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On the photoluminescence changes induced by ageing processes on zinc white paints

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Abstract

Recent research is focusing on the study of interaction mechanisms between pigments and binder, as they are crucial for understanding paint ageing and conservation issues. In this work, we investigate these mechanisms and follow the changes induced by ageing on zinc white paint by employing Fourier Transform Infrared (FTIR) and Time-Resolved Photoluminescence (TRPL) spectroscopies. The two techniques, applied on thermally aged mock-up samples and on a 19th oil painting, provide complementary information on the effect of the binder on the ZnO pigment particles. The characterization of the infrared absorption spectra confirms the well-known tendency of the formation of amorphous metal carboxylates in zinc white paint following ageing. At the same time, the ageing of paint film produces significant changes in the photoluminescence emission from defect centres of ZnO. The emission that is mostly affected by the changes of the micro-environment is the blue band (430 nm) - associated with surface defects - whereas the green emission (530 nm) is stable. The results demonstrate that the evolution of the pigment-binder system has detectable consequences on the crystalline structure of the pigment particles and we speculate that the main cause of the modifications is the functionalization of the pigment particle surfaces. The possibility to follow crystal structure changes with time-resolved photoluminescence can thus support chemical studies by providing information about pigment-binder interactions, metal carboxylate formation and paint deterioration.

Keywords. zinc white; metal soap; thermal ageing; painting; Time resolved photoluminescence; FTIR

1. Introduction

Zinc white is a pigment made of ZnO and it was the most widely distributed white between the 1840s and the middle of the 20th C. when it was replaced by titanium white [1]. Following this, the pigment has been used mainly as an extender and filler in paints. The presence of zinc white has a major impact on the conservation of modern paintings, since the pigment is reactive to the formation of metal soaps [2][3][4]. The ageing of paint is a complex process that involves chemical reactions between pigments and binders and the photo-oxidative drying of the binding medium, as illustrate in the following.

Many studies have demonstrated that the ageing of binder alone can be simplified into two phases. The first phase is relatively short and stabilizes after 10-15 days (depending on binder), which corresponds to a touch-dry film [5][6]. In the second phase, the system is more stable, and slow processes take place which lead to the ageing of the film [6][7]. It is important to consider these two stages separately. The first phase implies a significant autoxidation process followed by polymerization of the network, which leads to the hardening of the film [7][8][9]. The presence of a metal-based pigment (such as zinc white) catalyses the cross-linking process and activates a series of other chemical reactions between the organic part of the binder and the metal compounds. One significant consequence of the interaction is the formation of metal carboxylates, which can be detected by Fourier Transform Infrared (FTIR) spectroscopy [8][10]. It has been shown that in the case of oil and metal-based pigments, the unbound fatty acids present inside the oleic binder bond to metal ions and, via a hopping mechanism, cause the migration of metal ions from the metal oxide to the binding medium where the metal ions attach to the polymer network and form metal carboxylates [11][12]. Another mechanism suggested to occur in paint material is the adsorption of the organic acids on the pigment particle surface [10][13]. Such a surface functionalization has not been experimentally demonstrated for paint materials, but it is widely observed between metal oxide surfaces and organic compounds [14][15]. Despite the lack of experimental evidence, the functionalization of metal oxide particle is highly plausible even in paint materials and in our previous study we supported this hypothesis [16]. In fact, by employing Time Resolved Photoluminescence (TRPL) spectroscopy, we detected a significant modification of the photoluminescence (PL) emission of the zinc white mixed with binder with respect to the pigment powder. These changes were not simply related to a superposition of the PL of zinc white and the fluorescence of the binding medium, but were ascribed to an intrinsic modification of the zinc oxide crystal structure. The results confirmed the strong effect of the drying binder on zinc white and opened up questions about the temporal evolution of such a system.

As previously mentioned, in addition to the important interaction in the first drying phase, in the second ageing stage, there is a progressive oxidation of the binding medium, that also involves the hydrolysis of ester bonds and cleavage of fatty acid chains