It takes an age: Art pigments influence degradation of protein-based binders under UV light

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Binder breakdown

Natural organic materials were used in many old works of art as binders, to enable the paint pigments to stick to the canvas. Latex and animal glue are typical examples, and egg is used in authentic tempera. When restoration work is required, it is crucial to know the type of binder that is in place, to facilitate a successful and lasting repair.

Unfortunately, binders do not remain intact throughout the lifetime of the painting. They are degraded by daylight, heat, dirt, insects and mould which affect the quality of the painting and can cause considerable damage to the painting.

The protein-based binders are also affected by some of the pigments present, which appear to initiate changes in the amino acid compositions of the proteins. This phenomenon has been examined by several research teams in the past, but a team of European researchers has taken an original approach to the problem by comparing the mass spectra of degraded binders using principal components analysis (PCA).

Natalia Navas and co-researchers from the University of Granada, Spain, the Institute of Chemical Technology, Prague Charles and University, Prague, examined the influence of two conventional pigments on the degradation of rabbit glue under UV light. This is more harmful than visible or infrared light and causes breakdown of the binders as well as oxidising the pigments. The importance of the study is augmented by the recent, apparently contradictory, introduction of UV laser technology for cleaning and testing the surfaces of paintings.

A sticky study with rabbit glue

Rabbit glue is a traditional protein binder that consists of hydrolysed collagen. In this study, it was mixed with cinnabar, which is a red pigment, and azurite, which is deep blue. Cinnabar is an ore containing mercury sulphide, which is often sold as the synthetic compound under the name of vermilion. Azurite is hydrated copper carbonate.

The glue, with and without each of the pigments, was prepared according to recipes used by the Old

Masters to produce samples similar to those with which Medieval artists would have painted. It was spread onto a glass slide using a paintbrush in several successive layers, drying between each coat.

Artificial ageing was accomplished under UV light from a xenon lamp for up to 3000 hours. Samples were taken at intervals from 200 hours onwards to study the nature of the protein in the paints and these were compared with a pristine sample collected before irradiation was begun.

Each sample was treated with trypsin to break up the proteins present and the resulting peptide fragments were analysed by matrix-assisted laser desorption/ionisation mass spectrometry (MALDI MS). The spectra of fresh and aged samples were compared using PCA. The team also applied FTIR spectroscopy to examine the conformation of the collagen at different stages of ageing.

Pigments interact with binders

The mass spectra of fresh pure rabbit glue were different to those of the aged glue, confirming changes due to UV light irradiation. The spectra also differed from those of fresh glue-pigment samples, suggesting that addition of cinnabar and azurite brought about changes to the collagen before ageing began.

The PCA plots discriminated between pure glue samples aged in the period from 200-1500 hours. The protein was stable before that period and no further changes were observed afterwards. A large number of the tryptic peptides, differentiated by their m/z values, were associated with the discrimination.

The IR spectra suggested that the ageing process was related to a change in protein conformation. The UV irradiation breaks the hydrogen bonds that hold together the peptide chains in the beta-turn structure, so that the chains become independent and form an alpha-helix as the basic unit.

When cinnabar or azurite was added to the rabbit glue and aged, the resulting mass spectra and PCA also discriminated between fresh and aged samples. For both pigments, different ageing processes were at play compared with pure glue.

The mercury present in cinnabar initiated protein denaturation even before ageing began. The disordered protein then formed aggregates which coexisted with the random denatured coils.

For azurite, the copper ions formed complexes with the amide groups of collagen within the first 200 hours of ageing, after which the glue-pigment composite was stable to UV light. In this case, the beta-turn structure remained in place.

Navas reports that this is the first known study of MALDI MS with PCA in the field of cultural heritage. Along with the FTIR data, it illustrates how changes in the protein-based binders can be followed during ageing by UV light, and how these changes are modified by the presence of pigments.

The joint techniques can easily be applied to study the

effects of other internal and external influences such as organic pigments, oils, varnishes, dirt, and airborne gases and particles. The results will add to the all-important bank of knowledge which can be called upon before considering restoration of old works of art.

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- ***Journal of Mass Spectrometry* 2012, 47, 322-330** : "Collagen-based proteinaceous binder-pigment interaction study under UV ageing conditions by MALDI-TOF-MS and principal component analysi)"

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