Journal of Analytical and Applied Pyrolysis 113 (2015) 606–620

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

Characterization of additives of PVAc and acrylic waterborne dispersions and paints by analytical pyrolysis–GC–MS and pyrolysis–silylation–GC–MS

Miguel F. Silva, María Teresa Doménech-Carbó*, Laura Osete-Cortina

Instituto de Restauració del Patrimonio, Universitat Politècnica de València, Camino de Vera 14, València 46022, Spain

ARTICLE INFO

Article history:
Received 20 February 2015
Received in revised form 14 April 2015
Accepted 16 April 2015
Available online 23 April 2015

Keywords:
Additive
PVAc
Acrylic
Waterborn dispersions
Paints
Pyrolysis–GC–MS
Pyrolysis–silylation–GC–MS

ABSTRACT

Commercial formulations of poly(vinyl acetate) (PVAc) and acrylic dispersions and paints commonly used by artists include a number of additives such as surfactants, coalescing agents, defoamers and thickeners, which are designed for improving shelf-life, as well as chemical and physical properties of the resulting product. Recent studies have shown that additives present in paints play an important role in the alteration processes undergone by the painting during ageing and further in cleaning tasks planed in conservation interventions. However, the identification of additives is a difficult task due to the elusive character of these substances present at low concentration in the paint.

In this context, a four-step approach is proposed that includes analysis of paint samples together with analysis of their water extracted products by pyrolysis–gas chromatography–mass spectrometry (Py–GC–MS) and pyrolysis–silylation–gas chromatography–mass spectrometry (Py–silylation–GC–MS). This analytical strategy enables a better characterization of common additives present in commercial PVAc and acrylic paints and dispersions. In particular, the analysis of water soluble extracts, which are mainly composed by paint additives, avoids the interference of the major polymer pyrolizates. Experimental conditions concerning sample preparation and instrumental working conditions of both Py–GC techniques are optimized.

Both acrylic and PVAc paints presented poly(ethylene oxide) (POE) type fragments dominating the background of their pyrograms, especially when derivatized by means of hexamethyldisilazane (HMDS). For the first time, additives such as alkyl sulfate and alkyl ether sulfate with C_{10} and C_{12} alkyl chains, poly(ethoxylate) fatty alcohol and octylphenyl poly(ethoxylate) surfactants were identified, as well as polyvinyl alcohol (PVOH) protective colloids, hydrophobically modified ethoxylated urethane (HEUR) thickeners an defoamers. Their major fragments and corresponding mass spectra are discussed.

1. Introduction

Waterborne PVAc and acrylic dispersions are formulated by including a series of additives which are necessary during the polymerization processes as well as for stabilizing the product during storage, transportation, application and lifetime service.

Waterborne dispersions used for manufacturing paints are prepared with additives of different type such as initiators, chain transfer agents, buffers, surfactants, protective colloids and preservatives. In a second step, in which the latex is transformed into a suspoemulsion system by adding the pigment, the manufacturer will add other additives in view of achieving a number of desired properties. These may include wetting and dispersing agents, coalescing solvents, defoamers, preservatives, thickeners and rheology modifiers, freeze-thaw stabilizers and extenders [1–4]. It has been shown that the nature and amount of surfactants used in the manufacture of paints affects not only the film formation process but also important properties of the resulting paint film such as tackiness, water sensitivity and mechanical properties. For this reason, the identification of such compounds is highly relevant for conservation scientists, as they remain in the dried film playing an important role in the alteration processes that determine the aging behavior of the paint. It is worth mentioning that migration of surfactants to the surface is an alteration process frequently observed in aged paintings and reported as responsible for staining and inducing changes in gloss and color of the painting [5–13]. In addition to the migration problem, recent studies performed in aged acrylic

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* Corresponding author. Tel.: +34 963877835; fax: +34 963877836.
E-mail address: tdomenec@crbc.upv.es (M.F. Silva).

http://dx.doi.org/10.1016/j.jaap.2015.04.011
0165-2370/

samples have also shown that some additives contained in these paints are prone to degrade fast forming small agglomerates that remain trapped within the bulk film. This causes some acrylic films to become softer upon aging and, consequently, more prone to imprint and dirt picking [10,14].

Moreover, the solubility of additives influences the overall sensitivity of the paint to conservation cleaning treatments. The same applies to other conservation treatments such as consolidation or facing/protections, in which organic solvents or water are in contact with the paint surface for long periods of time [9,10,14,15]. Wolbers et al. [16] have stated that additives such as poly(acrylic acids), thickeners or surfactants may affect seriously the response of the paint to conservation treatments based on the use of aqueous solutions prepared at different pH and conductivity.

In the last decades the growing social implication in the safeguard of heritage has resulted in an increase of studies devoted to the analytical characterization of artworks. Nevertheless, most of the studies carried out have focused on the identification of the synthetic polymers used as biding medium of modern paints whereas studies focused on the identification of additives are scarce. An interesting overview of these applications has been provided by Anderson [17].

The specialized studies found in the heritage conservation field that have been addressed to the identification of additives in waterborne acrylics and PVAc dispersions, are generally focused on the characterization of surfactants and/or plasticizers. Fourier-transformed infrared spectroscopy (FTIR) and attenuated total reflectance-FTIR spectroscopy (ATR–FTIR) have been used to detect POE type additives in acrylic paints and binding media [10,13–15,18–23]. Non-ionic alkylaryl-POE type surfactants have been successfully identified in acrylic paint films by combining FTIR with size-exclusion chromatography (SEC–FTIR) [24]. Phthalate type plasticizers have also been detected by means of this analytical technique in PVAc films [25,26].

Other chromatographic techniques, such as high-performance liquid chromatography coupled with mass spectrometry and diode array detector (HPLC–MS–DAD) and (Py-GC–MS) have been used to detect these non-ionic alkylaryl-POE surfactants in acrylic formulations, as well as plasticizers in PVAc products [25–27]. Recently, a report described the use of Py-GC–MS in double-shot mode for the detection of oxidation products in aged acrylic samples [28]. HMDS has been proposed by the authors to perform Py-silylation-GC–MS on a series of PVAc-Vinyl Versatate (VeoVa) paints, for studying the additives otherwise difficult to characterize by means of the conventional techniques [11].

Matrix assisted laser desorption/ionization-mass spectrometry (MALDI-MS) and nanospray-electrospray ionization-mass spectrometry (nanospray-ESI-MS) have been used much successfully in determining POE chain lengths and sulfonated end groups from a series of surfactants both from test specimens and micro-samples extracted from artworks [29,30].

In the context of industrial applications, Py-GC–MS has been used to study lubricants, antioxidants and flame retardants [31–33]. Py-GC–MS has also been used for the study of the thermal decomposition of hindered amine light stabilizers as well as liquid chromatography-ultraviolet absorbance detection-evaporative light scattering detection [34,35]. Temperature-programmed pyrolysis hyphenated with metastable atom bombardment ionization mass spectrometry has also been used to detect light stabilizers in car paints [36].

Due to the importance of identifying the family of additives present in PVAc and acrylic paint layers before executing a conservation treatment, it is proposed here the combined use of both Py-GC–MS and Py-silylation-GC–MS for the study of commercial PVAc and acrylic dispersion paints, as well as their extractions in water. Both analytical methods reveal complementary information that allows, for the first time, the identification of a number of additive families such as ionic surfactants, HEUR thickeners, protective colloids and defoamers, as well as the characterization of other more common additives such as non-ionic surfactants. This provides, accordingly, a deeper insight into the composition of the acrylic and PVAc materials proposed for the study, but also expands the information of interest that can be achieved by these analytical techniques.

Table 1
Summary of products tested. PVAc: refers to poly(vinyl acetate), VeoVa: vinyl versatate. Sty: styrene. MMA: methyl methacrylate. 2EHA: 2 ethylhexyl acrylate. BA: butyl acrylate. BMA: butyl methacrylate. EA: ethyl acrylate.

Resin type	Commercial name	Color tested	Polymer composition
PVAc	Conrayt®	Pure dispersion	PVAc homopolymer
	Vinavil®	Pure dispersion	PVAc homopolymer
	Flashe®	Burnt umber	PVAc-VeoVa
	Flashe®	Raw umber	PVAc-VeoVa
Acrylic	Pébéo®	Titanium white	Sty-MMA-2EHA
	Pébéo®	Naphthol crimson	Sty-MMA-2EHA
	Liquitex	Gloss medium	BA-(BMA)-MMA
	Liquitex® Heavy Body	Cobalt blue	BA-(BMA)-MMA
	Liquitex® Heavy Body	Cadmium yellow	BA-(BMA)-MMA
	Liquitex® Heavy Body	Burnt umber	BA-(BMA)-MMA
	Liquitex® Heavy Body	Phthalocyanine blue	BA-(BMA)-MMA
	Royal Talens®	Gloss medium	BA-(BMA)-MMA
	Royal Talens®	Gel medium	BA-(BMA)-MMA
	Royal Talens®	Titanium white	BA-(BMA)-MMA
	Royal Talens®	Black oxide	BA-(BMA)-MMA
	Royal Talens®	Raw sienna	EA-MMA
	Royal Talens®	Naphthol red	EA-MMA

2. Experimental

2.1. Analytical reagents and reference materials

Hexamethyldisilazane (HMDS) was supplied by Sigma, Steinheim, Germany.

PVAc and acrylic products tested in this study are summarized in Table 1. These include waterborne dispersions and artists' commercial paints.

2.2. Preparation of specimens and samples

2.2.1. Model paint films

PVAc and acrylic test specimens were prepared as drawdowns as model paint films over Mylar® sheets. The products were cast directly as supplied and then dried in laboratory conditions for four years before testing. The resulting films have an average thickness of 0.15 mm.

2.2.2. Water extractions

A series of water extracts were obtained from the samples of model paint films in order to characterize water soluble additives. For this purpose, samples of the model paints weighting approximately 0.4–0.5 g were immersed in 50 mL of deionized water for 24 h at room temperature. The films were then removed, and the solution was dried at 50 °C in a laboratory oven until water was completely evaporated. A waxy-like solid extract was obtained for analyzing by Py-GC–MS and Py-silylation-GC–MS.

2.2.3. Preparation of samples for Py-GC–MS and Py-silylation-GC–MS

A series of samples from model paint films (a few μg) were scrapped with scalpel and introduced in a quartz tube with a small plug of quartz wool for analyzing by Py-GC–MS. In parallel, a series of samples of the waxy-like water extracts obtained after immer-