From egg tempera to oil painting – case studies of Domenico Ghirlandaio and Sandro Botticelli and the chemistry and microstructure of paints

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In a multiyear research project, the 14th to 16th century Florentine paintings in the Bavarian State Paintings Collections were studied to produce a catalogue of collection, including works by Fra Filippo Lippi, Domenico Ghirlandaio, Sandro Botticelli and Leonardo da Vinci. Special emphasis was placed on the transition from tempera to oil painting in the 15th century. Technical study revealed that besides tempera and oil painting, there are techniques "in between", showing characteristics of both techniques at the same time. Usually this is explained by "tempera grassa", i.e. egg tempera with added oil. However, binder analysis using gas chromatography mass spectrometry and amino acid analysis revealed that the type of technique did not necessarily correlate with the amounts of egg and oil in samples of the mentioned paintings. Particularly, there was no indication for "tempera grassa" as the link between the techniques, and oil paints did contain egg, which was also found for more traditional oil paintings before. What is the role of proteins in oil paints? Often they are neglected because they are difficult to identify in the presence of too much oil.

In recent years, consideration of basic principles of colloid chemistry and rheology (the science of flow of matter) lead to a new perspective in our understanding of the properties of paints and how they can be applied on paintings. A joint project of art technology, chemistry and rheology shifted the focus from sole chemical composition towards the formation of microstructures with varying distribution of paint ingredients on a micrometer length scale or below, depending on the presentation of materials and their colloidal interactions. It is well known in rheology that flow properties of dense suspensions (i.e. paints) are not determined by the binder alone but mainly by microstructures formed by pigment-pigment and pigment-binder interactions. Accordingly, samples with different applications of egg yolk and linseed oil mixed binders with lead white and ultramarine blue pigments were prepared and analysed by a broad range of chemical and mechanical methods. Pure oil paints were compared to egg yolk emulsified with oil ("tempera grassa"), capillary suspensions and egg-coated pigments in oil. Capillary suspensions develop if egg yolk (or water) is mixed into oil paints, e.g. with a brush, or even due to the uptake of humidity. The aqueous component forms gel structures with the pigments (the oil remaining in the pores of the gel), resulting in relatively stiff paints with a high yield stress, which is ideal for creating impasto. Egg-coated pigments in oil might be formed when pigments are ground with a bit of egg added as a wetting and anticaking agent, before dispersing the coated pigment in oil.

A multi-disciplinary and multi-analytical approach based on rheology, physical and analytical chemistry was carried out to investigate the chemical composition as well as the mechanical and physico-chemical properties of various paints. The focus was not only on wet paints, but also on their drying and curing behaviour, in order to correlate them with effects observed on tempera

and oil paintings. Steady shear experiments using different geometries for determining the yield stress, high shear viscosity or complex shear modulus, which influence the impasto of a paint, were used. Results were combined with gravimetric and thermogravimetric analyses, differential scanning calorimetry, oxygen uptake, gas chromatography mass spectrometry (GC−MS), analytical pyrolysis coupled with GC−MS and mechanical texture analysis. The presentation will show how the addition of egg yolk (protein) affects the drying and oxidation of the oil binder, which will also influence the paint ageing process. Adding egg during the preparation of the paints can be used to increase the pigment-binder ratio, avoiding problems caused by traces of humidity naturally occurring in the pigments during storage, and likely minimising well known binder-caused ageing problems such as darkening and crack formation. The distribution of protein, water and oil in paints will be correlated with the flow properties and the drying and curing behaviour of paints, demonstrating among others, that “tempera grassa” behaves like tempera and cannot explain observations from paintings showing characteristics “in between” tempera and oil techniques.