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Characterisation of preparation layers in nine Danish Golden Age canvas paintings by SEM–EDX, FTIR and GC–MS

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Abstract

This study explores the materials used in the preparation layers of nine paintings from the Danish Golden Age as a first approach to understanding the variation in use of materials in the nineteenth century as well as the potential for their degradation. Paintings on canvas have traditionally been suspected to be particularly sensitive to high moisture levels because of the changing quality of materials in the nineteenth century. The explanations have partly included the mechanisation of production methods and partly a more experimental approach to painting. Additionally, collagen-based glue sizing of the canvas is suspected to respond dimensionally to changes in relative humidity. In this study, pigments, fillers and binding media in the preparation layers of nine paintings by different artists were identified using scanning electron microscopy with energy dispersive X-ray spectroscopy, Fourier transform infrared spectroscopy and gas chromatography–mass spectrometry. The study shows a relatively low degree of variation in materials used in grounds. Surprisingly, no collagen-based binder was found in any of the nine paintings, suggesting that the canvases were not glue sized. All paintings contained calcium, lead, a drying oil and egg, even though only few contemporary recipes in painter's manuals included egg as an ingredient for preparation layers. These results suggest that the commercial producers of prepared canvas may not have followed the manuals that were written for painters. Egg may have been added in order to increase flexibility and durability of ready primed canvases that were stored and sold in rolls. Moreover, the egg–oil emulsion has the advantage of being more viscous than a pure oil paint and could thus be used without sizing the canvas, rendering the primed canvas less stiff and less responsive to changes in relative humidity. The advantages of using egg in the ground are obvious, and this use, as well as the lack of glue size, has implications for the long-term preservation of the paintings in changing environmental conditions. These results imply that these particular paintings might be less sensitive to relative humidity changes than expected due to the lack of hygroscopic glue.

Keywords: Danish Golden Age paintings, Nineteenth century, Preparation layers, Egg–oil emulsion ground, Gas chromatography–mass spectrometry (GC–MS), Fourier transform infrared spectroscopy (FTIR), Energy dispersive X-ray spectroscopy (SEM–EDX), Moisture sensitivity

Introduction

Danish Golden Age paintings were painted in the first half of the nineteenth century and are highly esteemed as an invaluable part of Danish cultural heritage. The painters involved in this study are Christoffer Wilhelm Eckersberg (1783–1853), also called 'the father of Danish painting', and some of his most famous pupils at the Royal Danish Academy of Fine Arts: Christen Schillerup Købke (1810–1848), Wilhelm Bendz (1804–1832) and Carl Christian Constantin Hansen (1804–1880), as well as Johan Thomas Lundbye (1818–1848), who was the pupil of professor J.L. Lund, Eckersberg's colleague at the academy.

This study concentrates on how the canvases used by these painters were prepared before paint application. The

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purpose of the preparation layers was to produce a uniform background for the painters to work on. In some cases, the procedure for preparing a canvas included sizing, which was the application of a layer of glue from bones, mammal skin, fish swim bladders, or flour paste to the raw canvas [1]. On top of this glue layer, one or more ground layers containing pigment, fillers, and binding media would then be applied. In some cases, a brownish or reddish layer with more inexpensive materials such as ochre or chalk that was bound in oil or suspended in an emulsion was used to fill the voids of the canvas. A thinner layer of more expensive materials was then added to supply the desired background colour. In some cases, painters probably applied their own ground(s) on top of a commercially primed canvas [2, 3].

The colour and texture of the ground layer could influence the tonality and surface appearance of the finished painting; in addition, the materials chosen for the preparation layers can affect the way a painting age. In Denmark as well as abroad, canvas paintings of the nineteenth century have been suspected to be extra sensitive to humidity and water, which cause shrinkage and cracking [4–6]. Theories regarding variations of preparation layers can be investigated through studies of historic recipes and mock-ups but, to understand the full potential of the preparation layers for influencing degradation, the historic painting materials must be characterised through analyses.

Colour and preparation layers have been studied for some painters from the Danish Golden Age [4, 7] as well as the previous generation. Thus, we know that there was a shift in the use of colours of grounds (from coloured to white) in Denmark from Nicolai Abildgaard [8] through Jens Juel [9] to Christoffer W. Eckersberg [7]. Previous studies furthermore suggest that painters primarily painted on Danish-produced canvases due to the high customs duties on canvases during the first half of the nineteenth century [5]. This behaviour suggests that canvases were locally produced and prepared except for a few specific instances. Eckersberg's journals show that he bought ready-primed canvases or employed a local craftsman to prepare his canvases [4, 7].

For a canvas that was prepared for commercial sale, we may assume that there were practical issues to consider such as their rolling, storing and shipping [10]. These issues means that flexibility would be an issue of importance, and the binding media plays a significant role in defining these qualities. Certain materials such as collagen-based glues would increase both stiffness and hygroscopic behaviour if used in the preparation of the canvases and might cause failure in the added paint layer [11, 12], whereas we would expect oils to provide more flexibility and less reactivity to moisture.

Recipes suggest that the binding media in grounds in the first half of the nineteenth century were mainly oil or glue or a mixture of both, but a variety of other materials was also introduced. The use of starch is well known [2, 13] and, used less frequently, casein, egg and natural rubber [14]. Grounds were required to have a certain absorbency, which was achieved with glue or an emulsion of oil and water as a binder [15]. However, as mentioned, a certain flexibility that would allow the primed canvases to be rolled for storage or shipping would have become increasingly important with the commercialisation of prepared canvases. It must have been a difficult balance to strike, as more oil provided more flexibility but less absorbency.

This study explores the materials (organic and inorganic components) used in the preparation layers of nine Danish Golden Age paintings in order to improve our understanding of the manufacturing processes and to achieve an impression of the degree of variation in the ground and size layers used at the time. It is furthermore a first approach to understanding the potential for physical degradation by mechanisms such as mechanical stress and to understand the possible sensitivity to changes in relative humidity in order to improve the decision-making platform for conservation and storage of the paintings.

Experimental methods

Golden age painting samples

Statens Museum for Kunst (the National Gallery of Denmark, SMK) possesses a number of samples from the tacking edges of paintings, which include the most prominent Danish Golden Age artworks. These samples were removed by conservators in the first half of the 1960s before conservation treatment, which was usually the application of a wax resin lining. This removal was done in order to have material for later research, and the samples are rather large by modern standards. The size varies from 2 × 50 mm to 20 × 240 mm.

Samples from paintings by influential artists have been chosen for this study (Table 1) and represent different trends and periods of the Danish Golden Age. The paintings furthermore represent different genres (portraits, landscapes and seascapes); two of the nine paintings were executed outside Denmark, namely, in Paris (no. 3) and Rome (no. 4). These canvases were therefore likely to have been prepared abroad.

The following techniques were used for the analytical investigation of the materials in ground samples:

Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM–EDX)

SEM–EDX was performed on cross sections taken from the pieces of tacking edge that were removed during conservation in the 1960s (see Table 1). Samples were

Table 1 Nine selected paintings

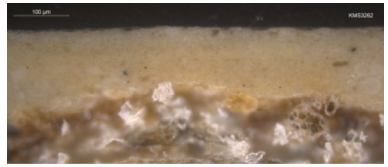
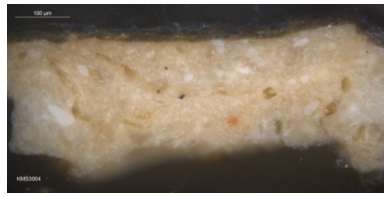
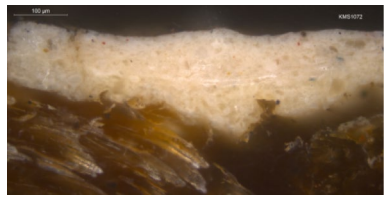
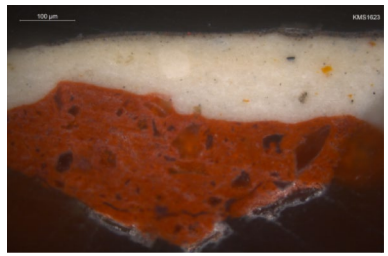
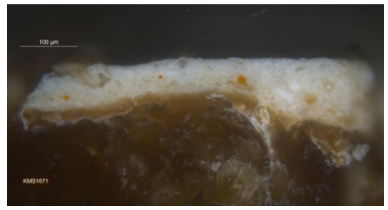
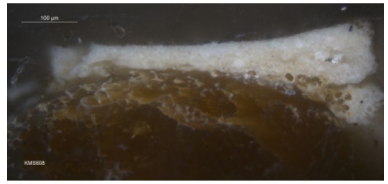
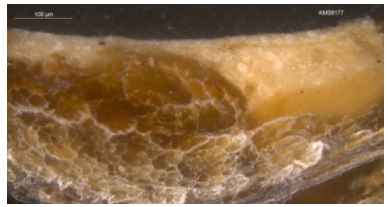
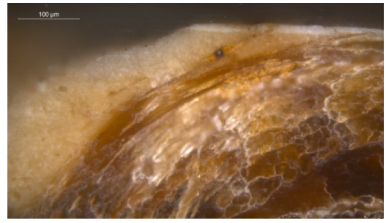
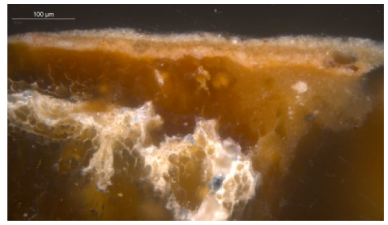
No.	Title artist, year, dimensions no., SMK painting accession no.	Cross section (dark field)	Conservation treatment
1	"The Opera Singer Christoffer Hvid", Bendz, W. 1825–27, 38.5 × 31 KMS3262		Previous conservation: 1913 glue–paste lined and new stretcher; 1964 wax–resin lined. Glue–paste residue and traces of paper are probably from the glue–paste lining from 1913
2	"The Artist's Sisters Signe and Henriette Reading a Book", Constantin Hansen, C.C., 1826, 65.5 × 56.0, KMS3004		Restored (method unknown) 1910, cleaned and "steamed" 1944, wax–resin lined 1963
3	"The Vesta Temple in Rome", Constantin Hansen, C.C. 1837, 75.5 × 100.0, KMS1072		Wax–resin lined in 1963. This painting was painted in Italy
4	"A View from the Château of Meudon", Eckersberg, C.W. 1813, 55.5 × 71.0 KMS1623		The painting was glue–paste lined in 1899 and wax–resin lined twice in the 1960s due to severe cracking. The red ground layer has poor adhesion to the canvas
5	"A Russian Fleet at Anchor near Elsinore", Eckersberg, C.W. 1826, 31.5 × 59.0 KMS1671		1901: new stretcher; 1912 cleaned; 1964 wax–resin lined (no previous lining)

Table 1 continued

No.	Title artist, year, dimensions no., SMK painting accession no.	Cross section (dark field)	Conservation treatment
6	"The Russian Ship of the Line "Asow" and a Frigate at Anchor in the Roads of Elsinore", Eckersberg, C.W. 1828, 63.0 × 51.0 KMS608		1906: yellow varnish possibly removed. Wax–resin lined 1963, no previous lining, good condition
7	"Nude Figure Sitting Boy" Købke, C.S. 1833, 58.3 × 48.7 KMS6177		The painting was wax–resin lined in the 1960s, but the detailed written report disappeared from the conservation archive
8	"Portrait of the Decorative Artist G.C. Hilker", Købke, C.S. 1837, 65.0 × 54.5 KMS1081		The painting was wax–resin lined 1963/64 and had no previous lining. There is an extensive crack pattern in the painting surface
9	"A Croft at Lodskov near Vognserup Manor, Zealand", Lundbye, J. Th. 1847, 71.0 × 93.0, KMS1644		1963: wax–resin lined

Cross sections were cut from the tacking edge of samples. Canvas has been included in order to make sure that all preparation layers were included

embedded in Serifix resin from Struers (methyl ethyl ketone peroxide, butanone and dimethyl phthalate), and the cross sections were polished with sandpaper. Cross sections were analysed in order to obtain elemental information using a Hitachi S-3400N equipped with a Bruker detection system. Spectra and elemental maps were recorded using 20-kV voltage, 50-μA probe current and 10-mm working distance.

Fourier transform infrared spectroscopy (FTIR)

A sample of the ground (approximately 0.5 × 0.5 mm) was taken with a scalpel. The sample was positioned in a Perkin Elmer Spectrum 100 Fourier transform infrared (FTIR) apparatus equipped with an attenuated total reflectance (ATR) diamond/ZnSe crystal. The side that had been closest to the canvas was in direct contact with the ATR crystal. Spectra were acquired in the range from 4000-650 cm^{-1} with a spectral resolution of 4 cm^{-1} and at a pressure of 100 N for 4 scans. To corroborate SEM–EDX results from the different layers, cross sections of sample numbers 4 and 9 (KMS1623 and KMS1644) were also measured by micro fourier transform interferometer (μFTIR). In these two specific cases, FTIR analyses were performed with a Bruker Tensor 24® spectrometer coupled to a Hyperion® 3000 microscope that was equipped with a focal plane array (FPA) detector. Measurements were performed in ATR mode with a 20× germanium crystal objective with a refractive index of 4.01 that has an anvil design in an 80-μm tip. An average of 32 scans was used in an accumulation range of 900–3600 cm^{-1} and at a spectral resolution of 4 cm^{-1}.

Gas chromatography–mass spectrometry (GC–MS)

Samples (between 0.2 and 1.0 mg in weight) were analysed with an analytical procedure based on a wet chemical pretreatment of the sample that includes extraction, desalting and hydrolysis steps. This procedure was done in order to separate the same microsamples into three fractions so that they could be separately analysed by GC–MS. The three fractions were: a *saccharide* fraction (solution of persilylated dithioacetal derivatives of aldoses and uronic acids that were derived from the hydrolysis of saccharide materials), an *amino acid* fraction (solution of tert-butyldimethylsilyl derivatives of amino acids that were derived from the hydrolysis of proteins) and a resinous lipid fraction (solution of trimethylsilyl derivatives of acids, alcohols and neutral compounds that were derived from the hydrolysis of lipids, resins and waxes). The procedure is described in detail in the literature [16].

A 6890N GC system gas chromatograph coupled with a 5973 mass selective detector single-quadrupole mass spectrometer equipped with a split-splitless injector and a 6890N GC system gas chromatograph (Agilent Technologies, Palo Alto, CA) coupled with a 5975 mass selective detector single-quadrupole mass spectrometer equipped with PTV injector, also by Agilent Technologies, were used. The MS transfer line temperature was 280 °C; the MS ion source temperature was kept at 230 °C, and the MS quadrupole temperature was at 150 °C. For the gas chromatographic separation, an HP-5MS fused silica capillary column (5% diphenyl/95% dimethyl-polysiloxane, 30 m × 0.25 μm i.d., 0.25 μm film thickness, Agilent Technologies) with a deactivated silica precolumn (2 m × 0.32 μm i.d.) was used. The carrier gas was used in the constant flow mode (He, purity 99.995%) at 1.2 mL min^{-1}. The mass spectrometer was operated in the positive EI mode (70 eV), and MS spectra were recorded both in total ion current (TIC) and single ion monitoring (SIM) modes.

Results

SEM–EDX and FTIR-ATR data are summarised in Tables 2 and 3, and GC–MS data relative to the three analysed fractions are reported in Tables 4, 5 and 6.

For the characterisation of the source of the proteinaceous material, the amino acid profile of each sample whose protein content was above the quantitation limit of the procedure was subjected to a multivariate statistical analysis that included a data set of 121 reference samples of animal glue, casein, and egg (whole egg, albumen and yolk) [17] using principal component analysis (PCA). The resulting score plot is presented in Fig. 1.

PCA score plot relative to the ground samples with a protein content above the QL, using a database of reference samples of animal glue, casein and egg.

Table 2 Elements identified by SEM-EDX on the nine selected paintings

No.	SMK accession no.	Elements
1	KMS3262	*Pb*, Ca (Al)
2	KMS3004	Ca, Pb (Si, Al, Fe, Na)
3	KMS1072	*Pb*, Ca (Mg)
4	KMS1623	Whitish layer: *Pb* (Ca, Al, Si, Fe, K) Red layer: Si, Fe, Al (Ca, K, Pb/S)
5	KMS1671	*Pb*, Ca (Al)
6	KMS608	*Pb*, Ca (Al)
7	KMS6177	*Ca*, Pb (Si, Mg, Al, K)
8	KMS1081	Whitish upper layer: *Pb* (Ca) Lower layer: *Ca* (Pb, Si)
9	KMS1644	Whitish and yellow upper layer: Pb, Ba, Fe (Si, Al, Na) Inter layer: particles of Si, Al, Na Lower layer: Ca

Italics elements are present in relatively high levels. Elements in parentheses are present at trace levels. Pb (lead), Ca (calcium), Al (aluminium), Si (silicon), Fe (iron), Na (sodium), Mg (magnesium), K (potassium), S (sulphur), and Ba (barium)

Table 3 Absorption features in the region between 4000 and 600 cm^{-1} and their assignments in the FTIR-ATR spectra of the samples collected from the ground samples

No.	SMK accession no.	Lipids	Proteins	Calcium sulphate and/or other compounds	Calcium carbonate	Lead carbonate (basic)
1	KMS3262	2921 s 2852 s 1720 sh	1638 s 1530 s 1327 sh 1240 w 1208 w 1151 w 1078 sh 1030 sh	ca. 1100 br	2515 sh 1795 w 1384 s br 875 vs 715 s	3536 sh 1400 s br 1045 s 756 br 680 s 838 s (neutral)
2	KMS3004	2921 m 2852 m 1708 w	1638 m 1530 vw 1151 w	Silicate ca. 1000 s br	2515 sh 1795 w 1391 s br 875 vs 715 s	1400 s br 756 br 680 s
3	KMS1072	2921 s 2852 s 1738 + 1715 sh	1638 s 1530 s 1327 sh	3530 w 3403 w 1622 w 1110 s br	1393 s br 875 vs 715 s	3536 sh 1400 s br 1045 s 756 br 680 s
4	KMS1623 Top layer	2921 s 2852 s 1730 sh				1400 s br 1045 s (+Pb carboxylates ca. 1515 cm^{-1})
	KMS1623 Bottom layer	2921 s 2852 s 1730 sh	1638 br 1537 br	Silicate ca. 1000 s br	1393 w br (carbonate)	
5	KMS1671	2921 s 2852 s 1720 sh	1638 s 1530 s 1327 sh 1240 w 1208 w 1151 w 1078 sh 1030 sh	ca. 1100 br	2515 sh 1795 w 1384 s br 875 vs 715 s	3536 sh 1400 s br 1045 s 756 br 680 s 838 s (neutral)
6	KMS608	2921 s 2852 s 1710 sh	1638 s 1530 s 1151 w 1030 sh	ca. 1100 s br ca. 673 w	2515 sh 1795 w 1384 s br 875 vs 715 s	3534 1400 s br 680 s 838 s w (neutral)
7	KMS6177	2921 s 2852 s 1738 sh 1715 sh	1638 s 1530 s 1327 sh 1240 w 1078 sh 1030 sh	3530 w 3403 w 1110 s br 673 s	1393 s br 875 vs 715 s	1400 s br 680 s
8	KMS1081	2921 s 2852 s 1720 m	1638 m 1530 m 1327 sh 1240 w 1208 w 1151 w 1078 sh 1030 sh	1620 br (w?) 1110 s (w?) 673 s (w?)	2515 sh 1795 w 1384 s br 875 vs 715 s	3536 sh 1400 s br 1045 s 756 br 680 s

Table 3 continued

No.	SMK accession no.	Lipids	Proteins	Calcium sulphate and/or other compounds	Calcium carbonate	Lead carbonate (basic)
9	KMS1644 Top layer	2921 s 2852 s 1730 sh		$BaSO_4$ with bands ca. 1170, 1112, 1075, 981 s		1400 s br 1045 s (+Pb carboxylates ca. 1515 cm^{-1})
10	KMS1644 Bottom layer	2921 s 2852 s 1738, 1710 sh 1169 w 1094 w			2515 sh 1795 w 1389 s br 875 vs 715 s	

Regarding basic lead carbonate, it is only possible to identify the main components due to the overlap of calcium carbonate, lead carbonate and calcium sulphate peaks. Lead carboxylates could also be present, with bands approximately 1500 and 1400 cm^{-1}; however, because the peaks are located on the same wavelengths as proteinaceous compounds and carbonates, they cannot always be identified

s sharp peak, *m* medium peak, *w* weak peak, *br* broad band, *v* very, *sh* shoulder band

Table 4 Amino acid profile (%) of samples with a protein content above the detection limit (DL) or quantitation limit (QL)

No.	SMK accession no.	Ala	Gly	Val	Leu	Ile	Ser	Pro	Phe	Asp	Glu	Hyp	Protein content
1	KMS3262	9.7	9.1	9.5	13.3	8.3	3.8	6.5	7.0	16.7	16.1	0.0	>QL
2	KMS3004	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	No	>DL <QL
3	KMS1072	12.4	3.5	6.4	10.2	4.9	8.1	6.6	5.7	13.8	28.4	0.0	>QL
4	KMS1623	6.0	15.7	5.1	11.1	4.9	5.9	10.6	7.5	6.5	26.5	0.0	>QL
5	KMS1671	13.8	13.9	13.0	19.2	11.9	7.2	1.8	6.1	10.4	2.7	0.0	>QL
6	KMS608	4.2	2.7	5.4	8.7	5.2	37.5	1.3	1.5	13.1	20.3	0.0	>QL
7	KMS6177	8.5	14.3	8.6	14.3	8.3	5.0	6.0	8.6	14.7	11.6	0.0	>QL
9	KMS1644	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	No	>DL <QL

Table 5 Characteristic parameters related to the identification of the source of the glycerolipid material in those samples with a lipid content above the QL

No.	SMK accession no.	A/P (azelatic acid/palmitic acid)	P/S (palmitic acid/stearic acid)	O/S (oleic acid/palmitic acid)	Σ Dicarboxylic acids %
1	KMS3262	1.4	1.4	0.0	49
2	KMS3004	2.6	1.3	1.3	63
3	KMS1072	1.1	3.7	–	36
4	KMS1623	2.6	1.3	0.1	63
5	KMS1671	1.5	1.3	0.0	51
6	KMS608	0.9	3.0	0.4	43
7	KMS6177	1.7	0.9	0.0	51
8	KMS1081	0.8	2.0	2.0	29
9	KMS1644	1.5	1.3	0.0	52

The meaning of the reported parameters are discussed in detail in the literature [20]

To determine the source of the saccharide materials, the data were compared to a database of saccharide profiles of reference materials [18], and when polysaccharide gums were hypothesised, they were identified using a decisional scheme that was reported in the literature [19]. The interpretation of the chromatograms relative to the lipid-resinous fractions was based on the recognition of molecular markers for resins and waxes and quantitative evaluation of mono and dicarboxylic acids for lipids [20].

Table 6 Relative aldose and uronic acid content (%) of samples with a sugar content above the DL

No.	SMK accession no.	Xylose	Arabinose	Rhamnose	Fucose	Galact uronic acid	Glucuronic acid	Glucose	Mannose	Galactose	Sugar content
1	KMS 3262	0	0	0	0	0	0	36	59	6	>QL
5	KMS 1671	0	0	0	0	0	0	34	58	8	>QL
9	KMS 1644	18	4	2	0	0	0	52	7	17	>QL

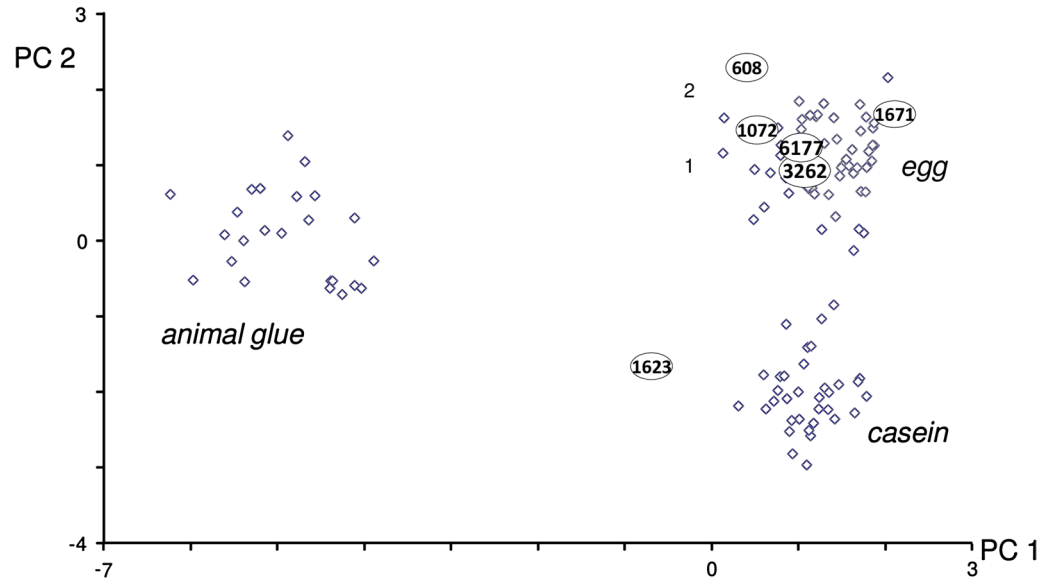


Fig. 1 Principal component analysis (PCA) score plot

Table 7 Overview of suggested content in the nine paintings

No.	SMK accession no.	Binders	Pigments and elements	Fillers
1	KMS3262	Drying oil (linseed or walnut) + egg	Lead carbonate	Calcium carbonate, perhaps calcium sulphate
2	KMS3004	Drying oil (perhaps linseed) + egg or casein	Lead carbonate	Silicon and calcium containing filler
3	KMS1072	Drying oil (linseed or walnut) + egg (whole or yolk)	Lead white + (Mg and Si)	Calcium sulphate and calcium carbonate
4	KMS1623	Drying oil and egg (whole or yolk)	Lower layer: iron earth pigment (Fe, Si, Al, Ca, K and Pb/S) Top layer: lead carbonate + (Ca, Al, Si, Fe, and K)	
5	KMS1671	Drying oil + egg (whole or yolk)	Lead carbonate	Calcium carbonate, perhaps calcium sulphate
6	KMS608	Drying oil (linseed or walnut) + egg	Lead carbonate, perhaps calcium sulphate	Calcium carbonate, perhaps calcium sulphate
7	KMS6177	Drying oil + egg (whole or yolk)	Lead carbonate, calcium sulphate	Calcium carbonate, calcium sulphate
8	KMS1081	Drying oil + egg (whole or yolk)	Lead carbonate	Silicon and calcium containing filler
9	KMS1644	Drying oil + egg or casein + gum	Top layer: lead carbonate, Fe, Si, Al, Na, Ca Lower layer: no clear identification	Top layer: barium sulphate Lower layer: calcium carbonate

Discussion

The SEM–EDX data allowed us to obtain the elemental composition and stratigraphic information of the ground layers. The EDX information was complemented by the molecular information on organic and some inorganic compounds that were obtained by FTIR. Analyses done with GC–MS on whole samples allowed us to specifically list the organic compounds that were used in grounds and possible size layers without pointing to the specific layers from which these compounds originate. The data are discussed in the following paragraphs and summarised in Table 7.

Generally, the analysed grounds are rather similar in composition, but minor differences have been noted. The FTIR and SEM–EDX analysis of the examined grounds generally confirmed the presence of lead carbonate and

calcium carbonate, and in five cases, calcium sulphate was also observed (KMS3262, KMS1072, KMS1671, KMS608, and KMS6177); however, due to the overlap of peaks in the fingerprint area, it is not always possible to confirm its presence. Silicon was observed in five paintings, and silicate was clearly observed by FTIR in two paintings (KMS1623 and KMS3004). Barium sulphate was only found in sample KMS1644. Calcium carbonate, calcium sulphate and barium sulphate were mainly used as fillers in oil grounds, as they become semi-transparent in oil, whereas lead white provided the white colour to the ground. Furthermore, they acted as dryers to catalyse the oxidation of the oil binder. Apart from a slight tinting of some of the white layers in the grounds, a light-brown bottom layer is the only variation to be found among the pigment composition of the nine grounds [4]. SEM–EDX results from painting number 4 by Eckersberg (KMS1623), which was painted in France, had a red iron earth pigment below the white top layer. The white grounds were also reported in a large survey of Eckersberg paintings [7] and recipes from other European countries [2], confirming a European trend of using white grounds in the period.

GC–MS analyses on the grounds of the nine paintings allowed the identification of a drying oil, most likely linseed or walnut oil, and egg. The oil seemed to have been combined with egg in different amounts in order to form a thick emulsion. It was not possible to determine if yolk or white had been used. The amino acid profiles of egg yolk and egg white proteins are in fact very similar [20], and the P/S ratio could not be used to determine the source of the oil or to verify the presence of the egg lipids. Walnut oil would in fact give rise to similar P/S values as a those of a mixture of egg lipids and linseed oil. The P/S ratios that were obtained were in fact quite low, and according to the literature, this could be interpreted as being due to linseed oil alone [21]. The absence of egg lipids cannot be verified, as egg might be present in relatively minor amounts and consequently not modifying the fatty acid profile of the drying oil. Moreover, it has been demonstrated that fatty acids escape a paint film in time, and considering that palmitic acid evaporates four times quicker than stearic acid [22], the P/S value is expected to significantly decrease over time [23]. The presence of lead white in the preparation layer should make the P/S parameters somewhat more reliable, as lead carboxylates are not volatile. In these samples though, saponification, if it occurred, was not complete, as the ν_{as} COO^- bands of the glycerolipid materials were still very well visible in the spectra, and the ν_{as} COO^- bands of the lead carboxylates, if present, were not distinguishable from the amide II band. The sugar profiles that were observed were in perfect agreement with the presence of egg [18].

Collagen-based compounds, such as animal glue, contain the amino acid hydroxyproline, and the absence of this amino acid in all nine samples ruled out the presence of collagen-based glues in the samples.

Animal glue size was thus not identified in any of the nine samples, although the samples were obtained with great care so that all layers from the canvas on up would be included. Interestingly, this result concurs with discoveries by Stools-Witlox, who concludes that a large proportion of nineteenth century recipes for canvas preparation do not mention a size layer [1].

Furthermore, the analyses evidenced the presence of egg in all cases, a binder that is rarely mentioned in contemporary European sources [1, 2]. However, new materials such as egg did start to occur in recipes in the nineteenth century due to the general trend of experimentation and innovation [1, 24]. As discussed above, the analyses do not clearly show which part of the egg was used because of the simultaneous presence of the drying oil. However, it is well known that egg yolk mixes well with oil due to its emulsifying powers [25, 26].

Conservation-based sources provide an impression of the practical implications of the use of egg–oil grounds. Paints with egg yolk are considered to be strong and durable and have a low tendency to turn yellow, compared to pure oil paints [26, 27]. While egg white is supposed to make brittle paints, yolk-based paints are considered more flexible and tough [28, 29]. A paint based on emulsion of egg and oil would have a higher viscosity than a pure oil ground, and, depending on the particular mixture and the openness of the canvas weave, it could be used directly on a canvas without the use of glue size to prevent it from sinking into the canvas structure.

With an egg–oil ground and no animal glue size, a merchant or artist would probably have been able to roll and store the canvas with ground with a smaller risk of cracks than would have been the case with a glue- or starch-based ground [25]. Furthermore, due to the lack of collagen-based glue, the preparation layer would be less dimensionally responsive at different relative humidity levels, and the risk of mechanical damage could be expected to be lower with this type of preparation. In painting KMS1644, a polysaccharide gum was found. The xylose/arabinose ratio was higher than one, and fucose was absent. Therefore, we can exclude the presence of tragacanth gum and suggest the presence of fruit tree or gum arabic [19], which could very well serve the similar purpose of providing flexibility; alternatively, it could have been used as a sizing agent for the canvas.

KMS3262 and KMS1671 seem quite similar in material composition in the analyses that have been used here, and the two paintings were also painted more or less at the same time but by two different artists. A thread count

conducted on these two canvas samples suggest that they are slightly different (KMS3262: 10.0 × 14.5 threads per centimeter and KMS1671: 15.2 × 14.5 threads per centimeter (or 12 × 14.7 when measured with automated thread count on the entire painting [7]), although both are tightly woven [4]. Whether the canvases are in fact different remains uncertain, but the results support the hypothesis that painters used the same supplier(s) of ground, and these suppliers may have had a premixed batch of ground that was applied to more canvases.

Conclusions

SEM–EDX, FTIR and GC–MS analyses of pigments, fillers and binders that were used in grounds of a group of Danish nineteenth century paintings seemed to indicate that the painters of the Danish Golden Age used similar materials. In all the paintings that were analysed, indications of egg–oil mixtures were found as well as lead white and calcium. The latest painting, from 1847, is a little different, as it also contains a gum and barium sulphate. This similarity indicates that certain recipes were favoured amongst the suppliers in Denmark for a period of time or amongst students of the same professor. Furthermore, the results question whether other contemporary countries used similar recipes, since two of these paintings were painted abroad. As animal skin glue seems to be absent in all cases, the findings indicate that these paintings have a relatively low response to relative humidity fluctuations. The presence of egg and gum may indicate a concern for practical matters such as rolling, stretching and storing preprepared canvases.

As all the paintings in this study were wax–resin lined in the 1960s, it does not seem possible to make more general conclusions by comparing the findings reported here and the current condition of the paintings.

Abbreviations

GC–MS: gas chromatography–mass spectrometry; QL: quantification limit; DL: detection limit; PCA: principal component analysis; PTV: programmed temperature vaporising; EI: electron impact; FTIR-ATR: Fourier transform infrared spectroscopy; *S*: sharp peak; *m*: medium size peak; *w*: weak peak; *br*: broad band; *v*: very; *sh*: shoulder band; SEM–EDX: energy dispersive X-ray spectroscopy.

Authors' contributions

CKA developed the concept of this work. AA, JvL, CKA and AV contributed to acquisition and analysis of the data. AA, IB, AV and JvL contributed to data interpretation. CKA provided context and all authors helped drafting/revising the manuscript. All authors read and approved the final manuscript.

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Competing interests

The authors declare that they have no competing interests.

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