Progress in Organic Coatings 123 (2018) 99–110

Contents lists available at ScienceDirect

Progress in Organic Coatings

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

Effect of proteinaceous binder on pollution-induced sulfation of lime-based tempera paints

A. Herrera[a], C. Cardell[a], J.S. Pozo-Antonio[b], A. Burgos-Cara[a,c], K. Elert[a,*]

[a] Dept. of Mineralogy and Petrology, Faculty of Science, University of Granada, Campus Fuentenueva s/n, 18071, Granada, Spain
[b] Dept. de Enxeñaría de Recursos Naturais e Medio Ambiente, Escola de Enxeñaría de Minas e Enerxía, University of Vigo, 36310, Vigo, Spain
[c] Sensient Colors UK Ltd., Oldmedow Road, King's Lynn, Norfolk, PE30 4LA, UK

ARTICLE INFO

Keywords:
Paint dosimeter
Calcite
Gypsum
Pigments
Chemical weathering
Pigment-binder interaction

ABSTRACT

Even though, atmospheric SO_2 contamination has been reduced over the last decades in Europe, practical experience has shown that sulfation of lime-based materials (i.e., lime-based tempera paint, lime mortar and plaster, as well as limestone) is still of importance, affecting monuments exposed to polluted air in urban centers. In order to evaluate the effect of organic binders (i.e., rabbit skin glue or egg yolk) on the chemical weathering resistance of lime-based materials, tempera paint dosimeters (i.e., paints containing calcite or mixtures of portlandite and calcite) were subjected to long-term outdoor exposure and accelerated SO_2-aging. SO_2-aging caused important morphological changes of the paint surface on the nano- and microscale. However, sulfation was significantly delayed in the presence of the organic binder. Furthermore, paints containing portlandite and calcite transformed faster into calcium sulfite hemihydrate and gypsum than paints containing only calcite. Calcium sulfite hemihydrate formation onto calcite always preceded non-epitaxial gypsum crystallization after dissolution of the sulfite precursor phase. These results suggest that a passivating product layer will not form onto calcite, and so sulfation will continue under suitable environmental conditions until all calcite is transformed into gypsum. Nevertheless, the organic binder strongly affected the mineralogical evolution of paints containing portlandite, resulting in the formation of organic-inorganic hybrid materials similar to biominerals. These hybrid materials generally have superior weathering resistance and might explain the absence of any clear signs of sulfation after prolonged outdoor exposure. The selection of lime-based tempera paints for conservation interventions must be made considering the prevailing exposure conditions. In polluted dry environments where carbonation of portlandite will be significantly delayed, the use of calcite-based tempera paints might be preferable, while tempera paints containing portlandite would be more suitable in humid climates where carbonation is fast, resulting in the formation of weather resistant hybrid materials.

1. Introduction

For decades atmospheric pollution has been recognized as one of the major threats to cultural heritage [1]. More recently, scientists have established that the damaging effects of pollution are enhanced by climate change, affecting a wide range of materials of the built heritage [2,3]. One of the classical examples of pollution-induced deterioration includes the formation of gypsum-rich black-crusts on limestone and lime mortars due to sulfation of calcite [4–7].

Even though, SO_2 concentration has been reduced drastically by ~75% since 1990 according to the European Environment agency [8], pollution-induced sulfation is still affecting monuments located in polluted metropolitan areas [9]. Actually, some experts suggest that there might not be any safe threshold and that resulfation of previously cleaned monuments could occur relatively rapidly. The formation of gypsum crusts is well documented for many monuments and historic buildings in Granada (southern Spain) [4]. However, sulfation is not limited to building materials and also affects painting materials. Sayre et al. [10] detected large amounts of gypsum ($CaSO_4{\cdot}2H_2O$) in decayed lime plaster from the Giotto frescoes in the Scrovegni Chapel, Italy, which they identified as a reaction product of calcium carbonate with atmospheric sulfur oxides (i.e., sulfur di- and trioxide) in the presence of moisture. While some research has been dedicated to the sulfation of pure lime in wall paintings [10,11], little is known on the effect of atmospheric SO_2 on lime-based binary systems, such as tempera paints, which contain an inorganic pigment and an organic binder.

Tempera paints applied in the fresco-secco technique have been extensively used in southern Spain and important examples include the

* Corresponding author.
E-mail address: kelert@ugr.es (K. Elert).

https://doi.org/10.1016/j.porgcoat.2018.06.017
Received 26 February 2018; Received in revised form 8 June 2018; Accepted 24 June 2018
0300-9440/ © 2018 Elsevier B.V. All rights reserved.

wall paintings of the Hospital of "San Juan de Dios" located in semi-open courtyards or the mural paintings of the Alhambra and the Moorish quarter (Albaycin, Granada) [12,13]. These wall paintings are exposed to relatively high levels of atmospheric pollution [9,14]. The high porosity of tempera paints and the underlying mortars make wall paintings very vulnerable to pollution-induced chemical weathering. Common damage patterns observed upon crystallization of gypsum include disaggregation, microflaking, and the formation of surface bloom [15].

In order to get a better insight into SO_2-induced deterioration of lime-based tempera paints, paint dosimeters containing either rabbit skin glue or egg yolk were exposed outdoors for 40 months in the historic city center of Granada. A second set of dosimeters was exposed to an accelerated SO_2-aging test to further study mineralogical and morphological changes upon sulfation of lime-based pigments in the presence and absence of an organic binder. To this end a wide range of analytical techniques were applied, including x-ray diffraction (XRD), laser particle size analysis, nitrogen adsorption, field emission scanning electron microscopy (FESEM), Raman spectroscopy, and spectrophotometry. Analytical results revealed a significant effect of the organic binders on the mineralogical evolution of lime-based tempera paints and their susceptibility to sulfation. The outcome of this investigation furthers the understanding of the chemical weathering process of lime-based tempera paints and allows for recommendations regarding the selection and preparation of adequate materials, not only for paintings conservation but also for applications involving the use of lime mortars or plasters exposed to polluted urban air.

2. Materials and methods

2.1. Pigments and binders

Three different lime-based pigments of different grain size (see Table 1) were purchased from Kremer Pigment GmbH & Co. (Germany): *Bianco di San Giovanni* standard (Ref. 11,415) with a mean particle size of ~60 μm, *Bianco di San Giovanni* coarse (Ref. 11,416) with a mean particle size of ~120 μm, and extrafine calcite (Ref. 58,720) with mean particle size of ~25 μm [16]. Note that *Bianco di San Giovanni* has been historically prepared by sun-drying small "cakes" of slaked lime in order to obtain a partial carbonation of portlandite upon reaction with atmospheric CO_2 [17]. Consequently, these pigments contain a mixture of calcium carbonate (i.e. calcite, $CaCO_3$) and calcium hydroxide (i.e. portlandite, $Ca(OH)_2$). Pigments were mixed with two different organic binders: rabbit skin glue (Ref. 63028, Kremer Pigment GmbH & Co) or locally purchased egg yolk.

Table 1
Nomenclature of samples.

Pigments	Material
CA-EF	Extrafine calcite
BSG-ST	Bianco di San Giovanni (standard)
BSG-C	Bianco di San Giovanni (coarse)
$CaCO_3$	Analytical grade calcium carbonate (calcite)
$Ca(OH)_2$	Analytical grade calcium hydroxide (portlandite)
Outdoor-exposed dosimeters and	Test duration
CA-EF-EY*	6, 12, 24, 36, 40 months
BSG-ST-EY	
BSG-C-EY	
CA-EF-RG*	
BSG-ST-RG	
BSG-C-RG	
SO_2-aged dosimeters and	Test duration
CA-EF-RG	5, 10, 34, 82 h
BSG-ST-RG	
BSG-C-RG	
$CaCO_3$-RG	
$Ca(OH)_2$-RG	
$Ca(OH)_2$-H_2O*	

* Paint dosimeters prepared with egg yolk (EY), rabbit skin glue (RG), or deionized water (H_2O).

2.2. Preparation of paint dosimeters

Two sets of samples were prepared for testing. For long-term outdoor exposure, paint dosimeters were prepared following traditional recipes according to organoleptic parameters in order to mimic the egg yolk- and rabbit skin glue-based tempera paints used by medieval artists [18]. The binder content of paints with adequate consistency varied slightly, because binder demand depends on the pigments mineralogical composition and pigment particle size [16]. Note that the paints' consistency was found adequate when droplets formed at the tip of the brush would not fall off easily. In practice, 5 g of pigment were wetted with deionized water before adding fresh egg yolk or an 8 wt% aqueous rabbit glue solution. The organic binder content calculated based on thermogravimetric analysis was 16.6 ± 3.3 wt% in the case of Bianco di San Giovanni-based paints and 9.5 ± 1.5 wt% in extrafine calcite-based paint [19]. Freshly prepared paints were spread directly onto glass slides with a paintbrush. The paint was applied in several layers once the previous layer was completely dry. The paints' film thickness was 0.53 ± 0.23 mm.

For the accelerated SO_2-aging test a second set of samples was prepared following the methodology above but with a fixed water/pigment/rabbit skin glue ratio of 2:1:0.1 wt/wt. Paints prepared with analytical grade calcium hydroxide ($Ca(OH)_2$, Guinama S.L.U., Spain) and calcium carbonate ($CaCO_3$, Labkem, Spain) were included in this test as reference materials. The former was also prepared without the addition of rabbit skin glue, maintaining the same water-pigment ratio. Note that only samples prepared with rabbit skin glue were included in the accelerated SO_2-aging test because they can be expected to be more susceptible to chemical weathering than their egg yolk-based counterparts. All paint dosimeters were dried under laboratory conditions (20 ± 5 °C and 40 ± 10% RH) for 1 week before testing. Dosimeters were labeled by adding to the pigments label the letter EY for egg yolk-based paints, RG for rabbit skin glue-based paints, and H_2O for dosimeters prepared with water. See Table 1 for the complete nomenclature of samples.

2.3. Outdoor exposure test

Dosimeters were placed vertically in an exterior eave of the Hospital of San Juan de Dios in Granada which faces SW and is adjacent to a highly trafficked street. Samples were exposed for up to 40 months (i.e., from January 2014 to July 2017) to direct sunlight but partially protected from rain. Sunlight exposure was ~10 h in summer and ~5 h in winter, the maximum T being 40 °C in summer and the minimum T being −3 °C in winter. The climate in Granada is characterized by significant diurnal T and RH variations of 20 °C and 50%, respectively. Average RH is ~40% in summer and ~75% in winter [20]. Granada is a non-industrialized city surrounded by up to 3500 m high mountains. As a result of its topography, low wind speeds, heavy traffic and intensive construction work, O_3 and particulate matter frequently exceeded the threshold values set by the EU directive 2008/50EC and the World Health Organization (WHO) [9,21–24]. Even though, SO_2 concentration was below the limit established by the Directive 2008/50/EC it exceeded that recommended by the WHO in several occasions [21–23]. Moreover, based on the annual mean concentration (i.e., 11.85 μg/m^3 SO_2 in 2013), Granada is among the cities with the highest SO_2 contamination in Western Europe according to the European Environment Agency [24]. Data on average concentrations of atmospheric contaminants during the outdoor exposure test are reported in Table 2. Previous studies [4,9,14,25] showed that atmospheric particulate matter was primarily constituted of soil dust (quartz, calcite, dolomite,

Download English Version:

https://daneshyari.com/en/article/7105316

Download Persian Version:

https://daneshyari.com/article/7105316

Daneshyari.com