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Raman analysis of complex pigment mixtures in 20th century metal knight shields of the Order of the Elephant

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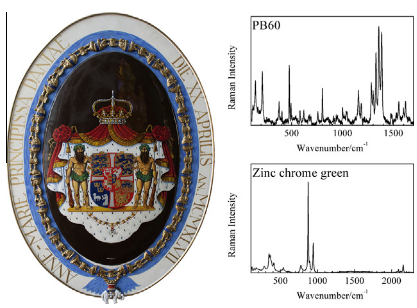
HIGHLIGHTS

- Raman analyses of complex pigment composition in artists' and industrial paint on metal support.
- Comparison between industrially applied paint layers and the artistic paint layers.
- Investigation of an important collection of Danish cultural history objects.
- Identification of composite inorganic pigment and synthetic organic pigments (SOPs).
- Characterization of artists' binding media on metal knight shields.

GRAPHICAL ABSTRACT



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ABSTRACT

The pigment composition of six painted metal knight shields of the Order of the Elephant dating from the second half of the 20th century belonging to the Danish royal collection were studied using Raman microscopy. By focusing a 785 nm laser with a 50× objective on particles in paint cross sections, it was possible to identify the following 20 compounds: hematite, goethite, chrome red/orange, chrome yellow, zinc chrome yellow, carbon black, toluidine red PR3, chlorinated para red PR4, dinitroaniline orange PO5, phthalocyanine blue PB15, indanthrone blue PB60, ultramarine, Prussian blue, lead white, anatase, rutile, calcium carbonate, barium sulphate, gypsum and dolomite. The components were frequently present in complex pigment mixtures. Additional information was obtained by elemental analysis with scanning electron microscopy–energy dispersive X-ray spectroscopy (SEM–EDX) to identify cobalt blue, zinc white and cadmium red, as well as to indicate the presence of zinc white in some pigment mixtures. The study allowed a comparison between the industrially applied preparation layers and the artistic paint layers applied by the heraldic painter. Differences in the choice of paint and pigment types were observed on the earliest knight shields, demonstrating a general delay of industrial materials into artist paints.

Introduction

The royal Danish award system is one of the oldest still practiced. Its roots date back to a Catholic confraternity founded in the mid-15th century by King Christian I, called the Fellowship of the Mother of God [1]. Due to the reformation in 1536, the confraternity was abolished, however it was later revived under the reign of King Frederik II (1559–88) as a Protestant order. The confraternity's original emblem of Virgin Mary and Child was thereby replaced by an elephant after which the revived order obtained its name. The Order of the Elephant is the most

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prestigious of the Danish royal orders, mainly bestowed on members of royal families and heads of state. The origin of the elephant is not clear, but it is known that elephants were originally part of Christian I's collar, from which the badge of Maria was hung [1].

In association with the strengthening of the monarchical power following the introduction of absolute monarchy in Denmark in 1660, the award system was taken into extensive use. During the reign of King Christian V (1670–1699), the Order of Dannebrog was founded in 1671 and statutes for both orders were formulated in 1693. In 1693–94 the Chapel of Orders was established in Frederiksborg Castle Chapel as a worthy setting for the annual assembly of the knights on Whit Tuesday. For this ceremonial occasion, the knights were assigned a fixed seat above which their metal knight shield was hung. The shield displayed the heraldic achievement components of the knight, such as coat of arms and motto, as well as name and date of ordination. A royal heraldic painter has since then been connected to the Chapter of the Orders.

Although the assembly was ceased already after the first gathering in 1694 [2], the production and subsequent display of the knight shields in the chapel continued – a tradition which remains in the present day.

In 1878 Frederiksborg castle was converted into the Museum of National History and the collection became open to the public. Today the collection counts about 2800 knight shields, 300 of which are of the Order of the Elephant.

The present paper is part of a comprehensive study, which is the first to investigate the production methods and materials used for the knight shields. More specific, the study covers knight shields of the Order of the Elephant dating from the late 1940s to 1990, as these show characteristic deterioration problems. A previous study presented the white ground and primer layers responsible for the striking variety in conservation states [3]. This study further investigates the pigment compositions of the paint layers.

The production of the knight shields is a multi-stepped process, whereby paint and gilding layers' common for all knight shields are applied by an external painter before the heraldic design is painted by the heraldic painter. Since industrial pigments used by the external painters [3] are often introduced into an artist's palette with years of delay [4–6], different pigment choices are expected to be observed in the different applications.

The investigation of modern pigment compositions is particularly challenging when taking into consideration the numerous pigment types available, as compared to the rather limited palette of old master paintings. The invention of the first synthetic aniline dye mauveine by Perkin in 1856 introduced the modern synthetic organic dye and pigment industry, which greatly influenced subsequent paint production. The synthetic organic pigments (SOPs) are not always used alone, but often mixed together [7] or added to inorganic pigments as a brightening agent or possible adulterant [4].

Raman microscopy has proven to be a powerful tool in the analysis of such complex pigment mixtures. This is largely due to its high spatial resolution and specificity, as well as its sensitivity to a large array of pigments of both inorganic and organic origin [7–11].

In this study Raman microscopy was the main technique used for pigment identification. Additional information on paint materials was obtained by optical microscopy (OM), scanning electron microscopy–energy dispersive X-ray spectroscopy (SEM–EDX) and Fourier transform infrared microscopy (μ-FTIR).

Experimental

Description of the knight shields

The knight shields investigated are depicted in Fig. 1(a–f) and are: (a) Prince Henry of Great Britain (1948), (b) General Dwight D. Eisenhower (1955), (c) President Urho Kekkonnen of Finland (1958), (d) Princess Anne-Marie of Denmark (1964), (e) Prince Hitachi of Japan (1967) and (f) Queen Silvia of Sweden (1990). Information of the knight shield and the heraldic painters are given in Table 1.

The six knight shields are representative for three successive external painters active in the period 1945–1990 [3]. The external painters are responsible for the preparation paint layers, i.e. layers which are common for all knight shields such as: the white frame; the brown central area, which functions as background for the heraldic design; and the blue sash surrounding the central area to which the golden chain of alternating elephants and towers is soldered. Their work is designated Prep1, Prep2 and Prep3 in Table 1. Thus, the knight shields have not been selected primarily to represent the heraldic painters of the period, who were Franz Šedivý (heraldic painter 1945–1967 and responsible for the first five of the chosen knight shields) and Aage Wulff (heraldic painter 1967–1994 and responsible for the latest knight shield).

As the shield may be painted years after the knight is appointed, the date of appointment cannot be used to date the production of the knight shield. However, the date the knight shield was hung in the chapel has in general been noted since the mid 20th century, and this date is considered close to the date of production (given in Table 1).

Cross sections

Tiny paint samples of the preparation and the heraldic paint layers were respectively made into cross sections by embedding in spofacryl resin between two PMMA blocks and polished wet with silicon carbide and then dry with micro mesh (granularity 2400–12,000).

Optical microscopy (OM)

The samples and cross sections were studied with an optical microscope Axioplan (Carl Zeiss) under incident white light and ultraviolet radiation with magnifications up to 1000×.

Raman microscopy

Raman analysis was carried out with a Renishaw inVia dispersive micro-Raman spectrometer equipped with a Peltier-cooled (203 K) near-infrared enhanced, deep-depletion charge coupled device (CCD) detector (576 × 384 pixels). The excitation source was a high-power diode 785 nm laser (Toptica Photonics XTRA, Graefelfing (Munich), Germany) operating in combination with a 1200 l/mm grating. Raman spectra were recorded from cross sections using the 50× objective of a direct-coupled Leica DMLM microscope with enclosure. The laser power was kept low at values between 0.1 and 1 mW by neutral density filters to avoid thermal degradation. Acquisition time was 10–80 seconds and accumulations from 1 to 5, depending on the circumstances to obtain a spectrum with a significant signal-to-noise ratio. Subsequently the spectra were baseline corrected with Raman software Wire 2.