Oil paints: the competition between cross-linking and oxidative degradation phenomena

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Paint consists of finely divided pigment particles dispersed in an organic fluid binder [1]. When a drying oil - a plant oil rich in triglycerides of polyunsaturated fatty acids - is used as a binder, the paint is an oil paint [1]. The air-curing process, during which a liquid oil paint layer converts to a durable film, is known as autoxidation [2]. The autoxidation of oil paints entitles the formation of peroxide species which evolve according to two main competitive phenomena - cross-linking and oxidation [3,4], of which cross-linking is fundamental for obtaining a durable film.

In the present study the chemistry of air-drying artist's oil paint curing and ageing up to 24 months was studied. The objective is to improve our molecular understating of the processes that lead to the conversion of the fluid binder into a dry film, and how this evolves with time, which is at the base of a better comprehension of degradation phenomena of oil paintings, and relevant to the artists' paint manufacturing industry. To this aim a methodological approach based on thermogravimetric analysis (TG), differential scanning calorimetry (DSC), gas-chromatography-mass spectrometry (GC-MS) and analytical pyrolysis coupled with gas chromatography and mass spectrometry (Py-GC-MS) was implemented. Model paintings based on linseed oil and safflower oil (a drying and a semi-drying oil respectively) mixed with two historically relevant pigments - lead white (a through drier) and synthetic ultramarine blue (a pigment often encountered in degraded painting layers) - were investigated. The oil curing under accelerated conditions (80°C under air flow) was followed by isothermal thermogravimetric analysis (TG). The oxygen uptake profiles were fit by a semi-empiric equation that allowed to study the kinetics of the oil oxidation and estimate oxidative degradation. DSC signal due to hydroperoxides decomposition and radical recombination was used to monitor the radical activity over time and to evaluate the stability of peroxides formed in the paint layers. GC-MS was performed at 7 and 24 months of natural ageing, to investigate the non-covalently cross-linked fractions, and Py-GC-MS to characterise the whole organic fraction of the model paintings, including the cross-linked network. Oil-pigment combination have a strong influence on the relative degree of oxidation of the films formed with respect to its degree of cross-linking. In particular, ultramarine blue painting layer is less cross-linked than a lead white based one, when other factors (oil type, additives, age, conservation conditions, etc) are the same. This tendency of ultramarine blue to favour oxidative degradation over cross-linking may be related to documented conservation issues of ultramarine paining layers, from the loss of cohesion to the establishment of water sensitivity.

References

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