IDENTIFICATION AND CLASSIFICATION OF SYNTHETIC ORGANIC PIGMENTS OF A COLLECTION OF THE 19TH AND 20TH CENTURY BY FTIR

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Abstract

This study presents an on-going project concerning the identification and classification of the synthetic organic pigments, which could be selected from the material collection of the Institute of Sciences and Technologies in Art at the Academy of Fine Arts in Vienna. The collection includes a large number of various pigments, dyes and binders. The results concerning the inorganic pigments are presented in an additional paper [1]. Data of more than 600 specimens of the early industrial period as well as the 2nd part of the 20th century were catalogued in a Microsoft ACCESS®-database. Extended research of source literature and the Colour Index [2] led to a first classification of dyes and pigments. Selected samples could be analyzed by means of energy dispersive x-ray fluorescence analysis (XRF) yielding the main elements with an atomic number higher than 11 (Na). Mainly extenders, fillers or substrates present could be characterized, which was helpful for the interpretation of the results obtained by FTIR.

Introduction

Despite the fact of increase in the use of modern pigments since their introduction early in the 20th century minority of those had been investigated on artefacts. Detailed data of use of these materials and FTIR spectra, which could be obtained by classifying and analysing the synthetic organic pigments of the collection, might be a helpful tool concerning future approach of analytical challenges. As a first step in this direction the organic synthetic materials of the pigment collection of the Academy of Fine Arts in Vienna have been catalogued by using the Microsoft database software package ACCESS®. The commercial names of the samples and, as far as possible, also their colour index names (CI) [2], chemical classification and manufacturer are taken into account as well as the relevant literature. Additionally, small amounts of the specimens were analyzed by x-ray fluorescence analysis (XRF) in order to determine the main and trace elements from Na – Pb. The main interest has been to built up a database with the FTIR spectra of all the samples in the material collection.

Experimental

The FTIR measurements could be carried out with a Perkin Elmer instrument Spectrum 2000 with an attached microscope (Perkin Elmer, i-series). Small samples on a diamond cell were prepared therefore and analyzed in the transmission mode. Due to the MCT-detector available a spectral range from 4000-580 cm⁻¹ could be registered.
Results and Discussion
In the studies carried out so far pure synthetic organic materials as well as pigments with substrates and containing also fillers or extenders have been investigated. Due to the great number of samples available only a few pigments are presented here as examples.

Synthetic organic pigments – pure materials
In Table 1 three pigments of our collection are summarized including their commercial names, chemical classification, colour index, institute-inventory-number as well as the elements, which could be detected by means of XRF:
FANALGELB (PY18, 49005) was introduced in 1924 and preliminary used in printing colours of the 20ies and 30ies of the 20th century.
PARAROT (PR1, 12070) was the first organic red pigment synthesized in 1885 and was manufactured for the first time in 1889 [4]. Formerly widely used, many manufacturers have stopped production [5] and nowadays PR1 is still in use for industrial printings only [7].
Although the reference spectra of both pigments were not available, FANALGELB and PARAROT could be classified as PY18 (Fanalgelb) and PR1 (Pararot) by using the Colour Index [2].
In contrast to the pigments mentioned above, ROTEXTRAKT/SIEGLE is not listed in the Colour Index [2] and could be identified as Pigment Violet 1 (PV1, 45170) by comparing the data of the Tate Organic Pigment Archive [3]. Pigment Violet 1 is described as a basic dye-based pigment of the PTMA type (also named Triarylcarbonium PTMA), which is prepared by complexing a basic dye molecule with a complex inorganic acid such as phosphotungstomolybdic acid (PTMA) [6]. First introduced in 1924 by I.G. Farben (Germany), PV1 was employed for printing colours, paints etc. Recently PV1 was found in a catalogue for artists’ paints formulations of Winsor & Newton/ Designers Gouache (W&N International Catalogue, 2003).
As can be seen in Figure 1, the pigment ROTEXTRAKT/SIEGLE (PV1), Inv. No. 938 of our collection, yields the same spectrum as the Fast Red Toner (PV1) of the Tate Organic Pigment Archive [3].

<table>
<thead>
<tr>
<th>Institute Inv. No.</th>
<th>Commercial Name</th>
<th>Chemical Classification</th>
<th>Colour Index Name</th>
<th>Historical notes and aspects of use</th>
<th>XRF</th>
</tr>
</thead>
<tbody>
<tr>
<td>951</td>
<td>Fanalgelb</td>
<td>Triarylcarbonium (PTMA/ phosphotungstomolybdic acid); lake of Thioflavine</td>
<td>Pigment Yellow 18 [PY 18, 49005]</td>
<td>Introduced 1924 (I.G. Farben, Germany); used in printing colours in 1920ies and 30ies, only minimal importance nowadays</td>
<td>W, Mo</td>
</tr>
<tr>
<td>759</td>
<td>Pararot</td>
<td>β-naphtol</td>
<td>Pigment Red 1 [PR 1, 12070]</td>
<td>Introduced 1895; widely used for paints; still in use preliminary for industrial printing</td>
<td>-</td>
</tr>
<tr>
<td>938</td>
<td>Rotextrakt, Siegle</td>
<td>Triarylcarbonium (PTMA/ phosphotungstomolybdic acid); derived from Rhodamine B</td>
<td>Pigment Violet 1 [PV 1, 45170]</td>
<td>Introduced 1924, I.G. Farben (Germany); printing colours etc., recently: used in artists paints formulations as W&amp;N/ Designers Gouache (W&amp;N International Catalogue, 2003)</td>
<td>W, Mo</td>
</tr>
<tr>
<td></td>
<td>Fast Red Toner, HY Pigments</td>
<td>Triarylcarbonium (PTMA/ phosphotungstomolybdic acid); derived from Rhodamine B</td>
<td>Pigment Violet 1, Tate [3]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1: Synthetic organic pigments - pure materials
Figure 1: FTIR spectra (4000-580 cm⁻¹) of pure pigments

**Synthetic organic pigments containing substrates/ fillers/ extenders**

As can be seen in Table 2, the sample Inv. No. 896, ECHT SCHARLACHROT G of the company Siegle contains barium and sulphur. Siegle & Co. was a subsidiary company of BASF and sold pigments for artists’ as well as decorative paints until they merged with BASF in 1970. As Siegle merely processed and marketed pure industrial products manufactured by other companies like BASF, their products were not listed in the Colour Index.

Figure 2 shows the results obtained by FTIR, where the spectra of the white pigment blanc fixe in our collection (Inv. No. 81) and of the Inv. No. 250 (β-naphtol, PR3) were used as reference materials. For comparison also the spectrum of Hansa Scarlet RNC (PR3) of the Tate Organic Pigment Archive [3] is depicted. The spectrum of ECHT SCHARLACHROT G of Siegle can be identified as a mixture of BaSO₄ and a β-naphtol pigment (PR3). As an example of this naphtol pigment LITHOLECHTSCHARLACH RN (Inv. No. 250) is considered in Figure 2.

Additionally, the spectrum of the red material is widely identical with the spectrum of Hansa Scarlet RNC [3], which was identified as β-naphtol (PR3).
Table 2: Synthetic organic pigments – containing substrates/fillers/extenders

<table>
<thead>
<tr>
<th>Institute Inv. No.</th>
<th>Commercial Name</th>
<th>Chemical Classification</th>
<th>Colour Index Name</th>
<th>Historical notes and aspects of use</th>
<th>XRF</th>
</tr>
</thead>
<tbody>
<tr>
<td>81</td>
<td>Schwerspat</td>
<td>BaSO₄</td>
<td>Reference: blanc fixe (Schwerspat)</td>
<td>Known since ancient periods</td>
<td>Ba, S</td>
</tr>
<tr>
<td>896</td>
<td><strong>Echt Scharlachrot G, Siegle</strong></td>
<td><strong>β-naphtol + BaSO₄</strong></td>
<td><strong>Pigment Red 3 [PR 3, 12120] + blanc fixe</strong></td>
<td>Toluidine Red PR 3: introduced 1905, still used in printing colours, paints etc.</td>
<td>Ba, S</td>
</tr>
<tr>
<td>250</td>
<td>Litholecht-scharlach RN</td>
<td>β-naphtol</td>
<td>Reference: PR 3</td>
<td>PR 3, see above</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>Hansa Scarlet RNC, Clariant</td>
<td>β-naphtol</td>
<td>Reference: PR 3, Tate [3]</td>
<td>PR 3, see above</td>
<td></td>
</tr>
</tbody>
</table>

Figure 2: FTIR spectra (4000-580 cm⁻¹) of Echt Scharlachrot G/ Siegle (Inv. No. 896) as well as the reference of the materials blanc fixe (Inv. No. 81), Litholechtscharlach RN (PR3, Inv. No. 250) and Hansa Scarlet RNC (PR3, reference Tate [3])

Conclusion/Perspectives
A few FTIR spectra were obtained for the selected synthetic organic pigments of the collection. The spectra were compared with the data of the IRUG-database [8] and the Tate Organic Pigment Archive [3].
Future research will focus on further investigations of paint manufacturers’ colour charts (Siegle & Co., Winsor & Newton, Talens etc.) to obtain data with regards to the application of synthetic organic pigments in the first half of the 20th cent. paints.
References


