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**Interactions of natural resins and pigments in works of art.**Tommaso Poli<sup>a</sup>, Anna Piccirillo<sup>b</sup>, Marco Nervo<sup>b</sup>, Oscar Chiantore<sup>a</sup><sup>a</sup> Università degli Studi di Torino, Dipartimento di Chimica, Via Giuria 7, Torino Italy  
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**Abstract**

The degradation process involving the formation of metal soaps in drying oils is a well-known problem due to cations from pigments reacting with free fatty acids from the oil. The aggregation of these carboxylates in semi-crystalline structures can lead to eruptions through the paint layers and 'blooming' on the surface. In this work, the metal soaps formation in presence of natural resins has been assessed and studied by means of Fourier transform infrared spectroscopy with experiments concerning the ageing of drying oil and different natural resins (shellac, dammar and colophony) in the presence of common historic pigments (smalt, ochre, umber, azurite, lead white, zinc white and titanium white). Mixtures of resins and pigments have been exposed to photo-ageing in solar box up to 1000 h, thermal ageing at 50 °C up to 1100 h and 6 month of room conditions exposure as reference.

The decrease in the intensity of the carbonyl band in the spectra, as well as the contemporary increase of the metal carboxylates (in the range from 1500 to 1650 cm<sup>-1</sup>) absorption bands, were used as the main indicators of metal soap formation. It has been observed that some pigments, particularly zinc white and smalt, present a 'catalytic' effect favouring the simultaneous formation of associated oxalates. The formation of oxalates and different degradation products from natural resins in the presence of pigments is particularly important, as it deeply affects the removability of varnishes and, more generally, the cleaning processes. Moreover, it permanently modifies the interface between painting and varnish layers as well as the aesthetic aspects of the painted surfaces. The influence of natural resins reactivity with pigments and their role in the oxalate formation is an issue still unexplored.

Key-words: natural resins; metal soaps; pigments; FT-IR; oxalates

**1. Introduction**

The pictorial organic materials have been studied in numerous works aiming at characterizing and understanding the film formation processes and the related decay patterns [1-11]. In particular, several studies have been published on the interaction between binding media and metal salts present as dryers or as pigments in painted artworks, focussing on drying oils or egg tempera [12-23]. The interaction of pigments and binding media may result in metal soaps formation on the painting layers which can influence the appearance and state of conservation of the film. The metal carboxylates, in particular, modify the painted surface aspect with the creation of protrusions that can determine weakening and sometimes the fall of the pictorial film [16, 17].

Numerous publications reported that pigments containing metals such as lead, copper, zinc, iron and aluminium, alkaline-earth metals like calcium and alkaline metals such as potassium induce carboxylates formation [10, 14, 15, 18-23]. In the case of drying oils, the metal carboxylates come from the reaction between the free fatty acids in the medium (coming from the hydrolysis of the triglycerides) and the cations in the pigments [17]; in the cases of egg tempera, the metal soaps come from the fatty acid components of the egg yolk [23].

The causes of the metal soaps formation reported in literature are many: nevertheless, humidity seems to play a crucial role in the formation of soaps. Variations of the relative humidity during the painting life or the introduction of polar solvents during restoration interventions could modify the delicate equilibrium of the systems [16]. It has been shown that high humidity with a basic pH value can destabilize many pigments [18] and surely, also, favours the hydrolytic processes. For

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