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Analytical study of modern paint layers on metal knight shields: The use and effect of Titanium white

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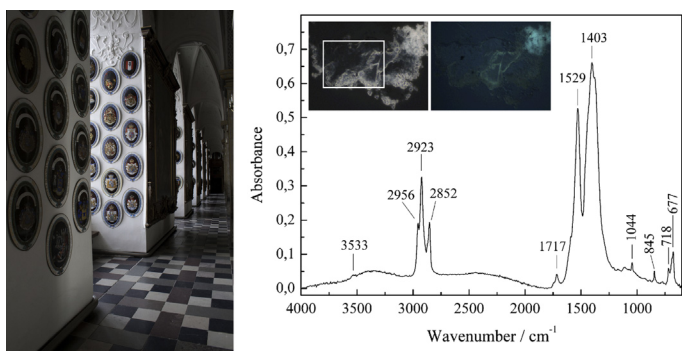
HIGHLIGHTS

- Investigation of the role of titanium white pigments in alkyd paint.
- Characterization of three different industrial coat systems on metal knight shields.
- Identification of lead corrosion products in the metal/paint interface causing paint delamination.
- Degradation of exposed pigmented paint layers containing anatase.
- Influence of the climatic conditions on the stability of the knight shields.

GRAPHICAL ABSTRACT



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ABSTRACT

Painted metal knight shields of the Order of the Elephant produced during the last part of the 20th century are characterized by a striking variety in their conservation state. Three different coat systems were identified and investigated by Fourier transform infrared microscopy (μ-FTIR), micro-Raman spectroscopy (MRS), scanning electron microscopy–Energy dispersive X-ray spectroscopy (SEM–EDX) and Thermally assisted hydrolysis and methylation-gas chromatography–mass Spectrometry (THM–GC–MS). Chalking of the white paint layer on the first group of knight shields displayed in the window niches was found to be related to the use of titanium white of the anatase type. A pristine condition of the second group could be attributed to priming of the lead rich metal support with a zinc potassium chromate based primer and the use of mainly stable white pigments in the top coat. Severe delamination of the paint layer of the third group was caused by the formation of lead corrosion products between the paint layer and the metal support. The results are discussed in relation to the climatic conditions as well as the historical context of contemporary paint production and availability in Denmark.

Introduction

The Order of the Elephant is the oldest and most prestigious order in Denmark and is primarily bestowed upon members of royal families and heads of state. Though its origin dates back to the mid-15th century it was not before the end of the 17th century during the reign of King Christian V that the order was established in the form still existing today. The statutes of the order of 1693 prescribe that a painted metal knight shield which displays the coat of arms and motto of the knight, is hung in the Chapel of Order in Frederiksborg Castle church. Since then, a heraldic painter has been affiliated with the royal award system. In 1878 Frederiksborg Castle was converted into The Museum of National History and the historical collection became open to the public. Today this unique collection counts about 300 elephant knight shields and constitute an important part of Danish cultural history and this paper is the first to provide an extensive study of part of this collection.

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A visual inspection of the knight shields revealed that problems in the paint layers can primarily be associated with the modern part of the collection. This includes brittleness of the white paint layer of some of the knight shields from the late 1940s and early 1950s, and severe delamination of the paint layer on knight shields from more recent times. These problems are not connected to the work carried out by the royal heraldic painter, who only paints the coat of arms and symbolum, but are related to the white coat system applied to the metallic surface prior to this step. These white coat layers, as well as other paint layers which are present on all knight shields, such as the brown colour of the picture plane and the blue sash around the picture plane, are today painted by external painters who are responsible for delivering an agreed number of prepainted knight shields to the Chapter of the Royal Danish Orders of Chivalry at regular intervals (Fig. 1). The external painters have their background in the industry whereas the heraldic painters traditionally have a background in pictorial art (Personal communication with Warden of the Chapel of the Royal Danish Orders of Chivalry Major Rolf Christensen and supplier of prepainted knight shields until 2011 Eli Diamant, February 2011).

The Chapter of Orders has no information on the suppliers of prepainted knight shields, and thus the external painters remain anonymous. However, based on minor differences observed in the way the standard paint layers have been applied, it is clear that the chapter had three main suppliers of knight shields in the period 1945–1990. Problems are only related to the first and the last suppliers, whereas the knight shields from the period pertaining to the second supplier remain in close to pristine condition (Table 1).

The term coat system is used for the prepainted layers to emphasize the materials' origin within the industry, thus firmly distinguishing these layers from the decorative paint layers applied by the heraldic painter. One or more of the following coat layers are included in a coat system: an anticorrosive primer applied directly to the metal in order to suppress corrosion and to ensure adhesion of the following coats to the metal substrate. The primer may be followed by an undercoat which provides a smooth and even surface for the topcoat or finishing layer. In general the undercoat contains a high amount of extender materials and is of low cost. The following topcoat provides the coat system with the final gloss and colour. It has good hiding power and contains no or only a small amount of extender materials. After application of the coat layers follows the paint and gild work of the heraldic painter. The stratigraphic build-up of the externally applied white coat system is seen in Table 2.

Fig. 1. Left: A knight shield before the coat of arms and symbolum are painted by the royal heraldic painter. Right: View through the Chapel of the Royal Orders at Frederiksborg Castle at the Museum of National History.

The aim of the study was to investigate the difference in conservation state of the applied paint layers by analyzing the multilayered white coat systems of the three different suppliers in order to provide an important basis for preservation strategies for the modern part of the collection.

Six representative knight shields, one from the beginning and one from the end of each supplier's period were studied. The data from this study is of significant importance for museums encountering similar challenges with painted objects of the same period e.g. modern art or industrial cultural heritage objects.

Experimental

Knight shields

The knight shields studied from each of the three periods were from the mid 1940s to mid 1950s, Prince Henry of Great Britain (1948) and General Eisenhower (1955), from the mid 1950s to mid 1960s, Princess Anne-Marie of Denmark (1964) and President Urho of Finland (1957), and from the mid 1960s to 1990, Prince Hitachi of Japan (1967) and Queen Silvia of Sweden (1990).

Cross sections

Paint samples were imbedded in spofacryl resin between two PMMA blocks and wet polished until the sample was reached, then dry polished using micro mesh (granularity 2400–12,000). The cross sections were studied with an optical microscope Axioplan (Carl Zeiss) under incident white light and ultraviolet radiation (excitation bandpass filter from 390 to 420 nm) with magnifications up to 1000×.

FTIR

μ-FTIR was performed in transmission mode using a Hyperion 3000 spectrometer equipped with a MCT (Mercury Cadmium Telluride) detector. The absorption spectra ranging from 4000 to 600 cm^{-1} were collected over 64 scans with a resolution of 4 cm^{-1}. Before measurement the sample was compressed in an anvil cell between two diamond windows and photographed under the optical microscope.

SEM–EDX

SEM analyses were carried out on gold coated cross sections and bulk samples using a JEOL JSM6300 scanning electron microscope with an energy dispersive X-ray spectrometer (SEM–EDX). The SEM–EDX was equipped with X-ray detectors Pentafet Si(Li) and BSE (Tetra Link), both from Oxford Instruments. The EDX-analyses were run at an acceleration voltage at 15 kV.

Raman

MRS analyses were carried out with a Renishaw inVia dispersive micro-Raman spectrometer equipped with a Peltier-cooled (203 K) CCD detector. The laser used operated at 785 nm (Toptica Photonics XTRA) in combination with a grating of 1200 l/mm. Analysis was carried out directly on the cross sections under a direct-coupled Leica DMLM microscope with enclosure using the 50× objective. The laser power used was kept low at values between 0.1–1 mW by neutral density filters to avoid any thermal degradation. Acquisition time was 10–80 s and accumulations from 1 to 5, depending on the circumstances, were used to obtain a spectrum with a significant signal-to-noise ratio. The spectra were subsequently baseline corrected with Raman software Wire 2.