentration, the measurements in the CIELab* color space provide an indirect indication of this concentration—and, therefore, of the degree of corrosion reached.

The variation in the CIELab* space is given by the Color Variation (ΔE) which is calculated using Equation 1:

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2} \quad (1)$$

Figure 3 shows an image of silver 500 coins with and without coating after the corrosion test. Figure 4 presents a diagram with ΔE values, representing the color change from the uncorroded to the corroded surface, as a function of concentration. This figure shows a decrease in ΔE with increasing concentration, following the same trend as the contact angle and indicating enhanced protection.

(a) (b) (c)

**Figure 3.** Images of silver 500 coins. In (a) control; in (b) coin without coating after exposure to $H_2S$ atmosphere for 24 hours; and in (c) coin with coating after exposure to $H_2S$ atmosphere for 24 hours.

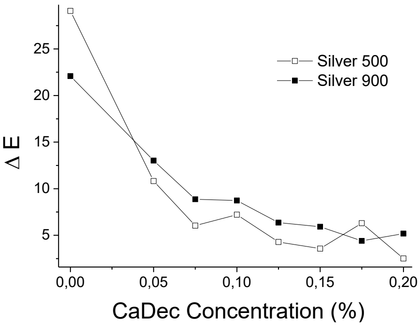


**Figure 4.** Diagrams of static contact angles as a function of CaDec concentration (%).

## Conclusions

The results indicate that the CaDec-P coating is a promising protective coating against the corrosion of silver cultural heritage objects. The relationship between hydrophobicity, measured by the contact angle, and the degree of corrosion, measured by ΔE, allowed for an assessment of the material's effectiveness.

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