

Removal of brownish-black tarnish on silver–copper alloy objects with sodium glycinate



João Cura D'Ars de Figueiredo Junior*, Samara Santos Asevedo,
João Henrique Ribeiro Barbosa

Department of Plastic Arts, School of Fine Arts, Universidade Federal de Minas Gerais, Avenue Antônio Carlos, 6627, Pampulha, Belo Horizonte, Minas Gerais, Brazil

ARTICLE INFO

Article history:

Received 4 May 2014

Received in revised form 26 July 2014

Accepted 17 August 2014

Available online 23 August 2014

Keywords:

Silver–copper alloy

Tarnish

Glycinate

Scanning electron microscopy

X-ray fluorescence

Infrared absorption spectroscopy

ABSTRACT

This article has the principal aim of presenting a new method of chemical cleaning of tarnished silver–copper alloy objects. The chemical cleaning must be harmless to the health, selective to tarnish removal, and easy to use. Sodium glycinate was selected for the study. The reactions of sodium glycinate with tarnish and the silver–copper alloy were evaluated. Products of the reaction, the lixiviated material, and the esthetics of silver–copper alloy coins (used as prototypes) were studied to evaluate if the proposed method can be applied to the cleaning of silver objects.

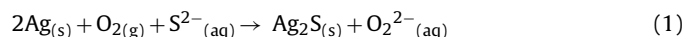
Silver–copper alloys can be deteriorated through a uniform and superficial corrosion process that produces brownish-black tarnish. This tarnish alters the esthetic of the object. The cleaning of artistic and archeological objects requires more caution than regular cleaning, and it must take into account the procedures for the conservation and restoration of cultural heritage. There are different methods for cleaning silver–copper alloy objects, chemical cleaning is one of them. We studied two chemical cleaning methods that use sodium glycinate and sodium acetylglycinate solutions. Silver–copper alloy coins were artificially corroded in a basic thiourea solution and immersed in solutions of sodium glycinate and sodium acetylglycinate. After immersion, optical microscopy and scanning electron microscopy of the surfaces were studied. The sodium glycinate solution was shown to be very efficient in removing the brownish-black tarnish. Absorption spectroscopy measured the percentage of silver and copper lixiviated in immersion baths, and very small quantities of these metals were detected. Infrared absorption spectroscopy and X-ray fluorescence characterized the obtained products. The greater efficiency of the sodium glycinate solution compared to the sodium acetylglycinate solution was explained by chelation and Hard–Soft Acid–Base Theory with the aid of quantum chemical calculations.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Silver objects are very common in art and objects like cutlery, daggers, dishes, etc. Despite the fact that we refer to them as silver, most of these objects are actually alloys of silver and copper, which are noble metals. Silver is very resistant to oxidation and this characteristic is attributed to strong intermetallic bonds and high energies of ionization. It is quite resistant to the attack of H^+ (Arrhenius and Bronsted acids) because it has a high standard electrode potential ($E^\circ = +0.80\text{ V}$) [1]. Copper is more instable than silver ($Cu^+ \rightarrow Cu^0$ $E^\circ = +0.52\text{ V}$ and $Cu^{2+} \rightarrow Cu^0$ $E^\circ = +0.34\text{ V}$) [1]. The

difference in the stability of these metals can lead to selective corrosion in the objects they compose. Red and black oxides, green carbonates, sulfates, and chlorides of copper can be observed due to the reaction of copper with gases in atmosphere or with corrosive solutions, depending on its storage [2]. Despite the stability of silver, it may react with oxygen and sulfur compounds (H_2S or COS) [3] and humidity in atmosphere, generating a brownish-black tarnish on the surface of objects. This tarnish can become black with time, and it is constituted mostly of acanthite (Ag_2S) (1) [2,4]. Sulfur compounds can also react with copper generating black copper sulfides [5]. All of these corrosion processes do not cause severe damages to the structure of a silver object, but they diminish its esthetic value.



* Corresponding author. Tel.: +55 31 3409 5287.

E-mail addresses: joaoc@ufmg.br (J.C.D. de Figueiredo Junior), samaranix@hotmail.com (S.S. Asevedo), joaohrb@yahoo.com.br (J.H.R. Barbosa).

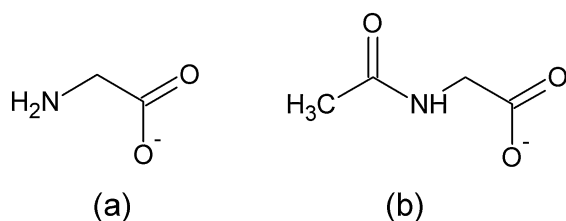


Fig. 1. Structural formulas of glycinate and N-acetylglycinate.

Conservators can achieve the removal of tarnish with different cleaning methods: mechanical, chemical, electrochemical [2], laser [4,6], and plasma [7,8]. Each one of these methods has advantages and disadvantages that make them all differently suited for cleaning. It depends on the object, its conservation state, the goal of the cleaning, and other criteria chosen by a professional of conservation and restoration of cultural heritage.

Among the cited cleaning methods, our research group studied improvements for chemical cleaning. Usually, chemical cleaning is based on using compounds that release H^+ in solution, basic compounds, or ligands that react with the products in tarnish [2]. Many problems may arise from these cleanings, one of them is the uncontrolled removal of corrosion products, non-corroded silver, and alloy constituents such as copper. This can lead to the loss of surface details such as drawings [2]. Another problem is the formation of coordination compounds of low solubility that can precipitate and remain retained in the object, these compounds can further react with the silver [2]. At least, the toxicity of the compounds utilized in cleaning should be cited. One example of a cleaning solution is the acidified thiourea, this substance removes the corrosion products of silver but reacts with non-corroded silver. If the cleaned object is not exhaustively rinsed with water, the thiourea, adhered to the surface of metal, deteriorates and produces more tarnish [9]. Thiourea is also considered to be a category 2 carcinogen according to the Globally Harmonized System of Classification and Labeling of Chemicals (GHS) [10].

According to [2], a cleaning solution should remove corrosion products and keep them in solution. Searching for alternative solutions that could satisfy the best of these conditions, we started a research project using amino acids for the cleaning of tarnish on silver–copper alloy objects. This article reports on the study of the use of two substances for the removal of tarnish: sodium glycinate and sodium N-acetylglycinate (Fig. 1).



Fig. 3. Brazilian silver coin out of circulation used as prototype.

N-acetylglycinate was already utilized to obtain water-soluble and light stable silver coordination compounds. These compounds were obtained by the reaction of N-acetylglycinate with Ag_2O [11]. Our objective was to test the reaction of N-acetylglycinate with Ag_2S in tarnish and evaluate it in the use of cleaning silver objects. Glycinate was tested with the same objective. The compounds obtained are polymeric, and $Ag(I)$ is coordinated by $-COO^-$ groups in the expected coordination compounds: silver(I) N-acetylglycinate, $\{[Ag(CH_3CONH_2CH_2COO)]_2\}_n$ [11], and silver(I) glycinate, $\{[Ag(NH_2CH_2COO)]_2 H_2O\}_n$ [12] (Fig. 2). Positive results were only obtained with sodium glycinate that was highly soluble in water and harmless to the health [13] as glycine is its precursor [14]. Sodium glycinate showed a high degree of selectivity for the $Ag(I)$ and $Cu(II)$ species present in tarnish. A discussion about different reactivities of ligands will be conducted with the aid of the Hard–Soft Acid–Base Theory and quantum chemical calculations.

2. Materials and methods

2.1. Artificial corrosion of prototypes and cleaning baths

Out-of-circulation Brazilian silver–copper alloy coins from the series “Brasileiros Ilustres–Duque de Caxias” were used as prototypes (Fig. 3). The coins are alloys of Ag and Cu , which was confirmed by X-ray fluorescence (spectrum not shown here). The coins were minted with silver 500 (50% Ag and 50% Cu) and had an initial mass of 8 g. The coins were chosen as prototypes because they have drawings on their surfaces that would allow us to perceive esthetic damages resulting from the proposed cleaning process. Firstly, the coins were washed with distilled water, then

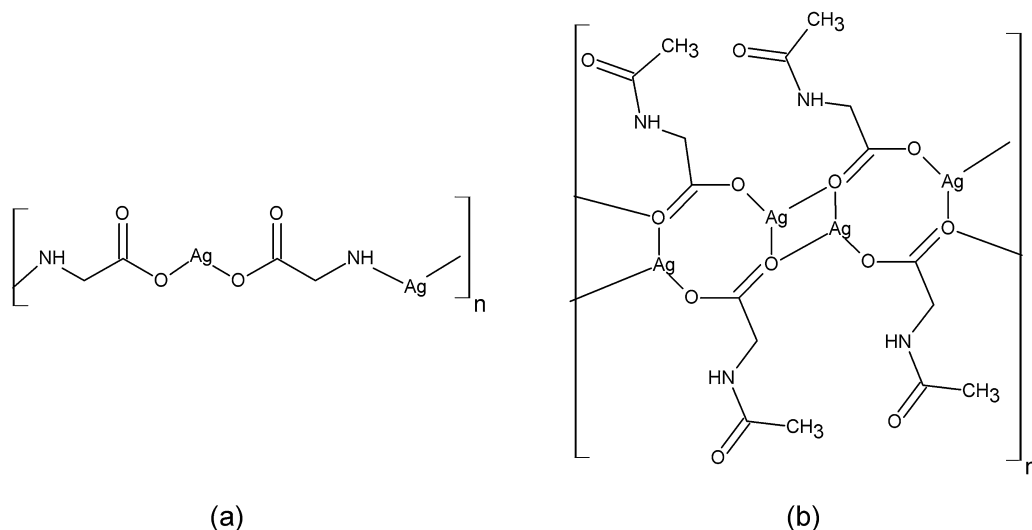


Fig. 2. Polymeric compounds of $Ag(I)$ with (a) glycinate and (b) N-acetylglycinate.

Download English Version:

<https://daneshyari.com/en/article/5360958>

Download Persian Version:

<https://daneshyari.com/article/5360958>

[Daneshyari.com](https://daneshyari.com)