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Polyurethane coatings in 20th 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.

1. Introduction

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.

2. Experimental

2.1. PU reference materials

The 115 PU reference samples analyzed in this study were collected or prepared between 2005 and 2015, and 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 divided into four subgroups. 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.

Table 1 List of the PU coating references analyzed by Py-GC-MS, presented with the

associated artists, outdoor sculptures and commercial names. The samples of two package solvent-borne (2KSBPU), two package water-borne (2KWBPU), one package water-borne (1KWBPU) and fluoropolymer polyurethanes (FPU) are divided into four subgroups.

*T=Topcoat, C=Clearcoat, P=Primer

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

2KSBPU					
Artist	**OPS**	**Trade names**	**Coating type***	**Sample x**	**Color***
R. Lichtenstein	*Three brushstrokes* (1984)	DuPont®/Imron® 2.1 HG-C™	C	2	Cl, Bl
R. Lichtenstein	*Three brushstrokes* (1984)	DuPont®/Imron® 2.1 HG™	T	5	Rd, W, Bk, Yel
R. Lichtenstein	*Three brushstrokes* (1984)	DuPont®/Imron® 5.0™	T	13	W, Bk, Gr, Bl, Yel, Rd, Br
R. Lichtenstein	n/a	Awlgrip®/(unknown)	T	3	W, Bk, Si
R. Lichtenstein	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
M. di Suvero	n/a	Tnemec®/Endura-Shield® II 1075	T	1	Bk
M. di Suvero	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
A. Calder	*Jousters* (1963)	MPC™/Satin MAP	T	3	Rd, Bk, W
A. Calder	*Jousters* (1963)	MPC™/42900SP Matte Clear	C	1	Cl
A. Calder	n/a	NCP ®/2KSBPU	T	1	Rd
A. Calder	*La Grande Vitesse* (1969)	Tnemec®/Endura-Shield® II 1074U	T	1	Rd
A. Calder	*Peau Rouge* (1971)	Tnemec®/Endura-Shield® 73	T	1	Rd
T. Smith	n/a	Tnemec®/Endura-Shield® Series 175	T	1	Bk
T. Smith	n/a	Akzo Nobel/Aerodur® 5000	T	1	Bk
C. Oldenburg / C. Van	*Corridor Pin Blue*	PPG/Deltron® DBU	T	1	Bl

Artist	OPS	Trade names	Coating type*	Sample x	Color**
Bruggen	(1999)				
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
n/a	n/a	DuPont®/Imron® 3.5 HG-D™	T	1	Bk
n/a	n/a	DuPont®/Imron® 2.1 HG, SG, FT, ST ™	T	21	Bk, W, Yel, Gr
n/a	n/a	DuPont®/Imron® 2.1 Pr-P ™	P	1	W
n/a	n/a	DuPont®/Imron® 2.1 HG-D™	T	1	W
n/a	n/a	DuPont®/Imron® 2.1 EZ-C™	C	1	Or
n/a	n/a	Awlgrip®/Awlcraft 2000®	T	3	Bk, W
n/a	n/a	Awlgrip®/Awlcraft 2000®	C	1	Cl

2KWBPU

Artist	OPS	Trade names	Coating type*	Sample x	Color**
A. Calder	Jousters (1963)	NCP ®/2KWBPU	T	9	W, Bk, Rd, Yel
A. Calder	Four Arches (1975) Intermediate Model	Spectrum Coatings/W-series	T	1	Rd
A. Calder	n/a	Formulated by J.A. Escarsega	C	1	Cl
A. Calder	n/a	Formulated by J.A. Escarsega	C	1	Cl
n/a	n/a	DuPont®/Imron® ZV-HG™	T	1	W

1KWBPU

Artist	OPS	Trade names	Coating type*	Sample x	Color**
n/a	n/a	DuPont®/Imron® 1.5 ST-D™	T	1	W
n/a	n/a	DuPont®/Imron® 1.5 PR™	P	2	W
n/a	n/a	DuPont®/Imron® 1.2 HG-C™	C	1	Cl

2KFPU

Artist	OPS	Trade names	Coating type*	Sample x	Color**
T. Smith	n/a	PPG/Coraflon® ADS Intermix	T	1	Bk
T. Smith	n/a	PPG/Coraflon® ADS Intermix low VOC	T	1	Bk
T. Smith	n/a	Sherwin-	T	1	Bk

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		Williams®/Fluorokem™ HS Satin			
T. Smith	n/a	Carboline®/Carboxane 950 Satin	T	1	Bk
T. Smith	n/a	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 1072V	T	1	Or
n/a	n/a	Tnemec®/Fluoronar® Series 1071	T	1	Bl

2.2. Py-GC/MS analysis

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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 x 0.25 mm x 0.25 µm) attached to a Frontier Vent-Free adaptor was used (40 M effective column length), with helium set to 1 ml/minute. 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 minutes, then 6°C /minute to 320°C with 9 minutes isothermal. 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 coreactants involved in the preparation of certain systems were analyzed individually by Py-GC/MS in the same fashion.

2.3. 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.

3. Results and discussion

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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.

3.1. Two package solvent-borne PU (2KSBPU)

3.1.1. Activators

The pyrograms obtained for the Awlgrip and AKZO activators similarly exhibit a dominant and sharp peak of hexamethylene diisocyanate 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 minutes. 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 (cyclohexane, butane 1- and hexane 1- isocyanato-), quinuclidone 3 and hexamethylenimine (hexane 1-, 6- diamine) 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.

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.

3.1.2. 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 nBMA polymers. The same three peaks of styrene, nBMA and 2-hydroxyethyl MA 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 minutes 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 anhydride phthalic, occurring at a slightly later retention indicates an anhydride phthalic-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 hexane diol were also detected. At a lesser proportion, Imron 2.1 co-reactants also contain acrylic resins modified with styrene, nBA and nBMA monomers were identified through their respective characteristic ion fragments.

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 anhydride phthalic peak arising at 9.09 minutes. The Py-GC-MS results also unveiled the presence of three acrylic species; EMA, C12MA and C14MA.

3.1.3. 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.
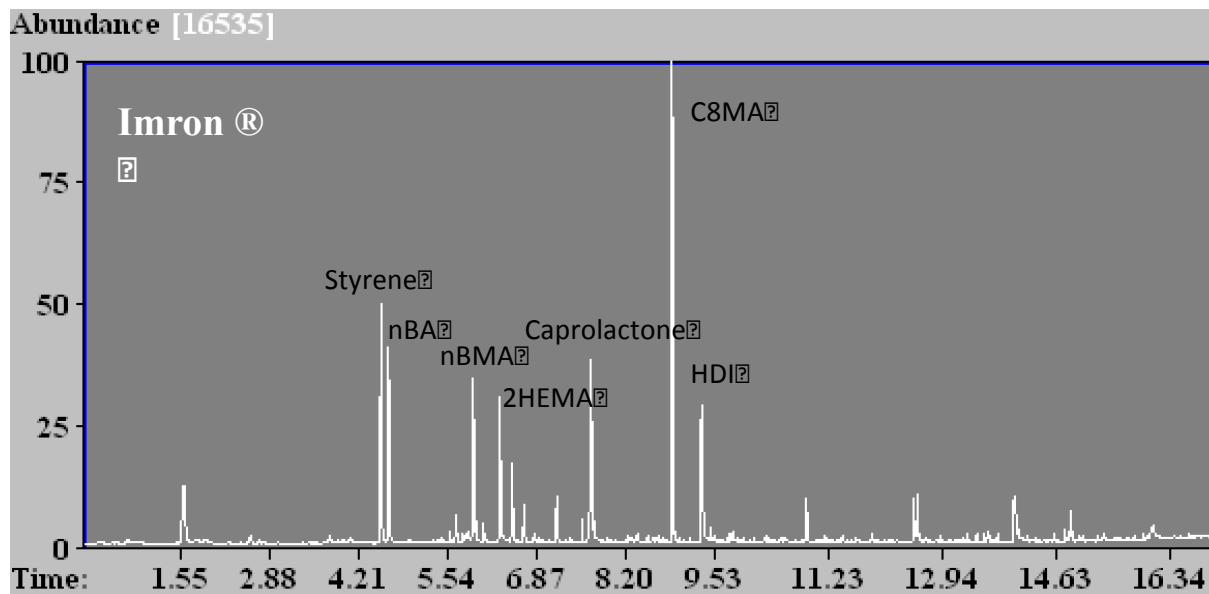
Fig. 1 Pyrogram produced for one 2KSBPU reference sample (Imron® 2.1 HG white topcoat from DuPont®) displaying peaks of styrene, acrylic species (nBA, nBMA, 2HEMA), phthalic anhydride, caprolactone and HDI.

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 primary based on acrylic resins, such as the Awlgrip, MPC and Endurashield Series samples, display easily distinguishable peaks of monomeric diisocyanate and acrylic monomers. The acrylic species recurrently identified, include nBMA, nBA, and 2HEMA. However, iBMA, 2EHA, EMA, C8MA, C12MA and C14MA monomers were also punctually detected.

The polyester resins were identified through the detection of characteristic polyester chemical precursors, such as phthalic anhydride (PA), caprolactone, adipic and benzoic acids, neopentyl glycol (NPG) cyclohexanedimethanol (CHDM) and 1-, 6- hexane diol. Note that polycaprolactone (PCL) polyols, allow making PU coatings with advantageous exterior durability are widely used in industry. The use of CHDM and 1-, 6- hexane diol 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 [9-10]. The Aerodur 5000 black topcoat from the Tony Smith Estate and the Akzo clear from 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 [11], while the detection of adipic acid indicates the use of alkyd resins [12-15]. Nevertheless, the Aerodur 5000 topcoat differs from the Akzo one by the absence of acrylic resin and the presence of bisphenol A, which is a characteristic compound of epoxy resins [6,16].

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.

3.2. Two package water-borne PU (2KWBPU)

3.2.1. Activators

HDI monomer eluting at 9.35 minutes was identified in all the pyrograms produced for water dispersible polyisocyanate resins. All of them display additional peaks identifying isocyanic acid, quinuclidone 3 and hexamethylenimine, in other words, the same decomposition products than those detected for the unmodified polyisocyanate resins discussed above. The PyGCMS 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 H2O 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 1-hexanol, 2- ethyl at 6.51 minutes in the pyrograms of aqueous resins. In PU industry, 2-ethylhexyl alcohol 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, 1-hexanol, 2- ethyl can be considered as a marker compound, relevant for the identification of waterborne PU systems.

3.2.2. Co-reactants

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

3.2.3. Activated systems

As shown in Fig. 2, the characteristic peak of 2-ethylhexyl alcohol 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 [8]. 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 for which 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 minutes. 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 minutes is identified as well. The formation of new compounds resulting from the pyrolysis decomposition process of a polyurethane dispersion (PUD) prepared with an IPDI polyisocyanate resin, could reasonably explain the presence of such strong peaks [17-18]. Because of the solubility of HDI crosslinkers in water, 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 H2O activator, supports this assumption. Additional peaks of NPG, hexane diol and adipic acid seen in the pyrograms of NCP samples suggest the use of PUD involving polyester polyols [8].

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 on a styrene-2EHA copolymer, although, nBA, nBMA and C8MA monomeric species were

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identified as well. The strong peak of 1-hexanol, 2- ethyl can be reasonably explained by the use of an activator containing 2-ethylhexyl alcohol-blocked isocyanates. The PUD identification is supported by the presence of the decomposition products PUD eluting at 13.67, 13.75 and 13.85 minutes, previously reported for the PUD-based coatings from NCP.
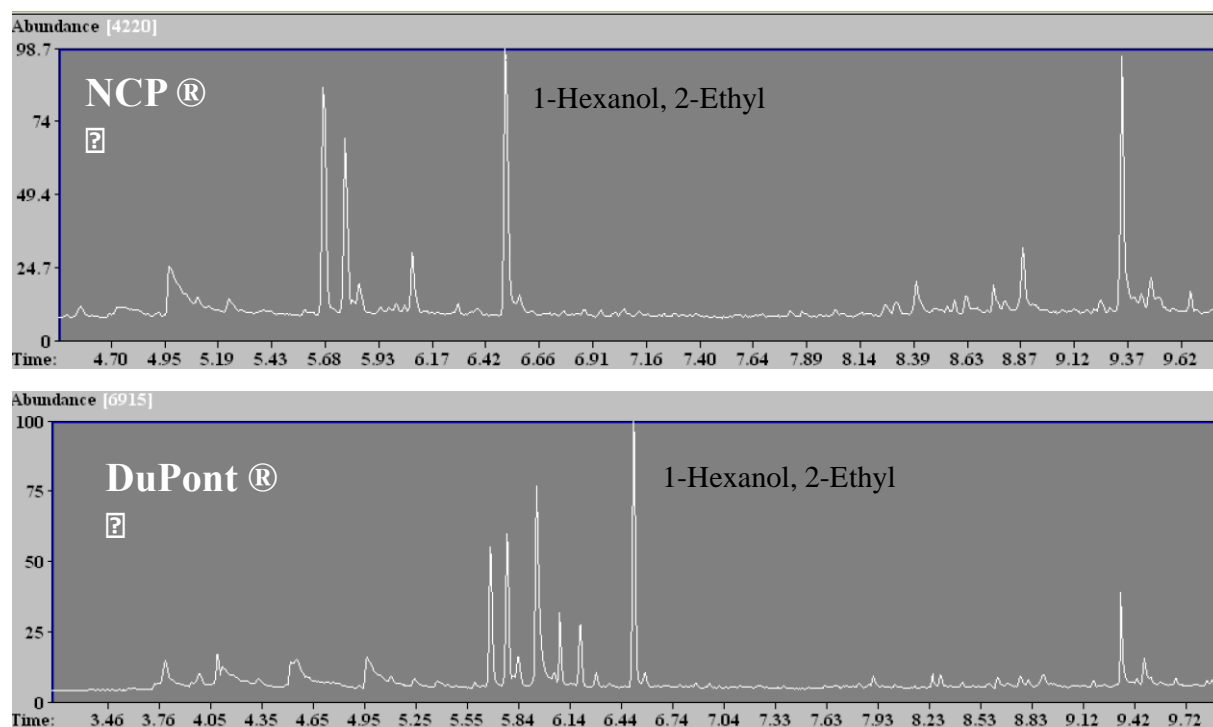
Fig. 2 Pyrograms of 2KWBPU reference samples, N9688A white topcoat from NCP® (top) and Imron® ZV HG white topcoat from DuPont® (bottom), displaying a dominant peak of 1-hexanol, 2-ethyl at 6.51 minutes.

3.3. One Package Waterborne PU (1KWBPU)

3.3.1. 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. However, the pyrograms produced for the

primer and the topcoat exhibit both a small peak of monomeric styrene while the clearcoat reference appears styrene free system using n-methyl-2-pyrrolidone (NMP). 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 3.2.3). 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 1-hexanol, 2-ethyl and diisocyanate monomeric species in the pyrograms produced for the former.

3.4. Fluoropolymer urethane (FPU)

3.4.1. Activated systems

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

A strong peak of HDI monomer and smaller peaks of cyclohexane isocyanato-and hexane 1-isocyanato 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, 2-cyclohexen- 1- one and benzene -1 chloro-3 - (trifluoromethyl).

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. The orange topcoat used for repainting the 1965 Murray's outdoor sculpture, *Duet*, is the unique Fluoranar sample containing bisphenol A. The presence of this compound suggests a binder mix with epoxy resin content. The pyrograms of the green Fluoranar 1072 topcoats used for Judd's coupons are distinguished trough styrene peaks significantly stronger.

The small peak areas of the acrylic monomeric species, identified in the FPU samples thanks to the Py-GC/MS technique, explain why no acrylic resin was identified from the FTIR

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spectra recorded for the same samples. 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.
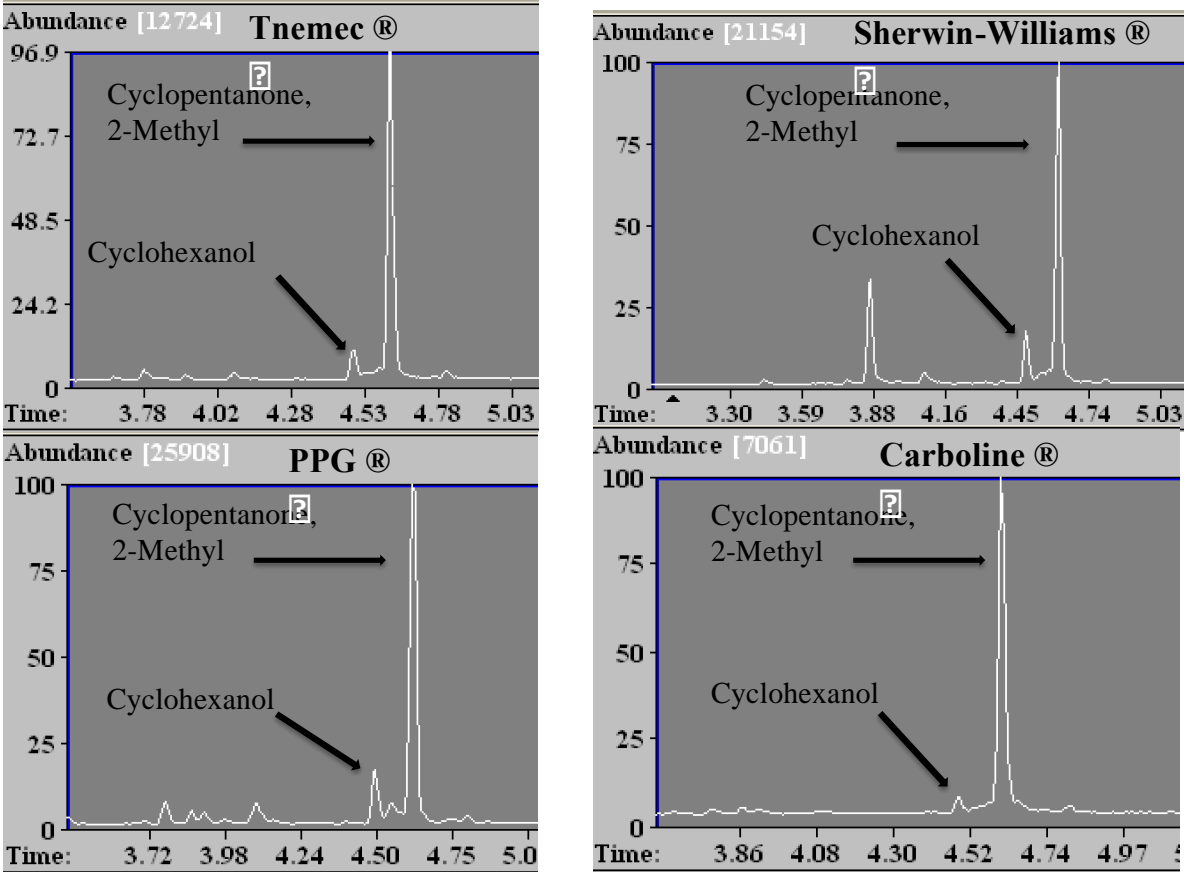

Fig. 3 Pyrograms of 2KFPU reference samples, Fluoronar Series 1072V® orange topcoat from Tnemec® (top left), Fluorokem HS® Satin black topcoat from Sherwin Williams® (top right), Coraflon ADS® Intermix black topcoat from PPG® (left bottom) and Carboxane 950® black topcoat from Carboline® (right bottom).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

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

X : identified in one or more reference sample(s)

X : identified in one or more reference sample(s) for each investigated system

- : not identified

	2KSBPU	2KWBPU	1KWBPU	2KFPU
Polyols				
Neopentyl glycol	X	X	X	-
cyclohexanedimethanol	X	X	-	-
hexane diol	X	X	-	-
2-Penten-1-ol, (Z)-	X	-		-
propylene glycol	X	-	X	-
cyclohexanol	-	-	-	X
1-,3- propanediol, 2- butyl, 2-ethyl	-	X	-	**-**
Polyacids				
phthalic anhydride (PA)	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
cyclopentanone 2-methyl	X	-	-	X
Aldehyde				
heptanal	X	-	-	-
2-pentanal, 2-methyl	X	-	-	-
Phenolic				
bisphenol-A	X	-	-	X
phenol	X	X	-	X
Polypropylene				

Propylene	X	-	-	-
PDU eluates				
Peak at 13.67 min	-	X	X	-
Peak at 13.75 min	-	X	X	-
Peak at 1.85 min	-	X	X	-
Styrene				
styrene	**X**	**X**	**X**	**X**
Siloxane				
Siloxane	-	X	-	X
Acrylates				
nBA	**X**	**X**	**X**	**X**
methoxyethyl acrylate	X	-	X	-
2-ethylhexyl acrylate	X	X	-	X
Methacrylates				
nBMA	X	X	X	-
EMA	X	-	-	-
C12MA	X	-	-	X
C14MA	X	-	-	X
2-Hydroxyethyl MA	X	X	-	-
ethylene glycol diMA	X	X	-	-
ethoxyethyl MA	X	-	-	-
iBMA	X	-	-	-
MMA	X	-	-	-
iso-Bornyl MA	X	-	-	-
C8MA	X	X	-	X
C16MA	X	-	-	-
Isocyanates				
cyclohexane isocyanato- (Isocyanic acid)	**X**	**X**	**-**	**X**
hexane 1- isocyanato-	**X**	**X**	-	**X**
benzyl isocyanate	X	-	-	-
benzene 1-isocyonato, 3-or-4- methyl	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
1- hexanol, 2- ethyl	X	X	-	X
3-hexen -1-ol, 2- ethyl	X	X	-	X
caprolactam	**X**	**X**	**X**	**X**
n-methyl-2-pyrrolidone	-	X	X	-

4. 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 primary identified are nBA and nBMA. Characteristic decomposition products of epoxy, aldehyde and silicone resins, resulting from pyrolysis were detected in several references. A dominant peak of ethylhexyl alcohol 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 ethylhexyl alcohol content might be considered as an indicator of 2KWBPU systems. Concerning the FPU samples, the produced pyrograms similarly display a dominant peak of cyclopentanone 2-methyl and a smaller peak of cyclohexanol. The combination of these two peaks appeared as a characteristic feature of the FPU pyrograms. As a result, the join presence of cyclopentanone 2-methyl and cyclohexanol provides a reliable criterion for the identification of FPU coatings.

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Competing interest

The authors declare that they have no competing interests.

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.

References

[1] T. Learner and R. Rivenc, *Conserving Outdoor Painted Sculpture: Outcomes from a Focus Meeting* , in L. Beerkens and T. Learner, eds. 2014. *Conserving Outdoor Painted Sculpture: Proceedings from the Interim Meeting of the Modern Materials and Contemporary Art Working Group of ICOM-CC, Köller-Müller Museum, Otterlo, the Netherlands, June 4–5, 2013.* Los Angeles, CA: Getty Conservation Institute, 13-22

[2] L. Beerkens and T. Learner, eds. 2014. *Conserving Outdoor Painted Sculpture: Proceedings from the Interim Meeting of the Modern Materials and Contemporary Art Working Group of ICOM-CC, Köller-Müller Museum, Otterlo, the Netherlands, June 4–5, 2013.* Los Angeles, CA: Getty Conservation Institute.

[3] B. Considine, J. Wolfe, K. Posner, M. Bouchard , *Conserving Outdoor Sculpture: The Stark Collection at the Getty Center,* Getty Conservation Institute (2010) ISBN 978-1-60606-010-0

[4] *The Conservation of Twentieth-Century Outdoor Painted Sculpture.* Report from focus meeting held at the Metropolitan Museum, New York, June 2012

[5] S.E. Stein *An integrated method for spectrum extraction and compound identification from gas chromatography/mass spectrometry data,* J. Am. Soc. Mass Spect.**,** Vol. 10, Issue 8 (1999) 770–781

[6] Z.W. Wicks, Jr., F.N. Jones, S.P. Pappas, D.A. Wicks*, Organic Coatings: Science and Technology*, 3rd Edition Wiley (2007) ISBN: 978-0-470-07906-5

[7] *The Chemistry of Polyurethane coatings*, BayerMaterialScience (report), http://www.bayermaterialsciencenafta.com

[8] D.K. Chattopadhyay, K.V.S.N. Raju, *Structural engineering of polyurethane coatings for high performance applications* , Prog. Polym. Sci. 32 (2007) 352–418

[9] T.P. Wampler, G.A. Bishea, W.J. Simonsick, *Recent changes in automotive paint formulation using pyrolysis-gas chromatography/mass spectrometry for identification*, J. Anal. Appl. Pyrolysis, 40–41 (1997) 79–89

[10] D. Thorburn Burns, K.P. Doolan,   *A Comparison of pyrolysis–gas chromatography–mass spectrometry and fourier transform infrared spectroscopy for the characterisation of automative paint samples*, Analytica Chimica Acta 539 (2005) 145-155

[11] J. Peris-Vicente, U. Baumer, H. Stege, K. Lutzenberger and J. V. Gimeno Adelantado, *Characterization of Commercial Synthetic Resins by Pyrolysis-Gas Chromatography/Mass Spectrometry: Application to Modern Art and Conservation*, Anal. Chem., 81,8 (2009) 3180–3187

[12] S. Wei, V. Pintus, M. Schreiner, *A comparison study of alkyd resin used in art works by Py-GC/MS and GC/MS: The influence of aging*, J. Anal. Appl. Pyrolysis, 104 (2013) 441-447

[13] R. Ploeger, D. Scalarone , O. Chiantore, *The characterization of commercial artists' alkyd paints*, J. Cult. Heritage 9, 4 (2008) 412–419

[14] M.R. Schilling, J. Keeney and T. Learner, *Characterization of alkyd paint media by gas chromatography-mass spectrometry*, Studies in Conservation 49 (2004) 197-201

[15] M.P. Colombini and F. Modugno, *Organic Mass Spectrometry in Art and Archaeology*, Wiley-Blackwell (2009) ISBN-10: 0470517034

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[16] T. Learner, *Analysis of Modern Paints*, Research in Conservation, Getty Conservation Institute, Los Angeles (2004)

[17] P.B. Jacobs, P.C. Yu, *Two-Component Waterborne Polyurethane Coatings*, J.Coat. Tech. 65 (1993) 45-50

[18] S.M. Cakic, J.V. Stamenkovic, D.M. Djordjevic, I.S. Ristic, *Synthesis and degradation profile of cast films of PPG-DMPA-IPDI aqueous polyurethane dispersions based on selective catalysts*, Polymer Degradation and Stability 94 (2009) 2015–2022

[19] C.R. Hegedus, A.G. Gilicinski, R.J. Haney, *Film formation mechanism of two-component waterborne polyurethane coatings*, Journal of coatings technology 68 (1996) 51-61

[20] J. Escarsega, *Water dispersible low-reflectance chemical resistance coating compostion,*

US patent 5691410 A (1997)

[21] S. Munekata, *Fluoropolymers as coating material* Progress in Organic Coatings 16 (1988) 113–134

[22] B. Krol, P. Krol, S. Pikus, K. Skrzypiec, *Synthesis and characterisation of coating polyurethane cationomers containing fluorine built-in hard urethane segments*, Colloid Polym Sci 288 (2010) 1255–1269