Scientific analysis of historical paint and the implications for art history and art conservation. The case studies of naples yellow and discoloured smalt.
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This thesis describes a research project in the field of technical art history. Subjects of this study are the production history of Naples Yellow and the discoloration of smalt. Naples Yellow, or lead antimonate yellow, is the most important synthetic yellow pigment in the history of the visual arts. The usage of lead antimonate covers a period of more than 3500 years, the first application of the pigment dating back to the 18th Egyptian dynasty (ca. 1500 BC). The production history of the pigment, notably over the past few centuries, is rather diverse and not well understood. This research project focussed on the European history of the pigment from the 16th to 19th century. The aim of this study was to describe different manufacturing methods and, subsequently, different forms of lead antimonate used at different periods over time. Secondly, the discoloration phenomenon of the blue painting pigment smalt was studied. Based on a number of analytical techniques a digital reconstruction was made showing the approximate original appearance of a smalt-discoloured painting.

Unraveling the history of the manufacture of Naples Yellow requires a close comparative research studying textual sources as well as scientific analysis of authentic pigment material. After interpretation of historical production literature, reconstructions of the pigments are made according to the descriptions in these sources. Subsequently, these reconstructions are studied using various analytical techniques. Both paths of research, scholarly interpretation of sources and scientific analysis of art objects, as well as some peculiarities of such interdisciplinary research are discussed in chapter 1.

During the Middle Ages the application of lead antimonate yellow seems to have been limited to the Eastern Mediterranean. In the early 16th century the use of the pigment is then suddenly taken over by Italian ceramic artists. The circumstances under which lead antimonate suddenly popped up in Italian Renaissance are investigated in chapter 2. Two contemporary Italian manuscripts are discussed in which the synthesis of lead antimonate yellow is described under the nomenclature of Potters’ Yellow. Reconstructions according to these pigment recipes show that at least three, possibly four different types of lead antimonate can be produced. Some of these types, notably lead tin antimonate, have been found in earlier studies. No evidence was found for a locally limited use of this type of Naples Yellow, as has been suggested in earlier studies. These findings should therefore be of interest to authenticity studies. Documentary and analytical evidence indicates that the knowledge on lead antimonate yellows originates from Middle East ceramical and glass industries. It is argued that the know-how on the production of lead antimonate yellows has been transferred through the migration of glass artists from the Eastern Mediterranean to Venice during the 15th century.
Chapter 3 deals with the introduction of lead antimonate yellow in Northern European painter studio’s after 1700. North European painters, however, hardly applied Naples Yellow before 1700. Instead, the traditional yellow pigment lead-tin yellow remained highly popular until about 1730, when it was replaced gradually by Naples Yellow. When the pigment was first imported from Italy, the origin of Naples Yellow remained a mystery to North European artists and craftsmen. Only during the second half of the 18th century Germans, Frenchmen and Dutchmen seemed to have learned to produce lead antimonate themselves. This development is discussed from technical, economical and art historical points of view. In addition, a contemporary Northern European manual is examined and pigments are reconstructed according to the descriptions given by the manual. The results show interesting characteristics of 18th century lead antimonates that clearly differ from earlier Italian types, which could be helpful in art historical authenticity questions.

Various original samples of 19th century lead antimonate yellow have been preserved in several historical pigment collections, such as the Hafkenscheidt collection at the Teylers Museum (Haarlem, Holland) and the Turner pigment collection at the Tate Gallery (London, UK). In chapter 4 pigment samples are subjected to extensive analysis, including synchrotron- as well as laboratory-based X-ray powder diffraction and single crystal electron diffraction. Again, chemical characteristics of these samples are discussed in the context of 19th century textual sources on lead antimonate yellow. In addition, a new phase of lead antimonate (Pb$_2$SbO$_x$, 4.5$\leq$x$\leq$6.5) has been discovered.

While the earlier chapters deal with chronological characteristics of lead antimonate production, chapter 5 is aimed at locating the geographical origin of the pigment. Lead isotope analysis (LIA) is used to determine the exact isotopic ratio of naturally occurring lead in lead-bearing material. Given the exact knowledge of isotopic characteristics of ores, it is in principal possible to deduce the ore source of the lead. LIA was performed on a few 18th and early 19th century samples of lead antimonate yellow. Samples were taken from historical pigment collections as well as a painting of known date and origin. The results show that the method can be applied successfully to the study of paint samples.

Chapter 6 discusses the digital colour reconstruction of a 17th century Dutch painting containing discoloured smalt. Smalt is one of the most common 17th century blue painting pigments. Smalt consists of cobalt-coloured potassium-enriched glass, that is ground to a fine, intensely blue powder. Being at the time a relatively cheap pigment, smalt was used as a substitute for other, more costly pigments roughly between the 15th and 17th centuries. As main disadvantage, however, smalt has shown to discolour over the years. The paintings of the Dutch painter Hendrick Ter Brugghen show severe signs of smalt discolouration. A dramatic example of such degradation can be seen in his painting St Luke. Employing a variety of analytical techniques, this chapter presents the digital reconstruction of the approximate original appearance of a painting suffering from severe small discolouration. The chapter also discusses the pictorial and art historical implications of paint discolouration.