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Analytical mass spectrometry of poly(ethylene glycol) additives in artists' acrylic emulsion media, artists' paints, and microsamples from acrylic paintings using MALDI–MS and nanospray-ESI–MS

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ABSTRACT

Poly(ethylene glycol) (PEG) compounds in artists' acrylic emulsion paint products from different paint manufacturers, ranging from base emulsions (Rohm and Haas, Röhm and Scott Bader), to modified emulsions and complete paints (Rowney, Winsor and Newton, Golden, Liquitex, Lascaux), were characterised with a newly developed mass spectrometric method which combines data from Matrix assisted laser desorption/ionisation mass spectrometry (MALDI–MS) and nano-electrospray ionisation mass spectrometry (nano-ESI–MS(MS)). MALDI–MS was used for the determination of the molar mass distribution (MMD) and calculation of the molar mass averages (M_w and M_n), the polydispersity index (D) and the relative amount of a specific distribution if multiple PEGs were present. Electrospray ionisation mass spectrometry was used for the end-group analysis. Three different classes of polymers was found being PEG, polypropylene glycol (PPG) and a block copolymer of polyethylene glycol/polypropylene glycol (PEG/PPG) with molar mass averages ranging from 400 to 4200 Da. PEG compounds with a nonylphenyl or an octylphenyl hydrophobic end-group are most common. The hydrophilic end-groups observed are hydroxide and/or sulphate.

Water extracts of microsamples from a palette by David Hockney dating from 1970 and samples paintings by Patrick Caulfield (1936–2005) and John Hoyland (born in 1934) were investigated with the same technique. Although some artist paint manufacturers use the same specific base emulsions to make their paints, the composition of the PEG compounds present in the water extracts of the palette and paintings samples made it possible, in some cases, to suggest a specific brand of paint used by the artist.

1. Introduction

The basic formulation of acrylic emulsion paint is water in which acrylic polymers are emulsified with surfactants. The acrylic emulsion is produced by the emulsion polymerisation technique [1]. Surfactants, based on poly(ethylene glycol) compounds (PEG), are used to keep the acrylic droplets dispersed in the water during the polymerisation and storage. During drying the water evaporates and the acrylic droplets fuse together to form a continuous film [2]. The molecular weight distribution of the surfactants and their end-groups are often unknown to the manufacturing color man who fabricates the paint (Marc Golden, personal communication). Since the surfactants loose their function after drying of the paint, their appearance at the surface of paintings can cause problems for the conservator [3–5]. A full characterisation of these compounds in paintings is therefore necessary and mass spectrometry plays a central role in the analytical process.

The analytical mass spectrometric methodology using MALDI–MS and nanospray-ESI–MS (MS) developed before [6] was applied to a large series of base emulsions, modified emulsions and paints from different manufacturers provided by the Conservation Department of Tate in London. Their choice is based on earlier studies by T.S.J. Learner on acrylic paint characterisation [1]. Our earlier study of Texicryl 13-031 base emulsion with our methodology [6] shows that several PEG components varying in molar mass and end-groups can be present within the water extract of one acrylic paint product. It is therefore expected that a large number of different PEG compounds may be present in the several acrylic emulsion products from different manufacturers. All results, molar mass averages (M_w and M_n), polydispersity index (D), the residual end-group mass (M_r) abundance (X) and structure of the PEG molecule are listed in Tables 1a and 1b. Water extracts from microsamples from palette and dried paints from paintings studied at Tate were also subjected to the MALDI–MS and nanospray-ESI–MS(MS). Questions relate to nature of the paint, the various surfactants and the possibility to link the painting to a particular brand of paint used by the artists.

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Table 1a
Characteristics of all PEG compounds present in the reference materials, acrylic base emulsions and modified emulsions.

Reference materials/emulsions		PEG						PPG[a]		PPG/PEG[b]
Brand	Product	X (%)	M_r (Da)	M_w (Da)	M_n (Da)	D	Structure of polymer	M_r (Da)	M_w (Da)	
Reference materials										
	Triton X-165	100	30	901	869	1.04	$C_8H_{17}C_6H_4-[OC_2H_4]_n-OH$			
	Triton X-305	100	30	1538	1503	1.02	$C_8H_{17}C_6H_4-[OC_2H_4]_n-OH$			
	Triton X-405	100	30	1769	1737	1.02	$C_8H_{17}C_6H_4-[OC_2H_4]_n-OH$			
	Triton N-57	100	0	541	528	1.02	$C_9H_{19}C_6H_4-[OC_2H_4]_n-OH$			
	Tergitol NP-9	100	0	643	619	1.04	$C_9H_{19}C_6H_4-[OC_2H_4]_n-OH$			
	Tergitol NP-40	100	0	1895	1861	1.02	$C_9H_{19}C_6H_4-[OC_2H_4]_n-OH$			
	Triton N-101 (reduced)	100	6	680	658	1.03	$C_9H_{19}C_6H_{10}-[OC_2H_4]_n-OH$			
Base emulsions										
Rohm and Haas	Primal AC-235	100	30	1806	1780	1.01	$C_8H_{17}C_6H_4-[OC_2H_4]_n-OH$			
	Primal AC-33	85	30	1809	1778	1.02	$C_8H_{17}C_6H_4-[OC_2H_4]_n-OH$			
		15	18	1273	1124	1.13 (C)	$H-[OC_2H_4]_n-OH$			
	Primal AC-634	100	30	1761	1733	1.02	$C_8H_{17}C_6H_4-[OC_2H_4]_n-OH$			
	Primal AC-73	100	30	1737	1709	1.02	$C_8H_{17}C_6H_4-[OC_2H_4]_n-OH$			
	Emulsion E-1801 (experimental one)	77	30	1770	1740	1.02	$C_8H_{17}C_6H_4-[OC_2H_4]_n-OH$			
		17	14	595	578	1.03	$C_9H_{19}C_6H_4-[OC_2H_4]_n-SO_4Na$			
		6	0	506	497	1.02	$C_9H_{19}C_6H_4-[OC_2H_4]_n-OH$			
Rohm	Plextol B-500	100	0	4260	4226	1.01	$C_9H_{19}C_6H_4-[OC_2H_4]_n-OH$			
Scott Bader	Texicryl 13-002	83	0	1419	1327	1.07 (B)	$C_9H_{19}C_6H_4-[OC_2H_4]_n-OH$			
		17	14	812	795	1.02	$C_9H_{19}C_6H_4-[OC_2H_4]_n-SO_4Na$			
	Texicryl 13-031	55	14	770	746	1.03	$C_9H_{19}C_6H_4-[OC_2H_4]_n-SO_4Na$ and $C_9H_{19}C_6H_3(SO_3Na)-[OC_2H_4]_n-OH$			Present
		34	28	871	854	1.02	$C_9H_{19}C_6H_3(SO_3Na)-[OC_2H_4l]_n-SO_4Na$			
		11	0	645	628	1.03	$C_9H_{19}C_6H_4-[OC_2H_4]_n-OH$			
	Texicryl 13-203	76	14	775	758	1.02	$C_9H_{19}C_6H_4-[OC_2H_4]_n-SO_4Na$ and $C_9H_{19}C_6H_3(SO_3Na)-[OC_2H_4]_n-OH$			Present
		17	28	811	800	1.01	$C_9H_{19}C_6H_3(SO_3Na)-[OC_2H_4]_n-SO_4Na$			
		7	0	676	653	1.04	$C_9H_{19}C_6H_4-[OC_2H_4]_n-OH$			
Modified emulsions										
Rowney	Rowney gloss medium	100	30	1828	1800	1.02	$C_8H_{17}C_6H_4-[OC_2H_4]_n-OH$			
Golden	Golden polymer medium gloss	85	30	1744	1709	1.03	$C_8H_{17}C_6H_4-[OC_2H_4]_n-OH$			
		5	18	1266	1099	1.15 (C)	$H-[OC_2H_4]_n-OH$			
Liquitex	Liquitex	100	30	1752	1723	1.02	$C_8H_{17}C_6H_4-[OC_2H_4]_n-OH$			
Lukas	Lukas acrylic binding medium (1993)	100	0	4112	3954	1.04	$C_9H_{19}C_6H_4-[OC_2H_4]_n-OH$			
	Lukas acrylic medium brilliant	100	0	4172	4138	1.01	$C_9H_{19}C_6H_4-[OC_2H_4]_n-OH$			
	Lukas acrylic medium matt (1993)	90	0	4214	4187	1.01	$C_9H_{19}C_6H_4-[OC_2H_4]_n-OH$			
		10	18	1523	1473	1.03	$H-[OC_2H_4]_n-OH$			
Lascaux	Lascaux medium 1	57	12	820	802	1.02	$C_{12}H_{25}C_6H_4-[OC_2H_4]_n-SO_4Na$			Present
		43	42	673	657	1.02	$C_{12}H_{25}C_6H_4-[OC_2H_4]_n-OH$			
	Lascaux medium 1 gloss (1994)	60	12	785	765	1.03	$C_{12}H_{25}C_6H_4-[OC_2H_4]_n-SO_4Na$			Present
		40	42	665	650	1.02	$C_{12}H_{25}C_6H_4-[OC_2H_4]_n-OH$			
	Lascaux acrylic varnish 575 matt (1994)	100	0	710	690	1.03	$C_9H_{19}C_6H_4-[OC_2H_4]_n-OH$			
	Lascaux acrylic varnish 575 gloss (1994)	100	0	669	651	1.03	$C_9H_{19}C_6H_4-[OC_2H_4]_n-OH$			
	Lascaux acrylic size 735	100	6	726	702	1.03	$C_{18}H_{37}-[OC_2H_4]_n-OH$			

[a] For the PPG MMDs observed with MALDI–MS are only the residue mass and the approximate molar mass is presented.

[b] For the PPG/PEG block copolymers only the presence is confirmed. The mass of the intact polymers, however, suggests the presented end-groups. B = bimodal and C = continuous trace.

2. Experimental

2.1. Materials

Triton X-165 (CAS No. 9002-93-1), Triton X-305 (CAS No. 9002-93-1), polyethylene glycol 600 sulphate (CAS No. 37340-69-5), polyethylene glycol 350 monomethyl ether (CAS No. 9004-74-4) and Brij 76 (CAS No. 9005-00-9) were purchased from Fluka (Buchs, Switzerland). Triton X-405 (CAS No. 9002-93-1), Triton N-101 (CAS No. 123359-41-1), trimethylolpropane ethoxylate (CAS No. 50586-59-9), 2,5-dihydroxybenzoic acid (CAS No. 490-79-9), sodium iodide (CAS No. 7681-82-5) and tetrabutylammonium hydroxide (CAS No. 2052-49-5) were purchased from Aldrich (Gillingham-Dorset, United Kingdom). Triton N-57 (CAS No. 9016-45-9), Tergitol NP-9 (CAS No. 127087-87-0) and Tergitol NP-40 (CAS No. 127087-87-0) were purchased from Sigma (St. Louis, USA). Ethanol (CAS No. 64-17-5) and methanol (CAS No. 57-56-1) were purchased from Biosolve (Valkenswaard, The Netherlands). Ion exchange resin (AG® 501-X8, 20-50 mesh) (CAS No. 60177-39-1/CAS No. 69011-20-7) was purchased from Biorad (Hercules, USA). Ammonium acetate

Table 1b
Characteristics of all PEG compounds present in acrylic paints, samples from a palette and samples from paintings.

Paints/Paint samples		PEG						PPG[a]		PPG/PEG[b]
Brand/artist	Product	X (%)	M_r (Da)	M_w (Da)	M_n (Da)	D	Structure of polymer	M_r (Da)	M_w (Da)	
Paints										
Lascaux	Lascaux acrylic paint yellow ochre 1994	100	0	714	691	1.03	$C_9H_{19}C_6H_4-[OC_2H_4]_n-OH$			
	Lascaux acrylic paint titanium white 1994	100	0	740	712	1.04	$C_9H_{19}C_6H_4-[OC_2H_4]_n-OH$			
Lukas	Lukascryl helio genuine yellow lemon	82	0	4088	4058	1.01	$C_9H_{19}C_6H_4-[OC_2H_4]_n-OH$	18	1200	
		18	18	599	578	1.04	$H-[OC_2H_4]_n-OH$			
	Lukascryl titanium white	81	0	4226	4178	1.01	$C_9H_{19}C_6H_4-[OC_2H_4]_n-OH$	18	1200	
		17	18	615	585	1.05	$H-[OC_2H_4]_n-OH$			
		2	2	387	378	1.02	$C_2H_5CH-(CH_2-[OC_2H_4]_n-OH)_3$			
Winsor and Newton	Artists' acrylic titanium white (1973)	95	0	1293	1207	1.07 (H)	$C_9H_{19}C_6H_4-[OC_2H_4]_n-OH$			
		5	14	761	746	1.02	$C_9H_{19}C_6H_4-[OC_2H_4]_n-SO_4Na$			
	Artists' acrylic Indian yellow (1973)	100	0	1007	927	1 09 (H)	$C_9H_{19}C_6H_4-[OC_2H_4]_n-OH$			
	Artists' acrylic titanium white (1994)	100	30	1673	1626	1.02	$C_8H_{17}C_6H_4-[OC_2H_4]_n-OH$	34	700	
	Artists' acrylic azo yellow light (1994)	76	30	1764	1736	1.02	$C_8H_{17}C_6H_4-[OC_2H_4]_n-OH$			
		24	0	946	922	1.03	$C_9H_{19}C_6H_4-[OC_2H_4]_n-OH$			
	Finity acrylic titanium white (1995)	94	30	1692	1652	1.02	$C_8H_{17}C_6H_4-[OC_2H_4]_n-OH$			
		6	32	486	481	1.01	$CH_3-[OC_2H_4]_n-OH$ or $OC_3H_7-[OC_2H_4]_n-OH$			
	Finity acrylic azo yellow medium (1995)	83	30	1648	1615	1.02	$C_8H_{17}C_6H_4-[OC_2H_4]_n-OH$	34	700	
		17	32	487	480	1.01	$CH_3-[OC_2H_4]_n-OH$ or $OC_3H_7-[OC_2H_4]_n-OH$			
Paint chips from a palette										
David Hockney	Mr and Mrs Clark and Percy (T01269) 1970–1971									
	Yellow	100	30	1839	1815	1.01	$C_8H_{17}C_6H_4-[OC_2H_4]_n-OH$			
	Brown	100	30	1765	1734	1.02	$C_8H_{17}C_6H_4-[OC_2H_4]_n-OH$	18	1200	
Paint chips from a painting										
Patrick Caulfield	Cream paint from Interior with a Picture (T07112) 1985–1986 sample H	95	30	1673	1572	1.06 (L)	$C_8H_{17}C_6H_4-[OC_2H_4]_n-OH$	18	1200	Present
		5	18	573	489	1.17 (S)	$H-[OC_2H_4]_n-OH$			
	White paint from Grill (T07150) 1988 sample A	44	0	1147	1014	1.13 (B)	$(C_9H_{19}C_6H_4-[OC_2H_4]_n-OH)$[c]			Present
		39	30	1262	1110	1.14 (B)	$(C_8H_{17}C_6H_4-[OC_2H_4]_n-OH)$[c]			
		17	18	798	724	1.10 (S)	$H-[OC_2H_4]_n-OH$			
	Dark green paint from Second Glass of Wiskey (T06727) 1992 sample A	73	0	704	685	1.03	$C_9H_{19}C_6H_4-[OC_2H_4]_n-OH$			Present
		27	30	1574	1542	1.02)	$(C_8H_{17}C_6H_4-[OC_2H_4]_n-OH)$[c]			
John Hoyland	Red paint from Gadal 10.11.86 (T04984) 1986 sample D	86	30	1164	1025	1.14 (B	$C_8H_{17}C_6H_4-[OC_2H_4]_n-OH$			Present
		14	18	627	580	1.08 (S)	$H-[OC_2H_4]_n-OH$			

The mass of the intact polymers, however, suggests the presented end-groups. B = bimodal, H = high mass tail, L = low mass tail and S = skewed.

[a] For the PPG MMDs observed with MALDI–MS are only the residue mass and the approximate molar mass is presented.

[b] For the PPG/PEG block copolymers only the presence is confirmed.

[c] The intensity in the ESI–MS spectrum was too low to do an MSMS analysis for the identification of the end-groups.

(CAS No. 631-61-8) was purchased from Janssen Chimica (Beerse, Belgium).

2.2. Samples

Acrylic samples were received both in liquid and dry form. The liquid samples consist of base emulsions (BE), modified emulsions (ME), varnishes (V) and liquid paints (LP). The dry samples are pieces from dried paint films (PF) or samples taken from a palette and from paintings.

The base emulsions Primal AC-235 (BE), Primal AC-33 (BE), Primal AC-634 (BE), Primal AC-73 (BE) and Emulsion E1801 (BE) were obtained from Röhm and Haas. Samples obtained from Lascaux include Lascaux medium 1 (ME), Lascaux medium 1 gloss (1994) (ME), Lascaux acrylic paint yellow ochre (1994) (PF), Lascaux acrylic paint titanium white (1994) (PF), Lascaux acrylic varnish

575 matt (1994) (V), Lascaux acrylic varnish 575 gloss (1994) (V) and Lascaux acrylic size 735 (V). From Röhm the base emulsion Plextol B-500 (BE) was obtained. Texicryl 13-002 (BE), Texicryl 13-203 (BE) and Texicryl 13-031 (BE) were obtained from Scott Bader Ltd. Golden polymer medium gloss (ME), Liquitex gloss medium and varnish (ME) and Rowney gloss medium (ME) were obtained from Golden, Liquitex and Rowney, respectively. From Lukas, Lukas acrylic medium brilliant (ME), Lukas acrylic medium matt (1993) (ME), Lukas acrylic binding medium (1993) (ME), Lukascryl helio genuine yellow lemon (LP) and Lukascryl titanium white (LP) were obtained. Samples from Winsor and Newton include Winsor and Newton artists' acrylic titanium white (1973) (PF), Winsor and Newton artists' acrylic Indian yellow (1973) (PF), Winsor and Newton artists' acrylic titanium white (1994) (PF), Winsor and Newton artists' acrylic azo yellow light (1994) (PF), Winsor and Newton finity acrylic titanium white (1995) (PF) and Winsor and Newton finity acrylic azo yellow Indian (1995) (PF).

The Tate (London, UK) provided paint samples from a palette and paintings. A yellow and a brown palette sample were obtained from David Hockney's palette for '*Mr and Mrs Clark and Percy*' (T01269) (1970–1971). Three paint samples were provided from paintings by Patrick Caulfield: a cream colored paint sample from '*Interior with a Picture*' (T07112) (1985–1986), white from '*Grill*' (T07150) (1988) and dark green colored paint sample from '*Second Glass of Whiskey*' (T06727) (1992). A red colored paint sample was obtained from John Hoylands' painting '*Gadal*' (T04984) (1986). The samples were provided by Dr. T.J.S. Learner while at Tate, London, UK.

2.3. Sample preparation

The liquid acrylic samples were painted out on aluminium foil and dried for two weeks. Subsequently the dry and dried samples were cut into small pieces (1–5 mm^2), about 100–1000 μg of sample was transferred into a vial and extracted with 2 ml Milli-Q water. The sample size for the palette samples and samples from acrylic paintings were typically 20–100 μg and were extracted with 200 μl. All samples were extracted for two weeks. The extract was transferred to a new vial and the water was evaporated under a stream of nitrogen.

2.4. MALDI–TOF–MS

For MALDI–TOF–MS analysis the residue recovered from the water extract (estimated 0.1–100 μg) was dissolved in ethanol. The amount of ethanol used roughly depended on the amount of residue. An aliquot of 4 μl of the solution was mixed with a 20 μl solution of 0.2 M 2,5-dihydroxybenzoic acid and 1 mM sodium iodide in ethanol. Sodium iodide was added to promote the formation of sodiated molecules during desorption and ionisation. A volume of 1 μl of the mixture was spotted on the MALDI target and dried at room temperature.

MALDI–MS was performed on a Bruker Biflex TOFMS (Bruker-Franzen Analytik GMBH, Bremen, Germany) and on a TofSpec 2E time-of-flight mass spectrometer (Micromass Limited, Wythenshawe, UK). The MALDI–MS systems were equipped with a nitrogen laser (337 nm). Spectra were obtained by averaging 50–100 spectra, with a typical laser fluency of 5×10^{-3} J/mm^2 using the reflectron mode, and a 20 kV acceleration voltage. Data were processed using the XMASS 5.0 software (Bruker Daltonik GMBH, Bremen, Germany) and MassLynx V3.5 software (Micromass Limited, Wythenshawe, UK).

2.5. Nano-ESI–QTOF–MS

For nano-ESI–QTOF–MS analysis the residue recovered from the water extract was redissolved in MeOH:H_2O (70:30). All samples were measured in the positive ion-mode and some in the negative mode. Ion exchange resin (Biorad, AG® 501-X8, 20–50 mesh) was added to the solutions intended for positive ion-mode analysis to remove all cations and anions. All solutions were filtered over 0.2 μm Spinex Centrifugal Filters (Phenomenex, Torrance, USA) to remove particles that could block the spray needle. A final concentration of 10 mM NH_4Ac or 10 mM $N(Bu)_4OH$ was used to enhance the ionisation process of the positive ion-mode and the negative ion-mode, respectively.

Nano-ESI–QTOF–MS was performed on a Q-ToF2 instrument (Micromass Limited, Wythenshawe, UK). The solutions were sprayed with Econo10 needles or BG-10-58-2-CE-20 needles (New Objective, Woburn, USA) with a flow of approximately 10–80 nl/min.

2.5.1. Positive mode

Typical settings used in the positive mode are a capillary voltage of 0.7–2.0 kV, cone voltage of 0 V, collision energy of 10 eV, TOF voltage of 9.1 kV and the detector set at 2.1 kV. For nozzle skimmer dissociation (NSD) the cone voltage was adjusted to 60 V. Tandem MS (MSMS) analysis was performed with a collision energy of 20–60 eV and the resolution was adjusted to select the mono-isotopic peak or the complete isotopic pattern. For NSD–MSMS analysis the cone voltage was set at 60 V, the collision energy at 20 eV and the resolution was adjusted to select the mono-isotopic peak or the complete isotopic pattern.

2.5.2. Negative mode

Analysis in the negative ion-mode was performed with a capillary voltage of 0.7–1.5 kV, cone voltage of 10–30 V, collision energy of 10 eV, TOF voltage of 9.1 kV and the detector was set at 2.3 kV. MSMS analysis was performed with a collision energy of 20–50 eV and the resolution was adjusted to select the mono-isotopic peak or the complete isotopic pattern.

Data were processed using the MassLynx V3.5 software (Micromass Limited, Wythenshawe, UK).

3. Results and discussion

A comprehensive overview of all characteristics established for each polymer analysed are listed in Tables 1a and 1b. Table 1a contains the polymer characteristics of the reference materials and the polymeric compounds found in the water extracts of the base and modified emulsions. Table 1b contains the polymeric compounds found in the water extracts of the paints, palette samples and paintings samples.

The mass spectrometric analysis of the samples shows three different classes of polymers: polyethylene glycol (PEG), polypropylene glycol (PPG) and a block copolymer of polyethylene glycol/polypropylene glycol (PEG/PPG).

Analysis by MALDI–MS facilitated the determination of the molar mass distribution (MMD), which was used to calculate the molar mass averages (M_w and M_n), the polydispersity index (D), the residue mass (M_r) and the relative amount of a specific distribution if multiple PEGs were present in one water extract. The residue mass was only used to correlate the PEGs identified with MALDI with the ones seen in the ESI–MS spectra.

The ESI–MS analysis, in the positive and negative mode, was used for the characterisation of the polar and apolar end-groups that are attached to the polymer chain. The masses of the end-groups were identified by ESI–MSMS analysis and/or nozzle skimmer dissociation (NSD) separately. A structural identification of the end-groups was possible by NSD in combination with MSMS analysis of the fragment bearing the end-group. Reference [6] details the methodology used.

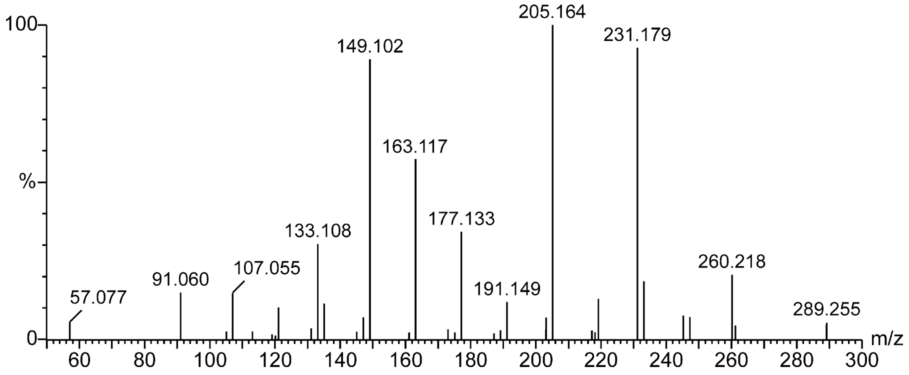

Fig. 1. Lascaux medium 1 gloss ESI$^+$–NSD–MSMS spectrum of m/z 289 (cone voltage = 60 V, collision energy = 20 eV).

The different polymeric compounds – polyethylene glycol (PEG), polypropylene glycol (PPG) and polypropylene glycol/polyethylene glycol block polymer (PPG/PEG) – are divided in three classes (see Tables 1a and 1b); for the PPG and PPG/PEG compounds none or only one MMD was observed, whereas for PEG compounds up to three MMDs were observed in a single water extract. These are presented separately as MMD 1, MMD 2 and MMD 3 in the tables. The end-group properties and polymer properties are presented for each PEG MMD. The end-group properties of the PEG compounds are the nominal residue mass (M_r) and the structure of the entire polymer molecule. The polymer properties include the weight average molar mass (M_w), the number average molar mass (M_n), the polydispersity index (D) and if multiple MMDs are present, the relative abundance in the MALDI–MS spectrum is depicted (X). For the PPG MMD the residue mass and molar mass averages are given. For the block polymer only the presence is verified since all block polymers observed are assumed to have the same structure. All these variables will be used to compare the polymeric compounds found in the reference materials and water extracts.

3.1. End-groups in PEGs

Not all PEG compounds found in the acrylic samples are described in the previous paper [6] .

In the earlier paper we described the details of PEGs with nonylphenyl in combination with a hydroxyl (M_r = 0) or sulphate end-group (M_r = 14). Some water extracts contained PEG compounds with residue end-group masses (M_r) of 42, 18, 32, 2, 6 and 12 Da. In the following paragraph we will discuss each PEG with a different end-group separately.

3.1.1. PEG compounds with a residual mass of 42 Da

PEG compounds with a residual end-group mass of 42 Da were found in the water extracts of the paint films of Lascaux medium. ESI–NSD–MS analysis in the positive mode (spectrum not shown) shows two major fragment ion series 89 + 44n, indicative of a hydroxyl end-group, and 289 + 44n. ESI-NSD–MSMS analysis on m/z 289 was used to determine the end-group structure (Fig. 1). Loss of 44 Da (m/z 289–m/z 245) confirms the presence of one EO (ethylene oxide) monomer, which was also observed for octylphenyl and nonylphenyl end-groups. The presence of a phenyl group was supported by a tropylium ion at m/z 91. Several fragments separated by 14 Da suggest the presence of an alkyl moiety. The mass of m/z 289 is 56 (C_4H_8) and 42 (C_3H_6) Da higher than the fragment ions of PEG compounds with octylphenyl and nonylphenyl end-groups, respectively. The loss of a monomer, the presence of a tropylium ion, an alkyl moiety and the mass difference with PEG compounds with octylphenyl and nonylphenyl end-groups suggest a dodecylphenyl end-group. The proposed structure of the PEG compounds with a M_r = 42 Da is therefore: $C_{12}H_{25}$–[C_6H_4]–[OC_2H_4]$_n$–OH.

3.1.2. PEG compounds with a residual mass of 18 Da

ESI–MSMS analysis of the PEG compounds with a M_r = 18 Da shows only one major fragment ion series (not shown), suggesting that the two end-groups are similar. The fragment distribution (89 + 44n) is indicative for two hydroxyl end-groups. The structure for PEG compounds with a M_r = 18 Da is: H–[OC_2H_4]$_n$OH.

3.1.3. PEG compounds with a residual mass of 32 Da

The MSMS spectrum of a PEG compound with M_r = 32 is shown in Fig. 2. Two fragment ion series are observed: 89 + 44n (*) and 59 + 44n (o). The first series is indicative for the hydroxyl end-group. The second one suggests a methyl (59–44 = 15 Da) end-group. A very small peak (0.2% of the base peak) at m/z 353 (loss of methanol 385–353 = 32 Da) supports the presence of a methyl end-group. MSMS analysis of m/z 385 of poly(ethylene glycol) 350 monomethylether (not shown) gave an solid iden-

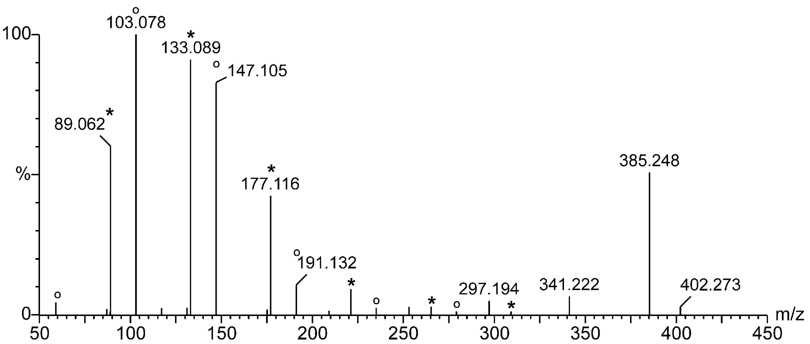

Fig. 2. Winsor and Newton Finity acrylic titanium white (1995) ESI$^+$–MSMS spectrum of m/z 402 (collision energy = 20 eV).

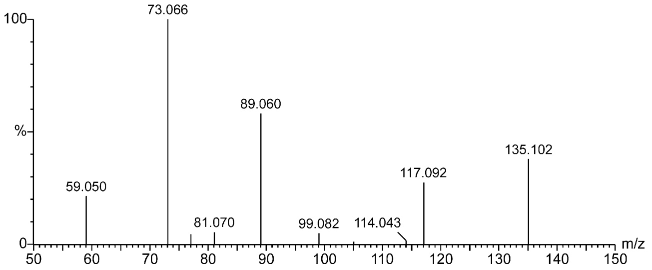

Fig. 3. Lukascryl titanium white ESI^+–MSMS spectrum of m/z 135 (collision energy = 20 eV).

tification. The structure for this PEG compounds is therefore: $CH_3–[OC_2H_4]_n–OH$.

3.1.4. PEG compounds with a residual mass of 2 Da

The PEG compound with $M_r = 2$ is observed in the water extract of Lukascryl white paint only. ESI–MS analysis in the positive mode only shows protonated polymer molecules instead of the expected ammonium adducts. MSMS analysis was performed on the cationised molecule with the lowest mass of that series. m/z 135 did not show monomer losses implying that this is the bare protonated end-group (Fig. 3). The subsequent losses of three H_2O molecules under MSMS conditions suggest the presence of 3 hydroxyl groups. MSMS analysis on m/z 135 of trimethylolpropane ethoxylate gave the same fragment distributions. The structure of this PEG is: $H_3C–CH_2–C–(CH_2–[OC_2H_4]_n–OH)_3$.

3.1.5. PEG compounds with a residual mass of 6 Da

The reference compound Triton N-101 (reduced) and the water extract of Lascaux acrylic size 735 contain a PEG compound with $M_r = 6$.

The structure of the Triton N-101 (reduced) is: $C_9H_{19}–C_6H_{10}–[OC_2H_4]–OH$. ESI–NSD–MS analysis of Triton N-101 (reduced) did not generate fragment ion series that contain the nonylcyclohexyl end-group. The hydroxyl containing fragment and a protonated PEG compound with two hydroxyl end-groups were observed. ESI–MSMS analysis of m/z 728 (Fig. 4) did not generate fragment ion series with the nonylcyclohexyl end-group either (*, 89 + 44n, $H–[OC_2H_4]_n{}^+$) (^, 239 + 44n, $H–[OC_2H_4]_{n+5}–OH + H^+$). However, in this spectrum the end-group mass can be calculated: 728 − 17 (NH_3) − 503 = 208. The nonylcyclohexyl end-group is only observed as a loss of nonylcyclohexene.

ESI–NSD–MS analysis (not shown) did not give specific fragment ions for the $M_r = 6$ PEG compound found in Lascaux acrylic size. ESI–MSMS analysis on m/z 816 was used instead (Fig. 5). Two fragment ion series 89 + 44n (*, hydroxyl) and 253 + 44n (o) contain the end-groups. The elemental compositions calculated for the fragment ion m/z 253 and a neutral loss of 252 Da (799 − 547) are $C_{18}H_{37}$ and $C_{18}H_{36}$, suggesting an octadecyl end-group. ESI–MSMS analysis of Brij 76 (octadecyl ethoxylate) was used as a reference to confirm the octadecyl end-group. The structure for the PEG compound in the water extract of Lascaux acrylic size with $M_r = 6$ is therefore: $C_{18}H_{37}–[OC_2H_4]_n–OH$.

3.1.6. PEG compounds with a residual mass of 12 Da

Fig. 6 shows the ESI–MSMS analysis of m/z 561 in the negative mode. The M_r (561 + 1 (H) − 12 × 44 = 34) in this case differs 22 Da with respect to the M_r calculated from the MALDI spectrum (M_r = 12 Da) which suggests that the polymer molecule was in the sodium salt form during MALDI–MS analysis. A small peak at m/z 261 in spectrum suggests a dodecylphenyl end-group and the 123 + 44n (*) is characteristic for the sulphate end-group. The corresponding structure of the PEG compound is therefore: $C_{12}H_{25}–C_6H_4–[OC_2H_4]_n–SO_4{}^-$.

3.2. PEG compounds in the various acrylic media

3.2.1. Reference materials

The characteristics for the reference materials, commercially available pure compounds and solutions in water that were chosen for this study are listed in Table 1a. The analytical results of the reference materials agree with the information supplied by the manufacturer. Some of the other reference compounds are described in Table 1a in the same way as the Triton X-series.

3.2.2. Base emulsions

The base emulsion contains the polymerised acrylic particles in the water phase that are stabilised by surfactants. Several base emulsions from Rohm and Haas, Rohm and Scott Bader were investigated.

3.2.2.1. Rohm and Haas. The base emulsions (Rohm and Haas, Röhm and Scott Bader) can contain up to 3 PEG MMDs. Of interest is the PEG compound present in all Rohm and Haas products. That particular PEG contains an octylphenyl and a hydroxyl end-group, which is similar to the end-groups found in the Triton X-series. Further classification should be possible by examining the polymer properties. The M_w and D are close to that of a specific Triton X-series product, namely Triton X-405. Therefore a complete identification of this PEG compound found in the water extracts of Rohm and Haas products is possible.

In some Rohm and Haas products additional PEGs were found with the double hydroxyl end-group, with a relatively high D in Primal AC-33, and two additional PEGs found in Emulsion E-1801. The additional PEG compound found in Primal AC-33 might be a by-product of the polymerisation procedure used to produce the octylphenyl PEG. One of the PEGs found in Emulsion E-1801, the

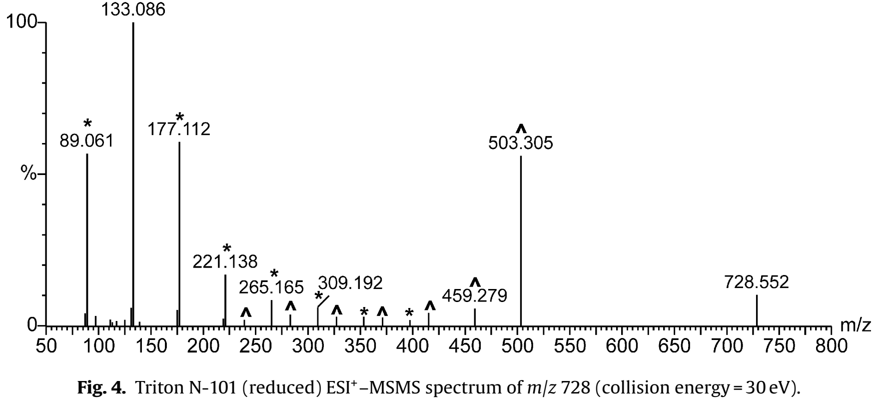

Fig. 4. Triton N-101 (reduced) ESI^+–MSMS spectrum of m/z 728 (collision energy = 30 eV).

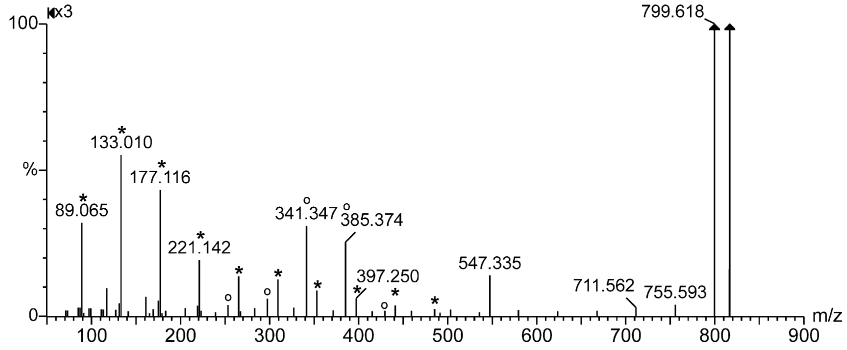

Fig. 5. Lascaux acrylic size ESI$^+$–MSMS spectrum of m/z 816 (collision energy = 25 eV).

one with a nonylphenyl and a hydroxyl end-group has the same end-groups as Triton N-57 or a Tergitol NP-series product. The M_W of that PEG (M_W = 506 Da) is closest to that of Triton N-57 (M_W = 541 Da), which suggests that Triton N-57 is used in Emulsion E-1801. An additional PEG compound was discovered in Emulsion E-1801 which has a nonylphenyl and a sulphate end-group. Unfortunately no reference is available in this case.

3.2.2.2. Röhm. The Röhm product Plextol B-500 contains the same apolar and polar end-groups as the Triton N-57 and the Tergitol N-series. The M_W, however, is relatively high and does therefore not match any of the reference materials. The commercial product used in the Plextol B-500 could therefore not be identified.

3.2.2.3. Scott Bader. The PEG compounds found in the water extracts of the Scott Bader emulsions all contain the same hydrophobic nonylpheno1 end-group. However, some PEG compounds found in Texicryl 13-031 and 13-203 contain a hydrophobic end-group with a rather polar sulphonic moiety attached to the phenyl ring.

The determination of the end-group structures with exactly the same mass depicted at M_W = 770 and 775 Da for Texicryl 13-031 and 13-203, respectively, was only possible by MSMS analysis, which revealed the presence of the different end-group moieties. The MSMS data of the M_W = 812 Da of Texicryl 13-002, however, points to the presence of only one polymeric structure.

The PPG/PEG block polymers with apolar end-groups are only observed in the water extracts of Texicryl 13-031 and 13-203 by ESI–MS analysis. The absence of this polymer in MALDI analysis could be due to different precipitation behaviour of the compound in comparison with PEG compounds during the drying process on the MALDI probe or due to a different desorption/ionisation efficiency. However, in first instance the solvation of this relatively apolar compound in water is not be expected at all. The extraction of PPG/PEG polymer molecules could therefore be enhanced by PEG molecules that have formed micelles (if the critical micelle concentration was reached).

3.2.3. Modified emulsions

The basis of a modified emulsion is a base emulsion that is modified by the addition of several additives to improve the physical properties. A modified emulsion therefore is paint without pigments. The modified emulsions are listed in Table 1a by their company name as Rowney, Golden, Liquitex, Lukas and Lascaux.

3.2.3.1. Rowney, Golden and Liquitex. The modified acrylic emulsions of Rowney, Golden and Liquitex all contain a PEG compound with an octylphenyl and hydroxyl end-group with a M_W of 1828, 1766 and 1752 Da, respectively. The characteristics of the PEG compounds agree well, with respect to their end-groups and M_W to the PEG compounds found in the water extracts of the Rohm and Haas base emulsions. This suggests that Primal emulsions were used by Rowney, Golden and Liquitex to make their own products. This observation supports a proposal that the three paint manufactures used Primal emulsions as basic material for their products (T.J.S. Learner, Tate Gallery, London, United Kingdom, personal communication, 2002). The additional PEG found at M_W = 1266 Da is probably a by-product as discussed earlier for the Primal AC-33 emulsion of Rohm and Haas. This by-product seen in the water extract could suggest the use of a Primal AC-33 emulsion. However, the intensity of this signal is rather low (just above the noise) and may therefore remain unnoticed in the analysis of the other Primal products.

3.2.3.2. Lukas. The modified emulsions of Lukas all contain a relative high M_W PEG compound of 4112, 4172 and 4214 Da with a nonylphenyl and hydroxyl end-group for the Lukas acrylic binding medium, medium brilliant and medium matt, respectively. The characteristics resemble the PEG compound found in the water extract of Plextol B-500 of Röhm, supporting the interpretation

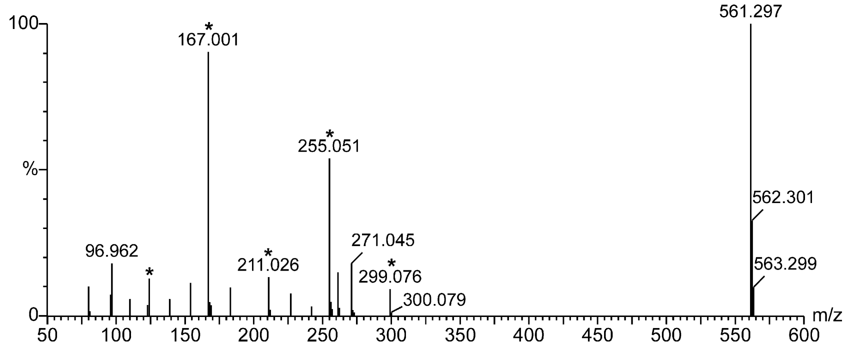

Fig. 6. Lascaux medium 1 ESI$^-$–MSMS spectrum of m/z 561 (collision energy = 40 eV).

that a Plextol B-500 was used by Lukas (T.J.S. Learner, Tate Gallery, London, United Kingdom, personal communication, 2002).

3.2.3.3. Lascaux. The Lascaux emulsions show a variety of non-ionic and anionic PEG compounds which differ in hydrophobic and hydrophilic end-groups. The water extracts of Lascaux medium 1 and medium 1 gloss contain PEG compounds that are not observed in other water extracts.The Lascaux acrylic varnishes contain PEG compounds that have a different hydrophobic end-group structure than the one observed in the extracts of the medium 1 extracts. The nonylphenyl and hydroxyl end-group in combination with the M_w of 710 and 669 Da for Lascaux acrylic varnish matt and gloss, respectively, suggest that a Tergitol NP-series product is used that is near to Tergitol NP-9 in composition.

Lascaux acrylic size 735 contains a PEG that was not observed in the other water extracts. The end-group structures identified are octadecyl and hydroxyl. Note that on the basis of the MALDI–MS analysis alone one can't discriminate between an octadecyl and nonylcyclohexyl end-group since they have the same nominal residue end-group mass. This implies that a high resolution MS or MSMS analysis is essential for the discrimination.

None of the PEG compounds identified for the Lascaux products agree well with one of the investigated base emulsions since octadecyl and dodecylphenyl are not found in any of the other water extracts. Only the Lascaux acrylic varnishes contain a nonylphenyl PEG with an M_w close to the ones identified for the PEG compound with nonylphenyl and hydroxyl end-groups found in Texicryl 13-031 and 13-203. However, the water extracts of the latter two contain additional anionic PEGs that are not observed in the Lascaux varnishes. This observation strongly suggests that Lascaux fabricates its own proprietary emulsions.

3.2.4. Paint

The paint products investigated were manufactured by Lascaux, Lukas, and Winsor and Newton (W&N).

3.2.4.1. Lascaux. The water extracts of Lascaux yellow ochre and titanium white (Table 1b) contain PEG compounds that have a nonylphenyl and hydroxyl end-group with an M_w of 714 and 740 Da, respectively. These polymer characteristics agree well with those of the other Lascaux products depicted in Table 1a namely the Lascaux acrylic varnish 575 matt and gloss.

3.2.4.2. Lukas. The water extracts of Lukascryl paints contains one PEG compound that is also found in the Plextol B-500 and Lukas binding medium, medium brilliant and medium matt, according to the nonylphenyl and hydroxyl end-groups and M_w. The paints, however, contain some additional polymeric compounds at $M_w = 599$ and 615 Da for Lukascryl Helio genuine yellow lemon and titanium white, respectively, and the trimethylolpropane ethoxylate at $M_w = 387$ Da for Lukascryl titanium white only.

3.2.4.3. Winsor and Newton. The Winsor and Newton paints available for study are from the production years 1973, 1994 and 1995.

The Artists' acrylic white and Indian yellow from 1973 both contain a relatively polydisperse PEG compound with a $M_w = 1293$ and 1007 Da, respectively. An additional PEG with nonylphenyl and sulphate end-groups is found in Artists' acrylic titanium white at $M_w = 761$ Da. PEG compounds with a nonylphenyl and a sulphate end-group were also present in the water extracts of Emulsion E-1801 and Texicryl 13-002, 13-031 and 13-203. The M_w of 595 Da of this compound in Emulsion E-180l is lower with respect to the one identified for the W&N Artists' acrylic titanium white (1973). The M_w of 812, 770 and 775 Da of Texicryl 13-002, 13-031 and 13-203 are much closer to the PEG found in this W&N paint. For the Texicryl 13-031 and 13-203, however, two different PEG compounds were identified with exactly the same mass whereas only one structure was identified for the W&N titanium white paint. The anionic PEG compound found in the water extract of Texicryl 13-002 also contains only one structure and bears therefore the closest resemblance to the PEG compound found in the water extracts of the W&N titanium white paint. In the Artists' acrylic Indian yellow this anionic PEG compound was not observed. This can be attributed to the absence of this compound or to the fact that the intensity is just too low since the abundance in the titanium white sample was also low (Table 1b). The other non-ionic PEG compound found in the titanium white (1973) water extract contains, just like the Texicryl 13-002, a nonylphenyl and a hydroxyl end-group. The M_w of 1293, 1007 and 1419 for W&N Artists' titanium white, Indian yellow and Texicryl 13-002 differ significantly from each other. On the other hand all MMDs are relatively polydisperse 1.07, 1.09 and 1.07 and with the exception of the paint samples from paintings no relatively high polydisperse (>1.04) polymers are observed with nonylphenyl end-groups. These clues suggest that W&N used Texicryl 13-002 for their paints in 1973, supporting a proposal by Learner that W&N used Texicryl products in 1973 to make their paints, although there is no exact match (T.J.S. Learner, Tate Gallery, London, United Kingdom, personal communication, 2002).

The W&N Artists' acrylic titanium white and azo yellow light paints produced in 1994 contain a PEG compound with an octylphenyl and hydroxyl end-group with a M_w of 1673 and 1764 Da, respectively. These characteristics closely resemble the ones found in Rohm and Haas products and Triton X-405. However, an additional PEG compound with a nonylphenyl and hydroxyl end-group for the azo yellow light paint was observed at $M_w = 946$ Da. Although PEGs with the nonylphenyl and hydroxyl end-group are also observed in products from Rohm and Haas, Röhm, Scott Bader and Lascaux, the M_w is significantly smaller than Plextol B-500 and significantly higher (approximately 200 Da) than the ones observed in Emulsion E-1801, Texicryl 13-031 and 13-203, Lascaux varnishes and Lascaux paints. This PEG might have been added by W&N as an additional compound in the formulation of their emulsions and paints.

The 1995 paints of W&N were suspected to be a Primal product (T.J.S. Learner, Tate Gallery, London, United Kingdom, personal communication, 2002). This proposal is supported by the presence of a PEG compound with octylphenyl and hydroxyl end-groups and a M_w close to that of the PEG found in the Rohm and Haas products and Triton X-405. An additional PEG compound was observed at $M_w = 486$ and 487 Da for the Finity acrylic titanium white and azo yellow medium (1995).

Poly(propylene glycol) was found in the water extracts of the Artists' acrylic titanium white (1994) and Finity acrylic azo yellow by MALDI with a M_w of approximately 700 and a residue mass of 34 Da. This compound is not observed by ESI–MS analysis however, so an end-group analysis was not possible. This compound is relatively hydrophobic in nature. ESI–MS analysis of all W&N paint extracts reveal that the PPG compound was also present in the other water extracts at low intensity.

3.3. Microsamples from a palette by Hockney and paintings by Caulfield and Hoyland

The PEG compounds found in the yellow and brown palette samples of David Hockney contain a PEG compound with a M_w of 1839 and 1765 Da, respectively, with octylphenyl and hydroxyl end-groups. These results suggest the use of a Rowney, Golden, Liquitex or W&N product. Learner (Tate, personal communication) proposed that David Hockney used Liquitex paint for this painting on the basis of information obtained from the artist and/or other sources. It is not possible to confirm this, because it is not possible to discriminate Rowney, Golden, Liquitex and some W&N paints on the basis of the PEG compounds in their water extracts. Analysis of additives other than water extractable polymers might support further authentication in this case. The more hydrophobic PPG polymer with a residue mass of 18 Da is only found in the water extract of a brown paint sample from this palette. The residue mass of 18 Da suggests two hydroxyl end-groups.

The characteristics of the PEG compounds found in the water extract of three painting samples from Patrick Caulfield's paintings and one painting sample from a painting of John Hoyland are discussed separately. The PPG/PEG block copolymer compound is found in all these painting samples.

3.3.1. Cream colored paint from "Interior with a Picture" (T07112) by Patrick Caulfield

The characteristics of the major PEG component identified in the water extract of Patrick Caulfield Cream colored paint from "Interior with a Picture" (T07112) are the octylphenyl and hydroxyl end-group, the M_w of 1673 Da and a rather high polydispersity of 1.06 due to the low mass tail. A PEG compound with these end-groups and M_w suggests that a Rowney, Golden, Liquitex or W&N product was used. It is supported by a communication from the Caulfield to Learner (T.J.S. Learner, Tate Gallery, London, United Kingdom, personal communication, 2002) that a Liquitex paint was used. The polydisperse skewed distribution at low mass with two hydroxyl end-groups and the low mass tail of the PEG compound with octylphenyl and hydroxyl end-groups suggests that these artefacts originate from the polymerisation procedure of the polymer. The PPG at a M_w of approximately 1200 Da has a residue mass of 18 Da, suggesting two hydroxyl end-groups.

3.3.2. White paint from "Grill" (T07150) by Patrick Caulfield

Three polydisperse PEG compounds were identified in the water extract of T07150. Due to the small amount of sample only the end-groups of the PEG compound with a M_w of 798 Da could be identified as a PEG with two hydroxyl moieties. The identification by MSMS analysis of the end-groups of the other two MMDs was not possible because the signal was too low and there was no sample left. However, the end-groups for the two PEG compounds with $M_r = 0$ and 30 Da are expected to be nonylphenyl and octylphenyl, respectively, according to the accurate mass of the intact polymer identified with ESI–MS analysis and the comparison with characteristics of PEGs found in other water extracts. The paint used in this case was proposed to be Liquitex (T.J.S. Learner, Tate Gallery, London, United Kingdom, personal communication, 2002). This assignment however, can't be confirmed since the PEG compounds found are too polydisperse.

3.3.3. Dark green paint from "Second Glass of Whisky" (T06727) by Patrick Caulfield

The water extract of T06727's green paint contained two PEG compounds. The end-groups of the major PEG compound were identified as a nonylphenyl and hydroxyl end-group. For the PEG compound with the residue mass of 30 Da the accurate mass identified with ESI– MS analysis suggests an octylphenyl and hydroxyl end-group. The M_w of 1427 Da of this compound is significantly lower than the ones observed for PEG compounds with an octylphenyl end-group in emulsions and paints discussed already. With respect to the reference materials the M_w is closest to Triton X-305. The M_w of the other PEG polymer in the water extract with a nonylphenyl and a hydroxyl end-group is close to the PEG compounds found in the water extracts of the Texicryl emulsions and Lascaux varnishes and paints. However, the Lascaux varnishes and paints are closer to the actual PEG composition of T06727 than the Texicryl emulsions since no anionic PEG compounds were found in the water extract of the paint chip. This observation supports a proposal by Learner (T.J.S. Learner, Tate Gallery, London, United Kingdom, personal communication, 2002) that this paint was a Lascaux paint. The additional PEG compound at $M_w = 1427$ might originate from another paint, other than dark green, present in the sample. Some dark green paint chips have small white parts, which may imply that the paint chips that were analysed were not completely pure paints.

3.3.4. Red paint from "Gadal" 10.11.86 (T04984) by John Hoyland

Two PEG compounds were identified in the water extract of the red paint of T04984. One bimodal MMD at $M_w = 1164$ Da with maximums at approximately m/z 750 and 1500 Da with an octylphenyl and a hydroxyl end-group. The second distribution at $M_w = 627$ with two hydroxyl end-groups shows a skewed MMD. The paint used has been proposed to be a Lascaux product (T.J.S. Learner, Tate Gallery, London, United Kingdom, personal communication, 2002). The end-groups and M_w of the PEG compounds found in the water extract of T04984 do not match any of the PEGs found in the Lascaux products. The highest maxima of the bimodal distribution at m/z 1500 Da coincides well with the M_w of Triton X-305. The lowest maximum at m/z 750 Da is somewhat lower than Triton X-165.

4. Conclusion

The mass spectrometric techniques applied in our methodology facilitate the analysis of the MMDs and end-groups of the PEGs found in the water extracts of pigmented and unpigmented acrylic emulsion paint films, paint samples from a palette and several small painting samples. Polymeric compounds other than PEG that were found in the water extracts are PPG and a PPG/PEG block copolymer.

The PEGs found in the extracts vary in their MMD and end-group composition. Their characteristic molecular features have potential for the identification of the commercially pure PEG products (such as Triton X-405) that were used in the base emulsions. This PEG compatibility agent was also found in modified emulsions and in paints of paint manufacturers, who were thought to use a specific base emulsion.

The results from the palette and paintings samples demonstrate the applicability of this method for microsamples from works of art. The composition of the PEG compounds present in the water extracts of the paints could be used, in some cases, to identify a specific brand of paint used by the artist.

Acknowledgements

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