Molecular studies of Asphalt, Mummy and Kassel earth pigments: their characterisation, identification and effect on the drying of traditional oil paint

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Summary

The organic black and brown pigments, asphalt, mummy and Kassel earth, are often used or claimed to have been used by painters in the 19th century. In particular paintings from the 19th century show paint defects that can be associated with these pigments. Examples of poor drying of the oil are observed as formation of premature cracks and phenomena, such as migration or sinking-in of layers. These phenomena are already reported in the contemporary literature, but they are also reported nowadays by conservators and restorers investigating 19th-century paintings. With all the indications about the negative influence of asphalt, Kassel earth and mummy pigments on the condition and aesthetic quality of the paintings, surprisingly little or no molecular evidence is so far available. What exactly are these pigments? Is it possible to identify them in painting samples? Are they the reason why the oil binding media dries so poorly? These are questions addressed in this dissertation. An introduction to the asphalt, mummy and Kassel earth pigments and the conservation problems related to the use of these pigments as well as the aims of this dissertation are discussed in Chapter 1.

With such considerations in mind, the primary goal of this thesis is to characterise 19th-century asphalt, mummy and Kassel earth pigments at a molecular level. The chemical composition of these pigments was investigated and compared to relevant pigment reference samples (Chapter 2, 3 and 4). Once the nature and composition of the 19th-century pigments was established, the next challenge was to try and identify them in original 19th-century paint samples. Because of the inconclusive and puzzling data resulting from this approach, the focus of the investigation was shifted from the identification of the pigments in the oil paint samples to the effect of the pigments on the composition of the oil binding medium. This study was limited to research on the effect of asphalt and to some extent Kassel earth on the chemical drying of traditional oil paint. Molecular changes that occur in reference pigments and in the oil binding medium itself during ageing of pigment-oil model systems (paints and solutions) are reported in the last chapter of the thesis and in annexes to that chapter. An attempt to identify the cause of poor drying of the oil in selected 19th-century paint samples is made in the same chapter.

The identification and characterisation of the 19th-century asphalt pigment (from the Hafkenscheid collection, in the Teylers Museum, Haarlem, The Netherlands) is presented in Chapter 2. The analytical work was in the first instance performed with Direct Temperature resolved Mass Spectrometry (DTMS). DTMS tandem MS (DTMS/MS) was to used to confirm the structure of some of the compounds present in the 19th-century sample. Then Pyrolysis Gas Chromatography Mass Spectrometry (Py-GC/MS) was applied to determine the distribution of molecular markers and so-called biomarkers. The results were used to develop an
analytical protocol for the identification of asphalt in paint samples. Furthermore the
analysis of $^{13}$C/$^{12}$C isotopic ratio was carried out to investigate the possible Dead Sea
provenance of the 19th-century asphalt sample. These data together demonstrate that
the 19th-century asphalt pigment from the Hafkenscheid collection is indeed a natural
asphalt of a Middle Eastern provenance. Moreover a rather good similarity to Dead
Sea asphalt is suggested.

The results of investigation of the 19th-century mummy pigment (from the
same Hafkenscheid collection) by mass spectrometric techniques are reported in
Chapter 3. First DTMS revealed a complex bulk composition that consists of oil
and/or fat constituents, medium aged mastic resin and beeswax. In addition to DTMS,
various GC/MS techniques were applied for the characterisation and identification of
molecular markers in the 19th-century mummy sample. For example Py-GC/MS was
effectively used to search for the presence of asphalt in the sample. The fatty acids of
the mummy pigment sample were investigated by an on-line transesterification
method (Py-TMAH-GC/MS). The results pointed to bacterial, fungal and/or human
origins of the fat component. Additionally the same technique revealed the presence
of a rather fresh (unaged) pine resin in the sample. Then on-column GC/MS was
applied for a better characterisation of the triterpenoid resin fraction and the results
demonstrated the presence of resin of mastic in the sample. The combination oil and
mastic resin point to the use of a megilp medium as a means to bind the pigment
mummy pigment powder. The presence of degraded asphalt, beeswax and possibly
human fat does not exclude the use of a real mummy parts as constituents of the
preparation of the 19th-century Hafkenscheid mummy pigment.

Chapter 4 presents the DTMS and GC/MS investigation of a series of Kassel
earth, Cologne earth and Vandyke brown pigments from the 18th- and 19th-century
(Vigani, Winsor & Newton and Hafkenscheid collections) as well as reference
pigments\(^1\). Compounds representative for fossil lignin from wood and for lipids and
custin from leaf remains were found, indicating that the pigment samples have a
composition reminiscent of the composition of lignite or brown coal formed from
tropical forests. Then multivariate analysis techniques using Principal Component
Analysis (PCA) applied to the DTMS data, classified the samples in two main groups:
samples with a relatively high abundance of fossil wood components and samples
with a high abundance of fossil leaf compounds. Moreover DTMS/MS confirmed the
structure of the montan waxes originating from the leaf surface wax layers. Next,
solvent extraction techniques were applied and revealed that fossil wood components
are more likely bound to the polymeric network of the samples, while the fossil leaf
components are weakly bound and mostly removable by solvents. The lipid and lignin
derived fractions in the Kassel earth, Cologne earth and Vandyke brown pigments
were further characterised by Py-TMAH-GC/MS. Therefore fatty acid and alcohol
moieties of the montan waxes were identified. Indications for the contribution of
lipids (from microorganisms involved in the degradation of wood) and evidence for
the type of wood that contributed to the lignite/brown coal deposits were also
obtained. Py-GC/MS studies gave information about the presence of plant resins and
bacterial biomarkers. As a result a protocol for the identification of Kassel earth,
Cologne earth and Vandyke brown pigments was derived. It is proposed to attribute a

\(^1\) including the Kassel earth pigments described in the *Artists' Pigments, A Handbook of Their History
and Characteristics*, vol. 3 in 1997 by Feller and Feller.
higher abundance in fossil leaf material to Kassel and Cologne earth type of pigments and a higher abundance in fossil wood material to the Vandyke brown type of pigments.

From a microanalytical point of view, DTMS was proved a valuable tool that allows the discrimination between asphalt, mummy, Kassel earth, Cologne earth and Vandyke brown pigments. The GC/MS techniques, on the other hand, reveal common and specific marker molecules, including the biomarkers, in these pigments, which should make the recognition of such materials much easier in the future. The less specific markers can give only indications for the presence of one of these pigments, but the presence of biomarkers is required for confirmation.

Chapter 5 focuses on the poor drying of oil paint with asphalt and Kassel earth pigment investigating the fate of pigment biomarkers, the influence of the pigment on the drying of oil and case studies of 19th-century paint samples. As a start, the protocols for identification of these pigments were tested on natural or artificially light aged reference pigments and paint model systems. The ageing techniques presented in this thesis created a link between the initial material, (pretreated) pigment and freshly prepared pigmented oil paint, and the aged pigmented paint as "final" product. Paint samples of known composition and ageing history were used for research and provided valuable information on the fate of marker molecules in paint. Therefore asphalt and Kassel earth oil paints prepared by H.C. von Imhoff and naturally aged at the Canadian Conservation Institute in Ottawa, and the 19th-century asphalt-linseed oil paint reconstructions made by R. Bottelle for the MOLART project and aged at the artificial light-ageing facility of the Limburg Conservation Studios (SRAL) gave a good insight into the influence of pigment preparation and ageing on the chemical drying of oil. Asphalt specific markers were traced in the pretreated pigments and in the oil paints with the various available MS techniques (DTMS, Py-GC/MS, on-column GC/MS, Py-TMAH-GC/MS). It was shown that the presence and abundance of these compounds is directly related to the pretreatment of the pigment, for example roasting, heating or solvent extraction and also to the preparation method of the oil paint. Thus, the analysis of the natural and light aged paint samples shows that even though some markers are lost or diminished in abundance, some of the asphalt biomarkers are preserved! A similar approach is described in the Annex A of Chapter 5 for a naturally aged, Kassel earth containing oil paint. This also shows that the (bio)markers of the pigment can be retrieved from the oil paint. So a number of these pigment-specific molecules or biomarkers remains identifiable in oil paint made with asphalt or Kassel earth pigment although there is a strong dilution in the paint preparation process, which will make it difficult to retrieve all those markers in original paint samples.

Simpler pigment-oil model systems prepared with asphalt and linseed oil in dichloromethane (DCM) and exposed to light, provide a more detailed chemical insight into the processes of oxidation and cross-linking that play a role in the drying of asphalt-oil paint. First, the changes in linseed oil and asphalt-linseed oil DCM solutions were traced with DTMS. Next, the discriminant analysis was applied to the DTMS data of the model asphalt-linseed oil and linseed oil solutions and revealed a different composition of the oxidising oil in the presence of asphalt. This was translated as a lower speed of drying of the oil. Additionally results of Fourier Transform Infrared Spectroscopy (FTIR) applied to an asphalt-oil mixture in comparison to oil alone supported the supposition that asphalt retards the drying of the oil. Drying of oil is known to involve oxidation and cross-linking reactions of the unsaturated triglycerides (TAGs) in oil. These mechanisms were proven with
Electrospray-Fourier Transform-Ion Cyclotron Resonance MS (ESI-FTICR-MS) and High Performance Size Exclusion Chromatography (HPSEC) techniques. On the molecular level, the technique of ESI-FTICR-MS showed that less oxygen was incorporated in the aged TAGs of the linseed oil in the presence of asphalt, which points to a different mechanism of the oxidation of the oil compared to linseed oil alone. HPSEC data of linseed oil DCM solutions (no asphalt) show a very limited formation of high molecular weight material. The presence of asphalt in an oil DCM solution increases the molecular weight of the asphalt fraction. In combination with DTMS results, this was interpreted as an indication that oil and asphalt components form a network macromolecule as a result of cross-linking reactions between the asphalt and TAGs. The oxidation and cross-linking reactions also influence the fatty acid and dicarboxylic acid distributions. The changing ratio between azelaic acid and stearic acid and the ratio between oleic (+ elaidic) acid and stearic acids were determined by GC/MS. They have been identified to be a measure for the condition of the chemical drying of the oil. Paint made with natural asphalt has still a comparatively high abundance of remaining oleic and elaidic acid and a relatively low abundance of azelaic acid as compared to the non-reactive stearic acid after 25 years of exposure. The preparation methods of asphalt pigments and asphalt paint according to 19th-century recipes change the antioxidising power of the asphalt, which can be deduced from the ratios of fatty acids and dicarboxylic acids. Unexpectedly, the same ratios determined for oil paint made with Kassel earth pigment demonstrated that Kassel earth apparently does not affect the chemical drying of oil paint. It is, therefore, possible to trace compounds specific to asphalt or Kassel earth in rather fresh oil paints as well as to get information about the drying of the oil paint using ratios of the fatty components. This points to a direct chemical correlation between the presence of the organic black and brown asphalt and Kassel earth pigments and the composition of the drying oil.

Detailed results similar to those acquired from the model systems could not be obtained from the original 19th-century paint samples. DTMS showed that the composition of painting samples is in reality more complex than the composition of asphalt oil paint model samples prepared according to 19th-century recipes. This is an indication that the painting technique itself plays an important role in determining the composition of the oil paint on the painting, too. Py-CG/MS and Py-TMAH-GC/MS indicate that in some samples the oil has dried better under the influence of driers, resins and possibly Kassel earth pigments, while in other samples the chemical drying of oil seems retarded due to the presence of vermilion, and components such as beeswax and paraffin waxes and/or possibly degraded asphalt. Nevertheless not enough evidence in the form of biomarkers was found for the presence of asphalt or Kassel earth pigments in these samples.

One can learn from these investigations that a study of the paint composition requires a search for specific pigment markers as well as an investigation of the drying state of the oil. These will offer answers to the questions regarding the cause of the poor drying of the oil binding medium in connection to asphalt, Kassel earth or mummy pigments.