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Pigment-binder interactions in calcium-based tempera paints

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ABSTRACT

Calcium hydroxide and calcium carbonate, or mixtures of both have been used for millennia as pigments or primers, often in combination with proteinaceous binders. Despite their historical importance and widespread use in wall paintings, little research has been dedicated to possible interactions between the inorganic pigment and the organic binder, and their impact on paint aging under variable environmental conditions. Here, paint dosimeters mimicking historic paints were exposed to artificial UV-aging and long-term outdoor exposure tests and analyzed using a wide array of techniques, including x-ray diffraction, scanning electron microscopy, attenuated total reflectance-Fourier transform infrared spectroscopy, thermogravimetry, laser particle size analysis, and spectrophotometry. Our results show that the prevailing environmental conditions (i.e., sheltered or directly exposed to rain and sunlight) and the presence or absence of proteinaceous binder have a significant influence on the mineralogical and morphological evolution of paints containing calcium hydroxide. The organic binder delays carbonation and induces the formation of hybrid materials similar to biominerals, incorporating organics into the inorganic carbonate matrix. Such a biomimetic effect significantly enhances the durability of the paint layer. Calcium carbonate pigments, in contrast, did not suffer mineralogical changes in the presence of organic binder. However, both, calcium carbonate and hydroxide caused conformational changes in the proteinaceous binder. Observed differences in pigment-binder interactions have an important influence on the paints' resistance to chemical weathering, explain different alteration patterns observed in historic paints under semi-open exposure conditions, and allow for recommendations regarding the most suitable material for wall painting conservation considering the prevailing environmental conditions.

1. Introduction

Throughout history calcium carbonate has been extensively used as a painting material, either as a pigment, often as an extender blended with more expensive white pigments, or as a primer [1]. The pigment can be made of ground limestone (marble) or chalk [2]. It shows good hiding power in water-based systems (i.e., tempera paints with egg yolk, casein, or rabbit glue binder) and is often mixed with animal glue when used as a primer. Early examples of its use as a pigment include the Lascaux and Roucadour cave paintings from the Palaeolithic period [3]. Apart from pure calcium carbonate, “Bianco di San Giovanni” (BSG) a white pigment made of partially carbonated lime has been used in fresco and tempera paintings. This pigment was first mentioned by Cennino Cennini in his “Il Libro dell Arte”, but was most likely used before Cennini's time [4,5]. According to Colalucci [6] Michelangelo used this pigment as a base for certain reds and yellows in the frescoes of the Sistine Chapel. Slaked lime ($Ca(OH)_2$) was also used as binding media for pigments applied in wall paintings (fresco technique). Earliest examples are found in Greece and Italy [1].

Despite their historical importance and widespread use as painting materials, little research has been dedicated to the interaction of calcium-based pigments and proteinaceous binders [2,5,7–9]. High pH, especially in the case of calcium hydroxide (pH = 12.5), might cause changes in the structure of proteins and will consequently affect the paint's stability over time [10].

Up to now, no detailed studies are available which would clarify this aspect. Furthermore, the calcium hydroxide in BSG-based paints inevitably carbonates once applied and exposed to ambient air and mineralogical and morphological changes that can alter the paints' properties will occur.

Here we examined the effect of different calcium-based pigments (pure calcium carbonate or calcium hydroxide, and mixtures of both) on conformational changes in rabbit glue used as organic binder. We also tracked the morphological changes of calcium-

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based pigments with or without organic binder under UV-aging conditions. Besides laboratory tests, paint dosimeters prepared following historic recipes, were placed over a period of 30 months in strategic locations in the city of Granada, Spain (i.e., the historic city center and the Alhambra monument), and textural, mineralogical, morphological, and conformational changes were examined using a wide range of analytical techniques, including x-ray diffraction (XRD), scanning electron microscopy (SEM), attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR), thermogravimetry (TG), laser particle size analysis, and spectrophotometry. Our ultimate goal was to further the current knowledge on pigment-binder interactions in order to help explain observed alteration patterns in historic paintings, and assist in the selection of appropriate conservation materials for wall paintings, especially those suffering *T* and relative humidity (RH) fluctuations in semi-open courtyards or halls.

2. Materials and methods

2.1. Materials

Pigments and rabbit glue were purchased from Kremer Pigmente GmbH & Co, Germany. The pigments and binder include “Bianco di San Giovanni” standard (No.11415), “Bianco di San Giovanni” coarse (No.11416), extrafine calcite (No.58720), and rabbit glue pearls (No.63028). According to the manufacturer, the average pigment particle size was <120 μm, 120 μm - 1 mm, and ~20 μm, respectively. Note that “Bianco di San Giovanni” was historically prepared by sun-drying small “cakes” of slaked lime to achieve a partial carbonation of $Ca(OH)_2$ [4]. Consequently, this pigment contains a mixture of calcium hydroxide and calcium carbonate of varying proportions, depending on the preparation method. Additionally, analytical grade calcium hydroxide ($Ca(OH)_2$, Guinama S.L.U., Spain) and calcium carbonate ($CaCO_3$, Labkem, Spain) were included in this study as reference materials.

2.2. Sample preparation

Two sets of dosimeters were prepared. The first set of samples was prepared following traditional medieval recipes according to organoleptic parameters in order to obtain paints with adequate consistency [11,12]. Since binder demand depends on the pigments' chemical composition and particle size, these paints contained varying amounts of binder (see TG results below). Rabbit glue pearls (8 g) were soaked in 100 ml deionized water for 24 h under occasional stirring before heating to just below 50 °C in a water bath until a homogeneous mixture was obtained. To prepare a tempera paint of appropriate consistency, pigments were first wetted with deionized water and afterwards mixed with sufficient animal glue paste. Dosimeters were prepared by applying paints as well as pure rabbit glue paste on glass slides using a brush. The dosimeters' dimensions were 15x20 × 1 mm. This set of samples was long-term exposed under ambient conditions at two locations in the city of Granada (see below for details).

The second set of samples was prepared in a similar fashion. However, the pigment-binder ratio was maintained constant at 10:1 wt/wt. This ratio has been chosen because it is close to the average binder content of paint dosimeters prepared according to traditional recipes and used for outdoor-exposure. In practice, 5 g of pigment was wetted with 4 g of deionized water and afterwards mixed with 6.5 g of rabbit glue paste (solid content 0.5 g). For comparison, samples made of 5 g calcium hydroxide mixed with 10 g of deionized water (without the addition of rabbit glue) were prepared. This set of samples was exposed to accelerated photo-aging in the laboratory (see below). Note that no attempt was made to study paints based on calcite-water mixtures, because drying resulted in a powdery pigment layer without any cohesion. Paint dosimeters are named according to the following system: A-B–C-D; A = type of pigment, B = particle size, C = type of binder, and D = type of exposure/location and duration. See Table 1 for the complete nomenclature of samples.

2.3. Outdoor exposure test

Paint dosimeters were placed in a semi-open courtyard of the Alhambra monument (“Patio del Harem”, Nasrid palaces) and on a balcony (first floor) of a residential building facing SW adjacent to a highly trafficked street in the historic city center of Granada. Whereas dosimeters were protected from direct sunlight and rain at the Alhambra, they were exposed to rain and sunlight (~5 h daily in winter and ~10 h daily in summer) at the location in the city center. After the 24-month outdoor exposure the overall sunlight exposure duration was estimated to be ~5800 h at an irradiance level of ~1090 W/m^2 [13].

During the outdoor exposure tests, the maximum *T* in summer and minimum *T* in winter were 40 °C and −3 °C, respectively, with diurnal variations of up to 20 °C. Diurnal relative humidity (RH) variations reached 50% with average RH ranging from ~40% in summer to ~75% in winter. The number of rainy days per month varied between 0 and 14 (Fig. 1) [14].

Granada is a non-industrialized city. However, particulate matter, NO_2, and O_3 concentrations frequently exceed threshold values [15] set by the EU directive 2008/50 EC [16]. Particulate matter is expected to deposit on exposed painted surfaces, causing soiling. According to Urosevic et al. [17] its main constituents at Granada are: soil dust (quartz, calcite, dolomite, phyllosilicates, and iron oxides/hydroxides), black carbon, secondary inorganic aerosols, and sea salt.

2.4. UV-aging test

Dosimeters were exposed in the laboratory to UV-C radiation emitted by a small tubular Pen-Ray Mercury Lamp (No. 90-0012-01, Utra-Violet Products Ltd, UK). The lamp emits a spectrum with the

Table 1
Nomenclature of samples.

Pigments	
Cal-EF	Extrafine calcite
BSG-ST	Bianco di San Giovanni (standard)
BSG-C	Bianco di San Giovanni (coarse)
$CaCO_3$	Analytical grade calcium carbonate
$Ca(OH)_2$	Analytical grade calcium hydroxide
Outdoor exposed dosimeters	Location and test duration
Cal-EF-RG-A[a]	A = Alhambra
BSG-ST-RG-A	Test duration: 6, 12, and 24 months
BSG-C-RG-A	
Cal-EF-RG-CC	CC = city center
BSG-ST-RG-CC	Test duration: 6, 12, 24, and 30 months
BSG-C-RG-CC	
UV-aged dosimeters	
Cal-EF-RG-UV	Total test duration: 1000 h
BSG-ST-RG-UV	
BSG-C-RG-UV	
$CaCO_3$-RG-UV	
$Ca(OH)_2$-RG-UV	
$Ca(OH)_2$-H_2O-UV	

[a] All pigments are mixed with rabbit glue (RG) except $Ca(OH)_2$–H_2O which is mixed with water.