

# Identification of additives in poly(vinylacetate) artist's paints using PY-GC-MS

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**Abstract** Commercial poly(vinyl acetate) (PVAc) paint formulations for artists include a number of compounds in addition to the PVAc polymer and pigments to improve the physical and chemical properties of the resulting product. Among the most common additives are surfactants, coalescing agents, defoamers, freeze–thaw agents and thickeners. These products significantly influence the behaviour of the dried film. Nevertheless, they are usually difficult to detect with conventional analytical methods given their low concentration. In order to identify these additives, present in the dried film as minor components, an analytical method based on in situ thermally assisted pyrolysis–silylation gas chromatography–mass spectrometry (GC-MS) using hexamethyldisilazane as a derivatisation reagent is proposed. This method improves the conventional GC-MS analysis performed by direct pyrolysis and enables the simultaneous identification of the PVAc binding medium and the additives included by the manufacturer in the commercial paint. Five different commercial PVAc paints have been analysed, namely, armour green, burnt umber, oriental red, raw umber and white from Flashe<sup>®</sup>. Internal plasticiser VeoVa consisting of C<sub>10</sub> fatty acids with highly branched chains has been recognised from the MS spectra. On the other hand, the differences found in the additive

content of the studied paints, in particular the poly(ethylene glycol)-type surfactant, are in good agreement with their mechanical properties.

**Keywords** Paints · PVAc · Additives · PEG · Py-GC-MS · HMDS

## Introduction

Artists' waterborne paints are prepared with a series of additives that seek the stabilisation of the paint during storage, transportation, application and lifetime service.

Prior to turning into a paint, the binding medium, or latex, counts upon several additives such as initiators, chain transfer agents, buffers, surfactants, protective colloids, preservatives and residual monomers. The paint manufacturer will then add several other compounds to achieve the desired properties for the paint, and these may include wetting and dispersing agents, coalescing solvents, defoamers, preservatives, thickeners and rheology modifiers, freeze thaw stabilisers, pigments and extenders [1, 2].

When the paint is applied, most of these components stay in the dried film, and for conservation purposes, their identification and the influence they have in the overall properties of the dried bulk material are of the outmost relevance. It has been shown that surfactants take an important part in the film formation process, surface tackiness, water sensitivity and overall mechanical properties of the resulting films, as well as they are also associated with changes in gloss, colour and staining [3–7]. Nevertheless, the way these additives interact and influence the ageing of these materials is quite unknown to date, since the development of the paint industry has been very much based on practical experimentation [1].

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The identification of additives is also of critical importance for conservation science when planning conservation treatments such as cleaning and consolidation, since solvents and water may have a direct effect in the overall paint film due to removal of possible additives.

Several analytical techniques and methods have been applied and developed in view of the identification and characterisation of additives in synthetic polymers. Nevertheless, most references found concern general industrial applications, and mainly tend to focus their studies in one type of additive. The more specialised papers on waterborne paints are generally focused on acrylic and poly(vinyl acetate) (PVAc)-type resins and focus in the detection of pigments, surfactants and/or plasticisers. A good review of analytical techniques applied for the characterisation of coatings has been provided by Andersen [8].

Thus, several authors have presented studies on the identification of surfactants, mainly poly(ethylene glycol) (PEG)-type surfactants, by means of Fourier-transformed infrared spectroscopy (FTIR) and attenuated total reflectance [4–7, 9–11]. Alkylaryl polyethoxylate-type surfactants have also been successfully identified by means of size-exclusion chromatography combined with FTIR spectroscopy [12]. And also, the use of chromatographic techniques, such as high-performance liquid chromatography coupled with MS and diode array detector and pyrolysis–gas chromatography–mass spectrometry (Py-GC-MS) have been reported to detect this non-ionic type of surfactant (alkylaryl polyethoxylate) used to stabilise acrylic formulations. These techniques have the analytical advantage of having high sensibility and reduce considerably the size of the samples tested [12, 13].

Recently, MALDI-MS and nanospray-ESI-MS have also proved to be successful in determining the structures of poly(ethylene glycol) additives from both test specimens and paint microsamples [14, 15].

The identification of plasticisers present in artist's commercial paints and binding media has been performed by spectroscopic techniques such as FTIR spectroscopy [16]. Nevertheless, Py-GC-MS has obtained much importance in the identification of these compounds, since it can discriminate with accuracy the type of plasticiser present in the paint's formulation [16–23].

In general studies, for industrial applications, Wang has published articles concerning the study of lubricants, antioxidants and flame retardants by means of Py-GC-MS [24–26]. Py-GC-MS has also been used by Blas o for the study of the thermal decomposition of hindered amine light stabilisers, as well as liquid chromatography–ultraviolet absorbance detection–evaporative light scattering detection [27, 28]. Temperature-programmed pyrolysis hyphenated with metastable atom bombardment ionisation mass spectrometry has also been used to detect light stabilisers in car paints [29].

Hexamethyldisilazane (HMDS) as derivatisation reagent for thermally assisted pyrolysis in GC-MS has already been applied successfully in the analysis of a number of organic compounds such as proteins, polysaccharide, lipids, terpenoid, acrylic and poly(vinyl) resins [30]. In particular, this method efficiently converts carboxylic and hydroxyl groups into their less polar trimethylsilyl ester (TMS) derivatives from fatty acids present in lipids [31]. Notable reduction of side reactions during pyrolysis is the main advantage of this method, and as a consequence, simpler pyrograms than those from thermally assisted hydrolysis methylation are obtained. In this paper, use of *in situ* thermally assisted pyrolysis–silylation GC-MS using HMDS is discussed for the identification of additives present in Flashe<sup>®</sup> waterborne armour green, burnt umber, oriental red, raw umber and white PVAc-based paint colours. In a first step, this method has been tested in a set of paint samples and has been compared with results obtained for the same samples analysed with direct pyrolysis. In a second step, water extractions of the paint samples have been analysed in order to detect minor water-soluble components present in the paint films and their corresponding peaks, retention times and mass fragmentation patterns.

## Experimental

### Analytical reagents and reference materials

Five different commercial PVAc paints have been analysed, namely, armour green, burnt umber, oriental red, raw umber and white from Flashe<sup>®</sup>. The paints were supplied by LeFranc & Bourgeois.

### Preparation of test specimens

Film specimens were prepared by casting commercial Flashe<sup>®</sup> vinyl paints colours over mylar<sup>®</sup> sheets. The colours prepared consisted of armour green, burnt umber, oriental red, raw umber and white. The products were left to dry for a year before testing, and the resulting films exhibited an average thickness of 0.15 mm.

### Preparation of extractions

Samples weighting approximately 0.4–0.5 g were immersed in deionised water for 24 h. The films were then removed, and the water was dried at 50°C in a laboratory oven. A waxy extract was obtained for analysis by Py-GC-MS.

### Preparation of samples for Py-GC-MS

Samples and extracts were scrapped with a scalpel and introduced in a quartz tube with a small plug of quartz

wool. For samples analysed with a derivatising reagent, 1  $\mu\text{L}$  of HMDS was afterwards added.

## Instrumentation

### Py-CG-MS

Pyrolysis–gas chromatography–mass spectrometry was carried out with an integrated system composed of a CDS Pyroprobe 1000 heated filament pyrolyser (Analytical Inc., New York, NY, USA) and an Agilent Technologies (Palo Alto, CA, USA) 6890N gas chromatograph coupled with an Agilent Technologies 5973N mass spectrometer and equipped with a pyrolysis injection system. An HP-5MS capillary column (5% phenyl methylpolysiloxane; 30 m, 0.25 mm i.d., 0.25  $\mu\text{m}$ ) was used.

In situ thermally assisted pyrolysis–silylation GC-MS using HMDS was performed with a temperature of pyrolysis of 700°C, for 10 s, using a precalibrated Pt coil-type pyrolyser (CDS Pyroprobe).

The pyrolyser interface and the inlet were set at 250°C. Samples were injected in split mode (split ratio 1:40).

The GC temperature was initially 50°C for 2 min, and then programmed at 5°C min<sup>-1</sup> to 100°C, then at 15°C min<sup>-1</sup> to 295°C, held for 10 min. The electronic pressure control was set to the constant flow mode with vacuum compensation. Helium gas flow was set at 1.2 mL min<sup>-1</sup>.

Ions were generated by electron-impact (EI) ionisation (electron energy 70 eV) in the ionisation chamber of the mass spectrometer. The mass spectrometer was scanned from  $m/z=20$  to  $m/z=800$ , with a cycle time of 1 s. Agilent Chemstation software G1701CA MSD was used for GC-MS control, peak integration and mass spectra evaluation. Tuning and calibration of the mass spectrometer were checked using perfluorotributylamine. EI mass spectra were acquired in the total-ion monitoring mode, and peak area (TIC) data were used to obtain values of peak area percentage. The temperatures of the interface and the source were 280 and 150°C, respectively. Compounds were identified by use of the NIST and Wiley Library of Mass Spectra and a library created by the authors for PVAc compounds.

## Results and discussion

### Optimisation of the analytical method

#### *Temperature of pyrolysis—derivatisation of samples*

A series of pyrolysis with derivatising reagent HMDS were performed at different temperatures ranging from 50 to 800°C on Flashe® oriental red samples in order to determine

the most adequate temperature conditions for the analysis of minor components for this type of paints. The pyrograms presented in Fig. 1 (A–C) show the results obtained at temperatures of 400, 550 and 700°C, respectively. According to these results, a general trend can be observed that provides useful information for establishing an analytical protocol.

Thus, analyses run at temperatures below 400°C show no major peaks that can be related to compounds of interest present in these paints. However, it is interesting to notice that there is a small trace of TMS of ethanoic acid, which is a product of the decomposition of poly(vinyl acetate) polymers chains during pyrolysis [3, 21]. In analyses performed with direct pyrolysis, the peak corresponding to ethanoic acid would appear as a fronting peak in the first minutes of the pyrogram. In contrast, in Fig. 1 A, the peak corresponding to the TMS form of the ethanoic acid appears as a well-defined peak. This result evidences the derivatising efficiency of HMDS for polar-type compounds such as organic acids, as presented in previously published studies [20, 21].

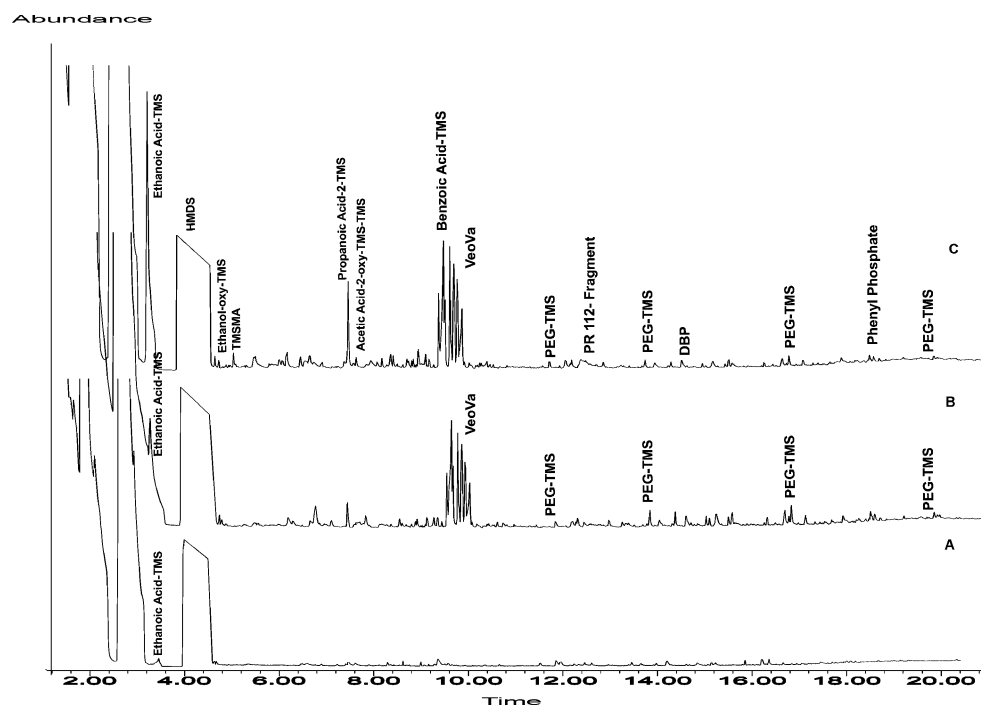
Above 400°C, several compounds of interest start to appear in the pyrogram, which provide good information about the polymer main chain and additives from the waterborne paint. Figure 1 B shows a pyrogram obtained at 550°C in which a series of peaks ascribed to vinyl versates (Veova) are pointed out. These products are commonly included as internal plasticisers in PVAc-based resins in order to lower the glass transition temperature ( $T_g$ ) of the resulting polymer. Therefore, they come as more stable substitutes for external plasticisers such as phthalate-type plasticisers, which tend to migrate to the surface of the polymer with time. Veova pyrolysis products and mass spectra characteristic fragmentation will be addressed thoroughly in the “Analysis of Flashe® paints by in situ thermally assisted pyrolysis–silylation GC-MS using HMDS” section of this paper.

Additionally, the analyses performed at 550°C show several small peaks along the pyrogram that correspond to PEG. These pyrolysates are useful for analysis since they indicate the presence of PEG-type surfactants in the paint formulation. These compounds appear in the derivatised form with HMDS, and present a characteristic masses  $m/z=45$ , 73, 116, 145 and 161. The ion with  $m/z=73$  appears in the derivatised products as it is the mass of the TMS group.

At 700°C, the analysis performed with HMDS gives much more complete information about the overall components of this vinyl paint, including peaks from the polymer chain and additives, and also possible fragments from distinct additives. The compounds identified are discussed in the following sections of this paper.

Pyrolysis performed at temperatures above 700°C presented similar peak profiles in the pyrograms with the downside of showing increased signal for secondary

**Fig. 1** Pyrograms corresponding to Py-GC-MS with HMDS of oriental red at different pyrolysis temperatures: (A) 400°C; (B) 550°C; (C) 700°C. These preliminary trials have revealed that pyrolysis conditions were optimised at 700°C on which concerns are the identification of the polymer chain, pigment fragments and main additives



pyrolysis products from the main polymer chain. Considering this, 700°C was the working temperature chosen for the analytical protocol used in the analysis of these vinyl paints.

#### Analysis of Flashe<sup>®</sup> paints by in situ thermally assisted pyrolysis–silylation GC-MS using HMDS

A set of Flashe<sup>®</sup> colours, namely armour green, oriental red, burnt umber, raw umber and white, was prepared as thin films and left to dry over a year period. These films have been analysed by in situ thermally assisted pyrolysis–silylation GC-MS using HMDS at 700°C in order to determine the overall composition of these products. The results obtained in the analyses of these samples are summarised in Table 1.

In general, the pyrolysis of PVAc-based polymers, at 700°C, results in the formation of peaks corresponding to ethanoic acid and benzene. These are the products of side group elimination from the backbone chain of the polymer, and the breakdown and rearrangement of the polyene chain during pyrolysis, respectively [3, 21]. In the pyrogram obtained for Flashe<sup>®</sup> oriental red presented in Fig. 1 C, ethanoic acid in the derivatised form is detected at low retention time. However, due to the presence of the derivating reagent at early retention time, the benzene peak is undetectable. According to the literature, one can still find some evidence of the formation of benzene later in the pyrogram, due to recombination and condensation reactions that occur during pyrolysis that form compounds such as 1,4-dihydronaphthalene, naphthalene and butyl benzoate

[21]. Nevertheless, for the products studied in this paper, and despite being PVAc-based paints, such compounds were not detected.

A further analysis of the pyrograms reveals traces of methacrylic acid (TMSMA), which is not detected with direct pyrolysis. This represents an improvement of the analysis achieved with the proposed method. Acrylic monomers are often present in PVAc formulations as co-monomers in order to improve overall mechanical properties and UV resistance [3]. The mass spectra shows characteristic ion fragments of  $m/z=158, 143, 73, 69$  and 41.

Propanoic acid and ethanoic acid 2-oxy-TMS are also detected in the pyrograms for all samples, and may be related to recombination reactions during the pyrolysis process. Benzoic acid-TMS was also found in the pyrograms as an intense peak, with ion mass spectra  $m/z=194, 179, 135, 105, 77$  and 51.

The set of peaks that appear between 9.3 and 9.9 min in the pyrogram of the studied PVAc paints are associated to the presence of versatates used as internal plasticiser. Vinyl versatates, also named VeoVa monomers (Shell), are understood to consist of several isomers of highly branched C<sub>9</sub> and C<sub>10</sub> vinyl esters [32]. They copolymerise with vinyl acetate by a simple addition polymerisation. Peak distribution corresponding to the VeoVa fraction that appears in the pyrogram of oriental red for Flashe PVAc paint obtained with in situ thermally assisted pyrolysis–silylation GC-MS using HMDS is shown in detail in Fig. 2. Retention time of the six main compounds of the VeoVa fraction, which did not overlap, together with  $m/z$  values of the main fragment ions, is summarised in Table 2. The close retention times

**Table 1** Summary of the compounds detected by means of Py-GC-MS in the Flashe<sup>®</sup> paint samples

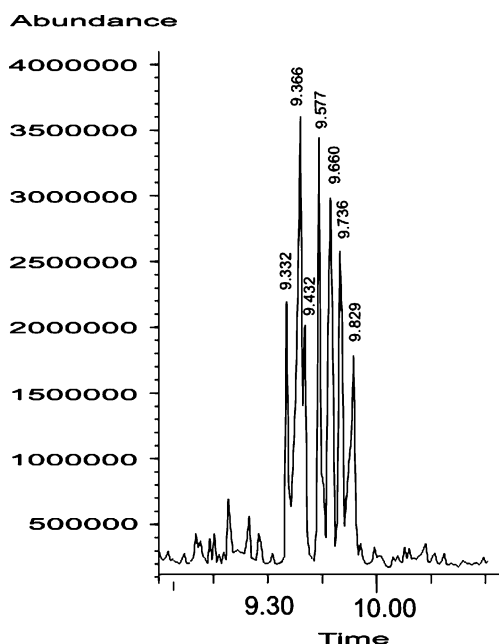
Colours	Flashe <sup>®</sup> oriental red		Flashe <sup>®</sup> armour green	Flashe <sup>®</sup> raw umber	Flashe <sup>®</sup> burnt umber	Flashe <sup>®</sup> white
Supplier	LeFranc & Bourgeois					
Declared composition by supplier	Vinyl paints					
Compounds identified	<i>m/z</i> ion fragments					
Ethanoic acid-TMS	117, 75, 45	√	√	√	√	√
2-Methoxyethanol-TMS	133, 103, 89, 73, 59, 45	–	√	√	–	–
2-TMS-oxy-ethanol	119, 103, 75, 73, 58, 45	√	–	–	√	–
Propanoic acid-2-methyl-TMS	145, 117, 75, 73, 58, 45	√	–	√	√	–
Methacrylic acid-TMS	158, 143, 73, 69, 41	√	√	√	√	–
Styrene	104, 78, 51, 39, 27	–	√	–	√	√
Phenoxy-TMS	166, 151, 77, 43	–	–	–	√	–
Propanoic acid 2-oxy-TMS	234, 191, 147, 117, 73, 45	√	√	√	√	√
Ethanoic acid 2-oxy-TMS	220 205, 147, 73	√	√	√	√	√
Benzoic acid-TMS	194, 179, 135, 105, 77, 51	√	√	√	√	√
Veova	See Table 2	√	√	√	√	√
Butanedioic acid-TMS	261, 147, 73, 55, 45	–	–	–	√	√
Pentanedioic acid-TMS	189, 142, 115, 87, 57, 43	–	√	–	–	√
Pigment traces		√ (PR112: 2,3,4-trichloro benzenamine) (195, 160, 124, 97, 62, 28)	–	–	–	–
Bis(2-butoxyethyl) phthalate	366, 223, 149, 56	–	√	–	–	–
Diethylene glycol dibenzoate	149, 105, 77, 51	–	√	–	–	–
Diglycol benzoate,	163, 105, 77	–	√	–	–	–
Isopropyl phenyl diphenyl phosphate	368, 251, 118, 77	√	√	–	–	–
PEG-TMS	45, 73, 101–103, 116–117, 145, 161 (...)	√	√	√	√	√

Only for oriental red paint sample was a fragment of an organic synthetic pigment, PR112, detected

suggested similar structures for these compounds. The mass spectra from all the peaks in this region are also very similar. They are dominated by  $m/z=73$  ascribed to the fragment ion  $[\text{TMS}]^+$ , which indicates that these compounds have been satisfactorily trimethylsilylated by HMDS. The presence of the  $[\text{M}-15]^+$  ion ( $m/z=229$ ) in the mass spectra of the main compounds appearing in the Veova fraction, which is ascribed to the loss of a methyl group from the TMS derivatives of the compounds, suggests that the group of compounds are highly branched isomers of the decanoic acid ( $\text{C}_{13}\text{H}_{28}\text{O}_2\text{Si}$ ) with structure close to that proposed by Learner [3, 19] that is shown in Fig. 3. Production on pyrolysis of  $\text{C}_{10}$  fatty acids presumably is taking place by a similar side group elimination mechanism to that discussed above resulting in the formation of ethanoic acid and benzene from the PVAc polymer. Identification of these compounds is in good agreement to that previously found by

Learner in Emultex VV536 PVAc emulsions using direct Py-GC-MS [19].

The rest of peaks that appear in the mass spectra of Veova compounds series exhibit low intensity if they are compared to the base peak. Nevertheless, two important processes described in general mass spectrometry treatises [33] that concern fragmentation of carboxylic acids and their derivatives have been identified in most of the mass spectra of the compounds composing the Veova fraction in our experiments. First of all, the  $\alpha$ -cleavage, which results in the formation of ion fragments  $[\text{COOTMS}]^+$  ( $m/z=117$ ) and the complementary  $[\text{M}-\text{COOTMS}]^+$  ( $m/z=127$ ), is observed in the mass spectra of the Veova series. The latter is of low abundance because this process probably is followed by a deprotonation that results in the fragment ion  $[\text{M}-\text{COOTMS}-\text{H}]^+$  ( $m/z=126$ ). Secondly,  $\gamma$ -cleavage that results in formation of fragment ion  $[\text{CH}_2-\text{CH}_2-(\text{C}=\text{O})-\text{O}-$

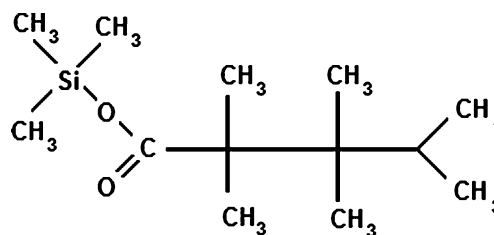


**Fig. 2** Detail of the oriental red pyrogram, which highlights the VeoVa fraction. Pyrolysis was performed with HMDS

TMS]<sup>+</sup> ( $m/z=145$ ), a minor peak in the mass spectrum. Low abundance of this fragment ion is probably due to the highly branched structure of the VeoVa fatty acids.

It is not easy to explain why McLafferty rearrangement is not taking place. Most probably, it is due to the particular structure of the VeoVa compounds, which are carboxylic acids highly branched at  $\alpha$ -,  $\beta$ - and  $\gamma$ -carbon (see Fig. 3) [33].

Characteristic peaks associated to  $\sigma$ -bond cleavage in the aliphatic chain, resulting in carbenium ions  $[C_3H_7]^+$ ,  $[C_4H_9]^+$ ,  $[C_5H_{11}]^+$ ,  $[C_6H_{13}]^+$  and  $[C_7H_{15}]^+$  are recognised at  $m/z=29$ , 43, 57, 71, 85, 97 and 113, respectively, in the mass spectra (Table 3). Characteristic accompanying pattern of peaks at  $m/z=[C_nH_{2n+1}]^+-2$  and  $m/z=[C_nH_{2n+1}]^+-4$  are also observed at the low-mass side of the corresponding peak of the carbenium ion, which is produced as result of dehydrogenation of these ions.



**Fig. 3** Proposed structure of an isomer of the trimethylsilylated- $C_{10}$  fatty acid appearing in the VeoVa fraction of Flashe<sup>®</sup> paints

Other interesting feature in the mass spectra of the VeoVa series is at  $m/z=159$  that is correlated with the fragment ion  $[M-C_6H_{13}]^+$ . Other fragment ions that appear in the mass spectra at  $m/z=202$ , 188, 174, 160 and 126 are harder to explain, but according to Learner [3] could result from the addition of a hydrogen atom to the charged carbon from a rearrangement reaction involving  $[M-C_3H_7]^+$ ,  $[M-C_4H_9]^+$ ,  $[M-C_5H_{11}]^+$ ,  $[M-C_6H_{13}]^+$  and  $[M-C_9H_{18}]^+$ . Peak at  $m/z=143$  that is particularly intense in mass spectra of all compounds has tentatively been ascribed to the formation of  $[C-CH_2-COOTMS]^+$ . This fragment ion at  $m/z143$  is found in deprotonated octanoic acid mass spectrum. This peak also appears, as a minor peak, in the mass spectra of  $C_{10}$  fatty acids associated to VeoVa fraction in Emultex VV536 PVA emulsion [3, 19]. In this last case, the fragment ion considered cannot be associated to a structure containing the TMS group because no trimethylsilyl derivatives are obtained by means of direct Py-GC-MS. In contrast to that, fragment ion at  $m/z143$  is a major peak in the mass spectra of Flashe<sup>®</sup> paints, which can be attributed to the presence of the group TMS in the fragment ion. Nevertheless, it should be noted that the proposed structure  $[C-CH_2-COOTMS]^+$  is hardly justified on the basis of the usual rearrangements and fragmentation pathways of fatty acids.

Along the pyrogram of oriental red, a series of peaks corresponding to PEG in their derivatised form with HMDS can also be identified, as explained in the previous section of this paper. These compounds have not been identified

**Table 2**  $m/z$  values of the characteristic ions found in the mass spectra of the TMS derivatives of the main compounds included in the VeoVa fraction appearing in the pyrogram of oriental red PVAc paint

Peak	VeoVa fraction Assignment <sup>a</sup>	$M_w$	$t_r$ (min)	Mass spectra data (70eV) Characteristic ions <sup>b</sup> : $m/z$
1	Unidentified decanoic acid, TMS ester	244	9.34	229, 202, 188, 173, 159, 143, 126, 117, 99, 85, 73, 71, 57, 43
2	Unidentified decanoic acid, TMS ester	244	9.43	229, 174, 159, 143, 126, 117, 85, 73, 71, 57, 43
3	Unidentified decanoic acid, TMS ester	244	9.57	229, 202, 188, 174, 159, 143, 126, 117, 85, 73, 71, 57, 43, 29
4	Unidentified decanoic acid, TMS ester	244	9.66	229, 202, 188, 173, 159, 143, 126, 117, 85, 73, 71, 57, 43
5	Unidentified decanoic acid, TMS ester	244	9.74	229, 174, 160, 143, 126, 117, 85, 73, 71, 57, 43
6	Unidentified decanoic acid, TMS ester	244	9.83	229, 174, 159, 143, 126, 117, 85, 84, 73, 71, 57, 43

<sup>a</sup> Assignment of structure based on the fragment ion pattern in the mass spectrum

<sup>b</sup> Base peak in italics

**Table 3** Main ion fragments identified in the VeoVa fraction

Compound	1	2	3	4	5	6
M <sup>+</sup>	244	244	244	244	244	244
[M-CH <sub>3</sub> ] <sup>+</sup>	229	229	229	229	229	229
[M-C <sub>3</sub> H <sub>7</sub> +H] <sup>+</sup>	202	–	202	202	–	–
[M-C <sub>4</sub> H <sub>9</sub> +H] <sup>+</sup>	188	–	188	188	–	–
[M-C <sub>5</sub> H <sub>11</sub> +H] <sup>+</sup>	–	174	174	–	174	174
[M-C <sub>5</sub> H <sub>11</sub> ] <sup>+</sup>	173	–	–	173	–	–
[M-C <sub>6</sub> H <sub>13</sub> +H] <sup>+</sup>	–	–	–	–	160	–
[M-C <sub>6</sub> H <sub>13</sub> ] <sup>+</sup>	159	159	159	159	–	159
[C-CH <sub>2</sub> -COOTMS] <sup>+</sup> ?	143	143	143	143	143	143
[M-COOTMS-H] <sup>+</sup>	126	126	126	126	126	126
[COOTMS] <sup>+</sup>	117	117	117	117	117	117
[C <sub>7</sub> H <sub>15</sub> ] <sup>+</sup>	99	–	–	–	–	–
[C <sub>6</sub> H <sub>13</sub> ] <sup>+</sup>	85	85	85	85	85	85
[C <sub>6</sub> H <sub>13</sub> -H] <sup>+</sup>	–	–	–	–	–	84
[TMS] <sup>+</sup>	73	73	73	73	73	73
[C <sub>5</sub> H <sub>11</sub> ] <sup>+</sup>	71	71	71	71	71	71
[C <sub>4</sub> H <sub>9</sub> ] <sup>+</sup>	57	57	57	57	57	57
[C <sub>3</sub> H <sub>7</sub> ] <sup>+</sup>	43	43	43	43	43	43

with direct pyrolysis but with the present method for every sample studied in this paper.

Besides the overall products detected in the general pyrograms, there are other compounds present in minor concentration, which seem to correspond to small variations for each colour formulation.

Organic pigments are, in general, very difficult to detect directly from microsamples since they are present in very low concentrations in paints due to their strong optical properties. The pyrogram corresponding to oriental red shows a minor peak corresponding to a fragment ascribed to the pigment red 112 (PR112), an azo pigment, which is in agreement with the indications supplied by the manufacturer. The mass spectrum of this pyrolysis product exhibits fragments ion at  $m/z=195$ , 160, 124, 97, 62 and 28, in agreement with that previously reported in literature [12]. In contrast to the behaviour of oriental red, green armour paint, which is prepared mainly with a green phthalocyanine pigment, does not exhibit any peak corresponding to this organic pigment. According to that reported in literature [19], phthalocyanine compounds do not undergo any kind of scission reaction on pyrolysis to produce fragments sufficiently volatile to pass through the GC column.

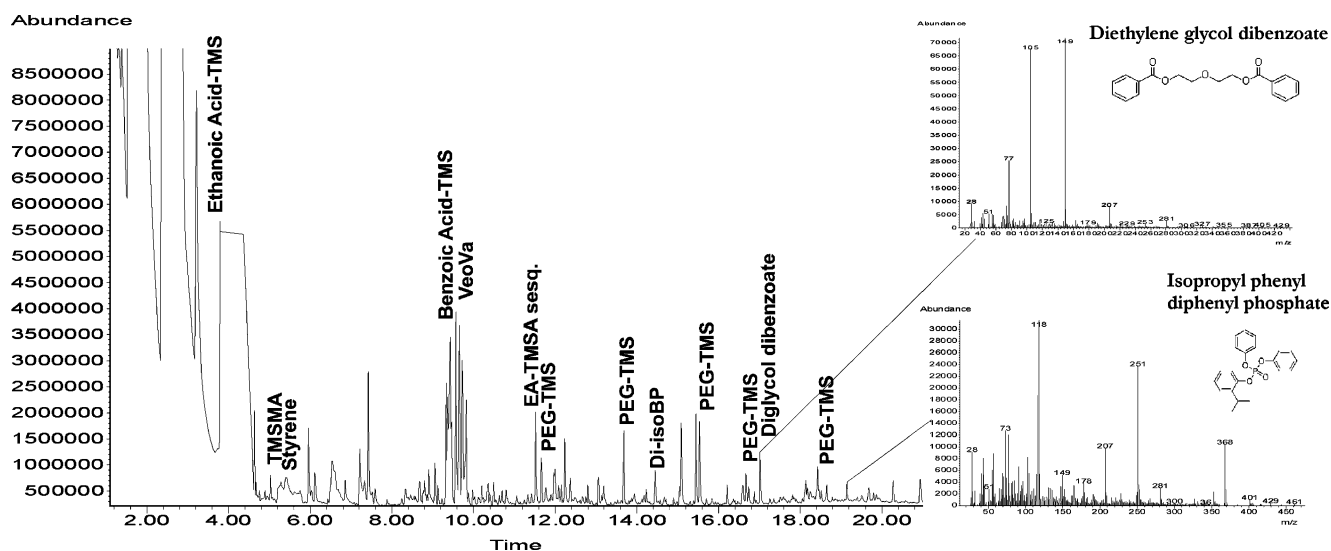
Moreover, it is interesting to note that dibutyl phthalate, used commonly as an external plasticiser, was also found in this paint sample, despite the internal plasticisation discussed previously by means of VeoVa. The mass spectra of phthalate-type plasticisers are typically dominated by peak at  $m/z=149$ . Phenyl phosphate has been also detected at trace levels. This

product is tentatively ascribed to a pyrolysis fragment of isopropyl phenyl diphenyl phosphate, found in some paints as a flame retardant. This product has also been identified in armour green colour.

A pyrogram corresponding to armour green is shown in Fig. 4. The results obtained from the analysis of this paint reveal the presence of styrene, a possible co-monomer for acrylic resins, which appear to have been included in this type of paint, since traces of TMSMA are also found in this sample as in oriental red. Another interesting compound is found at higher retention time that corresponds to a sesquimer of EA-TMSMA, which appears to be also an indicator of the presence of an acrylic resin as an additive in the fabrication of this paint. It is interesting to notice that all of these compounds seem to be present exclusively in their derivatised form, whereas they have not been detected in pyrograms obtained with direct pyrolysis.

Further in the pyrogram, a phthalate-type plasticiser (diisobutyl phthalate) has been identified and may have been included in the formulation in order to improve the overall physical properties of this paint.

Interestingly, relatively strong peaks corresponding to diethylene glycol dibenzoate, with characteristic ion fragments  $m/z=149$ , 105, 77 and 51 and diglycol benzoate  $m/z=163$ , 105 and 77 have been found together at high retention time in the pyrogram. These compounds are used commonly in industrial applications as plasticisers for PVAc-type resins and might as well have been included in this paint formulation in order to achieve desired performance properties.



**Fig. 4** Pyrogram corresponding to Flashe® armour green obtained at 700°C with HMDS. In this figure, the main compounds found in the paint samples are signed, which correspond mainly to acetic acid from the polymer main chain, VeoVa internal plasticisers, di-isobutyl

phthalate (*Di-iso-BP*) external plasticisers and PEG-type surfactants. Interestingly, the presence of styrene and methyl acrylate has been detected. Later in the pyrogram, diethylene glycol and isopropyl phenyl diphenyl phosphate have also been found

Finally, a strong peak corresponding to isopropyl phenyl diphenyl phosphate, a flame retardant additive, has been detected in this paint sample. Marker ion fragments detected are  $m/z=368$ , 251, 118 and 77.

#### Analysis of Flashe® paint extractions by Py-GC-MS with HMDS

The analysis of raw umber and burnt umber colours exhibited similar pyrogram profile to these previously described.

A series of deionised water extractions from Flashe® oriental red, armour green, raw umber, burnt umber and white films were prepared in order to separate possible minor water-soluble additives that may be hindered in the pyrogram due to the presence of major compounds such as polymer pyrolysates or secondary reactions that take place during pyrolysis. The waxy-like residues obtained from the extraction process for each colour of Flashe® paint films were analysed by Py-GC-MS with HMDS. The results obtained from the extractions of Flashe® vinyl paint samples are summarised in Table 4.

A pyrogram obtained for armour green extract is presented in Fig. 5. The presence of several peaks, which have not been detected in the general pyrogram obtained from the corresponding paint sample, can readily be observed. Well-defined peaks corresponding to styrene  $m/z=104$ , 78, 63 and 51 and methyl styrene are found early in the pyrogram and complement the results obtained previously for the paint samples. These compounds are also present in the extracts from the rest of paint samples. Interestingly, the analysis ran for armour green also revealed peaks

corresponding to *o*-xylene,  $\alpha$ -methylstyrene and methyl-naphthalene that may be related to recombination reactions promoted during pyrolysis.

Two intense peaks are found in the pyrogram that correspond to butanedioic acid and pentanedioic acid, both in the silylated form.

The water extraction of these paint films appears very useful to enhance the peak signal of PEG-type compounds in the pyrogram as signed in Fig. 5. Mostly, all PEG-type products appear in their derivatised form, which proves the efficiency of HMDS in the reprivatisation of –OH functional end groups. It is interesting to notice that, in the case of the analysis of the extract from white paint sample, it has been possible to detect the presence of PEG-type products with C=C double bond and C–C bond end groups. This might be an indicator of different cleavage pathways that occur during the pyrolytic process, which would be in good agreement with previous studies found in the literature [34].

#### Mechanical properties of Flashe® paints

Representative stress–strain curves obtained for the paints studied are presented in Fig. 6. For each sample, three replicates were obtained to confirm the consistency of the results. It is interesting to point out that the replicates of each colour exhibit similar characteristics in the elastic region but are somewhat discrepant in the elongation at break values. This is probably related to somewhat heterogeneous film formation properties of these paints, which has also been reported in the literature [35]. The results presented correspond to the replicates, which exhibited most plastic deformation.

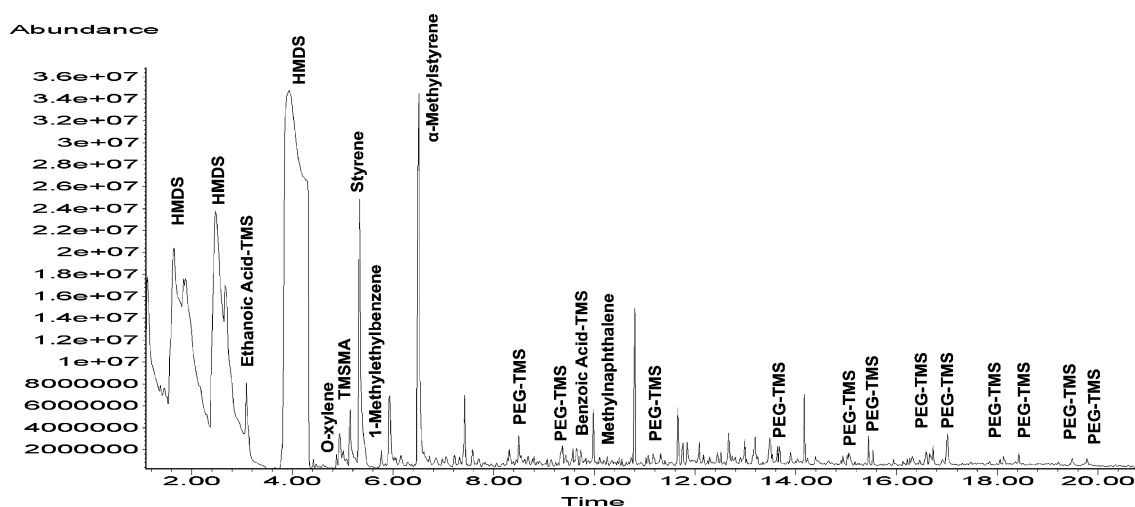


**Table 4** Main compounds detected by means of Py-GC-MS in the Flashe<sup>®</sup> extractions

Extractions		Flashe <sup>®</sup> oriental red	Flashe <sup>®</sup> armour green	Flashe <sup>®</sup> raw umber	Flashe <sup>®</sup> burnt umber	Flashe <sup>®</sup> white
Supplier		LeFranc & Bourgeois				
Declared composition by supplier		Vinyl paints				
Compounds Identified	<i>m/z</i> ion fragments					
Ethanoic acid, TMS ester	117, 75, 59, 45	√	√	√	√	√
Propanoic acid, 2-methyl-TMS	160, 145, 75,73, 58, 45	√	√	√	√	√
Ethanol, 2-[(TMS)-oxy]-TMS	119, 103, 85, 58, 43	–	–	–	–	√
<i>o</i> -Xylene	106, 91, 77, 65, 51, 39	–	√	–	√	√
Methacrylic acid-TMS	158, 143, 73, 69, 41	√	√	√	√	√
Styrene	104, 78, 63, 51, 39, 27	√	√	–	√	√
Vinylcarbitolether	160, 87, 72, 59, 45	–	–	–	–	√
$\alpha$ -Methylstyrene	118, 103, 91, 78, 51, 39	√	√	–	√	√
Phenoxy-TMS	166, 151, 77, 43	–	–	–	–	√
Propanoic acid-2-methyl-TMS	145, 117, 75, 73, 58, 45	√	√	√	√	√
Ethanoic acid 2-oxy-TMS	220 205, 147, 73	√	√	√	√	√
Vinyl ethyl carbitol	160, 85, 72, 59, 45, 31, 29	–	–	–	–	√
Divinylcarbitol	158, 117, 73, 71, 57, 45, 27	–	–	–	–	√
2-Pyrrolidinone, 1-ethenyl	111, 82, 68, 56, 41, 28	–	–	–	–	√
Methenamine	140, 112, 96, 85, 69, 53, 42	–	√	–	–	√
Benzoic acid	194, 179, 135, 105, 77, 51	–	√	√	√	√
Pentanedioic acid-TMS	276, 261, 158, 147, 73, 55	–	√	–	√	–
Butanedioic acid-TMS	247, 218, 172, 147, 129, 73, 55, 45	–	√	–	–	√
Hexanedioic acid-TMS	(290), 275, 147, 11, 83, 73, 55, 45	–	√	–	√	–
PEG-TMS	45, 73, 101–103, 116–117, 145, 161 (...)	√	√	√	√	√
Phosphate-TMS	314, 299, 73, 45	–	–	–	√	–

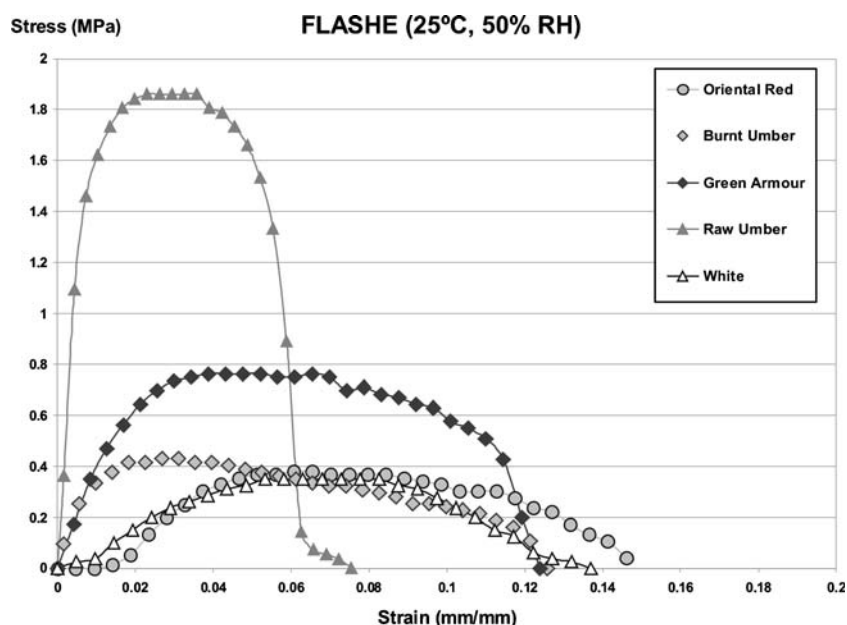
Between the different colours, there is an evident variation in the mechanical behaviour of the samples. Nevertheless, all samples showed the formation of cracks soon after the first strain increments were applied, and

started to break soon after (see Fig. 7). Oriental red exhibits an elongation of 14%, whereas raw umber reaches about 5% elongation. This implies a major difference between these vinyl paints and acrylic paints, which are reported to



**Fig. 5** Pyrogram obtained for Flashe<sup>®</sup> armour green extract. Peaks assigned correspond to ethanoic acid-TMS, *o*-xylene, styrene, methylethylbenzene,  $\alpha$ -methylstyrene and methylnaphthalene. PEG-type compounds were also identified

**Fig. 6** Stress–strain curve obtained for the Flashe<sup>®</sup> samples studied: oriental red, burnt umber, green armour, raw umber and white



elongate about 400% before breaking [36], at similar experimental conditions.

Regarding the ultimate elongation at break values, white and oriental red samples present similar mechanical behaviour, showing more flexibility, and this interestingly correlates with the overall pyrograms that present relatively less intense peaks correlated with PEG derivatives. In contrast, raw umber and green colours appear to have been formulated with a higher amount of PEG-type compounds, which may be related to the stabilisation of the pigment in the formulation. Considering that these colours present higher stiffness, when compared to other colours, it appears that these additives might be influencing the film formation process of the paints. The existence of external plasticisers and acrylic–styrene additives may possibly be attributed to an attempt to improve the overall mechanical properties of these films.

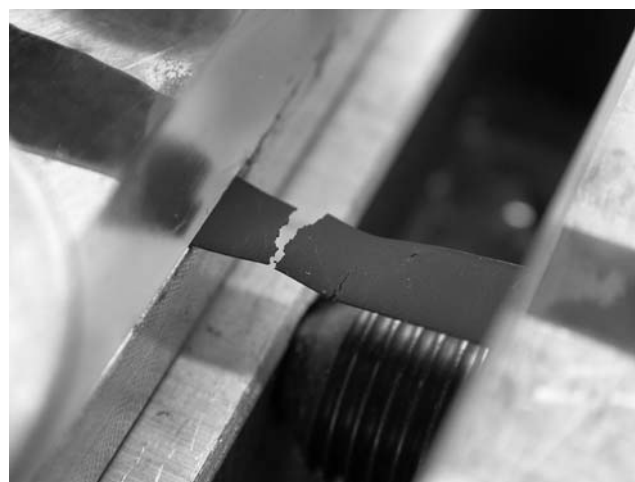
## Conclusions

In this paper, a new method consisting of the use of HMDS as a derivatising reagent in Py-GC-MS for analysis of PVAc paint samples is presented. The optimisation of the method allowed to improve data on additives and polymer analysis when compared to those from direct pyrolysis.

The method was tested on Flashe<sup>®</sup> PVAc-type paints and their corresponding water extracts, and the results indicate the presence of several monomers different from vinyl acetate. The presence of TMSMA and styrene can be related to the addition of co-monomers in the emulsion process, or can rather be related to the presence of more than one emulsion in the elaboration process of these colours.

Moreover, several additives have been identified, such as phenyl phosphate-type flame retardant products, glycol benzoates and phthalate-type plasticisers and preservatives such as methenamine. This indicates that the manufacturer includes a variety of products in search of desired properties of the paint.

The study of the mechanical properties of several paint samples allowed to characterise the tensile properties of these films as a function of the pigments and additives present in their composition. Interestingly, there appears to be a correlation between mechanical properties and the presence of PEG-type additives present in the formulations, as these compounds might be influencing the stiffness and plastic behaviour of the paint films.



**Fig. 7** Picture of armour green Flashe<sup>®</sup> paint sample breaking in the mechanical tester's gauge. The photo evidences the type of break these samples experience. Rather than a clean break, the sample experiences several simultaneous fractures with a saw-tooth-like pattern

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