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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5. On poorly drying 19th-century oil paints: reference materials, model systems and paintings

Abstract

Poor drying of oil paint observed in the paint of 19th-century paintings is often considered to be caused by the presence of geomaterials like asphalt or Kassel earth pigments. The objective of this chapter is to investigate in what way the pigments of asphalt and Kassel earth influence the drying of oil paint. The asphalt pigment itself, light exposed dichloromethane test solutions of the pigment in linseed oil and various reconstructed paints are investigated and the results are compared with 19th-century paint samples from paintings by Sir J. Reynolds, Th. Rousseau and J. Israels. This chapter is divided into three main sections focusing on (A) the fate of marker compounds in oil paint containing asphalt pigment, (B) the effects of asphalt and Kassel earth on the constituents in oil paint and (C) paint sample from paintings suspected of containing asphaltic materials.

Pretreatments of asphalt pigment are shown to affect the characteristic asphalt markers. Only hopanes and alkyl aromatics are preserved. Apolar solvents extract most of the biomarkers (i.e. the maltenes) from an asphalt sample. Asphalt specific compounds in light aged asphalt-linseed oil dichloromethane (DCM) solutions are rather well preserved. Artificially aged asphalt containing oil paint reconstructions show only the preservation of some hopanes and some alkyl aromatics. A kinetic FTIR study of linseed oil and linseed oil with asphalt shows that when asphalt is present a much longer induction time is necessary before the chemical drying of linseed oil starts. DTMS, Py-TMAH-GC/MS and ESI-FTICR-MS measurements point to a slower drying of the oil in the presence of asphalt in DCM solutions of asphalt and linseed oil compared to DCM linseed oil solutions alone. The chemical drying of the oil is monitored using ratios of C\textsubscript{16:1} and C\textsubscript{18:0} fatty acids, and the azelaic acid and stearic acid. Less oxidation and more cross-linking are observed by ESI-FTICR-MS and HPSEC for the oil triglycerides in the asphalt-oil solution. The data suggest that chemical interactions forming cross links occur between asphalt and linseed oil as a function of the light exposure time, i.e. the light ageing period. The chemical drying of the naturally aged Von Imhoff painted reconstructions (without drier) shows that asphalt retards the drying of linseed oil while Kassel earth does affect the drying. The oil seems to dry much better in the presence of driers and other materials as observed in the artificially aged oil asphalt paints prepared after 19th-century recipes. The 19th-century oil paint samples seem to have a complex composition (diterpenoid and triterpenoids resins, wax, vermilion, lead driers) with indications for lignite and possibly some degraded asphalt. The poor drying of the oil in these paints that follows from the fatty acid ratios determined seems to be more related to the overall paint composition, painting technique and restoration techniques than to the presence of a single culprit like asphalt.
Introduction

Defects in paintings such as darkening of the paint, premature drying cracks, migration or sinking-in of brown-black layers disturb the surface characteristics of paintings and therefore their aesthetic quality. These phenomena have been often observed in 19th-century paintings [1-10]. According to many authors these defects are considered to be caused by the addition of asphalt or asphaltic components to the paint [3-7, 11-16]. Specifically Roelofs in his book, intended to teach artists about oil painting technique, warns painters that asphalt is detrimental to a painting in the long run despite its short-term attractive effect. Further studies into the nature of these asphaltic components and related materials, and their effect on the drying of oil and oil paint are the main rationale for this chapter.

Paint samples from brown-black areas in 19th-century paintings displaying premature cracks and migration of layers were suspected to be asphalt containing oil paints and were investigated in an early stage of this study [7, 17-22]. As asphalt was not found to be an obvious main component in these paint samples, the research spawned a series of studies designed to understand the fate of asphalt derived organic matter in oil paintings. This is a main focus of the chapter. A previous study in chapter 2 describes the specific compounds that characterise asphalt in 19th-century pigment samples of defined origin that contain asphalt. The analytical protocol developed was applied in this chapter to samples from paintings. In this process some marker compounds pointed to lignitic material moving this investigation also into the direction of chemical markers of Kassel earth and Vandyke brown. These markers were discussed in a previous chapter (chapter 4). Effects of Kassel earth on oil paints are reported in this chapter. Whether Kassel earth was used as a substitute for asphalt is not clear [4, 5, 23], but other brown or black pigments certainly have been introduced on the palette of the painters and were used in the 19th century under the name of asphalt as discovered by Carlyle [4, 5]. Carbon black pigments e.g. ivory black and bone black are also mentioned as common substitute or adulterant for asphalt and Kassel earth [4, 5, 23]. Carbon black is not easily detected with the present techniques of analytical organic mass spectrometry however. Their effects on the oil paint itself are easier to detect.

Asphalt can be identified by organic mass spectrometry using pyrolysis gas chromatography mass spectrometry on the basis of the presence of marker compounds such as series of long chain alkanes and alkenes, alkylbenzenes, alkynaphthalenes, alkylbenzothiophenes, alkyl dibenzothiophenes and so-called biomarkers such as 17α, 21β hopanoids and gammacerane, C-ring monoaromatic steroids, 14α/β steranes and triaromatic steroid compounds (see chapter 2 and Scheme 1). In similar way characteristic markers of Kassel earth (Scheme 2) like alkylphenols, alkylmethoxyphenols and specific markers such as vanillic acid, montan wax derived acids and alcohols, and diterpenoids such as phyllocladane were defined as tools to trace this pigment (see chapter 4). Although this approach works fine on pure reference samples, quite a few of these characteristics could not be detected in the analysed samples from the selected 19th-century paintings. Some of the asphalt markers were observed in one sample and some of the Kassel earth in some other samples. (Results are discussed in the appropriate section.)

The rather scarce results obtained after a direct search for markers and biomarkers particularly in the 19th-century brown-black samples suggested that a
closer look at the influence of the pigment on the oil paint matrix pigmented with asphalt or Kassel earth was required.

This is another main focus of the chapter. Recipes for asphalt paint preparation in the 19th century point out that asphalt paint is not made simply mixing asphalt and oil together but requires several preparation steps [4, 5, 24] that might affect its overall chemistry. Similarly, Kassel earth also seems to have undergone pretreatment
Asphaltic oil paints reconstructed according to these recipes were prepared, painted out and artificially light aged in the course of the MOLART project by R. Boitelle [24, 25]. Results from a selection of these samples are reported in this chapter.

This chapter presents results on the VEGA asphalt, representative asphalt rich material donated by Shell quite similar in its properties to the asphalt from the Dead Sea used in the 19th century. Its chemical fate after roasting, exposure to solvents, accelerated ageing as such and in the presence of drying oil, and incorporation into oil paint as well as the chemical effect of the asphalt on the drying of the oil is discussed. This last aspect is investigated also for naturally aged reconstructions prepared with another asphalt material. A similar complete set-up for Kassel earth was not available but some aspects of these different conditions were tested as well and are reported in this chapter. Results from these experiments were used to put the analytical data from the 19th-century paintings into perspective, the concluding aim of this chapter.

**Experimental**

**Samples and sample preparation**

The untreated and roasted VEGA asphalt was analysed. Furthermore it was investigated as a fresh mixture of asphalt and linseed oil (5% asphalt in oil). It was analysed as well as an asphalt-linseed oil mixture in dichloromethane (2:1 weight/weight asphalt: linseed oil, per 1 ml solvent) and also after incorporation into paint according to 19th-century recipes, in both cases before and after artificial light ageing. For the dichloromethane (DCM) solutions samples of asphalt in DCM and linseed oil in the same solvent were prepared and aged in the same way for comparison. Control solutions of the latter solutions were prepared. A naturally aged asphalt containing oil paint, prepared however with another asphalt pigment (analysed by us but not reported here), was also investigated for reasons explained in the results and discussion section.

The untreated Kassel earth pigment used by Von Imhoff to prepare oil paints was analysed as reported in chapter 4. A naturally aged oil paint prepared with the same pigment and from the same series as the above-mentioned asphalt paint sample was investigated in this study. Moreover two other samples of the same series of naturally aged samples, an ivory black oil paint and a lead white oil paint were used for comparison.

Brown-black paint samples from selected 19th-century paintings by Rousseau, Israëls and Reynolds were regarded as appropriate for the current study, i.e. suspected to contain asphalt, because these three painters are said to have used asphalt pigments [7, 17-21, 26-28] while the defects observed on the areas of the paintings where the samples were taken, correspond to the defects associated in the literature with the presence of asphalt [3-7, 11-16]. Details about the symbols used for the samples, their appearance and the methods and materials used for their preparation as well as information on their ageing treatments are given below, in Table 1 (reference samples and oil paint reconstruction samples) and in Table 2 (19th-century oil paint samples).
Table 1. The label, composition and appearance of samples used for the asphalt paint preparation.

Legend: OP stands for oil paint, "c"- control samples (initial time), "a"- aged samples, VI stands for Von Imhoff [35-39].

<table>
<thead>
<tr>
<th>Label, Composition</th>
<th>Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Original material</strong></td>
<td></td>
</tr>
<tr>
<td>A, VEGA asphalt</td>
<td>black, glossy, sticky solid mass</td>
</tr>
<tr>
<td>A&lt;sub&gt;roasted&lt;/sub&gt;, roasted VEGA asphalt</td>
<td>brownish, mat, not sticky</td>
</tr>
<tr>
<td><strong>Roasted asphalt</strong></td>
<td></td>
</tr>
<tr>
<td>A&lt;sub&gt;heptane&lt;/sub&gt; (maltene) of A</td>
<td>colorless solution</td>
</tr>
<tr>
<td>A&lt;sub&gt;heptane residue&lt;/sub&gt; (asphaltenes) of A</td>
<td>dark brown-black residue</td>
</tr>
<tr>
<td><strong>Asphalt oil paint reconstructions</strong></td>
<td></td>
</tr>
<tr>
<td>OP&lt;sub&gt;Ac&lt;/sub&gt;, linseed oil: A, 1:2 (mg/ml DCM)</td>
<td>dark brown solution</td>
</tr>
<tr>
<td>LoAi, linseed oil: A</td>
<td>artificially aged for 1-12 weeks (i= 1-4, 8, 12); dark brown solution</td>
</tr>
<tr>
<td><strong>Asphalt extract and residue</strong></td>
<td></td>
</tr>
<tr>
<td>LoAc, linseed oil: A, 1:2 (mg/ml DCM)</td>
<td></td>
</tr>
<tr>
<td><strong>Asphalt-linseed oil dichloromethane (DCM) test solution</strong></td>
<td></td>
</tr>
<tr>
<td>LoAc, linseed oil: A</td>
<td></td>
</tr>
<tr>
<td>LoAi, linseed oil: A</td>
<td></td>
</tr>
<tr>
<td><strong>Asphalt oil paint reconstructions</strong></td>
<td></td>
</tr>
<tr>
<td>OP&lt;sub&gt;Ac&lt;/sub&gt;, William’s “Antwerp brown” (see below)</td>
<td>tiny particles in yellow-brown medium; elastic (skin like) before ageing</td>
</tr>
<tr>
<td>OP&lt;sub&gt;Ac&lt;/sub&gt;, Merimée’s English method (see below)</td>
<td>dark black, grain structure like before ageing</td>
</tr>
<tr>
<td>OP&lt;sub&gt;Ac&lt;/sub&gt;, Merimée’s other method (see below)</td>
<td>dark black and elastic (skin like) with visible warm brown particles in it before ageing</td>
</tr>
<tr>
<td>OP&lt;sub&gt;Ac&lt;/sub&gt;, William’s “Antwerp brown”; VEGA asphalt boiled to cinder, mixed cold with drying oil (linseed oil and litharge/lead oxide) applied on glass support; lead white linseed oil ground [4, 5, 24]</td>
<td>artificially aged for 3 months, [40, 41] tiny particles in yellow-brown medium; elastic (skin like); after ageing small lumps, semi-transparent and soft, have become visible carrying on top particles of white ground disrupted from the lead white ground</td>
</tr>
<tr>
<td>OP&lt;sub&gt;Ac&lt;/sub&gt;, Merimée’s English method: VEGA asphalt dissolved in oil of turpentine, mixed with mastic varnish (1: 2, mastic resin: gum turpentine) and drying oil (see above); ground and support as above [4, 5, 24]</td>
<td>artificially aged for 3 months, [40, 41] dark black, irregular structure</td>
</tr>
<tr>
<td>OP&lt;sub&gt;Ac&lt;/sub&gt;, Merimée’s other method: VEGA asphalt and shellac added to heated turpentine and drying oil (see above), mixed with beeswax; ground and support as above [4, 5, 24]</td>
<td>artificially aged for 3 months [40, 41] dark black and elastic (rubbery texture) with visible warm brown particles in it; particles of ground have protruded to the surface and there cracked open like a crust of bread [24]</td>
</tr>
</tbody>
</table>
Table 1 continued.

<table>
<thead>
<tr>
<th>Label, Composition</th>
<th>Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-VI, Von Imhoff asphalt paint sample: Düll asphalt, cold pressed linseed oil (standoil); wood support; gypsum-chalk-whiting ground [35-38]</td>
<td>Natural aged for 25 years</td>
</tr>
<tr>
<td>Ke-VI, Von Imhoff Kassel earth paint sample: Mülffellner-Rupf Kasselerbrown, standoil; ground and support as above [35-38]</td>
<td>Natural aged for 27 years</td>
</tr>
<tr>
<td>PbW-VI, Von Imhoff lead white paint sample: Düll lead white, standoil; ground and support as above [35-38]</td>
<td>Natural aged for 25 years</td>
</tr>
<tr>
<td>IvB-VI, Von Imhoff ivory black paint sample: Düll ivory black, standoil; ground and support as above [35-38]</td>
<td>Natural aged for 25 years</td>
</tr>
</tbody>
</table>

Table 2. The label, sample description and condition of the 19th-century paintings from which the samples originate.

<table>
<thead>
<tr>
<th>Sample's label</th>
<th>sample</th>
<th>Description painting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ro1 (286/1b)</td>
<td>brown paint + varnish</td>
<td>Unrelined, not known if cleaned, with severely darkened drying cracks and top layers shrunken into thick islands. <em>Restorer question:</em> What is the composition of the oil paint and the relation with poor drying of the oil? Is this an asphalt / Kassel earth containing paint?</td>
</tr>
<tr>
<td>Ro2 (286/5)</td>
<td>brownish glossy material; dark brown material</td>
<td>Wax-resin relined, cleaned, varnished, showing small drying cracks in the blue and brown areas. <em>Restorer question:</em> What is the composition of the oil paint and the relation with poor drying of the oil? Is this an asphalt / Kassel earth containing paint?</td>
</tr>
<tr>
<td>Ro3 (287/2a)</td>
<td>brown paint + varnish</td>
<td>Glue-lined, partly cleaned, condition of painting variable in different areas. <em>Restorer question:</em> What is the composition of the oil paint and the relation with poor drying of the oil? Is this an asphalt containing paint?</td>
</tr>
<tr>
<td>Re1 (1029/20)</td>
<td>bituminous paint, over red</td>
<td>Showing drying cracks, and severely darkened. <em>Restorer question:</em> What is the composition of the oil paint and the relation with poor drying of the oil? Is this an asphalt containing paint?</td>
</tr>
<tr>
<td>I1 (154/5)</td>
<td>light brown paint</td>
<td></td>
</tr>
<tr>
<td>I2 (154/2)</td>
<td>black paint</td>
<td></td>
</tr>
</tbody>
</table>
VEGA asphalt

For the analysis of the untreated VEGA asphalt a lump of the black sticky solid mass was analysed: sample A. The roasted asphalt, sample A_ro, was prepared by heating the asphalt on a glass slide above a gas torch \((t_{\text{flame}} \approx 400 \, ^\circ\text{C})\). The roasting of the asphalt was intended in order to investigate the difference in composition after exposure to a high temperature. The sensitivity of asphalt to solvents was tested according to the protocol used by Behar et al. for asphalt fractionation [29]. A few mg of VEGA asphalt were introduced in a gas chromatography vial of 2.5 ml and dissolved with a few ml of chloroform. The mixture was stirred using a VORTEX-GENIE mixer model K-550-GE (USA). Heptane was added to the mixture causing the precipitation of asphaltenes. The new mixture was centrifuged for 5 minutes in a CHRIST JOTA-RVC Gefriertrocknungsanlagen, type 100005 (Germany), the extract (maltene fraction) was removed with a Pasteur pipette and the procedure repeated. Heptane was added to the extract, the solution was centrifuged and the extract removed again. The procedure was repeated using the extract till no precipitate was formed, which is three times. The extract (maltene fraction), sample A_m, was concentrated by evaporation of part of the solvent under a stream of nitrogen, then subjected to on-column GC/MS measurement. The asphaltene residue, sample A_s, was dissolved in DCM and subjected afterwards to pyrolysis gas chromatography coupled with mass spectrometry (Py-GC/MS).

For DTMS analysis the VEGA asphalt was ground in DCM and the solution was applied to the Pt/Rh wire of the DTMS probe (see Experimental, DTMS).

Asphalt-oil dichloromethane test solutions

DCM test solutions of pigment and linseed oil are easy to prepare and require only a few weeks of artificial light ageing instead of months as necessary for artificial ageing of painted reconstructions. It was previously shown that such solutions produce similar changes as observed for atmosphere exposed drying of oil paint [30-33]. The rate of oxidation and cross-linking of the linseed oil in solution is much higher than observed for example in painted reconstructions. Natural ageing of painted reconstructions takes many years, and natural ageing of real paintings requires hundreds of years.

Test solutions of linseed oil (Lo), asphalt (A) and linseed oil-asphalt (LoA) in DCM were prepared, stored in glass vials, and artificially light aged for 12 weeks in a home-made light ageing device at FOM-AMOLF, Amsterdam, The Netherlands. Samples notations as reported in this chapter are: Loc, Loi \((i=1-4, 8, 12)\), LoAc, LoAi (idem as for Lo) and A12. The code numbers are equivalent to the number of weeks of artificial ageing. More details on the ratio “pigment: oil: solvent” are given in Table 1. The vials were opened daily to allow interaction of the solutions with atmospheric oxygen. The control samples and the several aged solutions were kept sealed under argon, at -18 \(^\circ\text{C}\). The following conditions were used for ageing of the samples: a halogen lamp (Philips Compact Plusline double ended lamp type 100 T3 Q/CL/CP 230V 100W R7s; 1600lm output, 2900K correlated temperature), radiant incidence 150 mW/m\(^2\) (UV), 3000 lux (VIS), UVA (ultraviolet/visible ratio) 50W/lm, 315 nm wavelength, ca. 30 \(^\circ\text{C}\) [34]. The test solutions were analysed as such by mass spectrometric techniques.
Asphalt and Kassel earth oil paint reconstructions

Fourier Transform Infrared Spectroscopy was used to determine the induction time observed for the drying of linseed oil and mixtures of linseed oil and VEGA asphalt or smalt (a well drying pigment when used in oil paint). A ratio of 5% weight/weight ratio of asphalt, or smalt to oil was used.

Painted test panels considered to be representative of the natural ageing of oil paints were sampled for the current investigations. These test panels had been naturally aged for about 25 years at Canadian Conservation Institute (CCI). H.C. von Imhoff has prepared these oil paints [35-37] using cold-pressed linseed oil (Mühlfellner-Rupf, Zurich, Switzerland) that was allowed to stand in dishes of 4 mm height for 3 weeks. The oil was mixed with the pigment until a workable paint was obtained, after the skin of the oil had been removed. The paints were then applied on sized and primed lime-wood and aged. Samples of four pigmented oil paints, without ground layers, were selected for this study: asphalt, Kassel earth, ivory black and lead white (the last two samples for comparison with the first two). The samples were labelled as follows: A-VI, Ke-VI, lvB-VI and PbW-VI, respectively. The test panel oil paints have undergone natural ageing at CCI: 22 ± 2 °C, RH 45.66 ± 5 %, radiant incidence 7950 mW/m² (UV), 318 lux (VIS), UVA 25 W/lumen for 3500 hrs/year since 1973. The panels were stored in wooden box at CCI from 1973 until 1990. In 1990 the panels were removed from their wooden boxes and hanged vertically on an interior wall of the Analytical Research Laboratory of CCI (1030 Innes Road, Ottawa, Canada) where they are still stored [38, 39].

Artificially aged paint reconstructions containing asphalt were available for this study. René Boitelle set up the painted reconstructions containing VEGA asphalt, as a part of the MOLART subproject “Drying problems in 19th-century paintings and the role of bitumen in the darkening of paint” [24]. After 8-10 months of curing, the reconstructions were artificially aged for 3 months in the ageing device at Stichting Restauratie Atelier Limburg (SRAL), Maastricht, The Netherlands. This time equals approximately 40 years of light conditions in a museum¹ [40-42]. The asphalt containing oil paints were prepared after three recipes from the 19th century. These are William’s “Antwerp brown” recipe, Merimée’s English method and Merimée’s other method [4, 5, 24]. The samples were labelled as OP₁, OP₂ and OP₃, respectively. More details about preparation of the oil paints are given in Table 1. The reconstructions were artificially aged at a temperature of max 29 °C, 27.5 % relative humidity, 10000 lux (VIS), at a wavelength of the light of 350-850 nm. More details about the ageing device at SRAL are given elsewhere [40, 41].

In the current research only the brown layer of all the oil paint reconstruction samples was analysed by mass spectrometry. Separation of layers of the oil paints was done under the microscope on a glass slide using a scalpel and a needle, cleaned before with ethanol. Suspensions of the samples in ethanol (EtOH) were analysed by DTMS and Py-GC/MS. Samples were ground in the TMAH transesterification agent instead of solvent for Py-TMAH-GC/MS. More details are available further in the Experimental’s Analytical techniques section.

¹ 200 lux for 7hrs/day is considered the average light intensity in a museum. At SRAL the samples are exposed to 10⁴ lux for 24 hrs/day; 92 days of exposure at SRAL imply 24/7 x 92 days of exposure x 10⁴/200 = 15771 days of 200 lux/day for 7 hrs= 43.2 years.
19th-century oil paint samples

Samples from 19th-century paintings with defects that would match the description of paints prepared with asphalt pigment were investigated for this study. These samples originate from areas of the paintings that have darkened and show drying cracks specific to a poor drying of the oil. The samples had a dark brown-blackish appearance (see Table 2) and were provided by several people. Joyce Townsend (Tate Gallery, London) provided a sample from a darkened painting by Sir Joshua Reynolds supposedly containing asphalt. The painting represents the ‘Death of Dido’, was painted around 1781 and belongs to the Royal Collection, London, United Kingdom (catalogue number 1029) [7]. In this experiments the sample’s code was Re1. J. Townsend described the sample before [28]. R. Boitelle provided two samples, coded I1 and I2, from ‘Alone’, a painting by Josef Israëls that was painted around 1880. The painting belongs to the Mesdag Museum, The Hague, The Netherlands (catalogue number 154). This painting also shows signs of darkening and poor drying of the oil paint [9, 21]. Van den Berg and Boon have been described the samples before [27]. Three other similar samples originate from a painting and a sketch by Théodore Rousseau, both hanging in the Mesdag Museum and both having the same name, ‘La descente des vaches’. The sketch (catalogue number 287) was painted between 1834-1835, while the painting (catalogue number 286) was painted about one year later, between 1835-1836. Unlike the sketch that shows small drying cracks in the blue and brown areas, the painting had severely darkened and the top layers had shrunked into thick islands of paint. The samples coded Ro1 and Ro2 were obtained from the painting’s darkened foreground. Sample Ro3 comes from a brown spot in the yellow foreground of the sketch. Some details are given in Table 2 and more details about the samples have been discussed elsewhere [26, 43].

Only the brown layers of the paint samples were analysed, after separation of layers as described for the oil paint reconstructions. In some situations traces of the varnish could not be entirely removed.

Analytical techniques

Direct Temperature-resolved Mass Spectrometry (DTMS)

The samples (pigments and oil paints) were analysed by DTMS as solutions or suspensions. These were prepared using 5-10 µg of sample and 15-25 µl of solvent (DCM for the pigments and EtOH for the oil paint samples). The test solutions in DCM were analysed as such. An aliquot of 1-2 µl of the suspension/solution was applied to the filament of a direct insertion probe for in-source analysis. DTMS experiments were carried out on a JEOL JMS SX-102 double focussing mass spectrometer (B/E) and a JEOL JMS-SX/SX 102A tandem mass spectrometer (B/E/B/E) [44, 45]. A resistively heated Pt/Rh filament (Pt/Rh 9:1, 100 µm) was used for the direct insertion probe. The filament was heated at a rate of 0.5 A/min to an end temperature of about 800 °C. Ions generated by electron ionisation (EI) in an ionisation chamber kept at 190 °C, were accelerated to 8 kV, analysed from m/z 20-1000 (about 1 s cycle time) and post-accelerated to 10 kV. A mass resolution of 1000 was used. A JEOL MS-MP 9020D data system was used for data acquisition and processing. To minimise the fragmentation reactions of the ions the DTMS spectra were acquired under low energy EI conditions at 16 eV. The test solution samples
were analysed in triplicate for discriminant analysis, and the spectra were summed over the TIC.

**Discriminant Analysis of the DTMS data**

Mass spectra were numerically analysed by discriminant analysis (DA) with the FOMpyroMAP multivariate analysis programme, a modified version of the ARTHUR package from Infometrix Inc. (Seattle, USA; 1978 release) and with the FOM developed Matlab® (The Mathworks Inc., Natick, MA, USA) toolbox ChemomeTrickss [46-49].

*Gas Chromatography Mass Spectrometry (GC/MS) analysis in various modes*: Py-GC/MS, Py-TMAH-GC/MS and on-column GC/MS

Typical amounts of sample used for GC/MS experiments were 10 μg for solid samples, or 10 μl solution for pyrolysis GC/MS measurements and 10 μl solution for on column GC/MS measurements. Solid samples were ground in DCM for Py-GC/MS experiments. For Py-TMAH-GC/MS experiments, the samples were homogenised in tetramethylammonium hydroxide (TMAH) 2.5% in water, and aliquots were applied to a ferromagnetic wire and dried in vacuo. The Curie point of the wires is given in Table 3.

**Table 3. GC/MS methods and oven programs used for analysis of the samples.**

<table>
<thead>
<tr>
<th>GC/MS method</th>
<th>Samples</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Py-GC/MS</td>
<td>A, A_{10}, A_{re}, A-VI</td>
<td>35(0)-4-320(10); 770 °C wire, 9 s Py</td>
</tr>
<tr>
<td>Py-TMAH-GC/MS</td>
<td>Lo, LoA, OP_{1-3}, A-VI, PbW-VI, IVB-VI</td>
<td>50(2)-6-320(10); 610 °C wire, 6 s Py</td>
</tr>
<tr>
<td></td>
<td>Ke-VI</td>
<td>50(2)-6-320(10); 610 °C wire, 6 s Py</td>
</tr>
<tr>
<td></td>
<td>Ro_{1-3}</td>
<td>35(0)-4-320(10); 770 °C wire, 9 s Py</td>
</tr>
<tr>
<td></td>
<td>Re_{1}</td>
<td>50(2)-6-320(2); 610 °C wire, 6 s Py</td>
</tr>
<tr>
<td></td>
<td>I_{1-2}</td>
<td>40(2)-6-352(6); 770 °C wire, 6 s Py</td>
</tr>
<tr>
<td>On column GC/MS</td>
<td>A_{e}</td>
<td>110(2)-3-320(10)</td>
</tr>
</tbody>
</table>

After drying of the sample, the wire was inserted into a glass liner, placed in the cold compartment of the pyrolysis unit, flushed with helium and then moved into the pyrolysis chamber (220 °C) of the FOM 5LX Curie point pyrolysis unit [50]. The experiments were carried out with a FOM-5LX Curie-point pyrolysis unit [50] mounted on a Carlo Erba series 8565 HRGC MEGA 2 gas chromatograph. For on-column GC/MS the sample was directly injected on column. For separation a fused silica SGE BPX5 column (25 m, 0.32 mm i. D., 0.25 μm film thickness) used with helium as a carrier gas at a flow rate of 2 ml/min. The oven temperature was

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2 Py-GC/MS stands for on line Pyrolysis GC/MS; Py-TMAH-GC/MS stands for on line transesterification Pyrolysis GC/MS.
programmed as shown in Table 3. For analysis of samples known to contain asphalt a longer oven program was chosen as shown in Table 3 to have a good separation of the asphalt markers and biomarkers. The paint samples are usually analysed with a oven program that follows the standard method for paint samples (see as well Table 3). The GC column was interfaced directly to a JEOL JMS DX-303 double focussing (E/B) mass spectrometer or a JEOL JMS-SX/SX 102A tandem mass spectrometer (B/E/B/E), using a home built interface kept at 300 °C. Ions were generated by electron ionisation (70 eV) in the ionisation chamber, accelerated to 3 kV (DX303) or 8 kV (SX/SX 102A), mass separated and post-accelerated to 10 kV before detection. The mass range was scanned from m/z 35-500, or m/z 40-800 respectively, with a cycle time of 1 s. A JEOL MS-MP 9020D data system was used for data acquisition and processing.

Electrospray Ionisation Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (ESI-FTICR-MS)

A modified 7.0e FTICR-MS instrument (Bruker-Spectrospin, Fällanden, Switzerland) equipped with a 7-Tesla superconducting magnet and an in-house designed external ion source was used for ESI-FTICR-MS measurements of the test solutions. Details of the instrumental parameters have been described before [51, 52]. The ICR cell used was a home-built open cell. The samples were mixed with DCM: EtOH (7:3, v/v) (1/100 µl) and 10mM NH₄Ac was added before analysis. Ions were generated using an atmospheric pressure electrospray ionisation interface, maintained at 3-4 kV, desolvated in a heated capillary, transported through several differentially pumped sections till trapping in the ICR cell at ~5 x 10⁻⁹ mbar. Data were processed using XMASS 5.0 software from Bruker Daltonik GmbH, Bremen, Germany.

High Pressure Size Exclusion Chromatography (HPSEC)

HPSEC or SEC was used only for the test solution in DCM. The samples were measured using a Shimadzu LC10 system, consisting of a SCL-10AD VP control panel, a LC-10AD VP pump, a DGU-14A degasser, a SIL-10AD VP autoinjector, a CTO-10AS column oven and a FRC-10A fraction collector (Shimadzu Benelux, ‘s-Hertogenbosch, The Netherlands). Separation was achieved on two columns used in series: PL gel Mixed D 5 µm (300 x 7.5 mm) and PL gel 5 µm 10³Å (300 x 7.5 mm) of Polymer Laboratories, Heerlen, The Netherlands. Three different detectors, connected in series, were used for detection: a SPD-10A VP UV/VIS-detector (Shimadzu) operated at 240 nm, a RID-10A refractive index detector (Shimadzu) and a 996 Photo Diode Array (PDA)-detector (Waters™ Chromatography B.V., Etten Leur, The Netherlands) operated at 195-500 nm, in combination with Class VP 5.03 (Shimadzu) and Millenium 32 (waters) software, respectively. The system was operated at a temperature of 40 °C or 30 °C with a flow rate of 1 ml/min and DCM was used as a mobile phase. The analysis time was of 25 min. Calibration was performed with polystyrene standards (Polymer Laboratories) with an average mass ranging from 570 to 370,000.
Fourier Transform Infrared Spectrometry (FTIR)

Initial chemical changes in a 5% (w/w) asphalt-linseed oil mixture were investigated using a FTS-6000 Bio-Rad FTIR imaging system (Bio-Rad, Cambridge, MA, USA), consisting of a Michelson interferometer (Bio-Rad FTS-6000), an IR microscope (Bio-Rad UMA-500) and a MCT narrow band detector. The fresh asphalt paint was applied as a thin film on a ZnSe disc. The disc was placed in a sample compartment of the BioRad FTS 6000 spectrometer. Spectra were averaged with a 30 minutes time resolution. The resolution of the spectra is 4 cm⁻¹ and the mirror speed was 5 kHz. Data were processed using WIN-IR Pro 2.5 software of Bio-Rad.

Results and discussion

A) Fate of marker compounds in oil paint that contains asphalt

The experiments planned required a relatively large amount of natural asphalt. A representative sample that would match the chemical properties of the Dead Sea asphalt was received from Shell. As discussed in chapter 2, the asphalt from the Dead Sea was considered to be the main source of asphalt in the past. The VEGA asphalt was investigated using the analytical Py-GC/MS protocol reported in detail in chapter 2. The full inventory of chemical marker compounds found made VEGA a good testing material to measure the effects of roasting and other 19th-century pretreatments on the chemical structure of the asphalt. VEGA was also used to make paint and to test the effect of ageing of the paint. The results of these investigations are reported in the next six sections. Apart from these paint studies, VEGA was also used to investigate its reactivity with drying oil. A similar but more limited approach for Kassel earth and Kassel earth containing oil paints is reported by Languri and Boon in Annex A of chapter 5 [53]. The main focus there is on the pigment and its fate in oil paint reconstructions. Some aspects of the effect of solvent extraction are also tested.

VEGA asphalt

The TIC and selected mass chromatograms for the hopanoid, monoaromatic steroid, all steroid biomarkers and aliphatic chain elements are depicted in Fig. 1a and those from the aromatic alkylbenzenes, alkynaphthalenes, alkylbenzothiophenes and alkyl dibenzothiophenes markers are presented in Fig. 1b. The same notation for markers as introduced in chapter 2 was used. Ratios of biomarkers calculated from their intensity in the partial mass chromatograms are shown in Table 4 and Fig. 2. The bar graphs in Fig. 2 were obtained by integration of the area of the peaks of interest (markers and biomarkers) in the partial mass chromatograms from the Py-(TMAH)-GC/MS data. The comparison between the abundance of the markers and biomarkers is absolute (bound to m/z values used) within each sample and relative from sample to sample.

3 The whole range of alkanes (m/z 85), hopanes (m/z 191), monoaromatic steroids (m/z 253), alkylbenzenes (m/z 77+91+105+119), alkynaphthalenes (m/z 128+142+156+170), alkylbenzothiophenes (m/z 148+162+176+190), alkyl dibenzothiophenes (m/z 198+212+226+240)
Fig. 1. Biomarkers (a) and markers (b) of the VEGA asphalt sample. Biomarkers: hopanoids (m/z 191), monoaromatic steroids (m/z 253) and the C_{25}-C_{35} n-alkane retention time window (m/z 85). Markers: alkylbenzenes (m/z 77+91+105+119), alkynaphthalenes (m/z 128+142+156+170), alkylbenzothiophenes (m/z 148+162+176+190) and alkyl dibenzothiophenes (m/z 198+212+226+240).
Table 4. Presence and absence of asphalt marker molecules and biomarkers in asphalt containing samples.

Legend: "i" stands for no. of C atoms in the alkyl chain, H, stands for hopane homologues (H_{27-37}), T_{s} and T_{m} for the H_{27} hopane homologues, G for gammacerane, MA, for monoaromatic steroids, C, for alkanes (i=6–max 38), B for benzene, B_{t} for alkylbenzenes (i=1-3), N for naphtalene, N_{t} for alkynaphtalene (i=1-3), BT, for alkybenzothiophenes (i=1-4), DBT, for alkyldibenzothiophenes (i=1-4). The eluting (alkane) windows are as follows: C_{29-36} alkanes for the hopanes, C_{26-29} alkanes for the monoaromatic steroids, C_{17-20} alkanes for the alkylbenzenes, C_{18-21} alkanes for the alkylnaphtalenes, C_{15-21} alkanes for the alkyldibenzothiophenes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Markers and biomarkers</th>
<th>Present</th>
<th>Absent</th>
</tr>
</thead>
</table>
| A      | hopanes: H_{27-29,32} (T_{s}, T_{m}, H_{29}, H_{30}, H_{31}, H_{32})  
gammacerane: G  
monoaromatic steroids: MA_{27,29}  
alkanes: C_{7-35}  
aromatics: B-B_{3,3}, N-N_{3}, BT_{1,4}, DBT_{1,4} |         |        |
| A_{10} | hopanes: T_{x, 1}, T_{m}, H_{29-32} (T_{x, 1}, T_{m}, H_{29}, H_{30}, H_{31}, H_{32})  
gammacerane: G  
akanes: C_{7-29}  
aromatics: B_{1-3}, N-N_{3}, BT_{1,4}, DBT_{1,4} |         | monoaromatic steroids |
| A_{c}  | hopanes: H_{27, 29-37} (T_{s}, T_{m}, H_{29}, H_{30}, H_{31}, H_{32}, H_{33}, H_{34}, H_{35}, H_{36}, H_{37})  
gammacerane: G  
monoaromatic steroids: MA_{27,29}  
akanes: C_{12-39} |         | B-B_{3,3}, N-N_{3}, BT_{1,4}, DBT_{1,4} |
| A_{rc} | hopanes: T_{x, 1}, T_{m}, H_{29-33}  
gammacerane: G  
monoaromatic steroids: MA_{27,29}  
akanes: C_{7-33}  
aromatics: B-B_{3,3}, N-N_{3}, BT_{1,4}, DBT_{1,3} |         | DBT_{4} |
| LoAc   | hopanes: H_{27, 29-35} (T_{s}, T_{m}, H_{29}, H_{30}, H_{31}, H_{32}, H_{33}, H_{34}, H_{35})  
gammacerane: G  
monoaromatic steroids: MA_{27,29}  
akanes: C_{7-34}  
aromatics: B_{1-3}, N-N_{3}, BT_{1,4}, DBT_{1,3} |         | B, DBT_{1,4} |
| LoAa   | hopanes: H_{27, 29-35} (T_{s}, T_{m}, H_{29}, H_{30}, H_{31}, H_{32}, H_{33}, H_{34}, H_{35})  
gammacerane: G  
monoaromatic steroids: MA_{27,29}  
akanes: C_{7-34}  
aromatics: B_{1-3}, N-N_{3}, BT_{1,4}, DBT_{1,3} |         | B, DBT_{4} |
| OP_{1c} | hopanes: T_{m}, H_{30-31} (T_{s}, H_{31}, H_{32}, H_{33}, H_{34}, H_{35})  
aromatics: B_{1}, B_{2,3}? , N_{3} |         | T_{s}, H_{30-31}(T_{s}, H_{31}, H_{32}, H_{33}, H_{34}, H_{35}) |
| OP_{1a} | hopanes: T_{m}, H_{30-31} (T_{s}, H_{31}, H_{32}, H_{33}, H_{34}, H_{35})  
aromatics: B_{2,3}, N_{3} |         | T_{s}, H_{30-31}(T_{s}, H_{31}, H_{32}, H_{33}, H_{34}, H_{35}) |
Table 4 continued.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Markers and biomarkers</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Present</td>
</tr>
<tr>
<td>OP₂c</td>
<td>hopanes: H₂₉, H₃₀</td>
</tr>
<tr>
<td></td>
<td>aromatics: B₁-₃, N?, N₂</td>
</tr>
<tr>
<td>OP₂a</td>
<td>hopanes: T₉₁, T₉₀, H₂₉, H₃₀</td>
</tr>
<tr>
<td></td>
<td>aromatics: B₂, B₃, N?, N₁-₃</td>
</tr>
<tr>
<td>OP₃c</td>
<td>hopanes: T₉₀, H₂₉, H₃₀</td>
</tr>
<tr>
<td></td>
<td>beeswax alkanes: C₂₅, C₂₇, C₂₉, C₃₁</td>
</tr>
<tr>
<td></td>
<td>aromatics: B₁-₃, N?, N₁, N₁ (2ⁿd isomer)?</td>
</tr>
<tr>
<td>OP₃a</td>
<td>hopanes: T₉₀, H₂₉, H₃₀</td>
</tr>
<tr>
<td></td>
<td>beeswax alkanes: C₂₇, C₂₉, C₃₁</td>
</tr>
<tr>
<td></td>
<td>aromatics: B₁-₃, N₁</td>
</tr>
</tbody>
</table>

The n-alkanes observed in the VEGA asphalt sample range from C₆ to C₃₅. It is obvious by comparison of the TIC with the mass chromatogram m/z 85 of alkanes that the aliphatic compounds have a stronger relative intensity than hopanoids and steroid compounds. The hopanoid and steroid elution windows are delimited by C₂₆-C₃₆ alkanes (m/z 85).

![graph](image)

**Fig. 2a.** Ratios of markers and biomarkers in VEGA asphalt samples and VEGA asphalt-oil test solutions. The labels are explained in Table 1.

In the lowest mass chromatogram of Fig. 1a the 17α, 21β(H) hopanoids (Tₕ and Tₘ, H₂₇ homologues, H₂₉-H₃₂ homologues; Scheme 1) characterised by the m/z 191 fragment ion are displayed. Gammacerane, the oleane type of pentacyclic hydrocarbon considered being highly characteristic of Dead Sea asphalt [54, chapter 2] is marked with G. The relative ratios of the hopanoid compounds are shown in Fig. 2 and Table 4, from where it appears that the Tₘ, H₂₉ and H₃₀ homologues are the highest in intensity. The middle mass chromatogram of Fig. 1a with the profile of
monoaromatic steroids (m/z 253), tentatively identified as the MA$_{27}$, MA$_{28}$ and MA$_{29}$ homologues, shows a similar pattern as observed in the Dead Sea asphalts [54, chapter 2]. Note that the mass chromatogram of m/z 253 also pulls out a series of alkane homologues. Other steroid hydrocarbons identified were 14α(H) steranes (m/z 217), 14β(H) steranes (m/z 218), monoaromatic and methyl-monoaromatic steroids (m/z 253, m/z 267), triaromatic steroids and methyl triaromatic steroids (m/z 231, m/z 245), but these will not be considered in the presented comparative studies.

![Mass chromatogram of m/z 253 showing monoaromatic steroids](image)

**Fig. 2b.** Ratios of markers and biomarkers in fresh and artificially aged oil paint reconstructions containing VEGA asphalt. The labels are explained in Table 1.

The aromatic compounds displayed by mass chromatograms in Fig. 1b, exhibit the whole range of homologues of alkylbenzenes coded B-B$_3$ (m/z 77+91+105+119), alkynaphthalenes coded N-N$_3$ (m/z 128+142+156+170), alkyl-benzothiophenes coded BT$_{1.4}$ (m/z 148+162+176+190), and alkyl dibenzothiophenes coded DBT$_{1.4}$ (m/z 198+212+226+240). The relative ratio between these markers is shown in Fig. 2 and Table 4 showing the alkylbenzenes as the highest in intensity of the aromatic compounds.

**Effect of roasting on the composition of asphalt**

The 19$^{th}$-century pretreatment of roasting affects the composition of the asphalt as can be deduced from the (bio)marker profiles in Fig. 3a and b. The TIC points out that the n-alkanes have almost completely disappeared. Some of the peaks at high elution times in the TIC are from hopanoid compounds as can be deduced from m/z 191 and the corresponding mass spectra. The mass chromatogram of m/z 253 shows that the monoaromatic steroids are also strongly affected. It is still possible to trace some of the n-alkanes (up to C$_{29}$) in the C$_{26}$-C$_{36}$ elution window. The hopanoids and gammacerane are present but some in diminished relative abundance as shown in Fig. 2 and Table 4 (T$_m$ and H$_{29}$ are still high in intensity, while the intensity of H$_{30}$ has decreased). The changes in the ratios of these different homologues suggest that these compounds are present in different chemically bonded forms. The relative ratio between the classes of biomarkers in the roasted VEGA
Fig. 3. Biomarkers (a) and markers (b) of the roasted VEGA asphalt sample. Biomarkers: hopanoids (m/z 191), monoaromatic steroids (m/z 253) and the C\textsubscript{23}-C\textsubscript{35} n-alkane retention time window (m/z 85). Markers: alkylbenzenes (m/z 77+91+105+119), alkylnaphtalenes (m/z 128+142+156+170), alkylbenzothiophenes (m/z 148+162+176+190) and alkyl dibenzothiophenes (m/z 198+212 +226+240).
asphalt mass chromatograms from Fig. 2, shows the hopanoids as the most resistant of the biomarkers as already suggested by Moldowan [55].

The aromatic compounds in Fig. 3b show preservation of the B-B₃, N-N₃, BT₁, 4, DBT₁,4 homologues. The alkylbenzene signature remains the strongest one, all the other aromatic compounds being decreased in intensity, as seen in Fig. 2.

Roasting clearly affects some of the (bio)markers like monoaromatic steroids, some of the hopanoids and the higher alkane homologues. The persistence of some of the hopanoid hydrocarbons and alkylaromatics is striking.

**Solvent sensitivity of asphalt marker compounds**

Since the roasting process affects the composition of the asphalt, the action of solvents on the composition of asphalt was also investigated. The effect of mixing in hot melts of resins was not investigated. Asphaltenes of VEGA were precipitated from a chloroform solution with heptane. The heptane solubles of the VEGA asphalt, i.e. the maltene fraction [29, 56], was subjected to on-column GC/MS. The relative ratios of markers and specific markers of the VEGA maltene fraction (not shown as partial mass chromatograms) are given in Fig. 2 and in Table 4. The asphaltene fraction [29, 56, 57] was analysed by Py-GC/MS and results are shown in Fig. 4a, b. The distribution of markers and biomarkers in the two fractions of the asphalt is shown in Fig. 2 and Table 4.

The n-alkanes in the maltene fraction range from C₁₂ (under the current experimental conditions) to C₃₉. Alkylaromatics were not detected. Monoaromatic steroid alkanes searched by the mass chromatogram of m/z 253 show the MA₂₇, MA₂₈ and MA₂₉ homologues. The series of hopanoids observed in the maltene fraction by the mass chromatogram of m/z 191 goes up to at least homologue H₃₅. Gammacerane is detected as the highest compound in the m/z 191 mass chromatogram.

The asphaltenes show a profile of n-alkanes after pyrolysis ranging up to C₃₂. The asphaltene fraction shows a full range of aromatic compounds similar to those observed earlier for the unfractionated VEGA asphalt. The profile of monoaromatic steroid hydrocarbons in Fig 4a resembles the distribution profile in the unfractonated sample but the ratio of the compounds differs from the maltene fraction. The hopanoids of the asphaltenes in the elution window from C₂₆-C₃₆ show a strongly differing profile compared to the maltenes. Trisnorhopanes are relatively prominent while the gammacerane is much lower in intensity. The whole profile resembles the unfractionated sample more closely. All the observations suggest that the maltene fraction is quantitatively smaller than the asphaltene fraction.

Aromatic compounds, which are known to be part of the cross-linked fraction of asphalt (asphaltene) [55-58] are absent in the maltene fraction. The ratio between the aromatic compounds in the asphaltenes, Fig. 2, shows a good match with the relative ratios observed for aromatic compounds in the unfractionated sample. This is in agreement with the information in the literature that aromatic compounds are interconnecting chains in the asphaltenes [56, 58] that are seen here as pyrolysis products.

The marker compounds of asphalt are affected by apolar solvents but the full range of markers present in cross linked fractions are retained and can be identified using Py-GC/MS. This is reassuring because it means that careful restoration treatment should not negatively affect the analytical tracing of the asphalt in oil paint. It is not entirely clear how boiling or other hot pretreatments affect the asphalt although some loss of the maltenes is to be expected.
Fig. 4. Biomarkers (a) and markers (b) of the asphaltene fraction of the VEGA asphalt. Biomarkers: hopanoids (m/z 191), monoaromatic steroids (m/z 253) and the C_{22}-C_{35} n-alkane retention time window (m/z 85). Markers: alkylbenzenes (m/z 77+91+105+119), alkylnaphtalenes (m/z 128+142+156+170), alkylbenzo thiophenes (m/z 148+162+176+190) and alkyl dibenzo thiophenes (m/z 198+212+226+240).
Fig. 5. Biomarkers (a) and markers (b) of the VEGA asphalt-linseed oil control as fresh DCM solution. Biomarkers: hopanoids (m/z 191), monoaromatic steroids (m/z 253) and the C_{23}-C_{33} n-alkane retention time window (m/z 85). Markers: alkylbenzenes (m/z 77+91+105+119), alkynaphtalenes (m/z 128+142+156+170), alkylbenzothiophenes (m/z 148+162+176+190) and alkyl dibenzothiophenes (m/z 198+212+226+240).
Fig. 6. Biomarkers (a) and markers (b) of the VEGA asphalt-linseed oil DCM solution artificially aged for 12 weeks. Biomarkers: hopanoids (m/z 191), monoaromatic steroids (m/z 253) and the C_{22}-C_{35} n-alkane retention time window (m/z 85). Markers: alkylbenzenes (m/z 77+91+105+119), alkynaphtalenes (m/z 128+142+156+170), alkylbenzothiophenes (m/z 148+162+176+190) and alkyl dibenzothiophenes (m/z 198+212+226+240).
Accelerated ageing of asphalt in linseed oil-dichloromethane solution

Accelerated ageing in dichloromethane solution has been very effective for the ageing of varnish resins, individual resin components and for study of the degradation of indigo [30, 31, 59]. The accelerated degradation of asphalt and asphalt oil mixtures under the influence of light was therefore studied in this way to simulate the degradation of these compounds under (photo)oxidizing conditions. In this section, the focus is on the effects on the marker signatures. HPSEC results that show that asphalt probably reacts with the oil are reported in section B. Fig. 5a and b shows the markers of the VEGA asphalt pigment after mixing with linseed oil in DCM (control test solution kept at –18 °C in the dark.). Fig 6a and b shows the results after 12 weeks of light exposure at room temperature.

Qualitatively all the hopanes, gammacerane, steroid and aliphatichydrocarbon compounds observed in the fresh VEGA asphalt are also observed in the fresh asphalt-oil solution. The ratios between the compounds however are not the same. Compared to the fresh asphalt, the asphalt oil solution in DCM shows a difference in the relative amount of the alicyclic hydrocarbons compared to the n-alkanes. The profile of the hopanoid hydrocarbons resembles the m/z 191 profile of the maltene fraction (not shown). The same is true for the monoaromatic steroid hydrocarbons. The aromatic fractions are largely unaffected although some of the dibenzothiophenes (DBT_{3,4}) are not detectable any more. Somehow, the solvent soluble fraction of the asphalt (maltenes) is affected by the dissolution in the oil dichloromethane solution.

Ageing after 12 weeks in the presence of oil leads to complexation of asphalt and drying oil (see section B). The question whether this would affect the marker compounds was studied by Py-GC/MS with tetramethylammoniumhydroxide as transmethylation reagent. The results on the fatty acid methyl esters are reported in the same section B treating the Effect of asphalt and Kassel earth on the composition of oil paint. The marker compound signatures in Fig. 6 show that the full range of marker compounds is still detectable. The mass chromatograms of 253 and 191 are very similar to the control sample and look like the distributions observed in the maltene fraction. Gammacerane and the whole series of hopanoids are present, with the same predominance of the H_{30}, H_{29} and H_{31} homologues as observed for the fresh solution. The monoaromatic steroid pattern and the presence of alkane series are well preserved. When comparing the ratios of markers and biomarkers with the control sample, in Fig. 2, the relative amount of aliphatichains appears diminished by a factor of two, compared to the relative amount of hopanoid compounds. In a similar way the hopanoids seem to have diminished compared to the monoaromatic steroids.

The alkylaromatic hydrocarbons in the Py-GC/MS data also show a high degree of similarity with respect to the fresh asphalt and the unaged solutions. It was evident that dibenzothiophenes were not always completely detectable. In the unaged sample for example, the DBT_{3} and DBT_{4} were absent although they could be detected in the corresponding sample without addition of oil. The full range of benzothiophenes was again detectable in the sample after 12 weeks of photooxidation. Linseed oil is known to react with sulphur compounds [60]. Whether this reactivity is an issue in these experiments is difficult to judge because there does not seem to be a consistent pattern. When comparing the ratios of aromatics in the aged sample and the control sample, Fig. 2, the alkylbenzenes show a much higher abundance compared to other aromatic compounds. Alkylnaphtalenes and the sulphur containing aromatics show similar ratios compared to the control sample.
Remarkably, the asphalt without the oil (not shown) shows a great resemblance after 12 weeks to the sample with drying oil suggesting that the asphaltic components are relatively resistant to the photooxidative regime that had been imposed. Asphalt can be severely photooxidised under external sunlight conditions leading to increased amounts of aromatic ketones, alcohols, carboxylic acids and sulfuroxides/sulfones [61]. The degradation conditions are much milder although the formation of these compounds can not be excluded. The used protocol may not be able to detect the effect of the oxidation processes expressed by these classes of compounds. Although there is no detectable effect on the asphalt itself, the effect of degradation in dichloromethane solution on the oil is very prominent (see section B).

**Asphalt oil paints**

Asphalt oil paints were prepared after 19th-century recipes [4, 5, 24] using the VEGA asphalt as pigment. Details about the preparation methods of the William’s “Antwerp Brown” paint (OP1), Merimée’s English asphalt paint (OP2) and another asphalt paint of Merimée (OP3) are given in Table 1. These paints were painted out on a lead white ground. The samples were artificially aged for 3 months at SRAL to an age that which equals approximately 40 years of light conditions in a museum (see the Experimental section). The asphalt containing oil paints were sampled before (controls) and after ageing. Samples were subjected to Py-TMAH-GC/MS analysis to study the fatty acids from the oil and to asphalt components in one analytical run. The pyrolysis and GC oven conditions are specified in Table 3. The distribution of markers in the samples is shown in Fig. 7a1,2, b1,2, Fig. 8a1,2, b1,2, and in Fig. 2.

Analysis of the control samples before ageing is showing that only some of the hopanoid and aromatic characteristics of the asphalt are preserved after preparation and drying of the paint. The monoaromatic steroid profile could not be detected, which prevents the use of the steroid compounds as asphalt markers in the paint. The aromatic compounds containing sulphur and the long chain n-alkanes could not be detected as well. Due to a flaw in the collection of controls, the actual pigments used in the preparation of the paints were unavailable for analysis. The pretreatment of the asphalt in the form of roasting and melting into resins before incorporation into the paint, however, very likely destroyed a number of the molecular features (see the effect of roasting on the composition of asphalt in section A). The hopanoid compounds were more resilient as was already clear from the analytical data of the roasted asphalt. A small population of hopanoids compounds could be detected. The H₃₀ and H₂₉ are the highest in intensity in all the OP₁ fresh paints. The Tₘ₉₃ trisnorhopane, the H₂₉, H₃₀ and H₃₁ homologues were found in OP₁. Only the H₂₉ and H₃₀ homologues are detected in OP₂. In the OP₃ sample the detected hopanoids are the Tₘ, and the H₂₉ and H₃₀ homologues. The Tₚ trisnorhopane, or its monounsaturated equivalent and the gammacerane are absent for all three paint samples and the highest hopane homologue, H₃₁, is observed only in OP₁.

The aliphatic chains of asphaltic origin are absent in all the paint samples. Some beeswax derived n-alkanes are detectable in the OP₃ sample. The beeswax provenance is confirmed by the recipe that mentions the use of beeswax and moreover the predominance of the odd alkane homologues C₂₅, C₂₇, C₂₉ and C₃₁ is specific for beeswax.

Few aromatic compounds survived the making of the oil paint. Benzene is absent in the analytical data of all three samples but toluene and alkylbenzenes up to
Fig. 7a, a2. Biomarkers and markers of the fresh VEGA asphalt oil paint reconstructions: William’s Antwerp brown method (a1, a2) used as control after curing. Biomarkers: hopanoids (m/z 191), monoaromatic steroids (m/z 253) and the C_{25}-C_{35} n-alkane retention time window (m/z 85). Markers: alkylbenzenes (m/z 77+91+105+119), alkynaphtalenes (m/z 128+142+156+170), alkylbenzothiophenes (m/z 148+162+176+190) and alkyl dibenzothiophenes (m/z 198+212+226+240).
Fig. 7b₁, b₂: Biomarkers and markers of the fresh VEGA asphalt oil paint reconstructions: Merimée English’s method (b₁, b₂) used as control after curing. Biomarkers: hopanoids (m/z 191), monoaromatic steroids (m/z 253) and the C₂₃-C₃₅ n-alkane retention time window (m/z 85). Markers: alkylbenzenes (m/z 77+91+105+119), alkynaphthalenes (m/z 128+142+156+170), alkylbenzothiophenes (m/z 148+162+176+190) and alkyl dibenzothiophenes (m/z 198+212+226+240).
Fig. 8a1, a2. Biomarkers and markers of the VEGA asphalt oil paint reconstructions artificially aged for 3 months: William’s Antwerp brown method (a1, a2). Biomarkers: hopanoids (m/z 191), monoaromatic steroids (m/z 253) and the C23-C45 n-alkane retention time window (m/z 85). Markers: alkylbenzenes (m/z 77+91+105+119), alkylnaphtalenes (m/z 128+142+156+170), alkylbenzothiophenes (m/z 148+162+176+190) and alkyl dibenzothiophenes (m/z 198+212+226+240).
Fig. 8b1, b2. Biomarkers and markers of the VEGA asphalt oil paint reconstructions artificially aged for 3 months: Merimée English’s method (b1, b2). Biomarkers: hopanoids (m/z 191), monoaromatic steroids (m/z 253) and the C_{23}-C_{33} n-alkane retention time window (m/z 85). Markers: alkylbenzenes (m/z 77+91+105+119), alkynaphthalenes (m/z 128+142+156+170), alkylbenzothiophenes (m/z 148+162+176+190) and alkyl dibenzothiophenes (m/z 198+212+226+240).
the C₃ substituted benzene are present. Naphthalene is absent only in OP₁, but the N-N₃ naphthalenes are present in all fresh samples. All the sulphur containing compounds are absent.

The analysis of the samples after artificial ageing is showing similar results as for the non-aged samples. With respect to the hopanes, the Tₘ, H₂₉ and H₃₀ homologues are traceable in the aged paint reconstruction (Table 4, Fig. 8a₁,b₁), H₃₀ or H₂₉ showing the highest relative intensity. The monoaromatic steroids are absent. Aliphatic chains characteristic for asphalt are not observed but alkanes originating from beeswax (C₂₇, C₂₉, C₃₁) were detected in the aged OP₃. Only some alkylbenzenes, some of the higher homologues, are present in the aged samples (Table 4). Benzene is absent in all three aged samples. Naphthalene is certainly absent in two of them, OP₁ₐ and OP₃ₐ. Their partial disappearance had been noticed already in the fresh and aged asphalt-oil solutions. Fig. 2 presents semiquantitative relationships calculated on the basis of mass chromatograms of the markers listed in Table 4. The difference between OP₃ control and aged is negligible. In OP₂ a difference is observed in the relative intensity of the hopanoids that are higher after ageing. The same phenomenon is observed in OP₁. Alkylmarkers are strongly affected by ageing in OP₁, but alkynaphthalenes become more prominent after ageing. The sulphur containing compounds as (di)benzothiophenes are also absent in the aged oil paint reconstructions.

In conclusion, marker compounds can be traced using the Py-TMAH-GCMS but their relative amounts are strongly affected by the preparation method of the pigment in the oil paint production process. Changes due to ageing appear to be of secondary importance. This introduces the possibility of tracing asphalt in complex paint samples with this technique.

Summarising this subsection, it can be said that asphalt (bio)markers in artificially light aged asphalt-linseed oil solutions are rather well preserved, which suggests that the conditions are too mild for extensive degradation of the asphalt molecule. The fate of marker compounds in oil paint that contain asphalt is certainly related to the pretreatments applied to the initial pigment. High temperatures have shown to severely affect the composition and signature of an asphalt. Only hopanoid markers and alkyl aromatics are preserved. This was confirmed when artificially aged asphalt containing oil paints prepared according to 19th-century recipes were analysed. In this case only some of the hopanes and some of the alkyl aromatics are still present. Solvent cleaning is inferred to have similar actions to solvent extraction of an asphalt. Apolar solvents were shown to remove part of the biomarkers, present in the maltene fraction. Only hopanes seem to be reliable for the identification of asphalt in the aged oil paint reconstructions. Unfortunately, the oil paint production process involving asphalt pigment is unknown when samples suspected to contain asphalt components are taken from a painting. As a consequence, the determination of asphalt in painting samples is surely difficult and the data will be hard to interpret.

B) Effect of asphalt and Kassel earth on the composition of oil paint

In the sections above, the emphasis was placed on the chemical nature of asphalt and Kassel earth as pigment materials. The next section will present data on the effect of addition of these pigments on the composition of the drying oil. Data are
presented on the kinetics of the drying of linseed oil in the presence of pure asphalt, on the accelerated ageing of oil with and without pure asphalt in solution and on the effect of asphalt and Kassel earth on the composition of drying oil paint.

**Fatty acids, dicarboxylic acids and their ratios in ageing oil paint**

Linseed oil as drying oil is a mixture of triglycerides (TAGs) containing mostly saturated C_{16} and saturated and unsaturated C_{18} fatty acid chains that will oxidise and cross-link upon exposure to light and oxygen [62-66]. The drying of linseed oil can be summarised as the “consumption” of double bonds. This is observed also in the Py-TMAH-GC/MS and ESI-FTICR-MS measurements of the linseed oil DCM test solutions (see further in section B). The decrease in the relative amount of unsaturated C_{18} fatty acids with the progress of chemical drying, preferentially affects the more unsaturated C_{18:3} and C_{18:2} fatty acids and only at a later stage the C_{18:1} fatty acids. It has been shown before that the monounsaturated C_{18} fatty acids react away about 1000 times slower than the polyunsaturated C_{18} fatty acids [67, 68]. The fact that C_{18:1} survives longer in the paint makes this compound a possible marker for monitoring the drying of (linseed) oil paint if it is compared to the saturated C_{18} fatty acid as an oil internal “standard”. For this reason the ratio, i.e. C_{18:1}:C_{18:0} FA, is used as a tool to monitor the drying of linseed oil. Values higher than one correspond to a still relatively high content in C_{18:1} fatty acid, i.e. a poor drying of the oil. Ratios lower than one are related to a good or normal drying condition of the oil. The lower the values below one, the more ideal the drying of that sample.

Chemical drying of drying oils introduces peroxides that are later on converted into volatile matter and residual matter enriched in oxygen containing functional groups like aldehyde and acids. Introduction of antioxidants like asphalt and related organic rich pigments are likely affecting this process. The relative amounts of dicarboxylic acids are possible markers for the degree of antioxidising activity. The ratio of azelaic acid (C_9 dicarboxylic acid) to stearic acid (C_{18} or C_{18:0} fatty acid), C_9 DA: C_{18} FA, is introduced as a measure of the chemical drying of oil. The unsaturated C_{18} fatty acids are considered the source of the azelaic acid in the advance of the drying process while the stearic acid is the indifferent component taken as an internal standard. Oil paints after a longer period of time change into an ionomeric structure because the glycerol ester bonds hydrolyse to form free acids among which unsaturated C_{18} fatty acids and dicarboxylic acids that react with metals (mostly lead) from pigments and driers [64-66]. The availability of such cations in asphalitic oil paints may be an issue in the overall stability of a century old asphalitic oil paint. I.e. the ionomeric stage is not reached. This is the explanation why a low relative amount of azelaic acid (a C_9 DA: C_{18:0} FA ratio much below one) is indicative for antioxidant activity. A rather high C_9 DA: C_{18:0} FA ratio (close to 1 or higher) is indicative for a normal, respectively a good drying of the oil paint.

**Kinetics of drying of an asphalt-oil mixture (FTIR study)**

FTIR was used to monitor the induction time for the drying of the linseed oil with and without asphalt following a method introduced by Muizebelt et al. [67-69]. Van der Weerd has described the setup [70]. The induction time is related to the time required for the *cis* double bonds originally present in the fatty acid chains of the oil TAGs to change into their *trans* configuration. The *trans* configuration favours the steric interaction between free radicals after the initiation reaction has taken place.
with the atmospheric oxygen as well as the reaction of the intact TAGs chains with the peroxi radicals formed (propagation reaction). [66-68, 71].

Results are shown in Fig. 9 for an asphalt-linseed oil mixture (5 % asphalt), pure linseed oil and linseed oil plus 5 % smalt. The y axis gives the intensity of the absorbance characteristic at 3010 cm⁻¹ of the trans C-C double bond. The x axis shows the induction time. The shortest induction time of 60 hrs is observed for the linseed oil plus smalt. The relative absorbance for 3010 drops very quickly leading to almost zero after 120 hours. Linseed oil alone shows a longer induction time of 80 hrs and shows a much slower drop off. The longest induction time of about 160 hrs is observed for the asphalt-linseed oil mixture. Thus asphalt clearly slows down the chemical drying of oil.

**Accelerated ageing of asphalt and drying oil in dichloromethane solution**

Comparative studies were performed on the accelerated ageing of linseed oil, asphalt and asphalt-linseed oil solutions in dichloromethane with DTMS, ESI-FTICR-MS, SEC and Py-TMAH-GCMS. Samples were exposed to light for 12 weeks. Samples were taken at once (control) and after one, two, three, four, eight and twelve weeks.

![Absorbance vs. Time graph](image)

**Fig. 9. Induction time of the oxidation of linseed oil, a linseed oil with 5 % smalt drier and a linseed oil with 5 % asphalt.**

The chemical composition of the linseed oil over the 12 weeks of exposure analysed by DTMS changes substantially leading to a rapid decrease of the polyunsaturated moieties and the appearance of cross linked fractions relatively enriched in saturated fatty acid moieties. The appearance of the asphalt DTMS spectra remains rather similar. The DTMS data obtained for the artificially light aged asphalt-linseed oil solutions and the linseed oil solutions for 1-12 weeks are compared by discriminant analysis (DA). The control samples of linseed oil or asphalt-linseed oil solutions are included in the discriminant analysis. The scatter plot of the first two discriminant functions (DF1 and DF2) is shown in Fig. 10a for linseed oil and
asphalt-linseed oil solutions. Linseed oil solutions are coded as “Lo” followed by a number indicative for the weeks of artificial light ageing (1, 2, 3, 4, 8, 12) or the letter “c” for the control samples. E.g. Lo1 is a linseed oil solution artificially aged for 1 week.

Fig. 10. Discriminant analytical map of the chemical composition (DTMS data) of VEGA asphalt-linseed oil DCM test solutions (right) in comparison with linseed oil DCM test solutions comparing initial state (control) and solutions artificially aged for 1, 2, 3, 4, 8 and 12 weeks (a). Mass spectrum of the DF2 (b).
Asphalt-linseed oil solutions are coded as “LoA” followed as well by a number (as above) or the letter “c”, having the same significance as for the linseed oil solutions. The distribution of samples along DF1 indicates the different composition of the samples, linseed oil solution, Lo, in the negative side of DF1 and linseed oil solutions containing asphalt, LoA, in the positive side of DF1 (see also the enlarged detail for LoA solutions). Another distribution of samples is observed along the DF2 axis. The control Lo solutions and the solutions aged for 1-4 weeks are very much grouped in the same area in Fig. 10a. The Lo solution aged for 8 weeks, Lo8, is further away on the DF2 axis and the Lo solution aged for 12 weeks even further away, on the positive side of DF2 axis.

These observations indicate that the DF2 axis represents the time axis and the distribution along this axis coincides with the changes in composition of the linseed oil solution from control to after 12 weeks of artificial light ageing. Similar assignments can be made also for the LoA solutions. It is clear that the composition of asphalt-linseed oil solutions (DF1+) along DF2 axis is almost constant in time compared to the composition of linseed oil solutions along the same axis. The enlargement shown on the right side of the figure points out that the composition of solutions of linseed oil in the presence of asphalt, LoA, also changes in time but much slower! So drying linseed oil changes qualitatively much more than when mixed with asphalt. Asphalt alone does not change too much on this time scale. It is believed that the access of oxygen to the oil triglycerides is hindered by physical interactions but also chemical interactions between asphalt and linseed oil. Indications for the chemical interactions between asphalt and oil are observed for example in the DTMS measurement of the 12 weeks LoA solution. Peaks characteristic for asphalt and linseed oil are present in the mass spectrum corresponding to the pyrolysis event in the TIC. The pyrolysis event in the TIC of a DTMS measurement corresponds to material chemically bound in a network. Linseed oil is represented by peaks corresponding to C16, C18;1 and C18 fatty acids (25% relative abundance) at m/z 256, m/z 264 and m/z 284, respectively, as well as peaks corresponding to C55 and C57 TAGs (3% relative abundance). These are symmetrically distributed clusters around m/z 854 (probably C55:4 TAG) and m/z 878 (probably C57:5 TAG). In the same LoA12 solution asphalt peaks are represented by m/z 191, 370, 398, 412, 426, 440, 454, 468 and 482 for hopanoids (30% relative abundance of the molecular ions), m/z 231 and 245 for triaromatic steroids, m/z 267 for methylmonoaromatic steroids, m/z 217 (218), 372, 386, 414, 428 for 14α(β) steranes (30% relative abundance of the molecular ions).

As suggested above the presence of both asphalt and linseed oil peaks in the chemically bound fraction of the LoA12 solution points to chemical interactions between the two. The oil component appears to have been drying (i.e. cross-linked and oxidised) to some extent, which is supported by the low relative abundance of TAGs and the much higher relative abundance of fatty acid moieties. Oxidation and especially cross-linking of the two are suggested and addressed again later on in the text. The spectrum for the positive side of DF2 (Fig. 10b) as already suggested by the DF1-DF2 plot, gives determining features in the mass spectrum of the 12 weeks aged linseed oil solution. The higher intensity peaks are observed in the fragment ion range below m/z 190. Fatty acids as such or released by elimination reactions are indicated by m/z 284 (C18:0), 264 (M-H2O of C18:1) and 256 (C16:0) and less specific fragment ions at m/z 185, 129, 98, 84, 73, 60 and 57. The ions at m/z 155 and 171 are assigned
to mid-chain hydroxystearic acids after observed in GC/MS data of dried linseed oil. Azelaic acid shows a specific fragment ion at m/z 152, which is inconspicuous in the spectrum in Fig. 10b. Very few peaks and of very low relative intensity are observed in the mass range above m/z 300. The absence of peaks typical for diglycerides and triglycerides in the fresh linseed oil (or the low content in double bonds) [66] together with the presence of peaks indicative of dicarboxylic acids as oxidative products of oil confirm the advanced state of oxidation of the oil after 12 weeks of artificial light ageing. As mentioned above when asphalt is present in the linseed oil solution less oxidation of the oil is observed (peaks of diglycerides and triglycerides are still present). To summarise, the presence of asphalt in the linseed oil solution is interpreted as impeding a normal drying of the oil (see the changes in chemical composition for the linseed oil solutions).

More information about the drying of the asphalt-linseed oil solutions was derived from ESI-FTICR-MS and HPSEC data by comparison with data obtained for linseed oil test solutions.

The oxidation of the oil was monitored as the oxygen uptake in the TAGs using ESI-FTICR-MS. The main triglycerides present in linseed oil are the TAGs containing C_{57} and C_{55} carbon atoms (the C_{55} TAGs and C_{57} TAGs), i.e. C_{18:n} and C_{16-18:n} where n has values between 0 and 3. Van den Berg has assigned the compounds in the ESI-FTICR-MS of linseed oil in an earlier study [66, 72]. Fig. 11 shows ESI-FTICR-MS data of the C_{55} and C_{57} TAGs area (m/z 850-980) for the control linseed oil solution (Loc), linseed oil solution after four (Lo4) and twelve weeks (Lo12) of artificial light ageing, and asphalt-linseed oil solutions after four (LoA4) and twelve weeks (LoA12) of artificial light ageing. The inserts in Fig. 11 display the compounds in the mass range up to m/z 1200. The clusters of TAGs are coded as C_{55} and C_{57}, corresponding to the number of carbon atoms in their structure. The numbers above each peak in the mass spectra in Fig. 11 correspond to the sum of the double bonds present in the fatty acid moieties of the triglycerides (Table 5). The clusters at higher m/z values in the same figure and inserts are oxidation products of the C_{57} TAGs. The number of the supposedly incorporated oxygen atoms after comparing the measured mass with the exact value is marked above as “+1”, “+2”, etc. The measured molecular masses for the compounds observed with ESI-FTICR-MS, which are triglycerides and their oxidised compounds, were compared with the exact (calculated) molecular mass. The exact and measured values of the C_{55} and C_{57} triglycerides are given in Table 5. The measured values in Table 5 originate from the ESI-FTICR-MS measurement done for the 4 weeks aged linseed oil test solution. A slight mass difference (error)\(^4\) from the exact mass is observed for the oil TAGs in the test solutions. Surprisingly, it was observed that the error was lower when the solutions were less aged\(^5\).

The fresh oil very quickly incorporates two atoms of oxygen during preparation of the control solution [66] and this is shown in Fig. 11 (see Loc). The C_{55} TAGs with 6, 5, 4 double bonds and the C_{57} TAGs with 9 double bonds are the main compounds of the Loc solution. At least 18 atoms of oxygen were incorporated in the C_{57} TAGs after 4 weeks of artificial light ageing (see Lo4 and insert, in Fig. 11).

---

\(^4\) The error, \(\varepsilon\), was calculated as the modulus of the difference between the exact mass of the compound and the measured value (\(\varepsilon = |M_{W_{\text{exact}}} - M_{W_{\text{measured}}}|/\text{amu}\)).

\(^5\) For example values of 10\(^{-1}\) were calculated for the control linseed oil solution and the 4 weeks aged linseed oil solution with a few values in the 10\(^{-2}\) or 10\(^{-1}\) range for the 4 weeks aged linseed oil solution. The 4 weeks aged asphalt-linseed oil solution gives mass errors of 10\(^{-2}\). The values of \(\varepsilon\) for the 12 weeks aged solutions are in both cases in the range of 10\(^{-1}\).
Fig. 11. ESI-FTICR-MS data showing compositional changes of ageing linseed oil triglycerides in linseed oil DCM test solutions: linseed oil control solution (a), linseed oil solution after 4 weeks of light ageing (b), linseed oil solution after 12 weeks of light ageing (c), VEGA asphalt-linseed oil solution after 4 weeks of light ageing (d) and VEGA asphalt-linseed oil solution after 12 weeks of light ageing (e).
The C_{55} and C_{57} TAGs with up to 6 and 9 double bonds remain the main compounds after 4 weeks but the relative amount of the C_{55} TAGs is higher compared to the original oil suggesting a preferential oxidation of the linolenic moieties in the C_{57} TAGs. After 12 weeks of artificial light ageing C_{57} TAGs with about ten atoms of oxygen are still observed in linseed oil (see Lo12 and insert in Fig. 11). After 12 weeks the relative intensity of the more unsaturated moieties in the unoxidised TAGs is decreased while the triglycerides with one to four oxygen incorporated have increased intensities.

Table 5. Possible combinations of fatty acid chains in the linseed oil triglycerides [62, 63, 66], the number of double bonds present in the correspondent triglycerides and their measured and exact molecular weight (MW). The position of the fatty acid chains given in the first column of the table is interchangeable.

<table>
<thead>
<tr>
<th>TAG</th>
<th>Double bonds no.</th>
<th>Measured MW (FT-ICR-MS)</th>
<th>Exact MW (calculated)</th>
<th>ε (x 10^{9} amu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{55} (C_{55}H_{94}O_{6})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C_{16}:0\text{-}C_{18}:3\text{-}C_{18}:3</td>
<td>6</td>
<td>850.708</td>
<td>850.705</td>
<td>3</td>
</tr>
<tr>
<td>C_{16}:0\text{-}C_{18}:3\text{-}C_{18}:2</td>
<td>5</td>
<td>852.721</td>
<td>852.721</td>
<td>0</td>
</tr>
<tr>
<td>C_{16}:0\text{-}C_{18}:3\text{-}C_{18}:1,2</td>
<td>4</td>
<td>854.737</td>
<td>854.736</td>
<td>1</td>
</tr>
<tr>
<td>C_{16}:0\text{-}C_{18}:3\text{-}C_{18}:0,1</td>
<td>3</td>
<td>856.752</td>
<td>856.752</td>
<td>0</td>
</tr>
<tr>
<td>C_{16}:0\text{-}C_{18}:2,1\text{-}C_{18}:0,1</td>
<td>2</td>
<td>858.770</td>
<td>858.768</td>
<td>2</td>
</tr>
<tr>
<td>C_{16}:0\text{-}C_{18}:1\text{-}C_{18}:0</td>
<td>1</td>
<td>860.783</td>
<td>860.783</td>
<td>0</td>
</tr>
<tr>
<td>C_{16}:0\text{-}C_{18}:0\text{-}C_{18}:0</td>
<td>0</td>
<td>low signal</td>
<td>862.799</td>
<td>-</td>
</tr>
<tr>
<td>C_{57} (C_{57}H_{92}O_{6})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C_{18}:3\text{-}C_{18}:3\text{-}C_{18}:3</td>
<td>9</td>
<td>872.687</td>
<td>872.689</td>
<td>2</td>
</tr>
<tr>
<td>C_{18}:2\text{-}C_{18}:3\text{-}C_{18}:3</td>
<td>8</td>
<td>874.706</td>
<td>874.705</td>
<td>1</td>
</tr>
<tr>
<td>C_{18}:1,2\text{-}C_{18}:3,2\text{-}C_{18}:3,3</td>
<td>7</td>
<td>876.718</td>
<td>876.721</td>
<td>3</td>
</tr>
<tr>
<td>C_{18}:0,1\text{-}C_{18}:3,2\text{-}C_{18}:3,3</td>
<td>6</td>
<td>878.733</td>
<td>878.736</td>
<td>3</td>
</tr>
<tr>
<td>C_{18}:0,1\text{-}C_{18}:2,2\text{-}C_{18}:3,2,3</td>
<td>5</td>
<td>880.751</td>
<td>880.752</td>
<td>1</td>
</tr>
<tr>
<td>C_{18}:0,1\text{-}C_{18}:1,2\text{-}C_{18}:3,2,2</td>
<td>4</td>
<td>882.769</td>
<td>882.768</td>
<td>1</td>
</tr>
<tr>
<td>C_{18}:0,1\text{-}C_{18}:0,1\text{-}C_{18}:3,2,1</td>
<td>3</td>
<td>884.785</td>
<td>884.783</td>
<td>2</td>
</tr>
<tr>
<td>C_{18}:0,0\text{-}C_{18}:0,1\text{-}C_{18}:2,1</td>
<td>2</td>
<td>low signal</td>
<td>886.799</td>
<td>-</td>
</tr>
<tr>
<td>C_{18}:0\text{-}C_{18}:0\text{-}C_{18}:1,1</td>
<td>1</td>
<td>overlap C_{57}\text{-}3 + 1O</td>
<td>888.815</td>
<td>-</td>
</tr>
<tr>
<td>C_{18}:0\text{-}C_{18}:0\text{-}C_{18}:0</td>
<td>0</td>
<td>overlap C_{57}\text{-}3 + 1O</td>
<td>890.830</td>
<td>-</td>
</tr>
<tr>
<td>C_{57}\text{-}3 + 1O</td>
<td>9</td>
<td>906.719</td>
<td>906.719</td>
<td>-</td>
</tr>
<tr>
<td>C_{57}\text{-}3 + 2O</td>
<td>9</td>
<td>922.713</td>
<td>922.713</td>
<td>-</td>
</tr>
<tr>
<td>C_{57}\text{-}3 + 3O</td>
<td>9</td>
<td>938.709</td>
<td>938.709</td>
<td>-</td>
</tr>
<tr>
<td>C_{57}\text{-}3 + 4O</td>
<td>9</td>
<td>954.704</td>
<td>954.703</td>
<td>1</td>
</tr>
</tbody>
</table>

The C_{55} TAGs with 4 double bonds (with symmetrically distributed peaks for 6, 3 and 2 double bonds) and the C_{57} TAGs with 5 (with 6, 7 and 4 double bond peaks symmetrically distributed) are the main compounds of the linseed oil solution. Other

\(^{6}\) as example, values from the FT-ICR-MS measurement for the test linseed oil solution aged for 4 weeks are shown
reactions than oxidation alone for example cross-linking reactions or formation of smaller oxidation products could possibly explain the lower relative abundance of the peaks of oxidised TAGs in the ESI-FTICR-MS measurement and the absence of the more oxidised TAGs.

After 4 weeks of artificial ageing oxygenated triglyceride ions with at least 4 incorporated oxygens are present in the asphalt-linseed oil test solution data (see LoA in Fig. 11). The ratio between C55 and C57 TAGs more closely resembles the original oil suggesting an antioxidant activity due to the asphalt. This clearly points to a slower oxidation of the linseed oil in the presence of asphalt. The way of oxidation of the oil in the presence of asphalt also seems to be different. An even number of oxygen atoms is preferentially incorporated in the fatty acid moieties of the oil in the asphalt-linseed oil test solution, while for the linseed oil test solution an odd number of oxygen atoms is preferentially taken up as seen in the data. Peroxidation of the oil moieties can lead to very high number of incorporated oxygen atoms [73]. This appears to be the case for the linseed oil experiment where higher relative intensities are observed with increments of 32 Dalton. At longer exposure time, the relative amount of these highly oxygenated species decreases. It was concluded that peroxides and other highly oxygenated triglycerides are converted into smaller compounds at this stage [74].

The range of oxygenated TAGs is much more limited when asphalt is present. The distribution of oxygenated triglycerides in the asphalt containing sample suggest that only one oxygen atom is reacting to the most reactive double bonds or that peroxides may not form. Longer exposure of the asphalt containing oil sample leads to a rapid decline of all triglycerides. After 12 weeks almost no free TAGs (i.e. unreacted by cross-linking or oxidation) can be detected (LoA12 in Fig. 11). In the same LoA12 sample, C55 TAGs with a very low relative abundance and with a distribution that resembles the distribution of unoxidised C55 TAGs in the LoA4 solution could be identified. The distribution of C57 unoxidised TAGs has a maximum at C57.6 and symmetry around this peak is also of low relative abundance and resembles the distribution of the homologues observed for the Lo12 solution. No more than 3 atoms of oxygen are detected as incorporated in TAGs in the LoA12 solution. That suggests that double bonds from TAGs are reacting away in a different way than by oxidation, for example via cross-linking reactions.

A few aspects can be summarised from ESI-FTICR-MS data. Less oxygen is incorporated in the asphalt-oil TAGs after 4 weeks compared to the oil alone. The ESI-FTICR-MS data point out that the incorporation of oxygen in TAGs of the asphalt-oil solution is about 60 % less. Oxidation of TAGs is perceived not only as formation of new clusters of oxidised TAGs but also as a decrease in relative abundance of the unoxidised unsaturated TAGs with ageing. A preferential oxidation of the more unsaturated moieties of the C55 and C57 TAGs is observed and which resulted in symmetry of the TAG clusters around a middle peak as a maximum. In other words the presence of asphalt in linseed oil solutions in DCM slows down the oxidation of the oil TAGs. The consumption of the unsaturations of the TAGs in such a mixture can take place by cross-linking reactions. Indications for cross-linking reactions have been discussed above, when DTMS results were discussed and other indications derived from SEC measurements are discussed further on.

SEC was used to give information on the cross-linking of the linseed oil or formation of asphalt-linseed oil networks upon the light ageing. The HPSEC results for the linseed oil and the VEGA asphalt-linseed oil DCM test solutions are shown in Fig. 12a and b. Polystyrene standards (PS) were used for the calibration, which
implies that the observed molecular weight (MW) values of linseed oil and asphalt in the SEC measurements are in fact apparent MW values. The MW values of the standards as a function of the retardation time are shown on the MW bar in Fig. 12.

When the linseed oil solution is analysed by SEC, there is a small difference between the MW curve of the linseed oil in the control test solution, Loc, marked as “1” (grey solid line “—“) in Fig. 12a, and the linseed oil in the 12 weeks aged linseed oil solution (Lo12) marked as “2” (black solid line “—”) in the same figure. A major peak (at RT~16 min) is observed for the fresh linseed oil solution (1) and is interpreted as the peak corresponding to the TAGs in the fresh linseed oil. As seen from the MW bar in Fig. 12a, the corresponding MW values of PS are around 1600 Dalton. This implies that SEC “sees” TAGs with molecular weights of about 900 Dalton as compounds with an apparent molecular weight of about 1600 Dalton.
A similar major peak is observed for the aged linseed oil solution (2), but a small shift is observed between the fresh and aged and fresh solution. Possibly this has to do with the increased relative abundance of C57 TAGs and their small oxidation products, compared to the C57 TAGs after 12 weeks of artificial light ageing as observed with ESI-FTICR-MS (for MW values and relative abundances see Lo12 in Fig. 11). Very small amounts of high MW (HMW) material with the apparent MW of ca 2900 Dalton are observed at retention time 15.5 min for Lo12. Two peaks of substances are observed in the aged linseed oil solution between 18-22 min RT that are interpreted as degradation products with a lower MW\(^7\) (LMW). DTMS and Py-TMAH-GC/MS confirm the presence of these smaller degradation products in the form of dicarboxylic acids and various diglycerides.

The chromatogram of the control asphalt-linseed oil solution, LoAc, the chromatogram of the asphalt-linseed oil solution aged for 12 weeks, LoA12, and the chromatogram of the asphalt solution aged for 12 weeks, A12, are compared in Fig. 12b. The chromatograms are marked as "1" (dark grey solid line “—”) for LoAc, “2” (black solid line “—”) for LoA12, and “3” (light grey solid line “—”) for A12. An unresolved envelope (ca 16-18 min RT) is observed in Fig. 12b for the LoAc solution (1). A peak corresponding to linseed oil is expected at RT 16 min in the LoAc solution. It is most probably hidden under the broad range of MW of asphalt, mixture of maltenes and asphaltenes that covers the apparent MW ranging from 1900 to values smaller than 500 Dalton.

For the A12 solution (3) a peak is also observed at ca 4000 Dalton (RT~15 min), which probably corresponds to aggregates formed by aged asphaltenes [56, 57]. The LoA12 solution (2) shows a common pattern with the control asphalt-linseed oil solution, i.e. the unresolved peak seen for LoAc. In the chromatogram of the same LoA12 solution another peak is observed at around RT 16 min with an apparent MW of ca 1600 Dalton. This peak has the same RT with the TAG peak observed in the linseed oil solutions (Fig. 12a) and it is interpreted as an oil peak. The LoA12 solution also shows a common pattern with the A12 solution, i.e. the HMW around 4000 Dalton (RT~15 min). This unresolved peak is somewhat broader than the peak observed for the aged asphalt solution, suggesting the formation of HMW other than cross-linked asphalt or cross-linked linseed oil. It is proposed that this HMW material is due to formation of cross-links between asphalt units and TAGs of the oil. It is proposed that asphalt in oil acts as a chemical trap for unsaturated TAGs creating a relatively large network molecule. A clear oxidation path for the ageing of the linseed oil in solution was seen in ESI-FTICR-MS results. From the same data it was clear that less oxidation occurs in the triglycerides of the asphalt-linseed oil solution. However only a very small amount of TAGs are remaining in the latter solution after 12 weeks of light exposure.

The consumption of double bonds (TAGs) in the LoA12 may be explained as suggested by SEC, i.e. the ageing of asphalt-linseed oil solutions take place differently (more cross-linking) compared to the linseed oil solutions (very little cross-linking). SEC of the oil itself demonstrates that a network of oil molecules is not formed under these conditions. Instead, the peroxidised TAGs seen by ESI-FTICR-MS are converted into smaller degradation products by further oxidation while some of the oxy-TAGs remain. The idea of cross-link formation between asphalt and linseed oil after 12 weeks of ageing is also supported by DTMS

\(^7\) The corresponding apparent MW values, below 500 Dalton, are not relevant for the interpretation of the data as they are out of the calibration range (for more details see the Experimental section).
observations that show the presence of peaks of both oil and asphalt in the pyrolysis event corresponding to network information.

Mono- and dicarboxylic fatty acids of the aged oils and oils plus asphalt were analysed by Py-TMAH-GCMS. The two ratios derived earlier using the stearic acid as the conservative property of the TAGs of the oils, C9 DA: C18:1 FA and C18:1: C18:0 FA, are used to estimate the chemical drying of linseed oil solutions with or without asphalt. The ratio of azelaic acid to stearic acid shows the progression of the oxidation of the C9 position in the unsaturated fatty acids. The ratio of the monounsaturated fatty acids (cis and trans C18:1) to stearic acid shows how much unsaturation of the oil is remaining. Light ageing of the oil in dichloromethane solution immediately leads to a decrease of the unsaturated fatty acid moieties and an increase in azelaic acid. Fig. 13 shows that the C18:1: C18:0 ratio decreases more slowly when asphalt is present in the oil mixture. After week 4 and 8, the ratio starts to decrease more quickly suggesting that a certain lag time has passed and that the antioxidative potential of the asphalt is decreasing. With initial values between 4.5 for the linseed oil control solution and almost 5 for the control asphalt-linseed oil solution, the C18:1: C18:0 FA ratio is still much higher than one (ca 2.5) after 12 weeks of artificial light ageing, when asphalt is present. For linseed oil solution aged 12 weeks the value is lower (ca 2). Azelaic acid increases relatively fast in the oil while its formation is slowed down when asphalt is present.

![Graph showing the ratio of fatty acids](image)

Fig. 13. Ratios of 9da/18:0fa and 18:1fa/18:0fa fatty acids obtained by GC/MS analysis of asphalt-linseed oil and linseed oil solutions in DCM, light aged for 0-12 weeks.

Summarising, the effect of asphalt on the oxidation of linseed oil could be observed easily when the linseed oil was photoxidised in dichloromethane solution. The results are considered to be relevant for the fate of oil in oil paints. Earlier studies on varnish and indigo in DCM test solutions have shown that similar compounds are being produced in solution as well as in the solid phase of paintings. Asphalt clearly affects the composition of the drying oil. The effect of asphalt on the oxidation of the linseed oil is a general slowing down of the rate of oxidation but the same kind of oil end products are being formed. The electrospray FTICR-MS data suggest that there
are different kinds of intermediate compounds formed when asphalt is present. There appears to be a high relative amount of peroxides that form in the oil compared to oil with asphalt. Further studies will have to corroborate this. Asphalt and linseed oil also react with each other as was deduced from the SEC and DTMS data. It is presently unknown what the reaction centres could be, although sulphur compounds in the asphalt are likely candidates. The reaction of asphalt with the oil starts immediately and may explain part of the antioxidant effect. The analysis of the TAGs by ESI-FTICR-MS suggests that a large proportion of the oil TAGs are indeed involved in the cross linking leaving only a small amount of free TAGs in solution after 12 weeks. The ratio of azaleic acid to stearic acid points out that oxidation of the double bonds keeps taking place, which suggests that not all double bonds are sequestered by the asphalt.

Asphalt and Kassel earth containing oil paints

Several sets of oil paint samples were available for analysis with Py-TMAH-GCMS. In Fig. 14 TICs of oil paint samples relevant for the drying of asphalt containing oil paints are shown. The C\text{18:1}:C\text{18} FA and C\text{9} DA: C\text{18} FA ratios of these samples are given in Fig. 15 and Fig. 16. Samples obtained from Von Imhoff (VI) test panels (at CCI) allow the comparison between a natural aged asphalt oil paint (A-VI) and oil paints with ivory black (IvB-VI), Kassel earth (Ke-VI) or plain lead white (PbW-VI). It is important to mention that these samples were prepared without addition of driers that could have promoted the chemical drying process of the oil in the paint. The asphalt used by von Imhoff in preparing the paint was analysed and found to be rather similar to the VEGA asphalt with the exception of the aromatic steroid hydrocarbons, which have different distribution. This difference is not considered to be of any significance for the effect of the asphalt on the drying of the oil paint. Fig. 14a shows the TIC of the asphalt oil paint after 25 years of natural ageing. The chromatogram shows a lot of peaks\textsuperscript{8} from asphalt as minor constituents and several major peaks from methyl ester of fatty acids (C\text{7}-C\text{18}, C\text{20}-C\text{24}) and dicarboxylic acids (C\text{6}-C\text{10}). A striking feature is the large peak from the C\text{18:1} fatty acid. The presence of the dicarboxylic acids with the quite high peak for the C\text{9} homologue indicates however that oxidation of the oil takes place but this does not go fast enough to decrease the amount of C\text{18:1} fatty acid [66]. The ratios of the C\text{18:1}:C\text{18} FA and C\text{9} DA: C\text{18} FA derived from this chromatogram are presented as bar graphs in Fig. 15. It is clear by comparison with the lead white paint that the chemical drying of asphalt paint is very strongly slowed down and incomplete. Interestingly, the ivory black oil paint has a relatively large C\text{9} DA: C\text{18} FA pointing to strong oxidation conditions but the C\text{18:1}:C\text{18} FA is still rather high. Kassel earth on the other hand has a low C\text{18:1}:C\text{18} FA although the geological origin and the organic nature of the Kassel earth might have suggested a potential antioxidant effect. The carbon in the ivory black has however a much stronger antioxidant effect. The other oil paints (OP\text{1}, OP\text{2} and OP\text{3}) were made with the VEGA asphalt pigment prepared according to 19\textsuperscript{th}-century recipes by Boitelle\textsuperscript{9}.

\textsuperscript{8} The following notation was used: "*" and "*9" for the nonanoic fatty acid methyl ester, "**" and "9da" for the nonadienoic dicarboxylic acid dimethyl ester, "aMe9 da" for the α methyl nonadienoic dicarboxylic acid dimethyl ester, "c" and "18:1" for monounsaturated C\text{18} fatty acid methyl ester and "0" and "**" for alkene or alkane and "\text{\textcopyright}" for hopanoid compounds from the asphalt component.

\textsuperscript{9} For details regarding the exact composition of the samples see Table 1 and the Experimental section.
Fig. 14. Py-TMAH-GC/MS Total Ion Current of asphalt aged oil paints without drier: CCI asphalt oil paint (a) and with drier: Wiliam’s Antwerp brown (b) and Merimée’s English method (c).

Example of notation: “•” and “9” for the nonanoic fatty acid methyl ester, “*” and “9da” for the nonadioic dicarboxylic acid dimethyl ester, “αMe9 da” for the α methyl nonadioic dicarboxylic acid dimethyl ester, “○” and “18: 1” for the monounsaturated C₁₈ fatty acid methyl ester, “○” or “●” for alkenes or alkanes and “▼” for hopanes from the asphalt component.
These paints were prepared with addition of litharge as a drying catalyst added to the linseed oil. The TICs of the Py-TMAH-GC/MS measurements are shown in Fig. 14 for samples OP$_{1a}$ (b) and OP$_{2a}$ (c). As observed for the A-VI sample a full range of fatty acids (C$_7$-C$_{18}$, C$_{20}$, C$_{22}$) and dicarboxylic acids$^{10}$ (C$_6$/C$_7$-C$_{10}$) methyl- or dimethyl esters are present. It is interesting to observe that the C$_9$ dicarboxylic acid is the second or the highest peak in the TICs of the OP$_{1a}$ or OP$_{2a}$ samples and moreover that the C$_{18}$:1 fatty acid peak is rather low. This indicates two possible influences on the drying of linseed oil in OP$_1$, i.e. the presence of driers and/or the deactivation of asphalt due to the roasting process.

![Graph showing relative ratio of fatty acid peaks](image)

\textit{Fig. 15. Degree of chemical drying expressed as ratio of 9da/18:0fa and 18:1/18:0 fa of naturally aged Von Imhoff asphalt and Kassel earth oil paints in comparison with an ivory black and lead white oil paint.}

In a similar way there are indications for three possible influences on the drying of linseed oil in OP$_2$, i.e. the presence of driers, the melting of the asphalt and/or the presence of resins. Surprisingly it seems that asphalt containing paint prepared according to the three selected 19$^{th}$-century recipes dries rather well after about 40 years of museum ageing (see Experimental section)! The oil characterising ratios of these oil paints are shown as bar graphs in Fig. 16. The fresh oil paints (OP$_{1c}$, OP$_{2c}$, OP$_{3c}$) already show a relatively high abundance of azelaic acid, which is probably due to a relatively long period of curing (8-10 months [24]) and the lead oxide present as a drying catalyst before exposure to light ageing. There is still a large relative amount of unsaturated fatty acids remaining however that decreases after ageing (OP$_{1a}$, OP$_{2a}$, OP$_{3a}$). The ratios of the three paints before ageing do not differ very much.

After ageing (equivalent to about 40 museum years) paint OP$_1$ is less oxidised compared to OP$_2$ and OP$_3$. In all three aged paints the azelaic acid is a dominant component and the C$_{18}$:1 is smaller than the C$_{18}$:0. The composition of the “asphalt pigment” itself seems to be the determining factor. The pigment in OP$_1$ was “boiled to cinder”, which substantially altered the properties of the molecular composition of the asphalt as seen above. The fatty acid and dicarboxylic acids of this oil paint

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$^{10}$ The α methyl C$_9$ dicarboxylic acid is a result of unwanted alkylation during the pyrolysis transmethylation process [50].
demonstrate that there is hardly any antioxidising effect left after this method of pigment preparation compared to the asphalt paint prepared by von Imhoff. However, the pigment is largely carbonised so it can still have an effect like the ivory black in the Ivb-VI paint. The “asphalt pigment” in OP₂ and OP₃ does not seem to affect the oxidation of the paint but the beeswax might considering the almost identical composition and preparation method for the two oil paints and the less oxidised oil in OP₃ (that contains beeswax). (The oil marker ratios are comparable to Kassel earth oil paint without drier.)

![Relative ratio graph](image)

**Fig 16. Ratios of 9da/18fa and 18:1/18:0 fa in asphalt paint reconstructions, before and after ageing.**

The pigment in these oil paints consists of “prepared” asphalt in a large amount of resin (mastic, gum turpentine and shellac). Since these resins are full of unsaturated hydrocarbons that could interact with the asphalt in similar ways as the unsaturated triglycerides in the oil-asphalt test solutions, it is possible that the potential effect of the asphalt itself on the oil paints neutralised to a large extent in the pigment preparation stage. This implies that the main effects on the drying of the oil are to be expected from other nondrying components in the oil paint such as the added resins and waxes. Earlier studies with resins and oil in DCM test solutions have shown that resins can strongly accelerate the oxidation of oils [32, 33].

Summarising this subsection, it can be said that several techniques have shown that the presence of asphalt in linseed oil paint or linseed oil DCM solutions hinders the drying of the oil. The induction time before oxidation and cross-linking of oil starts, is much longer in an asphalt-oil mixture compared to linseed oil alone. The chemical composition of the ageing oil seems to change much less in the presence of asphalt as observed by DTMS. A higher abundance of monounsaturated C₁₈ fatty acid is still observed (by Py-TMAH-GC/MS) in such an asphalt-linseed oil mixture compared to its linseed oil homologue solution. Examination of the linseed oil TAGs before and after ageing in the presence of asphalt have shown that less oxidation takes place even though the amount of TAGs diminishes. HPSEC experiments (supported by DTMS results) have explained this by the occurrence of chemical interactions between asphalt and oil units. The chemical drying of the naturally aged Von Imhoff
paint reconstructions containing no drier shows similarities between asphalt and carbon black pigments (like ivory black) in retarding the drying of oil but also the opposite effect of Kasselse on the drying of oil. The oil in the artificially aged asphalt-oil paints prepared after 19th-century recipes (i.e. with pretreated pigments, driers, resins and wax) is found to dry much better than the oil in the presence of only asphalt (Von Imhoff asphalt-oil sample).

C) Analytical data on selected 19th-century paintings

The paint samples from 19th-century paintings were taken on the supposition that the paint originally contained asphalt or other substances that caused premature cracking and darkening [7, 9, 21, 26-28, 43]. The samples were taken from brown-black darkened areas of several paintings: ‘Death of Dido’ by Sir Joshua Reynolds (1723-1792), sample Re1, ‘La descense des vaches’ by Theodore Rousseau, samples R01-R03, and the painting ‘Alone’ by Josef Israëls (1824-1911), samples I1 and I2. In the case of ‘La descense des vaches’ samples were available from both the beeswax/resin relined oil sketch (R03) and an unlined final painting (R01, R02), which are in the possession of the Mesdag museum. The research question addressed here is the composition of the oil paint, e.g. the presence or absence of asphalt or Kasselse pigments, and the additional organic material present that could influence the drying and darkening. Py-TMAH-GC/MS could be performed on most of the samples to determine the fatty acid and dicarboxylic acid distribution. Py-GC/MS and DTMS were used for molecular characterisation of the organic pigments and other organic materials in the paint. The results obtained by mass spectrometry are summarised in Table 6 and discussed further.

From the palmitic to stearic acid ratio (labelled as “p/s” in Table 6) it is suggested that the initial oil paint was prepared with linseed oil (L), as seen for samples Re1, I2, R01, R03 or poppy seed oil (P) like R02 [62]. The high p/s ratio derived from the Py-TMAH-GC/MS data obtained for the I1 sample could be possibly due to the presence of traces of beeswax in the paint. The marking features of the oil paint of these samples (C9 DA:C18:0 FA and the C18:1: C18:0 FA ratio) are shown as bar graphs in Fig. 17. Surprisingly, in all cases C18:1 fatty acids were found to be preserved. In the case of the Rousseau samples R02 and R03, and sample from the Israëls painting I2, the relative intensity of the C18:1 fatty acid (the C18:1/C18:0 ratio) is equal or larger than one, which points to poor drying of the oil paint even after 150 years. The low values for the C9 DA: C18:0 FA ratio for all the samples except RoI support the conclusion that the oil paint experienced a poor drying regime. The RoI sample seems to have experienced more oxidising conditions considering the C9 DA: C18:0 FA ratio of about 2. The poor drying of most of these paints could have been caused by the presence of antioxidising materials or by a lack of chemical driers. The latter supposition can be rejected because lead was found in all the sample by DTMS analysis, although it is possible that there is insufficient drier present considering the high abundance of non-drying organic components of the paints (except maybe in RoI) as shown in Table 6. All samples contain CO2 evolved by pyrolysis of a carbonate from an inorganic source. Considering that all the samples are dark the most logical explanation is that lead carbonate was used as a drier. DTMS and Py-GC/MS were used to determine the nature of the materials that could have interfered with the drying process.
Table 6. DTMS, Py-GC/MS and Py-TMAH-GC/MS results of 19th century paint samples.

Legend: "p/s" is the ratio between palmitic and stearic acid indicating the type of oil [62]. L stands for linseeds oil, P for poppy seed oil, Pb, Hg and S are the atomic symbols for lead, mercury, respectively sulphur. B stands for benzene, Bt stands for alkyl substituted benzenes, N stands for naphthalene, Nn for alkyl substituted naphthalenes, Ph stands for phenol, Phi stands for alkyl substituted phenols, Cx for n-alkanes (x= number of carbon atoms in the alkane chain and i= number of carbon atom in the alkyl substitute group).

<table>
<thead>
<tr>
<th>Sample's symbol</th>
<th>DTMS</th>
<th>Py-TMAH-GC/MS Py-GC/MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ro2 (286/5)</td>
<td>p/s= 4,7 → P Pb carbonate triterpenoids lignite (phenols) polysaccharides HgS (vermillion)</td>
<td>p/s= 4 → P alkanes: C9-C16, C16 alkylbenzenes: B1?, B2</td>
</tr>
<tr>
<td>Ro3 (287/2a)</td>
<td>p/s= 1,1 → L beeswax Pb carbonate triterpenoids (dammar)</td>
<td>p/s= 3 → L? asphalt/paraffin (alkanes: C9-C32)? alkylbenzenes: B, B1, B2 alkynaphthalenes: N, N1, N2 alkylphenols: Ph</td>
</tr>
<tr>
<td>Re1 (1029/20)</td>
<td>p/s= 0,9 → L? dicarboxylic acids (beeswax)? Pb triterpenoids HgS (vermillion)</td>
<td>p/s= 1,4 → L? lignite (phenols: Ph, Ph1, Ph2)? alkanes: C9-C10, C12 alkylbenzenes: B, B1, B2 alkynaphthalenes: N, N1, N2</td>
</tr>
<tr>
<td>I2 (154/2)</td>
<td>p/s= 2,5 → L dicarboxylic acids beeswax Pb carbonate (triterpenoids), (diterpenoids?) asphalt(C23-29,31 alkanes)? HgS (vermillion)</td>
<td>p/s= 2,6 → L lignite (phenols: Ph, Ph1)? alkanes: C9, C8, C11, C13-C17, C21, C23-C35 alkylbenzenes: B, B1, B2 alkynaphthalenes: N?, N1</td>
</tr>
</tbody>
</table>

No hopanoids nor steroid compounds characteristic for asphalt were found in the samples. Considering the fact that the hopanoid compounds are surviving well in the oil paint model studies (see above), it is concluded that asphalt as such can not have been the main antioxidising constituent. Small amounts of long chain n-alkanes that are potential indicator of sedimentary organic materials were observed by Py-GC/MS in the Rousseau Ro3 sample of the oil sketch (C6-C32 alkanes) and Ro1 sample of the oil painting (C27 and C29 alkanes), the Israels I2 sample (C21, C23-C35 alkanes), and the I1 sample (C21-C39 alkanes). Some of the n-alkanes are from the beeswax relining material like for the Rousseau sketch that was wax-relined [19]. The Reynolds painting was glue-lined [28] and the other have not been relined [21]. That suggest beeswax could have been used as a paint component in the other three paintings. And indeed beeswax esters could be demonstrated by DTMS to be part of
the sample’s composition in Ro1, Ro3, I2 and as trace in Re1 and I1 samples. Beeswax shows a strong odd predominance with C25, C27, C29 and C31 as main n-alkanes. Samples Ro3 and I1 contain a series of even n-alkanes as well. The distribution in I1 is gaussian (C20-C39) indicative of a petroleum origin. The distribution of the n-alkanes in Ro3 is rather flat and reminiscent of the VEGA n-alkane profile after roasting. If the observed aliphatic chains would be of asphaltic origin it is not clear why the asphalt biomarkers are absent. Alkyl aromatics specific for example to geomaterials/materials of organic provenance like are present as alkylbenzenes and as alkylnaphtalenes in the Ro3, Re1, I1 and I2 samples. Alkyl aromatic compounds and long chain aliphatic compounds as one would expect in non-degraded asphalt are present only in the Ro3, I1 and I2 samples.

![Graph showing ratios of 9da/18:0 and 18:1/18:0 for different samples](image)

**Fig. 17.** Degree of chemical drying of brown-black 19th-century oil paint sample expressed as ratios of 9da/18:0 and 18:1/18:0 fa.

Lignites like Kassel earth are potentially another source of paraffins (see chapter 4). The presence of phenol and some alkylphenols in some of the analysed paint samples suggests that Kassel earth like lignite was more probably used by Reynolds and Israëls and less likely by Rousseau. The partial mass chromatograms of phenol and higher homologues in sample Re1 from the ‘Death of Dido’ by Sir J. Reynolds, is shown in Fig. 18. In the uppermost window the correspondent TIC is shown.

A complete search for Kassel earth (bio)markers in DTMS and Py-GC/MS data revealed the absence of montan wax, phyllocladane and vanillic acid. Earlier studies on the fate of Kassel earth in oil paint demonstrated that montan wax, phyllocladane, vanillic acid, alkyl phenols and alkylmethoxyphenols survive the early stages of ageing [53]. However, montan wax and phyllocladane are sensitive to solvent extraction with apolar and polar solvents (chapter 4), so these features can be lost in the pigment preparation process (dewaxing) or due to restoration. Future work on reconstructions should prove if the presence of phenolic compounds in a paint sample is enough evidence for the use of a Kassel earth-like pigment. Alkylphenols
characteristic for Kassel earth are present in four of the samples, i.e. R0₂, I₂, I₁ and Rₑ₁, which represent poorly drying paint.

Other non-drying components discovered in the paint samples are beeswax esters, diterpenoid resins (in I₁, possibly also in I₂) and the triterpenoid resins of

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Fig. 18. Phenolic compounds in an oil paint sample (Rₑ₁) suspected of asphalt addition from 'Death of Dido' by Sir Joshua Reynolds.
dammar and probably mastic (Ro2, Re1, I1, possibly also in I2) [30, 45, 76]. In most of the cases beeswax is an acquired residue from the lining process. The same is probably true for the colophonium derived diterpenoids. The triterpenoids are probably from mastic in the case of the painting by Rousseau (Mesdag museum cat. no. 286) who is known to have used megilps (a mastic oil gel medium [4, 5, 77]) [17, 19, 20]. The dammar resin on the oil sketch from Rousseau is most likely from the varnish.

Three of the samples, Ro2, Re1 and I2, contain mercury and sulphur, which is interpreted as pointing to vermilion known to be a non-drying pigment. Peaks characteristic of polysaccharides are present in sample Ro2. Polysaccharides in forms of gums were used for example as paint ingredients in the 19th century [4, 5]. All these compounds detected do not amount to a large abundance of antioxidising materials in the paint that can explain the poor drying according to the indices used here. An attempt to correlate the poor drying of the oil in the 19th-century analysed samples and their composition is made in Table 7. Carbon blacks however can not be detected by the analytical methods used for this research. In the model experiments, the ivory black and the roasted asphalt showed antioxidant properties. It is postulated that such materials could have been introduced by the painters. Unfortunately, it is very difficult to detect these substances analytically. There is not enough evidence about the presence of these other “alike” pigments like ivory black, wine black, bone black, etc. [4, 5]) available to draw any conclusions about their role.

Table 7. Constituents and supposed causes for poor or good drying in the analysed 19th-century paint samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Oil</th>
<th>Pb carb.</th>
<th>Resins</th>
<th>Composition</th>
<th>Supposed cause poor drying</th>
<th>Supposed cause good drying</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ro2</td>
<td>P</td>
<td>+</td>
<td>ttp</td>
<td>+</td>
<td>HgS, sugars?</td>
<td>Pb carb.,</td>
</tr>
<tr>
<td>I2</td>
<td>L</td>
<td>+</td>
<td>(ttt,</td>
<td>+</td>
<td>B</td>
<td>HgS, B, Ph</td>
</tr>
<tr>
<td>Ro3</td>
<td>L</td>
<td>+</td>
<td>ttp</td>
<td>-</td>
<td>B</td>
<td>(ttt, dtp), Ph</td>
</tr>
<tr>
<td>I1</td>
<td>L/P</td>
<td>+</td>
<td>ttp,</td>
<td>-</td>
<td>B</td>
<td>B, C,H2n+2</td>
</tr>
<tr>
<td>Re1</td>
<td>L</td>
<td>+</td>
<td>ttp</td>
<td>(B)</td>
<td>(B), HgS</td>
<td>Ph, ttp, Pb</td>
</tr>
<tr>
<td>Ro4</td>
<td>L?</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>B</td>
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</tr>
</tbody>
</table>

In conclusion, all the analysed paint samples are characterised by a high abundance of organic materials in a complex matrix. The combination between such a composition, and a complicated painting technique seem to be the cause of the poor (physical and chemical) drying and darkening of these paintings and not the presence of a pigment like asphalt or Kassel earth. The restoration procedures like solvent cleaning and relining might be considered to be an additional cause in the deterioration of these paintings.
Discussion

As a starting point the prevailing viewpoint has been that pigments like asphalt, mummy containing asphalt and Kassel earth are the causes of poor drying in black-brown oil paintings from the 19th century. This belief was based on the information available in the literature about the materials and pigments used in the 19th century. Recipes from this period of paints containing asphalt [4, 5] in combination with remarks from the same period suggested that asphalt was included in paints, mainly after a heat pretreatment and that its use resulted in the formation of premature cracks in the paints. In a similar way it was supposed that mummy pigment is a pigment that should contain asphalt, at least this was one of the reasons why it was used. Another reason for the use of mummy pigments was their higher transparency than the transparency of asphalt paint and often a better behaviour in drying [4, 5]. Kassel earth pigment was used in the oil paint in the 19th century and preliminary results suggested it had an antioxidant activity in the drying of oil paint, rather similar to the asphalt pigment.

However when summarizing this research on this complex subject, other or new explanations have been found. Untreated asphalt indeed results in the poor drying of oil, which is clear from the DCM solution experiments. However analysis of heat pretreated asphalt has shown chemical modifications in the composition of asphalt. High temperatures applied to asphalt can be considered to resemble pyrolysis processes that result in a loss of aliphatic crosslinks and lead to an increase in the relative amount of aromatic compounds. A high amount of aromatic compounds is found also in carbon black pigments. The similarity of the roasted asphalt to carbon black pigments is possible and that would explain the slow oxidation of the oil component when either of these pigments are used. However such similarities were not investigated in this thesis. Nevertheless MS analysis of oil paints prepared with asphalt according to 19th-century recipes [4, 5, 24] and artificially light aged (ca 40 years of museum conditions) have unexpectedly indicated that the oil has dried to a great extent albeit with only small deformation, and wrinkles of the asphalt layers as reported by Boitelle [24]! The C_{18:1} : C_{18:0} FA ratio of oil from the aged artificially aged reconstruction samples is below one, compared with the ratio observed for the naturally aged asphalt oil paint (much higher than one). Nevertheless the time factor should not be totally neglected (the equivalent of 40 years museum ageing versus only 25 years of natural ageing.)

Oil paint containing the Kassel earth pigment without drier has shown a drying of the oil similar to lead white paint from the same series. From this it can be inferred that Kassel earth itself has no special influence on the drying of oil paint.

Analysis of 19th-century paintings supposed to contain asphalt or Kassel earth pigments have shown the presence of many other materials known to be the cause of poor drying of oil like megilp, vermilion, beeswax and other waxes, and polysaccharides. It can be inferred that the presence of the other non-drying constituents in the oil paint and the techniques used by the painters [7, 17, 20, 24] are more likely the causes for the disastrous poor chemical drying of oil paints in the 19th-century paintings and the physical behaviour and mobility of paint layers.
Conclusions

Artificial light ageing experiments and to some extent also natural ageing experiments on asphalt containing oil paints have shown the preservation of asphalt markers and biomarkers to some extent. Although the relative ratio between these compounds is modified in time or due to pretreatments of the pigment for example, hopanes, alkylbenzenes and alkynaphtalenes can survive for ca 40 years of museum conditions. However after 150 years no trace of hopanoids could be found in the analysed 19th-century samples. There are two possibilities: the absence of asphalt or its presence in such a form (degraded and cross-linked to the paint matrix) that makes it “invisible” for the mass spectrometer.

The effects of asphalt and of Kassel earth on the chemical drying of linseed oil paint were shown to be opposite. Asphalt has a strong antioxidant activity and retards the oxidation of oil paint. The formation of a network via cross-linking reactions is shown. Such a preference for cross-linking of triglycerides instead of oxidation is opposed to the situation observed for normal (linseed) oil paint. Interestingly but not totally unexpected, the overall drying effect of the oil paint is dependent on the composition of the paint including chemical modification due to heating of the pigments or solvent cleaning procedures.

Other ingredients than oil and asphalt like driers, resins or wax, when present completely change the drying behaviour of an “asphaltic paint”.

The investigations of samples from 19th-century paintings by Sir J. Reynolds, Th. Rousseau and J. Israëls very much agree with the observations made for artificially aged asphalt oil paints. Very little proof for the presence of geomaterials was found (few alkylphenols as lignite markers and long chain alkanes from a possible degraded asphalt although hopanes are absent; alkyl aromatics common for both Kassel earth and asphalt-like pigments were found). The chemical and physical behaviour of these paints is highly related to their complex composition rich in other non-drying components like vermilion, beeswax or megilps. The pretreatments of the pigments (roasting, melting, dewaxing) and restoration procedures (solvent cleaning and relining) certainly have an effect on the chemistry of the paint and the mobility of the paint layers.

References


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