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Study of color and structural changes in silver painted medieval glasses

Sofía Pérez-Villar *, Juan Rubio, Jose Luis Oteo

Department of Chemistry Physics of Surfaces and Processes, Instituto de Cerámica y Vidrio (CSIC), Kelsen, 5, 28049 Madrid, Spain

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Abstract

Silver was introduced into medieval glass by an ancient painting process using different clay minerals (ochre, illitic, montmorillonitic, and kaolinitic clays). The colorimetric properties, studied by UV–Vis spectroscopy, were dependent on the clay mineral as a result of different concentration of Ag ions diffused into the glass surface. TEM results showed the well known formation of silver nanoclusters which give the yellow coloration of the glass. The obtained results showed that clay properties such as specific surface area, pore volume and iron concentration (Fe_2O_3), are important factors that affect the yellow coloration. It is also observed that Fe_2O_3 acts as an oxidant agent for silver atoms providing the Ag_2O formation. This oxide cannot diffuse into the glass structure and avoid the ion-exchanged process. After Ag ion diffusion some structural changes occur in the glass as it has been shown by Raman spectroscopy. It is observed that the diffusion process leads to depolymerization of the glass network as it is determined by analyzing the Q^n components of Raman spectra. Two Raman bands at 148 and 244 cm^{-1} assigned to Ag–O bonds can be associated to the presence of Ag_2O on the glass painted surface.

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1. Introduction

Silver stain is one of the most interesting medieval pigments that correspond to a colored superficial layer formed by silver colloidal particles, responsible for the coloration [1,2]. The silver stain was not used by glass painters prior to the fourteenth century. This decoration appeared in the early Islamic world (Mesopotamia, 700 AD) [3,4] and spread to the West through the book 'El Lapidario del Rey Alfonso X' which was translated into Spanish by King Alfonso in the year 1279. The formula of this pigment was found in this book [5]. Craftsmen obtained this revolutionary pigment by applying a paint containing a mixture of silver salt, clays or ochres, water and arabic rubber on the glass surface. Afterwards, the painted glass was submitted to the heat-treatment to obtain the color [6]. This procedure is rather similar to that described by Colomban and used for painting ancient lustre pottery with gold and silver salts although in these cases the support was a lead glass [7,8].

Several authors [9–12] have demonstrated that the silver colloidal formation takes place as a result of an ionic exchange process, where silver ions are introduced into the glass structure at a temperature close to the glass-transition one. This reaction takes place during the contact of the silver ions with the glass surface. Different explanations exist about the silver coloration mechanism [9–13]. Araujo [9] explains this process as being one of silver reduction where an electron is extracted from a non-bridging oxygen atom (NBO) of the glass structure by means of the addition of alkaline ions. The use of high-field-strength ions such as Al_2O_3 limits both the number of NBOs and silver reduction and therefore, diminishes the coloration until it disappears. Inman [12] carried out structural studies by means of X-ray

* Corresponding author. Tel.: +34 917 355 840; fax: +34 917 355 843.
E-mail address: sofiapv@icv.csic.es (S. Pérez-Villar).

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absorption fine structure (XAFS) in aluminosilicate glasses and observed that the presence of a great quantity of NBO in the glass facilitated both the mobility of the cations and the mixed mobile ion effect (MMIE), favoring the diffusion in the glass. However, a different explanation for the silver reduction process was provided by Stookey [11] who discovered that when gold was dissolved in molten silicate glasses in an oxidized state it did not produce any coloration, and only under reducing conditions metallic gold was formed and coloration appeared at low temperatures. Similar conclusions can be applied to silver and copper. The reducing conditions can be achieved by a reducing atmosphere or by the presence of reducing agents (such as SnO or Sb_2O_3) in the glass composition [14]. On the other hand, different works [13,15–17] have also demonstrated that the incorporation of ionic silver into the vitreous structure by means of the ionic exchange processes can cause important structural alterations in the glass. By using infrared reflectance spectroscopy (IRRS) and ^{29}Si MAS-NMR Spectroscopy, Yamane et al. [13] proposed a very intuitive structural union model from the silver ions to the NBO of the glass structure. At the same time, Houde-Walter et al. [16] used the same techniques to determine the local environments of sodium and silver ions in sodium silicate glasses. This study concluded that the ion exchange with silver led to cation environments with much shorter cation-oxygen distances. All of these studies have been carried out by soaking the glass in a fused salt bath, however, medieval craftsmen used a paste where silver salt, clays, water and other additives were mixed together before painting. Very few studies have been published using the medieval painting process [18–21]. For example Roqué et al. [18] used a paste containing quartz, illite, calcite ($CaCO_3$), iron oxides (Fe_2O_3), gypsum ($CaSO_4 \cdot 2H_2O$), tenorite (CuO) and traces of silver oxide (Ag_2O). Similarly, Pradell et al. [19] used a basic mixture consisting of illitic clay (including quartz and iron oxides), cinnabar and silver nitrate. At the same time, Jembrish-Simbürger et al. has also studied the effect of different silver compounds (AgCl, $AgNO_3$, Ag_2SO_4, Ag_3PO_4, Ag_2O) mixed with ochres (SiO_2–Al_2O_3–Fe_2O_3) in the coloration obtained for a given glass [20]. However, Zhang et al. [21] used the ancient classical painting process but they only employed a mixture of Ag_2SO_4, $CuSO_4$, Na_2SO_4, and organic compounds such as screen oil as additive. All of these studies have confirmed the above mentioned conclusions obtained by conventional or soaking painting processes but the effect of the clay type has not been analyzed yet. The purpose of this work is to use different clays for the paint paste formulation and analyze the coloration obtained as well as their effect on the glass structure after the ionic exchange process. This study has been carried out by means of UV–Vis spectroscopy, transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDS) and Raman spectroscopy.

2. Experimental

2.1. Materials

We have prepared Medieval like glass samples by using the following raw materials: SiO_2, Al_2O_3, Na_2CO_3, K_2CO_3, $CaCO_3$, $BaCO_3$, ZnO and Sb_2O_3 all of them of reagent purity grade. Mixtures corresponding to the desired composition were melted by using sintered alumina crucibles, in a propane gas–air furnace at 1450 °C, and maintained for 2 h at this temperature. The melts were quickly cooled at room temperature by pouring and pressing between two stainless steel plates. The chemical composition of the prepared glass (determined by X-ray fluorescence analysis) is reported in Table 1. This medieval glass had a glass-transition temperature (T_g) of 533 °C. This glass was cut into pieces of $10 \times 10 \times 3$ mm^3. As it will be commented below, in all experiments three glass pieces have been used as substrate for each silver painting reproduction.

Silver stain reproduction was obtained following the traditional techniques described in the book of Le Vieil [6]. According to this book a silver stain can be prepared by using a mixture (slurry) of Ag salts, clays, binders and water. In order to study the effect of the clay type we have used $AgNO_3$ as Ag salt, Arabic rubber as agglomerate and different clays including ochres (iron oxides). Prepared slurries contained 16 wt% of $AgNO_3$ (Merck, analytical grade), 48 wt% of commercial clays and 36 wt% of a mixture of arabic rubber and water (Henkel). All the slurries were obtained by mixing the different components during 20 min under vigorous stirring. After that, medieval glass substrates were painted on one side. The thickness of this deposit was around 10 μm as observed by optical microscopy. Then they were dried at room temperature for 2 h, and heat-treated in air at 580 °C for 2 h. A heating rate cycle of 2 °C min^{-1} for heating and 1 °C min^{-1} for cooling was used. Finally, glass painted substrates was washed with distilled water to remove any residual slurry. According to the concentration of $AgNO_3$ used can be calculated the amount of silver atoms deposited on the glass surface, thus the obtained value was 17 atoms per nm^2 for each glass piece of the above given dimensions. At the same time, the redox elements (Sb_2O_3 and Fe_2O_3) existing in the glass structure (see Table 3) can be calculated that there are 14 and 0.3 atoms, respectively, per nm^2 of each glass piece.

Table 1
Chemical composition of prepared medieval silicate glass

Components	SiO_2	K_2O	CaO	MgO	Al_2O_3	Na_2O	BaO	ZnO	Fe_2O_3	Sb_2O_3	Others[a]
Medieval glass (wt%)	68.32	8.35	7.20	0.03	0.17	7.95	1.94	3.94	0.02	0.86	0.64

[a] Others: B_2O_3, TiO_2.