

Early synthetic organic lake pigments used by Vincent van Gogh at the end of his lifetime

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Abstract

Introduction

Throughout the centuries natural dyes from vegetable and animal sources were used for textile dyeing and as painting materials. This changed in the second half of the 19th century, due to the introduction of synthetic organic dyestuffs. The lecture will focus on two famous synthetic dye groups: the tri-aryl methanes and the hydroxy-phthaleins. The history, the chemical constitution, the production and the analysis of these dye groups will be shown. In addition, the use as artists' pigments of these dye classes in the last period of Vincent van Gogh's oeuvre will be presented.

History

Just months after the discovery of mauve (1856) another more important synthetic dye, namely fuchsine, was invented. The tri-aryl methane group was extended by methyl violet in 1861. After a successful technical dimethylaniline process large quantities of dimethylaniline were used in the production of methyl violet in 1866.

The first dye of the hydroxy-phthalein group was fluorescein (1871) and was used as a starting material for the development of other dyes of this class. By full bromination of fluorescein, the red dye eosin was obtained in 1873. The related Phloxines are obtained by bromination of di-chloro-fluorescein, respectively tetra-chloro-fluorescein.

In 1875 erythrosine G was made by the iodination of fluorescein to di-iodo-fluorescein. Full iodination of fluorescein in 1876 yielded erythrosine B, tetra-iodo-fluorescein. Two dyes related to erythrosine are the important Rose Bengals, prepared by complete iodination of di-chloro-fluorescein, respectively tetra-chloro-fluorescein.

Analysis

The tri-aryl methanes and the hydroxy-phthaleins are analysed with HPLC-PDA, using a gradient of water, methanol and phosphoric acid, the same system used for the analysis of natural dyes. Since the hydroxy-phthaleins are fluorescents, they can also be detected by fluorescence, improving the detection limit of at least a factor 100.

Properties

The dyes of the hydroxy-phthaleins can be used as artists' pigments by the precipitation on co-ordination metals. With aluminium salts and lead salts the series yields lakes of extreme brilliance and bright pure tone, ranging from an orange scarlet to bluish-red. The dyes of the hydroxy-phthaleins and the tri-aryl methanes on textiles and the lake pigments generally have a poor light-fastness. Seduced by the brilliance of the new colours, artists used them, but with disastrous results. This resulted in the

use of the non-complimentary terms 'coal-tar' and/or 'aniline' colours. At the end of the 19th and early 20th century writers warn the artists against using synthetic dyes. Even in the 1930s the lakes of the hydroxy-phthaleins and tri-aryl methanes should be forbidden in works of art that aspire to permanence.

Vincent van Gogh paintings

Technical examination of Van Gogh paintings has given a good insight into the red lakes he used. During his stay in Paris, 1886 till 1888, he mainly painted with a variety of natural organic dyes, such as: purpurin (probably Kopp's purpurin), redwood and cochineal.

Interestingly, in *Glass with Roses* (summer 1886, Paris) and in *Seascape at Saintes-Maries* (June 1888, Arles), methyl violet was identified.

In his southern-French period (1888-1890) he came in contact with another synthetic organic dye. In eight letters written in Arles, Saint-Rémy and Auvers-sur-Oise to his brother Theo, Vincent asked him to send laque géranium. In total, 44 paint tubes of this pigment from the artist's paint factory Tasset et L'Hôte in Paris has been mentioned. Laque géranium has been analysed by the ICN in twelve Van Gogh paintings (April 1888-July 1890). SEM-EDX demonstrated that the red paint contains the element bromine. The element chlorine was not detected, excluding the possible presence of Phloxines. HPLC-PDA and fluorescence analysis finally identified the 'laque géranium' as eosin lake.

In the eosin paint of *The Pietà* (September 1889, Saint-Rémy) and *Wheat Field under Clouded Sky* (July 1890, Auvers-sur-Oise), some red pigment particles contain the element iodine, showing that eosin was mixed with erythrosine.

A lead-containing eosin lake was used in *Two White Butterflies* (spring 1889, Arles). In the red transparent paint layer the element lead was identified by SEM-EDX. In the *Blossoming Pear Tree*, *View of Arles with Irises in the Foreground*, *The Pietà* (after Delacroix), *Enclosed Field with Ploughman*, *Wheat Field under Clouded Sky* and *Tree Roots and Trunks* (April 1888- July 1890, Arles, Saint-Rémy and Auvers-sur-Oise), an aluminium-containing eosin lake was used.

Conclusion

In his Paris period Van Gogh came in contact with methyl violet. Discovered in 1861 and put on the market in 1866 twenty years later methyl violet was used as an artist's pigment. Van Gogh painted between 1888 till his death in 1890 with lead and aluminium-containing eosin lake pigments. Fifteen years after the discovery of eosin it was used as an artist's paint. In two paintings made in Saint-Rémy and Auvers-sur-Oise the eosin was mixed with erythrosine.

Van Gogh was aware that the new colours could fade. In April 1888 he writes to his brother that he wants to overcome the problem of fading by applying excessively pronounced colours. It is clear that he was not successful in preventing the fading by this technique. Nowadays one can see this phenomenon on several of his paintings.

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