The use of X-ray micro- and nanoprobes to understand the natural degradation of semi-conductor materials used as artists' pigments

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Semiconductor materials such as HgS (vermillion red), CdS (cadmium yellow), As_2S_3/As_4S_4 (orpiment/realgar) and Pb_3O_4 (minium or red lead) as well as colored materials showing similar properties (such as $PbCr_{1-x}S_xO_4$, chrome yellow) have been frequently used as artists' pigments in several historical periods. Depending on the physicochemical conditions of conservation, these materials can be subject to natural degradation reactions which may lead to noticeable changes in color and/or mechanical integrity of the paint layers or paintings in which the pigments were used. In general, both physical and chemical agents can be identified as the cause of such unwanted transformations; usually (but not always) the simultaneous presence of several risk factors is required to allow these reactions to proceed at a noticeable pace. Light of different wavelengths and cyclic variations in relative humidity are among the most important physical agents contributing to paint degradation. In the category 'chemical agents', next to the components of the paint itself (binding medium, filler materials, other admixture pigments), also external chemicals can be identified as being the cause of alteration reactions. Sometimes these are very innocuous in nature such as NaCl (or related) particulates deposited on the painting surface or atmospheric CO_2. In several specific cases, we have observed that the degradation reactions not only involve a single-step chemical transformation, but may be comprised of (a) an initial photo-induced redox reaction followed by (b) some form of transportation or diffusion process of the initial secondary reaction products from the depth of the artifact towards the surface, which may optionally be followed by (c) other redox and/or precipitation reactions. Thus, pigment alteration frequently gives rise to strongly heterogeneous, layered materials of which the interlinked phases must be separately characterized on the micro- and nanoscale to allow for a better understanding of the sequence of reactions constituting a complete alteration pathway.

In this contribution, an overview of such recently investigated, spontaneously occurring transformations will be given, with emphasis on how synchrotron X-ray micro- and nanoprobe (and related) methods can be exploited to extract information from a limited number of paint micro samples. As specific cases, the degradation of HgS, CdS, Pb_3O_4 and $PbCr_{1-x}S_xO_4$ in works by Rubens and Van Gogh will be discussed [1,2,3]. Next to micro- and nano-analytical methods we have also found it very useful to employ electrochemical methods to monitor the redox transformations of simplified semi-conductor pigment/paint samples under various well controlled physico-chemical conditions [4]. Such information also facilitates the use of theoretical prediction models for the reactivity of (pairs of) photo-sensitive semi-conductor materials.

A final aspect to which attention will be given is the fact that the insights related to chemical alterations, usually obtained from a small number of paint micro samples of a given artefact, of which the representativeness may vary, can be put in the larger context of the entire work of art by combining results from micro- and nanoscopic (X-ray based) analyses with macroscopic (X-ray based) imaging information.

References

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