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A physicochemical approach to the investigation of the condition of oil paintings on paper supports

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The scope

The subject of this research is the physical chemical investigation of the condition of oil paintings and oil sketches on paper support. The research focuses on the study of the optical behaviour at different spectral regions and on the effect of the oil binder on the paper support to investigate the changes caused and the progress of deterioration. The optical behaviour is coupled with qualitative and quantitative analysis of the oxidation by-products of the degrading cellulose during ageing in original artworks and artificially aged mock-ups and thus to link the optical behavour to chemical degradation in order to provide criteria for the better evaluation of their condition.

The results



The methodology

Six original works of art, representative samples of the Greek artists of the 18th-20th century, belonging to the National Gallery - Museum of Alexandros Soutzos were investigated. The research was supported by experimental laboratory study of artificially aged mock ups made of linseed oil and different paper supports (pure cellulose Munktel, typical watercolour Montval and a Kraft type paper). The mock ups were submitted to close environment artificially aging according to ASTM D 6819-02 2002 standard (90 °C, 78%RH 1,4,7,14,21 and 28 ageing days). The methodology of research involved technical examination using non-destructive imaging techniques (UVF, multispectral imaging, FORS, colourimetry), microscopic techniques (optical VLM/FLM, UVF USB Microscopy in combination with SEM-EDX) as well the advanced VOC/MS analysis (HS-SPME-GC-MS) applied for the first time to the study of the effect of drying oils in paper except in our own preliminary studies, for the examination and the identification of the materials and the degradation products of the original artworks and the in depth study of extensive multi - parameter series of mock -ups before and after ageing.





Optical microscopy and SEM offered valuable information about the oil - paper system. Oiled mock-ups of the three types of paper, before ageing, present a similar condition: a layer of oil that almost completely covers the paper surface. The oil layer presents a surface profil which responds to the relief of the fibre net or might be attributed to the different adsorption degree of the oil locally, which is connected to the porosity of each paper and relevant surface tension properties.

Upon ageing the phenomena evolve in the same way for all three types of paper. There is a progressive but uniform sinking of the oil film, parts of the surface fibres are progressively more distinguished, holes and recesses appear, revealing the fibres and the fibre net. By the final stage of ageing the bulk of the oil film is still present at a lower level and the presence of holes and recesses is so extended that the oil layer seems to be fragmented.





N.Gysis, "Sewing studio" Oil painting, detail (NGASM). The comparative study of the same area in UV Reflection, UV Fluorescence, False Colour Infrared (FCIR) and Hyperspectral imaging (MuSIS HS) at 600 and 1000nm reveal information (the sketch, the pigments, the morphology) from different depth.

USB Dino light UV fluorescence Microscopy Ta=25°C without oil, ref with oil, ref IF=20mA S 0.8 5 0.6 표 0.4 F · 2 0.2 300 350 400 450 500 550 600 Wavelength λ (nm) 7days ageing 4 days ageing Dino light emission of LED

deteriorated paper fibre, SEM image at 3500x

The creamy oiled montval paper mock ups get an orange-brown hue from the 1st day of ageing and turn gradually darker to a warm brown colour upon the progress of ageing. The colour of the mock ups turn to an intense dark brown colour at the final stages of ageing.

It is likely that linseed oil application is principally responsible for the colour changes during ageing, though oxidation of the cellulose in the paper may also contribute to the colour change, especially if , as we suspect, the oil is enhancing the rate of oxidation of the paper, as indicated in our VOC emission studies.



In transmitted light, the three types of paper (cotton, montval and kraft) allow a limited amount of light to pass through, differing in quantity among the paper types, with kraft paper being significantly less transparent than the others. The oiled mock ups of the three paper types appear to allow gradually less light pass upon ageing, without getting absolutely opaque even at the 28th day of ageing.





Fluorescence of the oiled paper at different stages of ageing clearly demonstrate the oxidation effect of the oil.

Conclusions

Deep understanding of the paper - oil system optical alterations due to the deterioration were established through extensive studying of mock-ups. The catalytic effect that oil medium has on the acceleration of the entire degradation was examined and recorded in various ways. The research has shown that the presence of dried oil films accelerates the oxidative degradation of artists' paper including both cotton, and therefore rag paper and also wood based artists' papers. We can conclude that since drying oil clearly accelerates the destructive oxidation of the paper in the mock ups that it is having the same effect in the works of art in the collection studied. The associated loss of mechanical strength and deterioration of optical properties such as colour will also be accelerated in these works. A methodology based on non-destructive analysis was also established that enables the conservation scientists to have a better insight in the deterioration of the originals.

These findings will provide sound data on which informed decisions can be made regarding the conservation treatments for these works and that therefore this research will have an impact on the lifetime of these works making them available for public viewing for an extended period.

The presence of drying oil in paper greatly accelerates the emission of volatile cellulose degradation products both for cotton based and wood based papers. In the cotton paper it has greatly accelerated the emission of furfural, 2-ethyl furan, 5- methyl, 5- ethyl furfural and 5-pentylfuranone during ageing, while in the wood based papers has greatly accelerated the emission of furfural, 5-methyl furfural, 5- ethyl furfural and 5-pentylfuranone.

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