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Effect of tempera paint composition on their superficial physical properties-application of interferometric profilometry and hyperspectral imaging techniques

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ABSTRACT

Interferometric profilometry and hyperspectral imaging techniques combined with traditional analytical techniques such as spectrophotometry, stereomicroscopy, X-ray diffraction, scanning electron microscopy, particle size analysis, and thermogravimetry were used to characterize tempera paint mock-ups. These paint mock-ups were prepared as binary mixtures made by mixing either egg yolk or rabbit glue binders with one of ten pigments traditionally used by mediaeval artists, namely lime, calcium sulfate, white lead, minium, hematite, cinnabar, azurite, lapis lazuli, blue smalt and malachite. We evaluated the effects of mineralogical composition, pigment particle size and morphology, as well as the type and concentration of the binder on the physical properties of the paintś surface. Results showed that all the above compositional aspects had a direct influence on the paintś color, reflectance, and roughness. Moreover, mineral impurities and neoformed minerals due to pigment-binder interaction during paint preparation had a crucial effect on the superficial physical properties of paints. The analytical results proved the usefulness of interferometric profilometry and hyperspectral imaging techniques for the characterization of paint surfaces. The gained information will help conservation specialists in the evaluation of the impact of conservation treatments on the paint surface and the assessment of surface damage caused by weathering processes.

1. Introduction

Over the last decades research has been conducted on historical paints and paint mock-ups to fully characterize their composition and weathering mechanisms when subjected to different aging scenarios [1–5]. The conformation of paints (i.e., the pigment's mineralogical composition and particle size, the type and content of binder, as well as pigment-binder interactions) not only determines their surface texture and color, but also their susceptibility to chemical and physical weathering [3,4,6–8]. Since color change is one of the most obvious consequences of the impact of adverse indoor/outdoor environments on paints, color spectrophotometry has been one of the preferred non-invasive techniques to evaluate alteration [4,5,9–12]. Often this technique has been combined with more invasive analytical techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), Raman spectroscopy, and Fourier transform infrared spectroscopy (FTIR) to obtain more precise information on alteration processes involving compositional and conformational changes [3,6,13]. Many of these techniques require micro-sampling and are, thus, prohibitive in the case of valuable paintings.

More recently, non-invasive interferometric profilometry and hyperspectral imaging techniques have been introduced to the field of conservation science, providing useful additional information regarding superficial physical properties. The former allows high resolution measurements of surface roughness, and has been mainly applied for stone characterization [14]. Its application for the study of painting materials has been very limited [15]; recently Thei et al. [16] evaluated different consolidation treatments for urushi lacquer objects with this technique. Hyperspectral imaging techniques have been used for pigment identification [17,18], to evaluate the impact of conservation treatments [19], and to match paints for inpainting [20] based on their spectral features. However, until now the application of these imaging techniques has been often limited to case studies where only a small number of pigments/paints was analyzed [21,22].

Recently, a more general study using multispectral and hyperspectral imaging techniques was performed on paint [23]; however, this investigation did not consider pigment-binder interactions, pigment impurities, or particle morphology. Here we studied a wide range of

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pigments (i.e., lime, calcium sulfate, white lead, minium, hematite, cinnabar, azurite, lapis lazuli, blue smalt and malachite) in order to perform a systematic evaluation regarding the techniqueś potentials and limitations. The selected pigments were historically used in tempera paints for wall and panel paintings [24]. Mock-ups were prepared with pigments of different mineralogical composition, grain size and morphology using two different proteinaceous binders (i.e., rabbit glue and egg yolk) to evaluate the effect of pigment and binder properties as well as possible pigment-binder interactions on the paintś superficial physical properties (i.e, roughness, reflectance and color). To this end the above mentioned non-invasive techniques were combined with traditional analytical techniques, including spectrophotometry, stereomicroscopy, SEM, XRD, particle size analysis, and thermogravimetry (TG). The obtained results provided valuable information regarding shortcomings as well as potential applications of interferometric profilometry and hyperspectral imaging techniques for the characterization of painting materials and the evaluation of changes in the paintś superficial physical properties upon conservation treatments (e.g., impact of different cleaning methods) and physical and/or chemical weathering (e.g., assessment of changes during accelerated aging tests).

2. Materials and methods

2.1. Sample preparation

In this study we used forty-four tempera paint mock-ups prepared as binary mixtures mimicking real tempera paints. Each paint mock-up was prepared by mixing either egg yolk or rabbit glue with one of ten historic pigments (i.e. lime (calcite and/or portlandite), calcium sulfate (gypsum, bassanite and anhydrite), white lead, hematite, minium, cinnabar, azurite, lapis lazuli, blue smalt and malachite). Some pigments (i.e., lime, calcium sulfate, cinnabar, azurite and blue smalt) were purchased in different grain sizes in order to assess the effect of pigment particle size on the paint's superficial physical properties. All pigments were supplied by Kremer Pigments GmbH & Co. KG (Germany), except for cinnabar standard, which was supplied by Caremi Pigmentos S.L. (Spain). As mentioned before, the organic binders were of a proteinaceous nature; in particular, we used rabbit glue pearls (N°. 63028) from Kremer Pigments GmbH & Co. KG and egg yolk purchased locally.

Paint mock-ups were prepared according to Old Master recipes to achieve standards with adequate consistency similar to those used by mediaeval artists [25]. Consequently, these paints contained varying amounts of organic binder because binder demand depends on the pigmentś chemical composition and particle size; finer grained pigments commonly requiring more binder [24]. The procedure for the preparation of egg yolk-based paints can be consulted in [26], and for the rabbit glue-based paints in [6]. The paints obtained were applied in several layers onto glass slides (ca. 20 mm x15 mm x1 mm) using a paintbrush. The paint mock-ups were labeled by adding the letter E for egg yolk or G for rabbit glue to the pigments label, so as to clearly differentiate the powder pigments from the binary paint mixtures.

2.2. Analytical techniques

The pigments particle size was analyzed using a laser particle size analyzer (Mastersizer 2000LF, Malvern Instruments). Samples were dispersed in alcohol. One measurement was made per sample and the reported values are based on volume distribution.

The binder content of each tempera paint was determined by means of thermogravimetric analysis (TG) with a Shimadzu TGA-50H (Shimadzu Corporation) in flowing air (100 ml/min) at a constant heating rate of 10 °C min^{-1} (25–950 °C) as explained in [6,27].

Field emission scanning electron microscopy (FESEM) was used to study the pigmentśs morphological features (Auriga, Carl Zeiss, Germany). Equipment settings were 10^{-4} Pa vacuum and 3 kV beam accelerating voltage (secondary electron imaging mode). Samples were carbon coated.

The mineralogical composition of pigments and tempera paints was determined using X-ray diffraction (XRD, ẊPert PRO PANalytical B.V.) Analyses were performed using Cu-Kα radiation, Ni filter, 45 kV voltage, and 40 mA intensity. The exploration range was 3° to 60° 2θ and the goniometer speed was 0.05° 2θ s^{1}.The identification and semi-quantification (± 5%) of the minerals were carried out using Xpowder softare [28].

The viscosity of egg yolk- and rabbit glue-binder was measured using a Rheometer (R/S Rheometer, Brookfield Engineering Laboratories, Inc.) with a R/S MS-8 Din measuring system. Measurements were performed at 20 °C.

A stereomicroscope (SMZ 1000, Nikon) was used to examine the textural, structural and chromatic features of the paint mock-ups.

The color of tempera paints was characterized using CIELAB color space [29], measuring L* (lightness), a* and b* (color coordinates) and C^*_{ab} (chroma) by means of a Minolta CM-700d spectrophotometer. C^*_{ab} is calculated according to the following formula: $C^*_{ab} = (a^2 + b^2)^{1/2}$, where a* indicates the color position between red (positive values) and green (negative values) and b* between yellow (positive values) and blue (negative values). Fifteen random measurements on the entire surface of each mock-up (~20 × 15 mm) were obtained to provide statistically consistent results. The measurements were made in the Specular Component Included (SCI) mode, for a spot diameter of 3 mm, using D65 as the illuminant and an observer angle of 10°.

Reflectance spectra were obtained using an inhouse-built hyperspectral camera, which combines an imaging spectrograph with a monochrome matrix array sensor [30,31]. The equipment consisted of a CCD sensor Pulnix TM-1327 GE (1040 h x 1392 v pixel resolution) with an objective lens (10 mm focal length). An ImSpector V10 spectrograph with a spectral range of 400–1000 nm and a spectral resolution of 4.55 nm was positioned between the sensor and the lens. The camera scanned the surface, line by line, with a field of view of 51 × 0.89 mm, to obtain an image at each of the 1040 wavelengths. A cylindrical lens placed in front of the lamp focused the light so that the illuminated area was 15 × 1 cm. In order to move the sample, it was placed on a motorized XYZ translation stage in which the Z- axis is perpendicular to the sample surface. The paint mock-ups were fully scanned (ca. 20 × 15 mm). Once the hyperspectral images were acquired, the data were processed in a MATLAB programming environment in order to display the respective reflectance graphs.

Roughness was characterized by a non-contact optical profiling system using a profilometer (Wyko-NT 1100 (Veeco) with WycoVision®32 analytical software package). This equipment provides high resolution, 3D surface measurement, from sub-nanometer surface roughness to millimeter step-height. Two measurement modes are available: i) Phase-Shifting Interferometry (PSI) mode allowing high-resolution measurement of smooth surface and small steps, and ii) Vertical Scanning Interferometry (VSI) mode allowing the measure of rough surfaces and steps up to several millimeters high. In the current case, mean roughness data were obtained using the VSI mode (measurement range of 2 mm and vertical resolution of 1 nm for multi-measurement). The data were collected using a 5x magnification with an intermediate field of vision (FOV) lens of 1x. Using a motorized stage and the Data Stitching option, measurements were obtained of a 4 × 4 mm area by combining (stitching) 24 images. Reported values are based on one measurement.

The parameters computed for the characterizing of spatial and hybrid properties were Sa, Sdr and Str [32]. One measurement was made per sample. Sa is the height parameter in μm, measured over the complete 3D surface. Sdr is a hybrid parameter measuring the developed interfacial area ratio. It is expressed as the percentage of additional surface area contributed by the texture as compared to an ideal plane of the same size as the measured sample area. Str is the spatial parameter texture aspect ratio, which is a measure of the spatial