Defeyt *et al. Herit Sci (2017) 5:15*
DOI 10.1186/s40494-017-0129-2

Heritage Science

RESEARCH ARTICLE Open Access

Polyurethane coatings in twentieth century outdoor painted sculptures. Part II: comparative study of four systems by means of Py-GC/MS

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Abstract

Because PU coatings offer a compromise between aesthetic and performance expectations, unachievable with other types of industrial paints, they are currently recognized as the most appropriate option to coat sculptures intended for an outdoor setting. However, the PU class includes various systems, such as two package solvent-borne, two package water-borne, one package water-borne and fluoropolymer polyurethanes, which possess very different properties. 115 reference samples of PU coatings were investigated by means of Py-GC/MS, in order to outline the differences and the similarities existing, in terms of composition, between the major PU systems used for creating as well as for conserving modern painted outdoor sculptures. The Py-GC/MS study of an extended number of reference samples showed that the composition of equivalent PU systems strongly varies depending on the product line and the manufacturer. Furthermore the comparison of all the produced pyrograms allowed defining characteristic marker compounds helpful to discriminate specific PU paint systems.

Background

As evidenced by the numerous case studies reported in literature [1–4], PUs represent one of the most important class of industrial paints used in 20th outdoor painted sculptures (OPS), for making process as well as for posterior conservation treatments. The leading position of PU coatings noticed for painted artworks intended for an outdoor setting is due to the advantageous weatherability and durability generally associated with such products. However polyurethane is a generic class covering various paint systems that have their own properties. In practice, the uneven quality of PU coatings is indicated through variable significance and speed of the surface changes affecting artworks [2]. The PU coatings employed in OPS can be roughly divided in four systems, namely two package solvent-borne (2KSBPU), two package water-borne (2KWBPU), one package water-borne (1KWBPU) and fluoropolymer polyurethanes (FPU). The differences in terms of composition and performance existing between these four paint systems remain barely studied from a conservation point of view.

In the frame of the outdoor sculpture research project conducted at the Getty Conservation Institute (GCI), a part of the Modern and Contemporary Art Research Initiative, an extended number of PU reference samples were analyzed by means of the FTIR-ATR and Py-GC/MS techniques. This paper presents an overview of the obtained Py-GC/MS results. It outlines the differences and the similarities existing, in terms of composition between the investigated PU coatings and proposes some marker compounds helpful to discriminate certain PU systems.

Experimental

PU reference materials

The 115 PU reference samples analyzed in this study were collected or prepared between 2005 and 2015, and

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incorporate primers, topcoats and clearcoats. Various lines from manufacturers that are representatives of the PU industry, namely Dupont, PPG, Akzo, BASF, Tnemec, Carboline, Sherwin–Williams, NCP, Matthews Paints and Awlgrip, were investigated. The tested reference materials include:

Standard Color References supplied by collaborating Artists' Estates, Foundations, and Studios
Coupons made on request by industrials or fabricators
Swatches of replacement coatings used for OPS repainting
Laboratory prepared samples for the needs of this study

In Table 1, the 115 PU coating samples analyzed by Py-GC/MS are presented through the associated artists, outdoor sculptures and commercial names. For sake of clarity, the samples of two package solvent-borne (2KSBPU), two package water-borne (2KWBPU), one package water-borne (1KWBPU) and fluoropolymer polyurethanes (FPU) are presented separately. For a more accurate characterization of 2K PU coatings, available activators and co-reactants involved in the preparation of solvent-borne and water-borne systems were individually analyzed by Py-GC–MS.

Py-GC/MS analysis

Py-GC/MS analyses were performed on a Frontier PY-2020D microfurnace pyrolyzer interfaced to an Agilent 7890A GC/5975C inert MSD. A J&W DB-5MS-UI capillary column (30 M × 0.25 mm × 0.25 μm) attached to a Frontier Vent-Free adaptor was used (40 M effective column length), with helium set to 1 ml/min. The split injector was set to 320 °C with a split ratio of 50:1. The GC oven temperature program was 40 °C for 2 min, then 6 °C/min to 320 °C with 9 min isothermal. Fragments with a size of ca. 3 μm were taken from the PU reference materials in order to be analyzed by Py-GC/MS. Samples were placed into 50 μl stainless steel Eco-cups prior to analysis, and pyrolyzed at 550 °C. The Py-GC/MS results obtained for the 2KSBPU, FPU, 2KWBPU and 1KWBPU samples are presented separately. For a more accurate characterization of the activated and/or cured PU coatings, pure polyisocyanate resins and pure co-reactants involved in the preparation of certain systems were analyzed individually by Py-GC/MS in the same fashion.

Expert system for data processing

Although the analysis itself is easy to conduct, the abundance of the collected Py-GC/MS data have made challenging their evaluation. The key difficulty in Py-GC/MS data evaluation is recognizing the connection between the constitutive materials of the PU coatings and the sets of associated marker compounds formed by pyrolysis of these materials. Due to the extended number and the heterogeneous composition of the PU coating samples investigated in this study, the Py-GC/MS data were treated with an expert system for data processing. Scientists at the Getty Conservation Institute (GCI) and conservators at the J. Paul Getty Museum (JPGM), developed the latter for facilitated and more accurate Py-GC/MS data interpretation.

This expert system combines both components: processing with AMDIS (Automated Mass spectral Deconvolution and Identification System), and evaluation using Excel. AMDIS version 2.70 used in this study was bundled with the National Institute of Standards and Technology (NIST) MS library (version 2.0g), and AMDIS can also be downloaded for free from the NIST website (NIST 2015). Further information on AMDIS processes data can be found in [5]. Microsoft Excel 2013 was used with a customized workbook specifically developed for the present research.

Results and discussion

The Py-GC/MS results obtained for 2KSBPUs, 2KWBPUs, 1KWBPUs and FPUs are discussed separately. In the sections devoted to the 2KSBPU and 2KWBPU systems, the results obtained for the activators, the co-reactants and the activated systems are presented in three distinct parts. An overview of the compounds identified by Py-GC/MS in the reference samples of 2KSBPU, 2KWBPU, 1KWBPU and FPU is given in Table 2.

Two package solvent-borne PU (2KSBPU)

Activators

The pyrograms obtained for the Awlgrip and Akzo activators similarly exhibit a dominant and sharp peak of hexamethylene diisocyanate (HDI) monomer, which is consistent with the complete depolymerization of HDI resins on pyrolysis. By using the described experimental parameters, monomeric HDI elutes at 9.35 min. In the mass spectrum of HDI, the strongest peaks are the fragment ions at $m/z = 41$ and 56. Note the absence of the molecular ion ($m/z = 168$) in the spectrum.

The HDI peak is much less intense in the pyrograms produced for the Imron FG1333 and FG1633 activators. For both of them, important peaks identifying isocyanic acids (isocyanatocyclohexane, 1-isocyanatobutane and 1-isocyanato(1-$^{2}H_{1}$)hexane), 3-quinuclidone and hexamethyleneimine (HMI) were detected. Possibly, those compounds are decomposition products of the HDI polyisocyanates resulting from the pyrolysis. The presence of a very small peak identified as caprolactam has to be noticed as well.

Table 1 List of the PU coating references analyzed by Py-GC–MS, presented with the associated artists, outdoor sculptures and commercial names

Artist	OPS	Trade names	Coating type [a]	Sample n	Color [b]
2KSBPU					
R. Lichtenstein	*Three brushstrokes* (1984)	DuPont®/Imron® 2.1 HG-C™	C	2	Cl, Bl
	Three brushstrokes (1984)	DuPont®/Imron® 2.1 HG™	T	5	Rd, W, Bk, Yel
	Three brushstrokes (1984)	DuPont®/Imron® 5.0™	T	13	W, Bk, Gr, Bl, Yel, Rd, Br
	n/a	Awlgrip®/(unknown)	T	3	W, Bk, Si
	n/a	Akzo Nobel/Akzo topcoat 683-3-7	C	13	Cl, W, Bk, Yel, Bl, Rd, Gr
A. Caro	*Box piece E* (1971)	Nason®/FullBase 3.5 VOC	T	2	Rd
M. di Suvero	*Gandydancer's Dream* (1987-88)	DuPont®/Imron® industrial strength ultra low VOC™	T	2	Rd
	n/a	Tnemec®/Endura-Shield® II 1075	T	1	Bk
	n/a	Tnemec®/Endura-Shield® II 1074S	T	5	Rd, Or, Yel
A. Calder	*Spiny top* (1963)	DuPont®/Imron® 2.1 SG "E"™	T	1	Rd
	Jousters (1963)	MPC™/Satin MAP	T	3	Rd, Bk, W
	Jousters (1963)	MPC™/42900SP Matte Clear	C	1	Cl
	n/a	NCP®/2KSBPU	T	1	Rd
	La Grande Vitesse (1969)	Tnemec®/Endura-Shield® II 1074U	T	1	Rd
	Peau Rouge (1971)	Tnemec®/Endura-Shield® 73	T	1	Rd
T. Smith	n/a	Tnemec®/Endura-Shield® Series 175	T	1	Bk
	n/a	Akzo Nobel/Aerodur® 5000	T	1	Bk
C. Oldenburg/C. Van Bruggen	*Corridor Pin Blue* (1999)	PPG/Deltron® DBU	T	1	Bl
G.Hume	Back of snowman (Ink)	BASF/Glasurit® 22 line	T	1	Bl
R. Murray	*Nimbus* (1978)	Sherwin–Williams®/Polane®	T	1	Bl
n/a	n/a	DuPont®/Imron® industrial strength™	T	1	W
		DuPont®/Imron® 3.5 HG-D™	T	1	Bk
		DuPont®/Imron® 2.1 HG, SG, FT, ST ™	T	21	Bk, W, Yel, Gr
		DuPont®/Imron® 2.1 Pr-P ™	P	1	W
		DuPont®/Imron® 2.1 HG-D™	T	1	W
		DuPont®/Imron® 2.1 EZ-C™	C	1	Or
		Awlgrip®/Awlcraft 2000®	T	3	Bk, W
		Awlgrip®/Awlcraft 2000®	C	1	Cl
Artist	**OPS**	**Trade names**	**Coating type [a]**	**Sample x**	**Color [b]**
2KWBPU					
A. Calder	*Jousters* (1963)	NCP®/2KWBPU	T	9	W, Bk, Rd, Yel
	Four Arches (1975) intermediate model	Spectrum coatings/W-series	T	1	Rd
	n/a	Formulated by J.A. Escarsega	C	1	Cl
	n/a	Formulated by J.A. Escarsega	C	1	Cl
n/a	n/a	DuPont®/Imron® ZV-HG™	T	1	W
1KWBPU					
n/a	n/a	DuPont®/Imron® 1.5 ST-D™	T	1	W
		DuPont®/Imron® 1.5 PR™	P	2	W
		DuPont®/Imron® 1.2 HG-C™	C	1	Cl

Table 1 continued

Artist	OPS	Trade names	Coating type [a]	Sample x	Color [b]
2KFPU					
T. Smith	n/a	PPG/Coraflon® ADS Intermix	T	1	Bk
		PPG/Coraflon® ADS Intermix low VOC	T	1	Bk
		Sherwin–Williams®/Fluorokem™ HS Satin	T	1	Bk
		Carboline®/Carboxane 950 Satin	T	1	Bk
		Tnemec®/Fluoronar® series 1072	T	1	Bk
D. Judd	*Untitled* (1968)	Tnemec®/Fluoronar® series 1072	T	2	Gr
R. Murray	*Duet* (1965)	Tnemec®/Fluoronar® series 1072 V	T	1	Or
n/a	n/a	Tnemec®/Fluoronar® series 1071	T	1	Bl

The samples of 2KSBPU, 2KWBPU, 1KWBPU and FPU are discussed separately

[a] *T* Topcoat, *C* Clearcoat, *P* Primer

[b] *Bk* Black, *Gr* Green, *Gy* Gray, *Rd* Red, *Bl* Blue, *Yel* Yellow, *W* White, *Or* Orange, *Cl* Clear, *Br* Brown, *Si* Silver

Indeed, the use of epsilon-caprolactam as a blocking agent for isocyanates is quite common for engineering activators required in two components polyurethane coating systems [6, 7]. Blocking agents allow conserving unreacted isocyanates at storage temperatures. The recurrent presence of caprolactam could indicate activators containing isocyanate groups blocked by epsilon-caprolactam. However, caprolactam could also correspond to a residual product of the HDI cyclic trimer decomposition.

Co-reactants

The Py-GC/MS results obtained for the Aircraft 2000 co-reactants pointed out a binder mix with high contents in styrene and n-butyl methacrylate (nBMA) from a polymorphic form. The same three peaks of styrene, nBMA and 2-hydroxyethylmethacrylate (2HEMA) are observed in the pyrograms of the co-reactants used for clear, black and white Aircraft 2000 coatings. The co-reactant used for the Imron 2.1 topcoats seem richer in polyester resins. The intense peak seen at 7.73 min in the pyrograms of Imron 2.1 is caprolactone, a compound widely used in coating industry to prepare polyester resins for high-solids coatings [6]. The major peak of phthalic anhydride (PA), occurring at a slightly later retention indicates a phthalic anhydride-based polyester resin. Various other polyacid species, for instance, isobenzofuranone, benzoic and adipic acids were punctually identified. Polyols commonly used for making polyester resins in the coating industry, i.e. neopentyl glycol (NPG), cyclohexanedimethanol (CHDM) and 1,6-hexanediol were also detected. Additionally, in the case of the Imron 2.1 co-reactants, the identification of styrene, n-butyl acrylate (nBA) and nBMA monomers indicates the presence of styrenic acrylic resins in the binder mix.

The pyrogram produced for the Imron 5.0 co-reactant exhibits a single dominant peak with molecular ion at $m/z = 104$ and the characteristic $m/z = 78$ and 51 fragments of styrene in the related mass spectrum. Much smaller is the phthalic anhydride peak arising at 9.09 min. The Py-GC/MS results also unveiled the presence of three acrylic species; ethyl methacrylate (EMA), dodecyl methacrylate (C12MA) and decyl methacrylate (C14MA).

Activated systems

All the pyrograms produced for activated 2KSBPUs have in common a peak identifying HDI monomer. In the cases of the NCP, Nason and BASF references HDI was found in combination with isophorone diisocyanate (IPDI).

Basically, for most of the studied 2KSBPU samples, the formation of polyurethane linkages result from the reaction of polyisocyanate resins with hydroxy-terminated polyester and/or hydroxyl-substituted acrylic resins. Example of pyrograms produced for 2KSBPU samples made from hybrid resins is shown in Fig. 1.

The reaction of isocyanates with hydroxy-functional co-reactants yielding to urethanes is reversible at elevated temperatures [6]. As a result, the pyrograms of PU coatings primarily based on acrylic resins, such as the Awlgrip, MPC and Endura-Shield Series samples, display easily distinguishable peaks of monomeric diisocyanate and acrylic monomers. The acrylic species recurrently identified, include nBMA, nBA, and 2HEMA. However, iBMA (isobutyl methacrylate), 2EHA (2-ethylhexyl acrylate), EMA (ethyl methacrylate), C8MA (octyl methacrylate), C12MA and C14MA monomers were also punctually detected.

The polyester resins were identified through the detection of characteristic polyester chemical precursors, such

Table 2 Overview of the compounds identified by Py-GC/MS for the reference samples of 2KSBPU, 2KWBPU, 1KWBPU and FPU

	2KSBPU	2KWBPU	1KWBPU	2KFPU
Polyols				
NPG	X	X	X	–
CDHM	X	X	–	–
1,6-Hexanediol	X	X	–	–
(Z)-2-Pentenol	X	–		–
Propylene glycol	X	–	X	–
Cyclohexanol	–	–	–	X
2-Butyl-2-ethyl-1,3-propanediol	–	X	–	–
Polyacids				
Phthalic anhydride	X	X	–	X
Adipic acid	X	X	X	–
Caprolactone	X	–	X	X
Isobenzofuranone	X	–	–	–
Benzoic acid	X	–	–	–
Isobenzofurandione	X	X	–	–
Ketone				
2-Cyclohexen-1-one	–	–	–	X
2-Methylcyclopentanone	X	–	–	X
Aldehyde				
Heptanal	X	–	–	–
2-Methylpentanal	X	–	–	–
Phenolic				
BPA	X	–	–	X
Phenol	X	X	–	X
Polypropylene				
Propylene	X	–	–	–
PDU eluates				
Peak at 13.67 min (m/z 81)	–	X	X	–
Peak at 13.75 min (m/z 81)	–	X	X	–
Peak at 1.85 min (m/z 81)	–	X	X	–
Styrene				
Styrene	*X*	*X*	*X*	*X*
Siloxane				
Siloxane	–	X	–	X
Acrylates				
nBA	*X*	*X*	*X*	*X*
Methoxyethyl acrylate	X	–	X	–
2HEA	X	X	–	X
Methacrylates				
nBMA	X	X	X	–
EMA	X	–	–	–
C12MA	X	–	–	X
C14MA	X	–	–	X
2HEMA	X	X	–	–
EGDMA	X	X	–	–
Ethoxyethyl methacrylate	X	–	–	–
iBMA	X	–	–	–
Methyl methacrylate	X	–	–	–
Isobornyl methacrylate	X	–	–	–
C8MA	X	X	–	X
Cetyl methacrylate	X	–	–	–
Isocyanates				
Isocyanatocyclohexane	*X*	*X*	–	*X*
1-Isocyanato(1-$^{2}H_{1}$)hexane	*X*	*X*	–	*X*
1-Isocyanatobutane	X	–	–	–
1-Isocyanato-3-methylbenzene	X	X	–	–
HDI	X	X	–	X
IPDI	X	X	–	–
Trimethyl isocyanurate	X	–	–	X
Others				
3-Quinuclidone	X	X	–	X
1, 4-Pentadiene	X	X	–	X
2-Ethylhexan-1-ol	X	X	–	X
2-Ethyl-3-hexen-1-ol	X	X	–	X
Caprolactam	*X*	*X*	*X*	*X*
NMP	–	X	X	–

X, identified in one or more reference sample(s); *X*, identified in one or more reference sample(s) for each investigated system; –, not identified

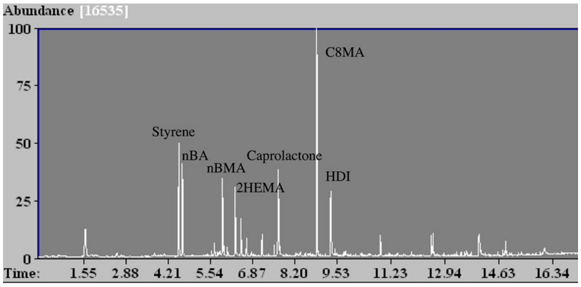

Fig. 1 Pyrogram produced for one 2KSBPU reference sample (Imron® 2.1 HG white topcoat from DuPont®) displaying peaks of styrene, acrylic species (nBA, nBMA, C8MA, 2HEMA), caprolactone and HDI

as PA, caprolactone, adipic and benzoic acids, NPG, CHDM and 1,6-hexanediol. Note that polycaprolactone polyols, allow making PU coatings with advantageous exterior durability are widely used in industry. The use of CHDM and 1,6-hexanediol as chain extenders in the PU industry has to be noticed as well [6, 7]. The significant peak of styrene arising in most of the pyrograms, pointed out the general use of styrenic polyester and/or acrylic resins in the PU coating formulations [8, 9]. The Aerodur 5000 black topcoat from the Tony Smith Estate and the unpigmented Akzo 683-3-7 reference from the Lichtenstein's studio, both produced by Nobel, are singular examples of styrene free 2KSBPU coatings. In both cases, the Py-GC/MS results led to the identification of adipic acid and heptanal.

The detection of heptanal is possibly due to the presence of aldehyde resins in the binder mixes [10]. In the same way, the presence of alkyd resins could be at the origin of the detection of adipic acid [11–14]. Nevertheless, the Aerodur 5000 reference sample differs from the Akzo 683-3-7 samples (pigmented and unpigmented) through the absence of acrylic resin and the presence of bisphenol A (BPA), which is a characteristic compound of epoxy resins [6, 15]. BPA epoxy resins can be used as co-reactants due to the presence of hydroxyl groups, which are cross-linked with isocyanates. On the other hand, the use of polyisocyanates cross-linked with epoxy resins, which have secondary hydroxyl groups, is a way of improving exterior durability of PU coatings.

Bisphenol A was also detected for the Deltron DBU, Nason Finishes and Imron Industrial Strength samples. The green coating from Polane, do not contain polyester or acrylic resins, it is made of a styrene–aldehyde hybrid binder. A styrene–nBMA copolymer with a relatively high polypropylene content was found in the NCP reference samples.

Two package water-borne PU (2KWBPU)

Activators

HDI monomer eluting at 9.35 min was identified in all the pyrograms produced for water-dispersible polyisocyanate resins. All of them display additional peaks identifying isocyanic acid, 3-quinuclidone and HMI, in other words, the same decomposition products as those detected for the unmodified polyisocyanate resins discussed above. The Py-GC/MS results obtained for activators made from HDI isocyanurates showed the decomposition of the cyclic trimer on pyrolysis. However, a very small peak of trimethyl isocyanurate was observed in the pyrogram of the H_2O activator from NCP. The most significant difference between the pyrograms of water-dispersible and regular resins lies in the presence of a dominant peak of 2-ethylhexan-1-ol (2-EH) at 6.51 min in the pyrograms of aqueous resins. In PU industry, 2-EH is used as blocking agent to make polyisocyante resins containing blocked isocyanate groups [7]. Because of a low reactivity, alcohol-blocked isocyanates are favored in the preparation of waterborne coatings with high stability [6]. Although, the peak area is variable depending on the sample, 2-EH can be considered as a marker compound, relevant for the identification of waterborne PU systems.

Co-reactants

The pyrogram produced for the anionic polyacrylate dispersion Bayhydrol, used in the 2K waterborne clearcoats, formulated at the GCI laboratory, primarily display the peaks of styrene, nBA and 2HEMA monomers. Smaller peaks of other monomeric acrylic species—nBMA and ethylene glycol dimethylacrylate (EGDMA)—are also present. The Py-GC/MS results did not reveal evidence of polyester resins (absence of characteristic precursors) but outlined the modification of the acrylic resin with styrene.

Activated systems

As shown in Fig. 2, the characteristic peak of 2-EH noticed for pure water-dispersible polyisocyanate resins remains readily identifiable in the pyrograms produced for activated waterborne systems. The differences of composition existing between the NCP, laboratory made and Spectrum coatings, clearly appear by comparing the produced pyrograms. On the basis of the Py-GC/MS results, the 2KWBPU samples may be divided in three subgroups. The first one includes the laboratory prepared clearcoats using anionic polyacrylate dispersion, as co-reactant [16]. Due to the absence of polyester resin in the binder mix the related pyrograms are relatively simple, the principal peaks being monomeric species of HDI, styrene, nBA and 2HEMA. The second subgroup includes all the NCP waterborne samples. The related pyrograms did not display any acrylic or styrene peak, but exhibit the three same dominant peaks, respectively seen at 13.67, 13.75 and 13.85 min. The mass spectra of these peaks have in common the fragment ion of IPDI, at $m/z = 81$. Interestingly, the IPDI monomer, eluting at 10.86 min is identified as well. The formation of new compounds resulting from the pyrolysis decomposition process of polyurethane dispersion (PUD) involving IPDI resin could reasonably explain the presence of such strong peaks [17, 18]. Indeed, due to the water solubility of HDI crosslinkers, cycloaliphatic diisocyanates such as IPDI are favored to make PUDs [6]. The absence of the IPDI peak and the dominant peak of HDI, in the pyrogram obtained for pure H_2O activator, supports this assumption. Additional peaks of NPG, 1,6-hexanediol and adipic acid seen in the pyrograms of NCP samples suggest the use of PUD involving polyester polyols [16].

The W series Spectrum Coating sample represents alone the last subgroup. In this case, the Py-GC/MS results led to the identification of a system based on hydroxyl functional PUD prepared with an acrylic–urethane hybrid resin [19, 20]. The acrylic resin mostly consists of a styrene–2EHA copolymer, although, nBA, nBMA and C8MA monomeric species were identified as well. The strong peak of 2-EH can be reasonably explained by the use of an activator containing isocyanates blocked with 2-EH. The PUD identification is supported by the presence of the decomposition products

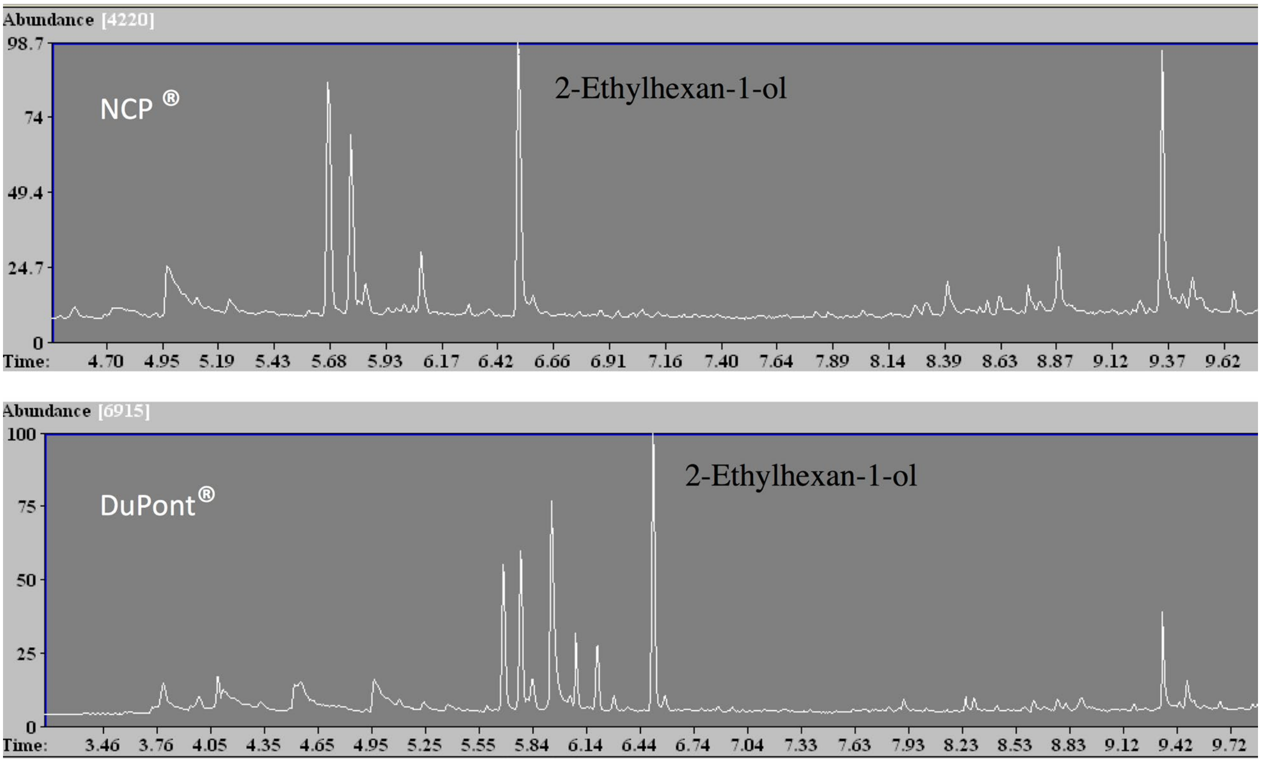

Fig. 2 Pyrograms of 2KWBPU reference samples, N9688A white topcoat from NCP® (*top*) and Imron® ZV HG white topcoat from DuPont® (*bottom*), displaying a dominant peak of 2-ethylhexan-1-ol at 6.51 min

PUD eluting at 13.67, 13.75 and 13.85 min, previously reported for the PUD-based coatings from NCP.

One package waterborne PU (1KWBPU)

Cured systems

The pyrograms obtained for the one package aqueous PU coating references, which include a grey primer, a clearcoat and a direct-to-metal white topcoat from Imron, present the same characteristic features. Despite obvious differences in terms of use, nBMA–adipic acid polyester PUD was identified in the three systems. The pyrograms produced for the primer and the topcoat have in common a small peak of monomeric styrene. The clearcoat reference involving *N*-methyl-2-pyrrolidone (NMP) appeared as styrene free. NMP is a water-miscible solvent commonly used to make PU dispersions [19]. In addition, the 1KWBPU pyrograms similarly exhibit the three characteristic peaks outlined for 2KWBPUs based on PUD (see "Activated systems"). The 1K samples pyrograms have in common two other peaks with a major fragment ion at $m/z = 81$. The most significant differences observed between the 1K and the 2K aqueous PUD systems are the missing peaks of 2-ethylhexan-1-ol and diisocyanate monomeric species in the pyrograms produced for the former.

Fluoropolymer urethane (FPU)

Activated systems

All the FPU pyrograms exhibit the same characteristic pattern, which is illustrated in Fig. 3. This one includes a dominant peak of 2-methylcyclopentanone, eluting at 4.62 min and, a smaller peak of cyclohexanol at a slightly earlier retention time (4.49 min). On the basis of the Py-GC/MS results obtained from the FPU samples, this combination of peaks appears as a diagnostic feature of FPU coatings.

A strong peak of HDI monomer and smaller peaks of isocyanatocyclohexane and 1-isocyanato(1-$^2H_1$)hexane are other common features noticed for the FPU pyrograms. Styrene was also identified in every case and, most of the obtained pyrograms display peaks identifying caprolactone and 2-cyclohexen-1-one.

The samples from the Fluoranar series have in common low siloxane content. Note the presence of several siloxane peaks in the Carboline 950 pyrogram as well. The peak identifying trimethyl isocyanurate in the pyrogram of the Tony Smith's color standard, prepared with a black Fluoronar 1072 topcoat, is consistent with the use of an activator based on HDI isocyanurate [21, 22]. The orange topcoat used for repainting the 1965 Murray's outdoor sculpture, *Duet*, is the unique Fluoranar sample containing bisphenol

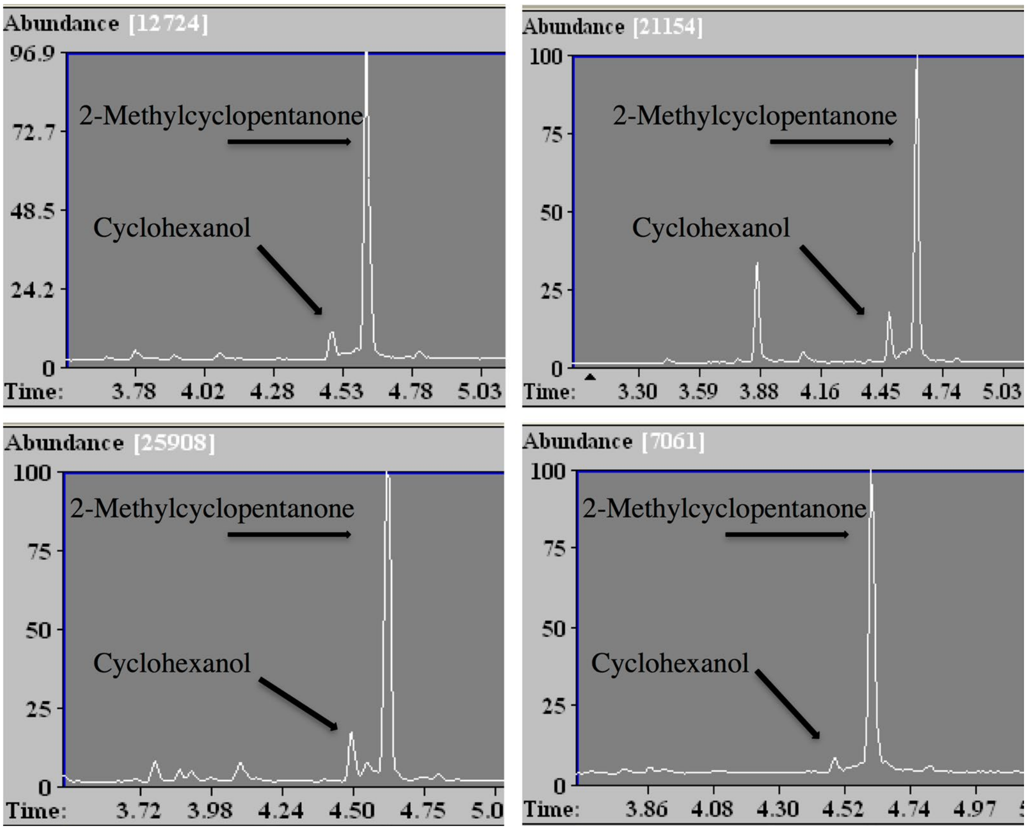

Fig. 3 Pyrograms of 2KFPU reference samples, Fluoronar Series 1072 V® orange topcoat from Tnemec® (*top left*), Fluorokem HS® Satin black topcoat from Sherwin–Williams® (*top right*), Coraflon ADS® Intermix black topcoat from PPG® (*left bottom*) and Carboxane 950® black topcoat from Carboline® (*right bottom*). The dominant peak of 2-methylcyclopentanone at 4.62 min and, the much less intense peak of cyclohexanol at 4.49 min are characteristic features of FPU pyrograms

A. The presence of this compound suggests a binder mix with epoxy resin. The pyrograms of the green Fluoranar 1072 topcoats used for Judd's coupons are distinguished by styrene peaks significantly stronger.

The small peaks identifying the acrylic monomeric species, in the FPU pyrograms, indicate binder mixes poor in acrylic resins. That is why the identification of acrylic resins from the FPU references by using FTIR spectroscopy was not possible. A small peak of 2EHA monomer appears in the Fluoronar 1072 and 1071 pyrograms, while a small peak of nBA monomer is present in the pyrograms of both Caraflon coatings from PPG. An additional peak of bisphenol A is observed for only one of them. In the case of the Fluorokem coating from Sherwin&William, the produced pyrogram display peaks identifying a C12MA-C14MA copolymer.

Conclusions

The Py-GC/MS study of 2KSBPU, 2KWBPU, 1KWBPU and FPU reference samples pointed out very different compositions for equivalent products and allowed determining marker compounds reliable for the identification of specific PU systems. The pyrograms obtained for two package PU systems systematically exhibit a peak identifying HDI monomer. Inversely no diisocyanate monomers were found in the pyrograms produced for the one package waterborne PU references. Most of the investigated PU coatings are based on binder mixes involving styrene, acrylate, methacrylate and phthalic anhydride polyester resins in various proportions. Acrylic monomeric species primarily identified are nBA and nBMA. Characteristic decomposition products of aldehyde and silicone resins, resulting from pyrolysis were detected in several references. A dominant peak of 2-ethylhexan-1-ol characterizes the pyrograms recorded for the 2KWBPU samples. In PU industry, this alcohol is widely used as blocking agent in the preparation of polyisocyanate resins offering waterborne coatings with high stability. For this reason, the detection of high 2-ethylhexan-1-ol content might be considered as an indicator of 2KWBPU systems. Concerning the FPU samples, the produced pyrograms similarly display a dominant peak of

2-methylcyclopentanone and a smaller peak of cyclohexanol. The concomitant presence of these two peaks appeared as a characteristic feature of the FPU pyrograms. As a result, the join presence of 2-methylcyclopentanone and cyclohexanol provides a reliable criterion for the identification of FPU coatings.

Authors' contributions

CD conceived the study and coordinated it. CD carried out the Py-GC/MS measurements and discussion of the results and drafted the manuscript. MS discussed and helped to interpret the results. JE gave theoretical background on PU and their practical formulation. JL carried out the preparation and classification of the samples. RR supervised the study and participated in the interpretation of the data. All authors read and approved the final manuscript.

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Acknowledgements

The authors sincerely thank Julie Wolfe, J. Paul Getty Museum, who provided insight and expertise that greatly assisted this research. We would also like to show our gratitude to Joy Mazurek, Getty Conservation Institute, for her valuable advice and technical assistance with Py-GC/MS measurements.

Competing interests

The authors declare that they have no competing interests.

Received: 5 November 2016 Accepted: 15 March 2017

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