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A multi-analytical study of early twentieth-century industrially produced cobalt blue paints from Edvard Munch's studio

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Abstract Based on the necessity of understanding the dynamics behind the darkening and degradation phenomena of cobalt blue oil paints observed in Edvard Munch's paintings, ten industrially produced cobalt blue oil paint tubes from the artist's studio were investigated. The synergic use of μ-Raman, ATR-FTIR, GC–MS and SEM–EDS techniques led to an overall characterization of the paints. The goal of this research was to further investigate the composition of these industrially produced cobalt blue oil paints and examine their implications in the observed deterioration and darkening phenomena in the blue painted areas in Munch's artworks. Pigments, binding media admixtures and additives present in the manufactured formulations were assessed. The analysed paints were characterized by complex mixtures, featuring the presence of non-drying or semi-drying oils, metal soaps and preservatives. Additionally, extenders, among others clay minerals and white pigments, and adulteration with other blue pigments were identified. The extensive detection of metal soaps in the analysed paint tubes, together with the specific deterioration patterns observed in Munch's paintings investigated, led to some preliminary considerations on the role of these components based on the reported literature.

1 Introduction, context and presentation of the case studies

This study stems from the necessity of understanding the dynamics behind the uneven darkening and degradation phenomena in some areas of Edvard Munch's paintings containing cobalt blue oil paints. Previous assessment concerning the conservation state of the paintings set the basis for understanding these phenomena [1, 2], but the full understanding of the mechanism behind them is far from being achieved. Three paintings have been observed with Hirox 3D microscopy in the cobalt blue degraded areas (Figs. 1 and 2).

The presence of this pigment has been mapped by elemental scans with MA-XRF in previous studies [1–3]. The present article sheds light on the topic investigating selected commercial oil paint tubes from the artist's studio, assessing the formulation of ten cobalt blue oil paint tubes in terms of binding media, additives and adulterants. This approach could help identify important factors affecting the stability of the paints, as well as provide insights into the composition of industrially manufactured oil paints used in modern artworks.

The same methodology was adopted for another important study on ultramarine blue paints, which was useful in understanding the composition and potential degradation issues related to this pigment found in commercial paints from Munch's atelier [4].

1.1 MUNCH's collection

The MUNCH museum's collection consists of close to 28,000 artworks, among which an impressive collection of original artist materials that have been found at the death of Edvard Munch on his property at Ekely and bequeathed to the City of Oslo. These materials represent an extremely relevant asset for research purposes both on the artist and on early modern artists' materials. The inventory includes palettes, brushes, easels, bottles with binding media and varnishes and early inventions of spray guns, as well as bags of dry pigments, crayons, watercolour boxes and a large collection of collapsible paint tubes, mostly used. Specifically, the vast variety of over 900 paint tubes, from thirty-one different brands and twenty manufacturers, represents an asset to this investigation as reference for historical industrial paint manufacture [4, 5]. The paint tubes came from several different countries, both from renowned and still operating paint manufacturers, like Winsor & Newton, and from now forgotten brands such as Ambor (France), manufactured by Morin et Janet [5]. Moreover, the collection of paint tubes covers a notably long period of time, spanning between

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Fig. 1 From top left: *The Death of the Bohemian* (1915–18), *Old Man in Warnemünde* (1907); *The Drowned Boy* (1907–1908)

1864 and mid-1940s [5]. A selection of ten cobalt blue oil paint tubes by eight different brands was made and studied for the current research project (see Experimental).

This study took its start from the recurrent observation of specific degradation phenomena in blue painted areas of Munch's paintings. Three canvas paintings from the Munch Museum collection were investigated using a Hirox 3D digital microscope: *Old Man in Warnemünde* (1907), *The Drowned Boy* (1907–1908), *The Death of the Bohemian* (1918–1920), as shown in Fig. 1. All three paintings appear to have areas where the paint is applied directly from the tube to the canvas—with long, thick lines of paint of approximately the same width, ending in bulging dots—and present extensive use of cobalt blue, as ascertained by previous studies [1–3]. In these areas where thick blue paint is applied, issues with adhesion to the underlying layers were noted, leading to significant cracking and paint loss and uneven darkening in the paint strokes. Moreover, the paint exhibited cohesion problems and was crumbly and porous, and the darkening was observed along the edges of cracks and thicker areas, progressing in a patchy way, with presence of black grains (Figs. 2 and 3).

1.2 Industrial manufacturing of modern paints

Since the invention of the collapsible metal tube in 1841 [6], the paint production industry has experienced significant growth, followed by the development of new formulations, often protected by patents. To extend the shelf life, maintain desired handling properties, accelerate the time of drying of the paint and reduce production costs, the simple and well-known composition of traditional oil mixtures of the previous times became increasingly complex. This complexity is attributed to the addition of extenders, additives, fillers and newly synthetized colorants and pigments [4–9]. Furthermore, alongside the traditional siccative oils (mainly linseed, poppyseed and walnut oils), other drying or semi-drying oils were introduced as cheap substitutes for linseed oil [6–9]. These additions and changes obviously influenced the final characteristics and behaviour of oil films, often exhibiting negative consequences and sometimes even unanticipated changes in some colours, which different authors have attributed to the interaction between the different components of the new formulations [1, 4–9].

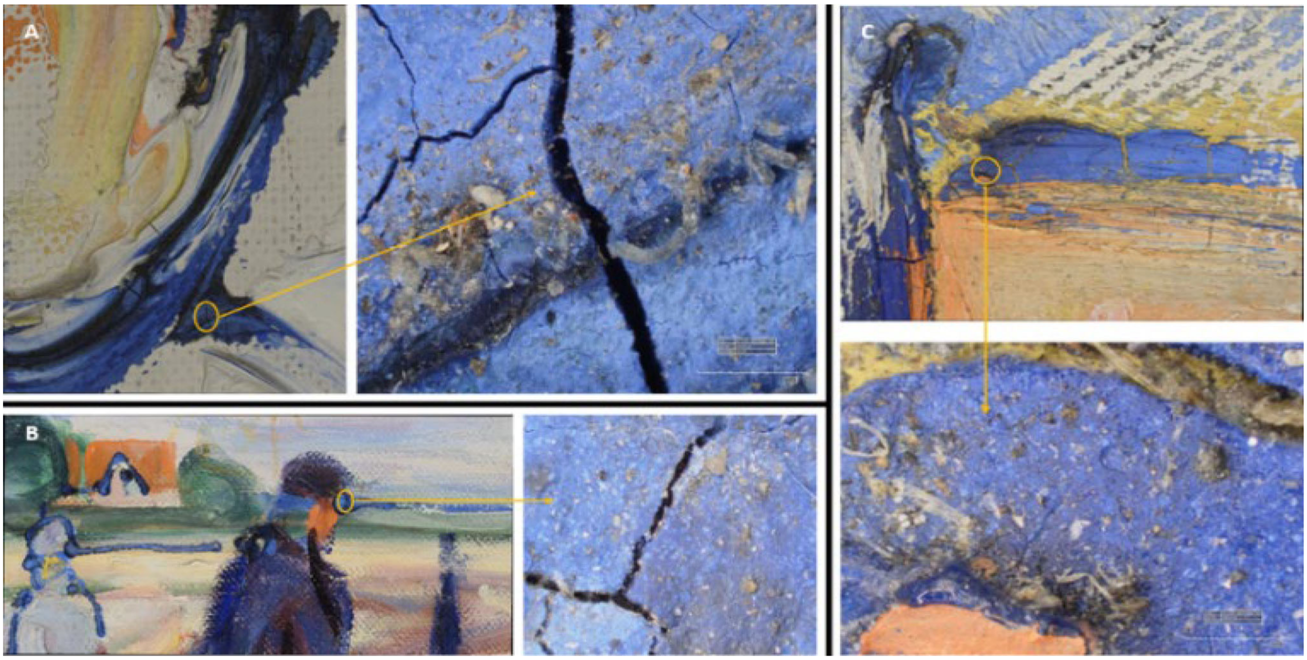

Fig. 2 Details from the case studies, showing dirt accumulation, darkening, cracking and loss of cohesion. **A** Detail from The Death of the Bohemian, left: 90 × scan, right:140 × detail; **B** detail from The Drowned Boy, left: 30 × scan, right: 140 × detail; and **C** detail from Old Man in Warnemünde, top: 90 × scan, bottom: 140 × detail

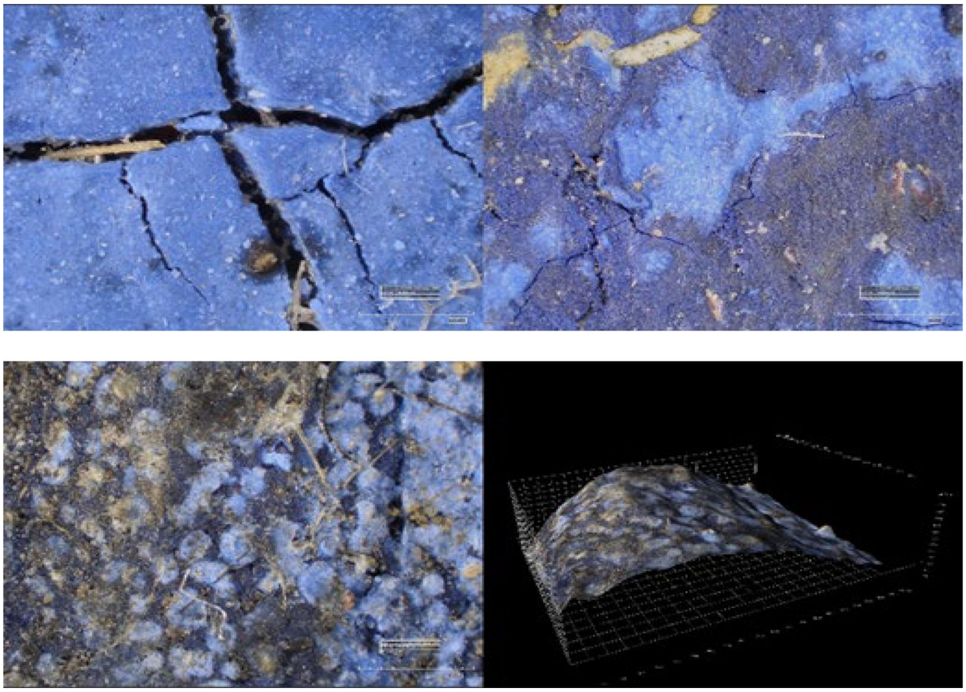

Fig. 3 Details of the three paintings investigated with the Hirox microscope. 140 × magnification lenses. From top left: detail from *The Drowned Boy* (1907–1908) (house in the background); detail from *Old Man in Warnemünde* (1907) (door in the background); detail from The Death of the Bohemian (1918–1920) (central figure's shoulder); and Hirox 3D image of the surface topography in correspondence of the detail from *The Death of the Bohemian*: it can be noticed how the lighter spots appears to be in correspondence of depressed areas

1.3 Cobalt blue pigment

Cobalt blue is a mixed oxide of cobalt and aluminium ($CoO \bullet Al_2O_3$) or alternatively cobalt (II)-aluminate ($CoAl_2O_4$). The structure of the mineral belongs to the class of normal spinel structure [10]. It became available as artist material soon after its discovery in 1803 by Louis Jacques Thénard, after whom it is also known as *Thénard blue* [10].

The production of the colour varied, implying the use of either arsenate and aluminate and/or arsenate phosphate, and therefore the final composition of the paint may vary according to the production process used [10, 11]. Many subsequent preparation mechanisms involve the coprecipitation of an insoluble cobalt salt (nitrates or sulphates) with hydrated alumina from a solution of alum [10].

Despite being one of the most expensive colours in artists' palettes in modern times, it seems that genuine cobalt blue rarely has been extended. Varieties of cobalt blue containing zinc white as an admixture yield greenish-toned blue, while the addition of zinc salts in the manufacture tends to counteract the violet undertone sometimes possessed by the pigment [10]. In a survey of modern pigments, it was found that cobalt blue used by several artists also contained chromium [11].

Cobalt blue is generally regarded as stable, which means that the pigment shows little or no reactions or changes when exposed to light, heat, chemical agents and/or chemical pollutants, in the atmosphere [9–11]. Early sources note that cobalt blue is not discoloured by hydrogen sulphate [9]. Nevertheless, in the early years after its development, it was observed that the pigment developed a greenish tone, ultimately darkening towards black if exposed to polluted air for prolonged time [9, 10]. This deterioration reflected the behaviour of a poorly made specimen, since insufficient heating of cobalt blue salts with alumina during the manufacturing process or impure ingredients would have affected the stability of cobalt blue [10]. This has been specifically ascribed to the reaction between the arsenate present as residue of production and the atmospheric sulphur, resulting in the formation of yellow arsenic sulphide [9]. Others attribute this effect to the yellowing of the oil medium [9, 10] or with the admixture with zinc white, leading to a greenish tinge [10]. These observations resulted in the shifting of the preferred production method towards the one implying the use of phosphate instead of arsenate.

The phenomena mentioned before are of particular interest for the present study, since it shows similarity with the identified darkening patterns in different paintings by Munch containing cobalt blue. For the purposes of this study, we consider it of great relevance to mention that cobalt (II, III) oxide (Co_3O_4) has a black colour.

Cobalt blue pigment is known for its drying properties. Nonetheless, cobalt blue has a very high oil-absorption index, meaning it needs a significant amount of oil to form a uniform paint film, which can be related to the activity of metal cations. Therefore, it can be expected that cobalt oil paint films, being highly absorbent, will experience slower drying times. Indeed, the catalytic activity during oxidative polymerization decreases with the content decrease in cobalt cations dissolved in the oil phase. In addition, both the size and shape of pigment particles as well as the presence of other minerals in the matrix might contribute to making the catalytic activity decrease [12, 13]. On the contrary, it can be expected that a greater quantity of pigment absorbed by the drying oil corresponds to a more important catalytic activity, and therefore, a greater drying speed with a consequent increase in the stiffness of the paint films has been observed in a study by Fuster-Lopez et al. [13], where mechanical properties of commercial paints containing cobalt blue have been investigated. Furthermore, in the same study, it was also observed that the addition of other drying agents modifies the activity of cobalt [13]. These observations are relevant to the context of this paper, as the mechanisms dictating the drying behaviour of the paint and its velocity, as well as the strategies adopted to speed it up, might result in unforeseen pigment-binder interactions leading to discoloration [4].

2 Experimental

The analytical methodology used complementary non-invasive and micro-invasive analytical techniques to gather relevant information both from the paintings and the paint tubes samples, as the ones adopted in [4].

2.1 Sampling

Ten samples were obtained from the selected tubes of cobalt blue oil paint, produced in the early twentieth century (Table 1).

2.2 Hirox 3D digital microscope imaging

A Hirox 3D Digital Microscope HRX-01 captured the images of investigated areas in the selected case studies, thanks to a ST-T500 Horizontal T-Stand (dimension 500 mm x 500 mm), which allowed for the inspection and automated XYZ scan of objects vertically placed. The lenses adopted were two: HR-1020E Telecentric polarized lenses for acquiring the scans ranging from 10 × to 90 × magnification and HR-2500E ranging from 20 × to 2500 × magnification for smaller details. The HRX-01 software was used to move in XY and Z axes to achieve automated stitching (gigapixel panorama), as well as 3D depth maps using focus variation.

2.3 ATR-FTIR spectroscopy

ATR-FTIR analyses were performed with an Alpha II Bruker spectrometer equipped with a synthetic diamond crystal, in the 4000 to 350 cm^{-1} wavelength region. The background was measured with 24 scans before each acquisition, while samples were investigated into 48 scans, 4 cm^{-1} resolution. Data were processed with OMNIC Specta 2.1.175 and Origin 2018 software.

2.4 µ-Raman spectroscopy

A DXRTM3 Thermo Scientific Raman Microscope coupled with 785 nm excitation laser was used to acquire µ-Raman spectra in the 3300 –100 cm^{-1} spectral range, with 5 cm^{-1} resolution. 20 to 100 scans were performed. The laser power and the time of scans

Table 1 List of paint tubes and analyses

Id Tube	Colour on label	Binder on label	Brand	Production country	Analyses performed
MM.I.01648	Bleu de cobalt Céleste	Oil	Ambor	France	ATR-FTIR, µ-RAMAN, GC–MS
MM.I.02117	Bleu de Cobalt	Oil	Lefranc	France	ATR-FTIR, µ-RAMAN, GC–MS
MM.I.02113	Bleu de Cobalt	Oil	Lefranc	France	ATR-FTIR, µ-RAMAN, GC–MS
MM.I.02216	Kobaltblau hell	Oil	Mussini ölfarben Schmincke	Germany	ATR-FTIR, µ-RAMAN, GC–MS, SEM–EDS
MM.I.01661	Blau de Cobalt glaukos	Oil	Ambor	France	ATR-FTIR, µ-RAMAN, GC–MS
MM.I.02198	Cobaltblau hell	Oil	Lusk & Holtz	Germany	ATR-FTIR, µ-RAMAN, GC–MS
MM.I.2302	Dunkel kobaltblau		Schoenfeld	Germany	ATR-FTIR, µ-RAMAN, GC–MS
MM.I.2328	Extra høy kobaltblaa	Oil	Vilhem Pact	Denmark	ATR-FTIR, µ-RAMAN, GC–MS
MM.I.02380	Cobalt blue	Oil	Winsor & Newton	England	ATR-FTIR, µ-RAMAN, GC–MS
MM.I.02265	Kobaltblau licht	Oil	Rembrandt Talens	Netherlands	ATR-FTIR, µ-RAMAN, GC–MS

were adapted to each sample, respectively, ranging from 4–18 mW and 1–5 s/scan. The acquisition and elaboration of the spectra were possible thanks to OMNIC Specta 2.1.175 software.

2.5 SEM–EDS

One sample (MM.I.02219) was analysed with scanning electron microscope (SEM) Jeol JSM-5600LV coupled with energy-dispersive spectrometer (EDS) Oxford Instruments ISIS Series 300, with a resolution of 133 eV at MnKα (5.9 keV). Secondary and back-scattered electron images were acquired, and EDS was used to perform both point analyses and mapping of selected significant elements (Co, Al, Sn, Pb and Na) identified with point analyses. The analysis was carried out in BES mode, low vacuum (80 Pa), working distance 20 mm. Spot analysis was carried out at accelerating voltage 40 kV and acquisition time 3 min for point, then the most significant elements for each spot were selected to acquire the maps, and the maps were acquired at 40 kV for around 15 min each, while 22 kV and the Scan4 mode were used for image acquisition. Isis SEMQuant software managed EDS spectra acquisitions, which were elaborated also with Origin8.5.

2.6 GC–MS

The GC–MS methodology adopted for the analysis of the organic fraction from paint tubes is the one proposed by Izzo [7] and further developments [4, 14–18], where all the experimental details and instrumental conditions are fully described and reported.

Both qualitative and quantitative analysis were performed. The GC–MS results were expressed in terms of molar ratios between significant fatty acids (i.e. P/S palmitic to stearic, A/P azelaic to palmitic, %D percentage of dicarboxylic acids, A/Sub azelaic to suberic, O/S oleic to stearic) to unravel specific characteristics of the binding medium and organic additives. The presence of peculiar fatty acids (considered as markers) was assessed through NIST library, and using a specific library created at Ca’ Foscari University for nineteenth–twentieth-century commercial oil paints [13, 15–19].

Table 2 Summary of results obtained from the analysed samples, divided into binding media and blue pigments detected and other organic and inorganic compounds identified. Binding medium identification is based on date reported in Table 6

Sample name	Binding admixture	Pigments	Minor organic compounds	Inorganic compounds
MM.I.01648—Ambor	Linseed oil	Cobalt blue	Metal soaps	Chalk, Aluminium oxide
MM.I.01661—Ambor	Linseed oil	Cobalt blue, Prussian Blue	Pinaceae resin, Animal fats	Aluminium oxide, Clay minerals, Cobalt oxide
MM.I.02113—Lefranc	Linseed oil + Sunflower oil?	Cobalt blue, Ultramarine blue	Venetian turpentine, Beeswax, Free fatty acids	–
MM.I.02117—Lefranc	Linseed oil + Sunflower oil?	Cobalt blue, Cobalt oxide	Metal soaps	–
MM.I.02198—Lusk & Holtz	Linseed oil	Ultramarine blue,	Shellac resin, added Stearates	Chalk
MM.I.02216—Mussini	Sunflower oil + Peanut oil	Cobalt blue, Cobalt oxide, lead white	Proline (protein?), Levulinic acid, Metal soaps (Lead soaps)	Lead sulphate, Lead white
MM.I.02265—Rembrandt Talens	Linseed oil	Cobalt blue, Cobalt oxide	Free fatty acids, Levulinic acid	–
MM.I.02302—Schoenfeld	Oil (Safflower/Sunflower oil?)	Cobalt blue, Cobalt oxide	Shellac resin, Pinaceae resin, Levulinic acid, Free fatty acids	–
MM.I.02328—Villh. Pacht	Oil (Sunflower/linseed oil? + Castor oil)	Cobalt blue, Prussian blue	Margaric acid, Shellac resin, Levulinic acid	–
MM.I.02380—W&N	Sunflower oil, Castor oil,	Cobalt blue, Cobalt oxide, Co-Zn spinel	Free fatty acids, Zn palmitate, Shellac resins, Pinaceae resin, Levulinic acid	–

3 Results

3.1 Paint surface observations in three paintings

Hirox 3D digital microscope was used to observe the condition and appearance of the paint surface: this permitted to assess the different degradation phenomena and their development in cobalt blue areas of the three paintings under investigation (Fig. 3). In all three paintings, the darkening appears to expand in a patchy way, affecting the whole thickness of the paint strokes, and darkened areas exhibit a crumbly texture, wet and waxy appearance between the cracks, dirt built-up around the brushstroke's hedges and the comparison of black crystals, together with the presence of lighter-coloured grains. In some areas, it was possible to observe a whitish efflorescence and alternation of discoloured and darkened spots, giving the surface the appearance of scales (Fig. 3, bottom).

3.2 Micro-invasive analyses

In Table 2, a summary of the analytical results obtained from all analysed samples is given.

With few exceptions, the analysed paint samples are composed of a cobalt blue pigment bound in lipidic binding media. The presence of a drying oil is confirmed both by ATR-FTIR (Fig. 4) and μ-Raman spectra thanks to the presence of peaks, respectively, at 2925 cm^{-1}, 2855–2850 cm^{-1}, 1740 cm^{-1}, 1710 cm^{-1}, 1625 cm^{-1}, 1460 cm^{-1}, 1410–15 cm^{-1}, 1242 cm^{-1} and 1165–60 cm^{-1} for ATR-FTIR, and at 3100–3000 cm^{-1}, 3000–2800 cm^{-1}, 2885–2880 cm^{-1}, 2855–2850 cm^{-1}, 1720 cm^{-1}, 1690 cm^{-1}, 1660 cm^{-1}, 1610–1600 cm^{-1}, 1440–30 cm^{-1}, 1380 cm^{-1}, ~ 1300 cm^{-1}, 1296 cm^{-1}, 1136 cm^{-1} and 1065–60 cm^{-1} for μ-Raman (see Tables 3 and 4 for the band attribution) [20–23]. Cobalt blue pigment was identified thanks to its characteristic peaks at 800 cm^{-1}, 650 cm^{-1}, ~ 550 cm^{-1} and 473 cm^{-1} in ATR-FTIR spectra and at 690 cm^{-1}, 620 cm^{-1}, 520–10 cm^{-1} and ~ 200 cm^{-1} in μ-Raman spectra [10, 24].

The presence of metal soaps is confirmed by ATR-FTIR and μ-Raman spectra in more than one case (samples MM.I.02216, MM.I.02380, MM.I.01648), as pointed out by the detection of characteristics peaks in the regions around ~ 1500 cm^{-1} (υ_a(COO) in metal soaps) in ATR-FTIR and ~ 1430 cm^{-1}, ~ 1290 cm^{-1}, ~ 1130 cm^{-1} and ~ 1060 cm^{-1} in μ-Raman [22]. Specifically, Pb stearate (peaks at 1461 cm^{-1}, 1441 cm^{-1}, 1295 cm^{-1}, 1173 cm^{-1}, 1126 cm^{-1}, 1063 cm^{-1} and 885 cm^{-1} in μ-Raman spectra [22]) and Zn soaps (broad peak at 1594 cm^{-1} in ATR-FTIR spectrum [21]) were identified, respectively, in samples MM.I.02216 and MM.I.02380 (Fig. 5). Spectroscopic analyses also revealed the presence of different compounds besides the expected ones. Specifically, μ-Raman allowed to detect the presence of different cobalt compounds and oxides (Co_3O_4) in several samples (MM.I.01661, MM.I.02117,

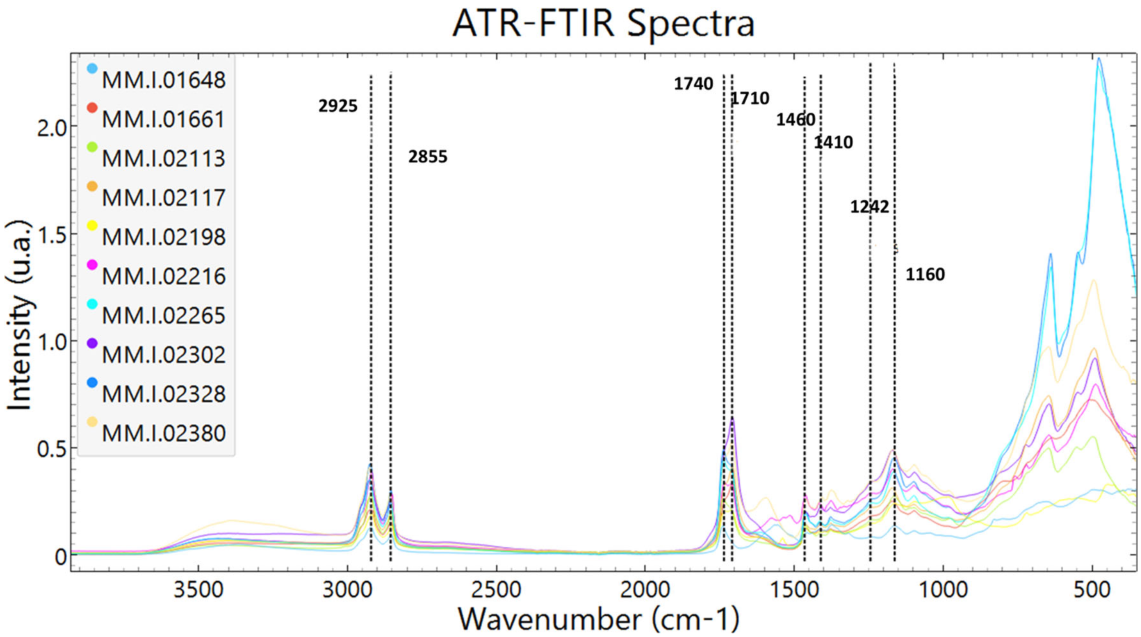

Fig. 4 ATR-FTIR spectra of the samples analysed showing the bands attributed to the presence of oil-based binding medium

Table 3 ATR-FTIR band attribution based on specific literature [10, 20–24]

Region (cm^{-1})	Band attribution
2925 cm^{-1}	$\upsilon_{as}(CH_2)$
2855–2850 cm^{-1}	$\upsilon_s(CH_2)$
1740 cm^{-1}	υ(C=O) in esters
1710 cm^{-1}	υ(C=O) in –COOH groups of free fatty acids
1625 cm^{-1}	υ(C=C) dialkyl; υ(C=O) amide I for proteins
1585–40 cm^{-1}	υ_a(COO) in metal soaps
1460 cm^{-1}	$\delta(CH_2)$
1410–15 cm^{-1}	$\delta(CH_2)$
1242 cm^{-1}	$\delta(CH_2)$; $\delta(CH_3)$
1165–60 cm^{-1}	C–O–C (ester) stretching
1095 cm^{-1}	υ(C–C) + δ(C–C-C)
800 cm^{-1}	Co–O in Cobalt blue pigment
650 cm^{-1}	Co–O in Cobalt blue pigment
~550 cm^{-1}	Co–O in Cobalt blue pigment
473 cm^{-1}	Al-O in Cobalt blue pigment

MM.I.02198, MM.I.02265, MM.I.02302, MM.I.2380) thanks to the presence of specific bands between 690 cm^{-1} and 170 cm^{-1} [24]. In the same region, cobalt–zinc aluminate spinel Zn:$Co_xAl_{3-x}O_4$ ($0 \leq x \leq 3$) was also detected in sample MM.I.02380 [24].

Another interesting finding is represented by the detection of Prussian Blue in μ-Raman spectra in correspondence of darker aggregates in samples MM.I.02328 and MM.I.01661, where the characteristic peaks at 2151 cm^{-1}, 2092 cm^{-1}, 533 cm^{-1} and 271 cm^{-1} have been identified [25]. In sample MM.I.02198, ultramarine blue was detected instead of cobalt blue in ATR-FTIR (980 cm^{-1}) and μ-Raman (580 cm^{-1}, 547 cm^{-1} and 252 cm^{-1}) spectra [25, 26].

Several inorganic fillers have been identified in the ATR-FTIR and μ-Raman spectra, such as clay minerals (ATR-FTIR spectra of sample MM.I.01661; broad band ~ 3400 cm^{-1}, 1095 cm^{-1} and ~ 700 cm^{-1}), Al oxides (ATR-FTIR spectra of samples MM.I.01661 and MM.I.02216; 719 cm^{-1} and 488 cm^{-1}) and calcium carbonate (μ-Raman spectra of sample MM.I.02198; ~ 1086 cm^{-1} and 288 cm^{-1}) [25–28]. Sample MM.I.02216 revealed the presence of lead soaps (1516 cm^{-1}, 1462 cm^{-1} and 1417 cm^{-1} in FTIR spectrum and 1440 cm^{-1}, 1417 cm^{-1} and 1294 cm^{-1} in μ-Raman spectrum) [22].

Table 4 Raman band attribution after [10, 20–24]

Region (cm^{-1})	Band attribution
3300–3100 cm^{-1}	υ(N–H), υ(O–H)
3100–3000 cm^{-1}	υ(= (C–H))
3000–2800 cm^{-1}	$\upsilon(C - H)$
2885–2880 cm^{-1}	$\upsilon_{as}(CH_2)$
2855–2850 cm^{-1}	$\upsilon s(CH_2)$
1720 cm^{-1}	υ(C=O)
1690 cm^{-1}	υ(C=O)
1660 cm^{-1}	υ(C=C) dialkyl; υ(C=O) amide I for proteins
1610–1600 cm^{-1}	υ(C=C)
~ 1540 cm^{-1}	Inorganic C
1440–30 cm^{-1}	$\delta(CH_2)$
1380 cm^{-1}	$\delta(CH_2)$
~ 1370 cm^{-1}	Inorganic C
~ 1300 cm^{-1}	υ(CC) alicyclic, aliphatic chain vibrations
1296 cm^{-1}	$\delta(CH_2)$
1136 cm^{-1}	$\delta(CH_2)$; $\delta(CH_3)$ asym
1065–60 cm^{-1}	υ(CC) alicyclic, aliphatic chain vibration
690 cm^{-1}	A_{1g} spinel vibrational mode in Cobalt blue pigment
620 cm^{-1}	F_{2g} spinel vibrational mode in Cobalt blue pigment
520–10 cm^{-1}	F_{2g} spinel vibrational mode in Cobalt blue pigment
~ 200 cm^{-1}	F_{2g} spinel vibrational mode in Cobalt blue pigment

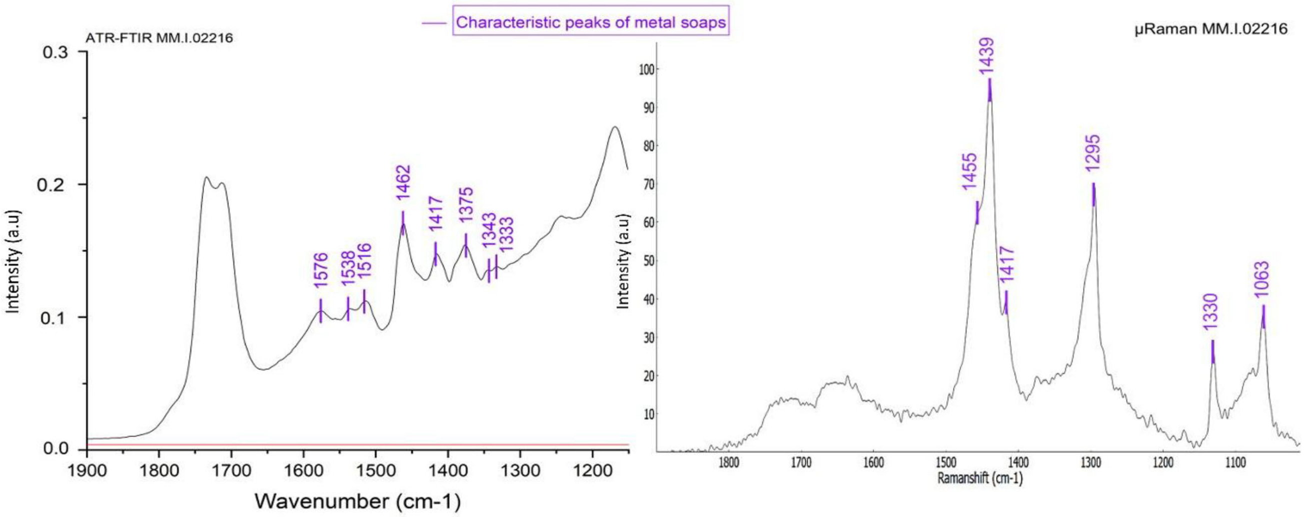

Fig. 5 ATR-FTIR (left) and μ-Raman spectra (right) of sample MM.I.02216 showing peaks attributed to the presence of metal soaps

3.3 SEM–EDS analysis

Sample MM.I.02216 was investigated also with SEM–EDS (Fig. 6), after being embedded in resin and covered by a 10 nm gold layer. From the BES image of MM.I.02216 (Fig. 6), the separation of the binding medium (darker area) from the pigment is clearly visible. The EDS results show the expected elemental composition of $CoAl_2O_4$, with small amounts of Pb and Sn in spectrum c, supposed to come from the collapsible tube made of tin.

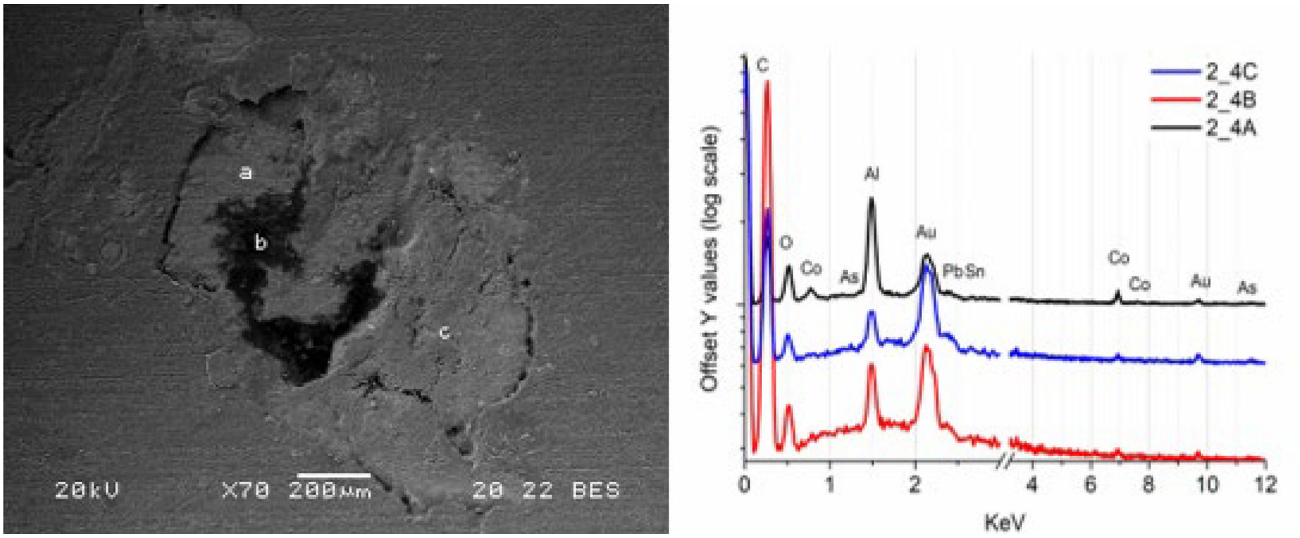

Fig. 6 SEM–EDS results for sample MM.I.02216. On the left side, back-scattered electron image taken at 70x, indicating the areas on which energy-dispersive spectroscopy was performed (spectra a, b, c)

3.4 GC–MS analysis

In general, the GC–MS results display all the typical fatty acid profile present in cured drying oil films (listed in Tables 5 and 6). These fatty acids include short-chain fatty acids, dicarboxylic acids (such as pimelic, suberic, azelaic and sebacic acids), as well as saturated long-chain fatty acids (such as myristic, palmitic, stearic, arachidic and behenic acids). Additionally, the presence of unsaturated fatty acids was detected, in particular oleic acid. The analysis also revealed the presence of glycerol (and its derivatives, according to the derivatization methodology).

Furthermore, a substantial presence of oxidised octadecanoic acids (among them: oxo-, hydroxy- and methoxy-octadecanoic acids) was detected, suggesting their formation as a result of the oxidative degradation of unsaturated fatty acids, originally present in the fresh oils used in the paint formulations [7, 13–16, 18, 29]. Similarly, the abovementioned dicarboxylic acids were found as the typical tertiary oxidation by-products resulting from the oxidative polymerization of the unsaturated fatty acids in the triglycerides within the cross-linked network [7, 13–16, 18, 29]. As concerns the degree of oxidation reached by samples, different molar ratios (%D, A/P and O/S, as reported in Table 6) can provide an overview: nevertheless, it has to be stressed that the condition and appearance of the paint tubes samples were different, ranging from completely dried out samples to tacky, still liquid and spreadable ones.

Few cases, in which the samples appeared to be dried and hard to the touch, revealed high concentrations of oleic acid. This can be determined by several factors: for instance, the thickness of the resulting film, the presence of different layers inside the sample with different degrees of oxidation or the formation of metal soaps (oleates).

As expected, in dried samples high content of palmitic and stearic acids was observed (with averages of, respectively, around 21% and 12.5%), compared to the unsaturated fatty acids originally present in the fresh oils. These saturated fatty acids are, in fact, supposed to be relatively stable during drying and curing, since they lack of instable double bonds that could function as active sites for the progression of oxidation and polymerization, differently from what happens for unsaturated linolenic, linoleic and oleic acids [7, 29].

The identification of the specific source of oil is often difficult to be achieved for modern and contemporary oil paints only by considering the P/S ratios, differently from traditional drying oils [7, 13–16, 18]. Nonetheless, the combination of both molar ratios and specific markers detected in the samples allowed for some hypotheses. Therefore, the binding admixtures reported in Table 2 were proposed according to qualitative and quantitative analyses and their comparison of ad hoc data in the literature [7, 29–32].

Table 7 summarizes the known P/S ratios and specific markers for different oils used as reference for our interpretation.

Linseed oil, safflower/sunflower oil, castor oil, peanuts oil and rapeseed oil were hypothesized to be present in some samples. It should be emphasized that while linseed oil, sunflower oil and safflower oil are indeed drying and semi-drying oils with known abilities to form durable and aesthetically pleasing films, other oils (e.g. castor seed oil) have no film-forming ability and can therefore be thought of as adulterants/additives in the paint admixtures.

Levulinic acid, whose use has been associated to preservative purposes, was detected in different samples (MM.I.02198, MM.I.02216, MM.I.02265, MM.I.02302, MM.I.02328 and MM.I.02380).

Moreover, alongside drying oils, the presence of minor (organic) addition of other materials has been assessed for almost all samples, thanks to the detection of specific markers. Aleuritic acid, one of the main aliphatic components of shellac resin, was

Table 5 Qualitative results for GC–MS analysis by brands. Fatty acids and other compounds are presented (as methyl esters)

	Detected compound	Ambor		Lefranc		Lusk & Holtz	Mussini	Rembrandt talens	Schoenfeld	Vilh. pacht	Winsor & Newton
		MM.I.01648	MM.I.01661	MM.I.02113	MM.I.02117	MM.I.02198	MM.I.02216	MM.I.02265	MM.02302	MM.I.02328	MM.I.02380
Compounds detected	Pimelic acid, methyl ester						v		v	v	v
	Levulinic acid, methyl ester					v	v	v	v	v	v
	Octanoic acid, 8-hydroxy-, methyl ester	V	v		v	v	v	v		v	
	Proline						v				
	Terephthalic acid, methyl ester										
	Decanoic acid, 9-oxo-ME	v	v		v					v	
	Caprylic acid, methyl ester		v	v	v						
	8-Methoxytetradecanoic acid	v	v	v	v				v	v	v
	Undecanedioic acid, 4-oxo-, dimethyl ester		v						v	v	v
	Butanoic acid, methyl ester					v	v	v	v		v
	Pentadecanoic acid, methyl ester		v			v	v	v			
	Palmitoleic acid, methyl ester	v	v	v	v		v	v	v	v	

Table 5 continued

Detected compound	Ambor		Lefranc		Lusk & Holtz	Mussini	Rembrandt talens	Schoenfeld	Vilh. pacht	Winsor & Newton
	MM.I.01648	MM.I.01661	MM.I.02113	MM.I.02117	MM.I.02198	MM.I.02216	MM.I.02265	MM.02302	MM.I.02328	MM.I.02380
Aleuritic acid, methyl ester, trimethyl ester					v			v	v	v
3-Oxo-1,8-octanedicarboxylic acid, dimethyl ester	v	v	v	v					v	
Margaric acid, methyl ester		v							v	
Marker stand oil			v							
Octadecanoic acid, 9,10-epoxy-, methyl ester	v	v	v		v	v		v	v	v
Octadecanoic acid, 10-oxo-, methyl ester	v	v	v	v	v	v	v	v	v	v
Methyl Dehydroabietate			v							
Octadecanoic acid, 9,10-dihydroxy-, methyl ester	v	v	v	v	v	v	v	v	v	v
Tetradehydroabietic, 7-methoxy-, methyl ester		v	v			x		v		v
Eicosane, methyl ester										
Ethyl stearate, 9,12-diepoxy						v		v	v	
Erucic acid, methyl ester					v	v	v			
Behenic acid, methyl ester	v	v	v	v	v				v	

Table 5 continued

Detected compound	Ambor		Lefranc		Lusk & Holtz	Mussini	Rembrandt talens	Schoenfeld	Vilh. pacht	Winsor & Newton
	MM.I.01648	MM.I.01661	MM.I.02113	MM.I.02117	MM.I.02198	MM.I.02216	MM.I.02265	MM.02302	MM.I.02328	MM.I.02380
Larixol acetate			v							
Methyl Ricinoleate									v	v
Heptacosane, methyl ester										
Lignoceric acid, methyl ester				v		v				
Hexacosanoic, methyl ester				v						
Docosane, methyl ester										
Cerotic acid, methyl ester										
Hentriacontane, methyl ester										
Melissic acid, methyl ester			v							

Table 6 Quantitative results for GC–MS analysis. Fatty acids and other compounds are presented in their methyl esters form, as a result of the preparation method adopted. Fatty acids presence is reported in percentage (%)

	Detected compound	Ambor		Lefranc		Lusk & Holtz	Mussini	Rembrandt talens	Schoenfeld	Vilh. pacht	Winsor & Newton
		MM.I.01648	MM.I.01661	MM.I.02113	MM.I.02117	MM.I.02198	MM.I.02216	MM.I.02265	MM.02302	MM.I.02328	MM.I.02380
Fatty acids (W%)	Suberic acid, methyl ester	6.10	14.01	2.42	9.89	9.64	12.82	10.06	17.84	9.85	11.16
	Azelaic acid, methyl ester	24.96	34.77	11.67	28.38	24.97	30.55	30.16	37.53	27.00	28.50
	Sebacic acid, methyl ester	2.24	6.08	1.33	3.86	3.25	6.15	3.03	5.00	2.63	5.43
	Myristic acid, methyl ester	1.54	1.25	1.06	1.30	3.91	1.32	1.53	1.46	1.41	1.15
	Palmitic acid, methyl ester	23.03	21.63	22.30	20.37	20.91	20.38	24.23	16.99	24.08	18.12
	Oleic acid, methyl ester	9.41	3.43	24.76	11.05	8.29	6.17	5.52	3.04	8.45	10.93
	Stearic acid, methyl ester	13.95	11.87	11.10	14.36	19.45	10.71	13.84	7.54	13.44	8.59
	Linoleic acid, methyl ester	6.21	0.19	15.03	0.26	0.09	0.09	0.05	–	0.22	0.28
	Linolenic acid, methyl ester	1.74	0.37	–	0.31	0.22	0.28	0.26	–	0.20	–
	Glycerol	10.82	6.40	10.34	10.23	9.27	11.53	11.31	10.61	12.73	15.85
Molar ratios among fatty acids	A/P	1.08	1.61	0.52	1.39	1.19	1.50	1.25	2.21	1.12	1.57
	P/S	1.65	1.82	2.01	1.42	1.08	1.90	1.75	2.25	1.79	2.11
	%D	33.29	54.86	15.41	42.13	37.86	49.52	43.25	60.37	39.48	45.09
	O/S	0.67	0.29	2.23	0.77	0.43	0.58	0.40	0.40	0.63	1.27
	A/Sub	4.10	2.48	4.83	2.87	2.59	2.38	3.00	2.10	2.74	2.56

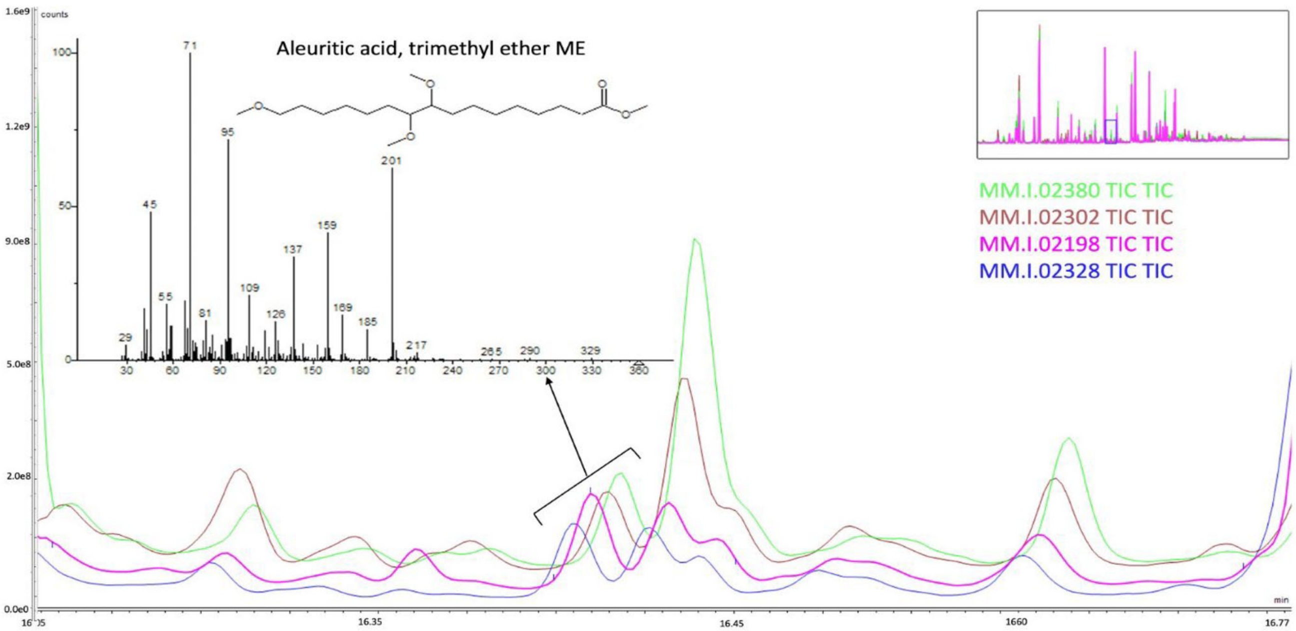

Fig. 7 Chromatograms and total ion current (TICs) chromatograms of samples MM.I.02198, MM.I.02302, MM.I.02328 and MM.I.02380, showing the presence of aleuritic acid. Mass spectra of aleuritic acid is shown

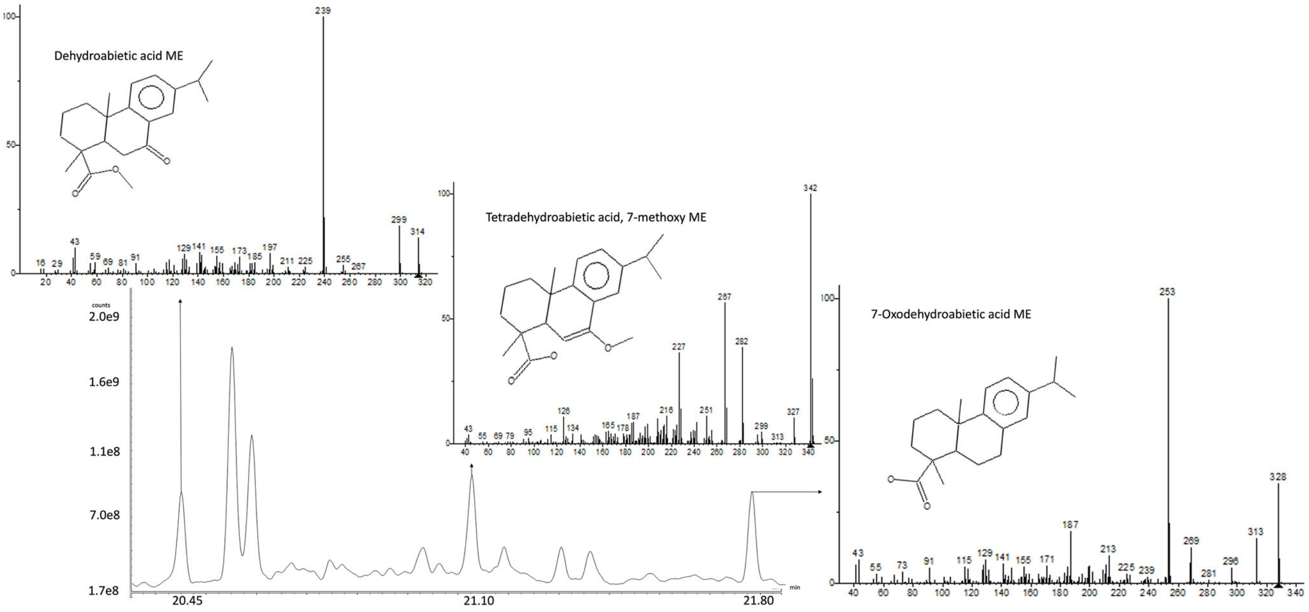

Fig. 8 Chromatogram of sample MM.I.02302. Peaks corresponding to Pinaceae resin markers (Dehydroabietic acid ME, Tetradehydroabietic acid, 7-methoxy ME and 7-Oxodehydroabietic acid ME) are shown, and their mass spectra reported

identified in samples MM.I.02198, MM.I.02302, MM.I.02328, MM.I.02380, suggesting the use of this component in the binding mixture [30] (Fig. 7).

The presence of at least one of the specific markers for the resins from the *Pinaceae* family (dehydroabietic acid, tetradehydroabietic, 7-methoxy-, 7-oxodehydroabietic acid) has been identified in samples MM.I.01661, MM.I.02113, M.I.02302 and MM.I.02380 (Fig. 8) [30].

In particular, sample MM.I.02113 shows the presence of the specific markers for Venetian turpentine (larixol and larixol acetate) [30]. Samples MM.I.01661 and MM.I.02216 showed the presence of margaric and pentadecanoic acids, which suggests the use of animal fat or other animal-originated compounds in these paints [33].

Even if the methodology adopted is specifically design to identify the lipidic and terpenic fraction, sample MM.I.02216 appeared to contain traces of proline, suggesting a protein-based component in the binding medium. The presence of margaric acid and

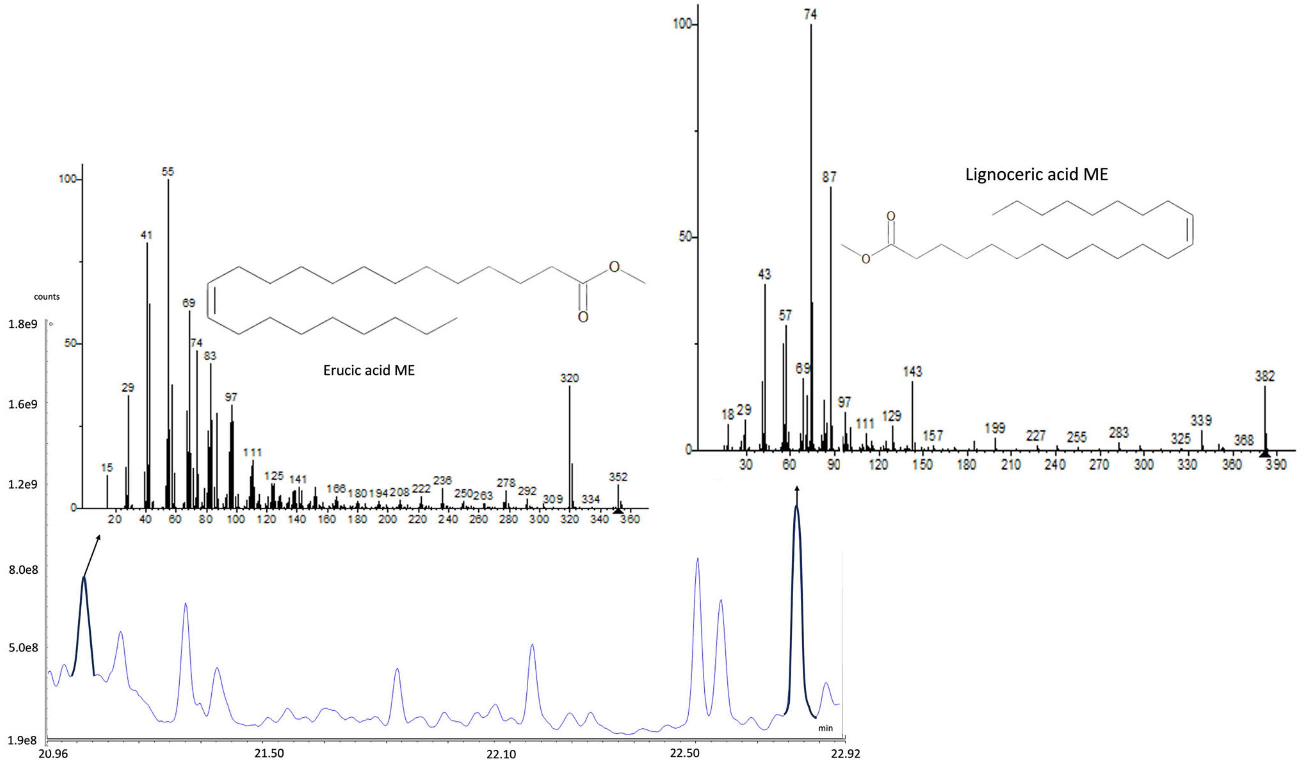

Fig. 9 Chromatogram of sample MM.I.02216. Peaks corresponding to erucic and lignoceric acid are shown, and their mass spectra reported

pentadecanoic acid, usually retrieved in animal fats more than vegetable oils, might confirm the presence of components of animal origin [33].

The A/P ratio is still consistent with the one expected for drying oils [7], suggesting that the presence of a proteinaceous component, which cannot be clearly detected with the derivatization method applied, is related to minor quantities. It is relevant to consider that *Mussini ölfarben Schmincke* was a famous brand for its production of temperas; therefore, complex formulations containing animal-based and proteinaceous materials are consistent with the peculiarities of this brand production. The presence of proteinaceous materials could be confirmed by the presence of a peak at 1534 cm^{-1} (bending N–H) in ATR-FTIR spectra.

Beeswax and other waxes have been identified in sample MM.I.02113 thanks to the presence of long-chain fatty acids and alkanes (lignoceric acid, melissic acid, cerotic acid, hexacosanoic, docosane, hentriacontane) (Fig. 9).

Lastly, azelaic-to-suberic acid ratios (A/Sub) might be useful to assess pre-heating treatments performed during oil preparation [7, 29]: in this study, certain samples interestingly showed values associated with the presence of pre-heated oils, ranging between values of 2.5–3 (see Table 6).

4 Discussion

4.1 Pigments, binding media and additives in industrial paint tubes

In the present study, we analysed ten paint tubes labelled as cobalt blue oil paints, by eight different brands, to uncover some of the characteristics of the commercial paints used by Edvard Munch and their production.

The complexity in the composition of the paints is rarely represented by the wording on the paint tubes labels, which are differentiated by the brand by which they were produced, and often differing among paints from the same manufacturer.

Besides linseed oil, other drying oils such as sunflower or safflower oil have been detected as substitutes. Beside, several frequent semi- or non-drying oils, including castor seed oil and peanut oil, have been identified. Indeed, peanut oil was identified within the *Mussini ölfarben Schmincke* brand. This is in accordance with what was recently found in a study concerning ultramarine blues by the same brand [4] and exposes the necessity of addressing specific conservation issues when preserving artworks that contain these components, as it has been discussed previously [4, 15].

Moreover, samples from the paint tubes produced by *Ambor* and *Mussini ölfarben Schmincke* showed traces of animal fat. This result is in accordance with the literature regarding *Mussini ölfarben Schmincke* [4] and represents a new finding *for Ambor* brands.

Table 7 Known P/S ratios and specific markers for different oils used as reference for our interpretation [7, 29–32]

Kind of oil	P/S	Any special fatty acid
Linseed oil	1.6 (±0.3)	–
Stand oil	1.3 (±0.4)	Cyclic compound (7-(o-pentylphenyl)-heptanoic acid; 9-(o-propylphenyl) nonanoic acid)
Poppy seed oil	3.9 (±1)	–
Sunflower oil	3.3 (±0.2)	Eicosanoic (arachidic) acid; Docosanoic (behenic) acid
Safflower oil	2.8 (±0.3)	Eicosanoic (arachidic) acid
Castor oil	1 (±0.1)	Hydroxyoctadecanoic (ricinoleic) acid; 9,12-dihydroxyoctadecanoic acid
Tung oil	4 (±0.2)	9,11,13-octadecatrienoic (α-eleostearic) acid
Cottonseed oil	9.5 (±0.5)	–
Soya been oil	3.8 (±0.5)	–
Rapeseed oil	3.7 (±0.3)	11-eicosenoic (gonoid) acid; 13-docosenoic (erucic) acid; 13,14-dihydroxydocosanoic acid
Peanut oil	3.7 (±1)	Tetracosanoic (lignoceric) acid; Docosanoic (behenic) acid

The common use of shellac resins in paint formulation is testified by the detection of aleuritic acid [30, 34] in many samples from different brands. Additionally, the detection of terpenic compounds from the *Pinaceae* family in many samples, either alongside or as a substitute for shellac resin, confirms the widespread inclusion of these materials in the production of early twentieth-century oil paints, likely serving as thickeners. In fact, besides *Rembrandt Talens*, no brand among the ones analysed showed the complete absence of such materials in the paint formulation (see Table 7 for more details).

Levulinic acid is another additive vastly implied in the paint formulations analysed from *Ambor*, *Lefranc*, *Mussini ölfarben Schmincke, Schoenfeld*, *Rembrandt Talens*, *Vilhem Pacht* and *Winsor & Newton*. The presence of this additive has been found to be used as a preserver, preventing microbial growth and prolonging shelf life [35].

The proof of the use of free fatty acids as additives to improve the consistency and rheological characteristics of the paint [14, 33] has been found in Vilhem Pacht paints, thanks to the detection of margaric acid.

Waxy materials (such as beeswax) were found in a tube by LeFranc as stabilizers to impart the right consistency and to keep the pigment in suspension [7, 15].

GC–MS analyses—even if the protocol used was aimed to mainly identify the lipidic, terpenic and waxy fraction—allowed to identify the presence of proteinaceous materials (proline) in a sample by *Mussini ölfarben Schmincke*. The complexity of this latter paint, which includes proteinaceous materials, resins, animal fats, waxes together with vegetable oils, suggests a mixture that cannot be identified as simply "oil" paint tubes, as it was instead reported on the original tube's label. This is in accordance with previously found in oil paints by this brand [4], which was also better-known for its temperas.

Few inorganic extenders have been also retrieved in the cobalt blue paints.

The composition of cobalt blue paints by *Ambor* was comprised of calcium carbonate, Al oxides and clay minerals.

Lead white was found in *Mussini ölfarben Schmincke* paint sample.

Zinc soaps have been found in at least a sample belonging to a cobalt blue paint by *Winsor & Newton.* Since neither ZnO nor any other source of Zn cations has been retrieved in those samples, their presence is to be attributed to the deliberate addition of such components to the paint formulations. Indeed, metal carboxylates have been commonly used as dispersion agents in oil paint formulations since the early twentieth century [7, 15, 29, 36]. The presence of Zn soaps is of particular relevance since their presence has been found to be the cause of different degradation patterns both as paint additives and as secondary products resulting from the interaction between the oil medium and the inorganic fraction [15, 16, 37].

Finally, other pigments have been found as adulterants or substitutions for cobalt blue in some of the paint tubes analysed, due to the high costs of this pigment.

Prussian blue has been found as an extender to cobalt blue paints in paint tubes by *Ambor* and *Vilhem Pacht*.

Moreover, ultramarine blue pigment has been found in small quantities in one of *LeFranc* cobalt blue paint tubes, and as a substitute of cobalt blue pigment in *Lusk & Holtz* "Cobaltblau hell" paint tube. These results are in accordance with what was found by the authors in a recent study concerning ultramarine blues by the same brands from MUNCH's collection [4], suggesting that the specific admixtures of above reported components represent a characteristic that differentiates the manufacturers and is consistent within the early twentieth-century paint production.

4.2 Considerations concerning the presence of metal soaps in paint tubes formulation and their possible role in the degradation patterns observed in Munch's paintings

Due to the extensive detection of metal soaps in the paint tubes analysed, together with the specific deterioration patterns observed in Munch's paintings investigated, some preliminary considerations on the role of these components based on the literature are reported.

Metal soaps are common additives used as dispersion agents [7, 36–38], as well as secondary products of the interaction between free fatty acids present in paints and metal cations present in the inorganic fraction of the paint [39–41].

Metal soaps are reported to be responsible for free fatty acids exudation from the paints, as well as efflorescence, formation of crater-like holes and ductile cracks [39, 42–44]. This phenomenon may generate a change in the pH of the surface that might eventually lead to corrosion and redox reactions, catalysed by the metal ions coming from cobalt blue pigment and other reactive metal ions [22, 45]. These transformations may explain the specific degradation pattern observed in *The Death of the Bohemian* painting (illustrated in Fig. 2, bottom), forming worm-like preferential corrosions and chemical alterations pathways [46]. Therefore, it is plausible that the redox process may be the reason behind the formation of black grains observed in the paintings.

It has indeed evidenced by Baij et al. [41] that metal soaps crystallization can lead to the breakdown of pigments.

Even in instances where redox reactions did not occur, the presence of metal soaps could still be responsible for the colour alterations observed on the painting: cobalt or other metal soaps might have crystallized forming darker aggregates [47]. The crystallization of these aggregates is consistent with what discussed by Hermans et al. [39], in which the authors pointed out that conservation treatments involving the use of moderately high temperatures (up to 70° C ca) could trigger the formation of metal soaps aggregates. As a matter of fact, treatment reports of the selected case studies point towards the use of hot spatula in different consolidation treatments, and conversations with the museum's conservators confirmed this as a fairly common practice for flattening of cupping of the paint layers up to recent years [48].

Furthermore, the presence of excessive quantities of stearates (more than 10–20% in weight) has been found responsible for the acquired water sensitivity, loss of cohesion due to reduced binding capacity of the medium and embrittlement of painted layers [11, 37, 49, 50], as well as efflorescence of fatty acids on the surface of twentieth-century paintings. These problems are among the ones observed and described for the Munch's case studies, supporting the hypothesis of metal soaps as a valuable explanation for these degradation phenomena.

As discussed by different authors, correlations between the presence of different additives and/or degradation products and water sensitivity as well as brittle and underbound paints have been found and proposed as possible causes [43, 51–53].

Burnstock et al. [51] suggested that the presence of aluminium and zinc stearates might be linked to a series of transformations in the paints that could explain the experienced water sensitivity in many twentieth-century paintings.

Tempest et al. [43] argued that the presence of added metal soaps can enable the presence of a low pigment volume paints, which could lead to a soft sticky film that never fully polymerizes, resulting in an open polymer network susceptible to swelling by polar solvents. Furthermore, free fatty acids, either as an integral additive or as a product of hydrolysis of the metal stearates, may migrate to the paint surface during drying of the film under normal environmental conditions, again enhancing the water sensitivity of the paint surface [43].

Even if it was not possible to compare the results of this study with samples from the paintings and validate the role played by the metal soap at this stage, many of the effects reported above have been observed in paintings from the Munch Museum collection, as been pointed out by Strand-Ferrer [1] and this study. The embrittlement of the paint resulting in cracking, losses and overall porous paint could have also contributed to the permeation of moisture and pollutants into the paint layers, further accelerating the chemical degradation of the paints.

Further analyses on paintings samples should be carried out to verify these hypotheses.

5 Conclusions

The results of this study shed light on the complex composition of industrial oil paints used in early twentieth-century artworks. Beside the significance related to the understanding of the industrial knowledge of paint manufacturers of that time, these findings are of high interest in the field of modern art materials due to their connection with Edvard Munch and his paintings. The study's extensive analysis reveals the complexity of these paint formulations and poses a challenge for the preservation of artworks, highlighting the importance of gaining a deeper knowledge of paint materials.

One of the central findings of the present research revolves around the distinct additives identified in the oil paints by the different brands investigated. Among them animal fats, resins like shellac and a *Pinaceae* resin, levulinic acid as a preservative and beeswax for consistency and stabilization were detected, illustrating the mismatch between original labels on the tubes and their content. The presence of Zn oxide and lead white further complicates the paint's composition and paint behaviour. The presence of various other metal soaps in more than one paint tube analysed was attributed to the intentional incorporation of these compounds into the paint formulations.

Furthermore, the study explored potential connections between degradation in paintings containing cobalt blue pigment and the paint tubes compositions, in relation to what reported in the literature.

Moreover, a comparison between the results obtained, the observations of Munch's paintings, their conservation history and the literature suggested the possible role played by metal carboxylates. The present study identifies this as a valuable research venue to be investigated in future studies.

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Author contributions Beatrice Giorgia Boracchi contributed to conceptualization, data curation, investigation, methodology and writing (original draft). Eun-Jin Strand Ferrer was involved in conceptualization and writing (original draft). Margherita Gnemmi contributed to investigation and methodology. Laura Falchi was involved in investigation. Irina Crina Anca Sandu contributed to conceptualization, resources, supervision and writing (original draft). Francesca Caterina Izzo was involved in resources, fundings, supervision, methodology and writing (original draft).

Data availability The authors confirm that the data supporting the findings of this study are available within the article.

Declarations

Conflicts of interest There are no conflicts to declare.

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