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Polyurethane coatings in 20th century outdoor painted sculptures. Part I: Comparative study of various systems by means of ATR-FTIR spectroscopy

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Corresponding Author:	Catherine Defeyt, Ph.D Universite de Liege BELGIUM
Corresponding Author Secondary Information:	
Corresponding Author's Institution:	Universite de Liege
Corresponding Author's Secondary Institution:	
First Author:	Catherine Defeyt, Ph.D
First Author Secondary Information:	
Order of Authors:	Catherine Defeyt, Ph.D
	Julia Langenbacher
	Rachel Rivenc
Order of Authors Secondary Information:	
Opposed Reviewers:	

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Catherine Defeyt

Centre Européen d'Archéométrie

Allée du 6 Août 10, Sart Tilman B15

University of Liège

B-4000 Liège, Belgium

Tel. +32 43663639

Email: Catherine.defeyt@ulg.ac.be.

Julia Langenbacher

Getty Conservation Institute, Science Department, Getty Center Drive 1200, CA90049 Los Angeles (USA)

Email : JLangenbacher@posteo.de

Rachel Rivenc

Getty Conservation Institute, Science Department, Getty Center Drive 1200, CA90049 Los Angeles (USA)

Email : rrivenc@getty.edu

Polyurethane coatings in 20th century outdoor painted sculptures. Part I: Comparative study of various systems by means of ATR-FTIR spectroscopy

C. Defeyt[1, 2], J. Langenbacher[1] and R. Rivenc[1]

[1] Getty Conservation Institute, Science Department, Getty Center Drive 1200, CA90049 Los Angeles (USA).

[2] University of Liège, Centre Européen d'Archéométrie, Allée du 6 Août 10, 4000 Liège, (Belgium), Tel. +32 43663639, Catherine.defeyt@ulg.ac.be.

Abstract

Like acrylics and alkyds, polyurethanes (PUs) represent an important class of industrial paints adopted by 20th and 21st artists; primarily by those creating outdoor painted sculptures (OPS). Because PU coatings offer a compromise between aesthetic and performance expectations, unachievable with other types of paints, they are commonly recognized as the most appropriate option for painted artworks intended for an outdoor setting. However, the PU class includes various systems and subgroups possessing very different properties.

Through the FTIR-ATR study of 137 PU coating references from the Getty Conservation Institute (GCI) reference collection, this paper outlines the differences and the similarities existing, in terms of the composition, of two package solvent-borne, two package water-borne, one package water-borne and fluoropolymer polyurethanes. The comparison of the obtained FTIR-ATR results allowed determining markers helpful to discriminate specific PU subgroups by means of ATR-FTIR spectroscopy. The goals of this paper are to provide to the conservation professionals a better understanding of the versatility and diversity of PU coatings and to facilitate the identification of the various types initially used by the artists.

1. Introduction

As part of the outdoor sculpture research project at the GCI [1], nearly two hundreds reference samples of industrial paints, used for making and/or conserving modern outdoor painted artworks, were collected. Representing 85% of the build collection, PU coatings appeared by far as the most significant class of industrial paints related to OPS. The examination of case studies reported in literature confirmed this predominance [2,3]. Indeed, many outdoor artworks from the late 20th century have originally been painted with polyurethanes, and PU topcoats and clear coats appear also as the favored option in case of a full repainting of exterior sculptures. The OPS by Roy Lichtenstein, Robert Adams, Mark di Suvero and Alexander Calder from the Fran and Ray Stark Sculpture Collection at the Getty Center are relevant examples among others [3]. Generally, the advantages associated with polyurethane coatings are their excellent weathering characteristics and chemical/mechanical resistance. These interesting properties explain the leading position of PU coatings in the aerospace and automotive refinish industries, where high performances are essential. Nevertheless, due to the large diversity of PUs and the specific requirements of the conservation field, making the most appropriate choice often becomes a very complicated task [4]. Unlike the PU foams [5,6], the PU paints remain barely studied in cultural heritage. In the present paper, the different PU systems, namely two package solvent-borne, two package water-borne, one package water-borne and fluoropolymer polyurethanes are reviewed and compared by means of ATR-FTIR spectroscopy.

2. Chemistry

PUs represent an extremely versatile class of compounds because of the extended list of monomeric materials, comprising diols, diisocyanates and chain extenders, as possible chemical precursors.

2.1. Isocyanates

The synthesis of urethane polymers is based on the isocyanate reactions. Isocyanates are highly reactive chemicals containing the functional group –N=C=O. The reaction of an isocyanate with an alcohol yields a urethane. The preparation of polymeric materials primary involves a di- or polyisocyanate reacting with a di- and/or polyol. A large variety of branched or crosslinked polymers may be obtained by adjusting the functionality of the isocyanate or hydroxyl-containing reactant [7].

The properties of the obtained PU products are strongly influenced by the nature of the diisocyanates used for synthesis. Typically, aliphatic diisocyanates give coatings with higher oxidative and ultraviolet stabilities, than their aromatic counterparts. As a result PUs prepared from aliphatic diisocyanates offer coatings with superior weather resistance. Hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI) are the most common monomeric aliphatic diisocyanates encountered in the sector of exterior PU coatings. Those are usually converted into higher molecular weight resins to reduce toxic hazard and to increase functionality. However, in the 1960s the urethane coatings were most often prepared with aromatic diisocyanates, primary TDI or its derivatives, because of their ease of handling and rate of reaction at lower costs [8].

2.2. Polyols

The isocyanate groups can react with any compound containing reactive hydrogen atoms. Products bearing two or more hydroxyl groups in the molecule are called diols or polyols. Along with the hydroxyl groups, polyols may contain other functionalities such as ester, ether, amide, and acrylic. Polyols with low functionality form linear PUs while polyols of high functionality give crosslinked polymers. In addition, polyols with low molecular weight produce rigid PU with a high concentration of urethane groups in the polymer chain [7]. Polyester and acrylic polyols are conventional coractants, employed for tailoring high performance PU coatings. Such polyols contain ester and/or acrylic and hydroxylic groups in their backbone. Note that the acrylic polyols, which are generally more expensive, present the advantage of imparting the characteristic properties of acrylics, e.g. thermal stability, to the resulting PU products [7, 9].

2.3. Additional compounds

Esters, ketones and ether esters are suitable solvents for clear and pigmented PU coating systems. Traditional extenders, such as barytes, calcium carbonate, talc, kaolin, mica, and silica may be used in one- and two-component systems. Among the conventional inorganic pigments, titanium dioxide, titanium yellow, various iron oxides, cadmium reds and yellows, some carbon blacks and chrome oxide green are suitable for most of the 2K PU systems. Organic pigments frequently found in the PU paint formulations, include quinocridone and perylene reds, monoazo and isoindoline yellows, and phthalocyanine blues and greens. The use of organic pigments from other classes may involve undesirable effects on the curing process of PU paint films [10]. Commercial PU coatings contain various additives, such as catalysts, flattening, leveling, thickening and anti-foaming agents. The presence of catalysts offers advantageous rates of polyurethanes reaction at lower temperatures. Those used in PU industry essentially consist on tertiary amines and tin complexes compounds [9].

3. History

In 1937, Otto Bayer and his coworkers achieved to produce a urethane polymer in the laboratories of I.G. Farben [11], with properties comparable to the polyamide 66 (Nylon), discovered shortly before by W. Carothers at DuPont. Polyurethanes are structurally related to polyamides, the recurring link being NHCOO instead of NHCO. The urethane linkage was already recognized in the previous century, but the breakthrough achieved by Bayer's team was the formation of new long-chain macromolecules resulting from the polyaddition reaction of diisocyanates with dialcohols. The founding principles of the polyurethanes chemistry were first reported in the German Patent (DE728981) published in 1942 [12]. Although World War II seriously impacted the market growth, the industrial scale production of PU products started in Germany, in the1940s [8]. Bayer wrote the first review on his research in polyurethane chemistry in 1947 [13].

Before their uses as architectural, domestic and automotive paints, the main applications of PU coatings were clear wood varnishes, leather finishes, maintenance and protective paints. Starting from 1952, most of the early PU coatings were made of polyester-polyisocyanate polymers. In the 1960s, the gradual decrease of costs for diisocyanates and other chemical precursors contributed to the market expansion of the PU coatings [14]. At this time, in the US, urethane oils, obtained by reacting diisocyanates with drying oils or their derivatives, were the most widespread type of PU coatings.

For a long time, solvents were necessary for applications requiring low viscosities. In the early 1970s, while the first polyurethane dispersions (in water) were patented [15], more than 90% of the paint and coatings sold worldwide were low solids (5-20% by weight) solvent-bornecoatings. The increased demands for improved technical performance and/ or minimized environmental contamination have motivated research on the development of new PU coating systems. High solids PU coatings (>60% of non-volatile solids by weight) have been developed in response to the legislation for reducing VOC (volatile organic compound) emission, introduced in the US in 1970 [16]. Latest developments in improving the surface properties of PU coatings exposed to drastic conditions consist on the engineering of binders with high fluorine content. At the end of the 20th century, DuPont, Sherwin-Williams Co., PPG Industries Inc., Akzo Nobel Coatings Inc., Bayer AG and BASF Corporation dominated the worldwide PU industry.

4. Subgroups of PU coatings

4.1. Two Package solvent-borne PU (2KSBPU)

The term "solvent-borne" indicates systems with solvents as primary volatile liquid components. For a long time, solvent-borne PU coatings have remained the standard for applications where low viscosities and high performance were essential. 2KSBPU coatings consist of an activator pack (Part B) and a co-reactant pack (Part A), containing active ingredients, respectively polyisocyanates (-N=C=O) and hydroxyl groups (-O-H). Conventionally, Part A indicates the package containing the co-reactants, pigments, fillers, and catalysts, while Part B is used for the polyisocyanate resins. Two pack systems can only be used as two component coatings. The polyaddition process starts directly after mixing Part A and B and the curing process may be completed at ambient temperature. The concentration of polyisocyanates, most often HDI, varies from 40% to 95% depending on the manufacturers and the product lines. OH-functional polyester and/or acrylic resins are the most common polyols used in PU coating industry.

4.2. Two Package water-borne PU (2KWBPU)

In the early 1960s, Otto Bayer first suggested the preparation of aqueous polyurethane systems by the incorporation of ionic groups [11]. The efforts made by formulators since the end of the 20th century to tailor new 2KWBPU products, derived from the increasing request of high performance and environmentally harmless coatings [17, 18]. The GCI reference collection incorporates only few 2KWBPU samples, however such systems have been marketed in a large scale since the 2000s [9].

Like their solvent-borne counterparts, 2K water-borne coatings are obtained by mixing polyisocyanate crosslinkers (Part B) with compounds bearing hydroxyl groups (Part A), which are, in this case, aqueous polyols such as polyurethane, polyacrylic or polyester dispersions [19]. Water-borne PU systems also require the use of water dispersible polyisocyanates. Hydrophilically modified polyisocyanates are generally favored because of their enhanced water dispersibility [10].

4.3. One Package water-borne PU (1KWBPU)

Generally speaking, the one component water-borne PU systems consist of modified polyurethane dispersions (PUDs) or acrylic-polyurethane dispersions. Systems using only PUDs are fully reacted PU polymers dispersed in water and/or co-solvents. Aqueous acrylic-polyurethane systems may be prepared by using blends of PUDs with water-reducible acrylic resins or by polymerizing acrylates into PUDs [9]. The film formation occurs at ambient temperatures and results from the evaporation of water and/or co-solvent. The 1KWBPU systems allow achieving isocyanate free coatings and often contain a relatively low proportion of n-methyl-2-pyrrolidone (NMP), a water-miscible solvent commonly used to make PU dispersions [19].

4.4 Fluoropolymer Urethane (FPU)

Latest developments undertaken for improving outdoor durability of industrial paints resulted in the engineering of fluoropolymers (FPs), which are macromolecular binders with high fluorine content [20]. Thanks to the very strong C-F bonds in organic molecules and the weak intermolecular interactions of the fluorocarbons, the presence of trifluoromethyl groups (-CF3) in polymeric materials affect advantageously their chemical reactivity. As a result, fluorine-containing PUs exhibit higher resistivity towards aggressive environments, and are gaining importance as binders for exterior coatings [21].

The 2014 repainting of the Long Beach Robert Murray's *Duet* (1965) with a fluoropolymer urethane (FPU) topcoat (Fluoronar 1072V from Tnemec) illustrates the interest of such coatings for conserving painted outdoor sculptures.

5. Experimental

5.1. PU reference materials

The GCI reference collection contains 137 PU coatings from various manufacturers, namely Dupont, PPG, Akzo, BASF, Tnemec, Carboline, Sherwin Williams, NCP, Matthews Paints and Awlgrip. It includes primers as well as pigmented and unpigmented topcoats, dating from 2005 to 2015. The sources of supply are:

- Standard Color References supplied by collaborating Artists' Estates, Foundations, and Studios (EFS)

- Coupons made on request by specialized companies or fabricators
- Swatches of replacement coatings used for OPS repainting
- Laboratory prepared samples for the purpose of this study

Additionally to the 137 activated and/or cured PU coating samples, presented in Table 1, FTIR-ATR measurements were performed on some unmixed polyisocyanates and co-reactants as well.

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	25	W, Bk, Gr, Bl, Yel, Rd, Or, Gy, Br, 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 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
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	T	1	Bk

		Intermix low VOC			
T. Smith	n/a	Sherwin-Williams®/Fluorokem™ HS Satin	T	1	Bk
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

Table 1 Description of the PU coating references from the GCI collection investigated in this study.

*T=Topcoat (pigmented), 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

5.2. FTIR-ATR measurements

The FTIR-ATR measurements (Fourier transformed infrared spectroscopy attenuated total reflectance) were performed with a portable A2 Technologies Flexcan spectrometer. This instrument is equipped with a diamond crystal. The FTIR spectra were recorded in the 4000-650 cm^{-1} region, collecting eight scans and using a spectral resolution of 4 cm^{-1}. Three spectra from different areas were recorded for each reference sample. For a better characterization of the activated and/or cured PU coatings, pure polyisocyanate resins and co-reactant s involved in the preparation of the corresponding systems were analyzed individually by FTIR. In this paper, the FTIR results obtained from the 2KSBPU, FPU, 2KWBPU and 1KWBPU samples will be discussed separately.

6. Results and discussion

6.1. Two Package Solvent-borne PU (2KSBPU)

6.1. 1. Activators

The FTIR spectra obtained from three different Imron activators (FG1333, FG1633 and FG0162) exhibit similar IR features identifying HDI isocyanurate, a trimer with a cyclic structure, see Fig. 1, widely used as precursor in the PU coating industry. The positions of the IR bands observed for FG1333 are listed and assigned by referring to literature [22,23,24] in Table 2. As shown in Fig. 2, the three sharpest and strongest absorptions respectively arising at 1680, 1455 and 765 cm-1 are in complete accordance with the FTIR data reported for HDI isocyanurates. The IR absorptions at 2930 and 2860 cm^{-1} (CH2 stretching deformation modes) and 1760 cm^{-1} (C=O stretching vibrations) also support this identification. The absorbance at ca. 2270 cm^{-1} is characteristic of unblocked isocyanates (out of plan stretching mode of the NCO groups), and more or less intense depending on the rate of isocyanate consumption [25, 26].

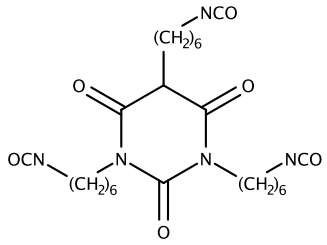

Fig. 1. HDI isocyanurate indicates a HDI trimer containing an isocyanurate ring.

Imron® FG1333™	NCP® H2OB	HDI isocyanurate	Intensity	Band assignment
3330	3330	3330	m	Secondary Urethane N=H stretch/NH bonded/N-H stretching vibration band
2930	2930	2936	m	νa CH_2
2860	2860	2856	m	νs CH_2
2270	2270	2263	m	Isocyanate asymetric N=C=O stretch/ NCO out of phase
1765	1765	1765	w	Free C=O stretch
1680	1680	1680	vs	H bond C=O stretch/Tertiary Urethane C=O/C=O bonded
1630	1630	1627	m	Carbonyl groups in urea bonds (C=O)
1565	1565	1574	m	Secondary amide RCONHR'
1515	1515	1513	sh	δ-NH and νa C-N
1455	1455	1455	vs	δ-CH_2
1425	1425	1425	s	δ OH
1375	1375	1375	m	δ-C(CH_3)
1330	1330	1334	m	NCO in phase/ CH_2
1250	1250	1248	m	(O=)C-O-C stretch/ Urethane C-O stretch
1155	1145	1155	w	νa C-N-C
1091	1089	1090	w	νa C-O-C
865	865	865	w	νs C-N-C
765	765	765	s	C-N skel str
730	730	730	m	CH_2 in phase rock

Table 2 IR band positions recorded for Imron® FG1333, NCP H2OB and pure HDI polyisocyanurate resin (Bayhydur® 303 supplied by Bayer) and their assignment by referring to literature [22,23,24].

νa=asymmetric stretch, νs=symmetric stretch, δ= deformation

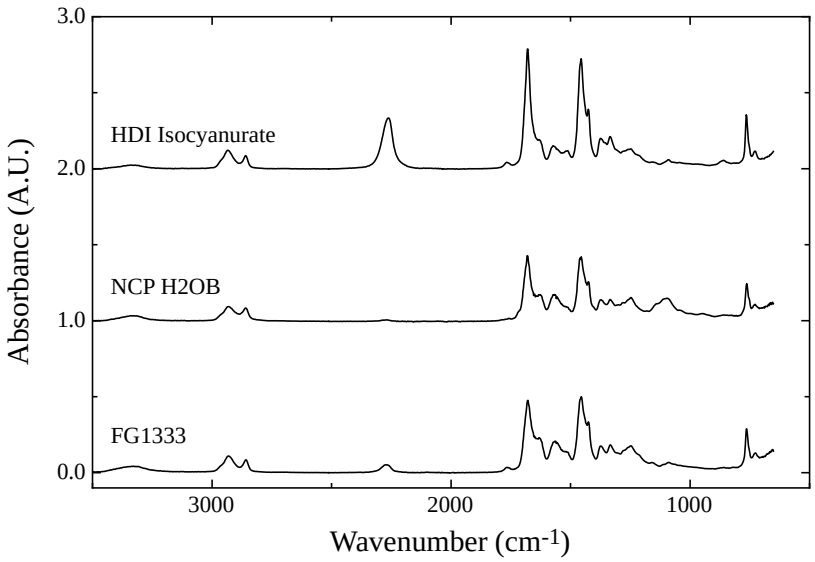

Fig. 2. FTIR spectra of Imron® FG1333, NCP H2OB and HDI polyisocyanurate resin (Bayhydur 303 supplied by Bayer) recorded in the same conditions.

The band at 1680 cm^{-1} may be attributed to the H-bond C=O stretching modes in isocyanurates, while the absorption at 1455 cm^{-1} probably results from to the CH2 bending in the backbone of the HDI monomer. The thin and sharp peak commonly observed at 765 cm^{-1} may be explained by the C-N skeleton stretch in HDI trimers with a cyclic structure [27]. As consequence, the IR absorptions occurring at ca. 765 cm^{-1} may be used as a marker for identifying isocyanurate based PU systems.

The Imron activator spectra have in common additional IR features: a smooth absorption at ca. 3330 cm^{-1} (N-H stretching), a sharp band at 1630 cm^{-1} (carbonyl groups in urea bonds C=O) emerging from the stronger band at 1680 cm^{-1}, a broad band at 1550 cm^{-1} (secondary amide RCONHR'), a thin and sharp band at 1430 cm^{-1} emerging from the stronger band at 1455 cm^{-1}, two medium bands of equal intensity at 1370 and 1330 cm^{-1}, a band at 1250 cm^{-1} equivalent in intensity but relatively larger than the two previous ones, a very weak peak at 1090 cm^{-1}, and a band at 730 cm^{-1} (CH2 in phase rock) which is significantly less strong than the nearest band observed at 760 cm^{-1}.

The FTIR spectra obtained from the Awlgrip G3010 and H3002 activators, display identical

patterns with a dominant band centered at 1515 cm^{-1}. This absorption may be considered as a combination of N-H deformation and C-N stretching vibration (amide II band) of the urethane group [28].

Unlike the Imron spectra, here the 1630 and 1680 cm^{-1} bands are similar in shape and intensity and an additional strong and sharp band is detected at 1210 cm^{-1}.

6.1.2. Co-reactants

In this section samples of unactivated co-reactants included in part A of Imron 2.1, Imron 5.0 and Aicraft 2000 are discussed. All the related FTIR spectra exhibit a dominant band at ca. 1730 cm^{-1}, which may be assigned to the carbonyl stretching vibrations. The studied Imron products have a binder primary based on a mixture of polyester and styrene modified acrylic resins. The styrene identification is supported by the presence of two high and sharp bands at 760 and 701 cm^{-1} and two small ones at 3062 and 3029 cm^{-1}, commonly used as diagnostic peaks for styrene modified resins [29].

In the case of Imron 2.1 spectra, the relatively intense absorptions at 2934, 2865, 1472, 1448, 1385, 1166 and 710 cm^{-1} suggest the presence of a pEMA-2EHA-styrene terpolymer in the binder mix. The FTIR measurements performed on the Awlgrip products have led to the identification of a styrenic acrylic polymer. The styrene was readily identified thanks to the characteristic features displayed at 3029, 749 and 702 cm^{-1}. In addition, the intensity and the position of the IR bands at 2960, 1452, 1383, 1240, 1145, 1068 and 961 cm^{-1} are in agreement with the FTIR data reported for acrylics made of nBMA homopolymer [29].

6.1.3. Activated systems

In the FTIR spectra obtained from Imron 2.1 systems activated with FG1333, FG1633 or FG0162, the HDI isocyanurate signature remains prominent. The spectra of pure Imron FG1333 and Imron 2.1 white topcoat activated with FG1333 are compared in Fig. 3a. The strongest and sharpest bands at 1680, 1455 and 765 cm^{-1} noticed for activators alone are easily recognizable in the FTIR patterns resulting from the mixed systems. The disappearance

of the characteristic free N-C-O band at ca. 2270 cm^{-1} results from the isocyanate consumption inherent to the urethane linkage formation [25]. The IR bands attributed to the HDI isocyanurate crosslinkers still clearly appear in the spectra, regardless the date of the reference samples. Indeed, the characteristic absorptions at 1680, 1455 and 765 cm^{-1} are easily recognizable in the spectra recorded for Imron 2.1 paint swatches, made in 2006, in the frame of the repainting campaigns conducted on Lichtenstein's *Three Brushstrokes* and Calder's *SpinyTop*.

Although the activator required for the Imron 5.0 line was not investigated alone, the presence of additional peaks at 1680 and 1462 cm^{-1} in the spectra of the activated system may be attributed to the aliphatic polyisocyanate resin contained in part B. The IR absorption observed at ca. 765 cm^{-1} cannot be reasonably attributed to the activator because of the presence of the styrene-modified acrylic resin in the system.

As illustrated in Fig. 3b, the spectra obtained from Aircraft 2000 systems activated with Awlgrip G3010 primary exhibit the IR bands induced by the nBMA-styrene polymer identified in the part A. However, the FTIR spectra also show the Awlgrip activator fingerprint that is formed by the four bands arising at 1690, 1635, 1523 and 1461 cm^{-1}. The doublet peaks at 1690 and 1635 cm^{-1} as well as the two bands of relatively equal intensity at 1523 and 1461 cm^{-1} and the small band at 1338 cm^{-1} correspond to the characteristic IR features identified for the Awlgrip activators. Obviously, regarding the 1460 cm^{-1} absorption, the contribution of the acrylic resin cannot be ignored.

All the EnduraShield Series spectra display the same salient FTIR features, especially in the 1300-700 cm^{-1} region, regardless of the line and the color of the analyzed samples (see Fig. 3c). The dominant IR absorption centered at 1080 cm^{-1} and the two high and sharp bands at 799 and 800 cm^{-1} are attributed to the abundant presence of crystalline silica (10-30% by weight) in the part A of EnduraShield Series. The 1150 cm^{-1} band due to C-O stretching groups is partly overlapped by the broad and strong absorption assigned to siloxane bonds in the 1200-1000 cm^{-1} region [30]. The bands at 3061, 3028, 1724, 763 and 698 cm^{-1} indicate the use of styrene modified acrylic resin. The diagnosis IR bands used for the PU identification arise at 1680, 1525 and 1460 cm^{-1}.

The remaining 2K SBPU reference samples include black, blue and red swatches prepared with Aerodur 5000 (Akzo), Deltron DBU (PPG), Glasurit 22 (BASF), and Nason Fullbase 3.5

topcoats. The related FTIR spectra are shown in Fig. 3d.

These samples constitute a set of color references used for repainting particular outdoor sculptures by Tony Smith, Claes Oldenburg, Gary Hume and Anthony Caro. Interestingly, the related FTIR spectra show similar IR features at 2930, 2860, 1680, 1520 and 1462 cm^{-1}. These absorptions may be attributed to the polyisocyanate resins used to activate the systems.

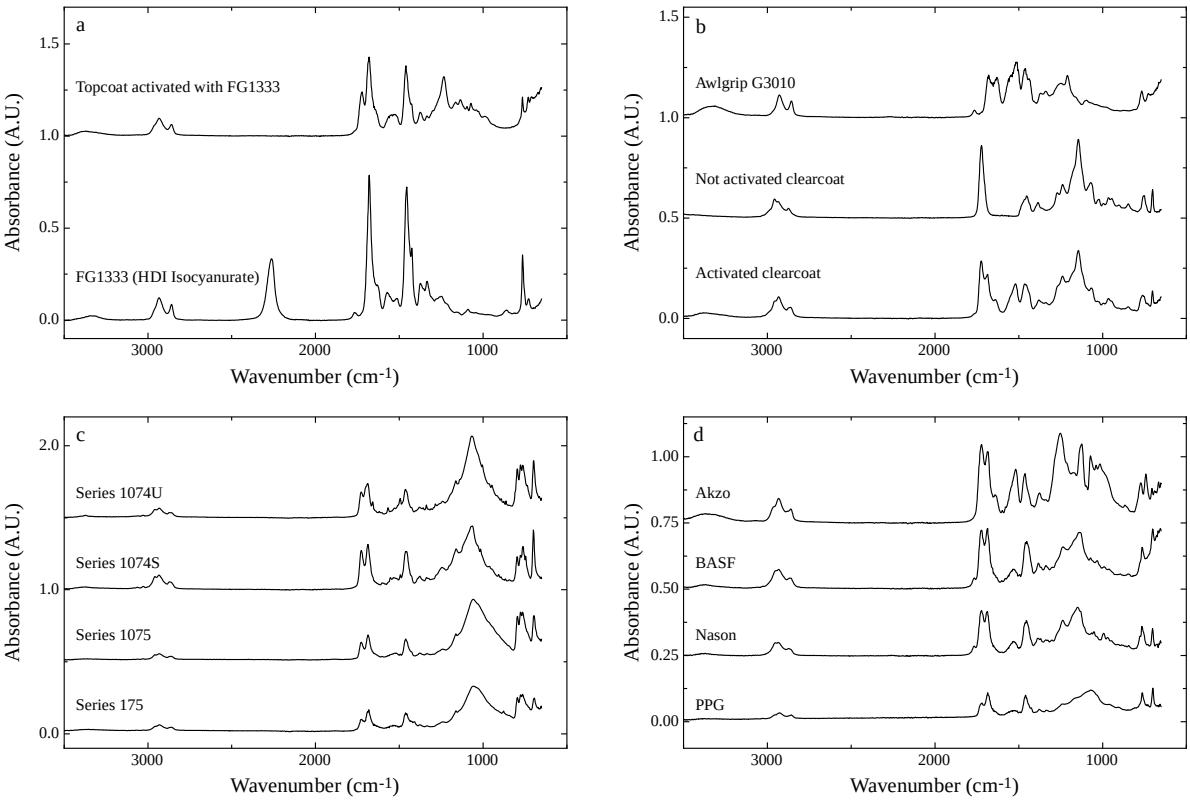

Fig. 3. FTIR spectra of various 2KSBPU samples: (a) Imron FG1333 and Imron 2.1 white topcoat activated with FG1333; (b) Awlgrip G3010 convertor, Aircraft 2000 clearcoat unactivated and activated with G3010; (c) black, red, orange and yellow EnduraShield topcoats from the 175, 1074U, 1075 and 73 Series; (d) Akzo Nobel (Akzo 683-3-7 clear), PPG (Deltron DBU blue), Nason (FullBase 3.5 VOC red) and BASF (Glasurit 22 blue).

6.2. Two Package Water-borne PU (2KWBPU)

6.2.1. Activators

All the 2KWBPU samples involve the use of a water-dispersible polyisocyanate resin based on HDI. The FTIR spectra recorded for pure H2OB and FG572 activators, recommended for the NCP and Imron ZV-HG lines, and for pure hydrophilically modified polyisocyanates prepolymers supplied by Bayer (Bayhydur XP2547 and XP2487) exhibit the same pattern. Note that H2OB is made of hydrophilically modified HDI polyisocyanurates (Bayhydur 303, Bayer).

Actually, the FTIR fingerprints obtained for the investigated water dispersible and regular polyisocyanates resins are very similar. The obvious similarity between all the activator spectra (except Awlgrip) underlines the recurrent use of HDI isocyanurate prepolymers in two package PU systems. The IR absorption at 2270 cm^{-1}, induced by the NCO groups from unreacted isocyanates, appear noticeably more intense for the FG572 product. In addition, the Bayhydur XP2547 spectra are distinguished by the presence of a broad and relatively strong IR band at 1765 cm^{-1}.

6.2.2. Co-reactants

In NCP topcoats, the part A is made of a hydroxyl functional polyurethane dispersion (PUD) dissolved in water/n-methyl-2-pyrrolidone (Bayhydrol XP7110E, Bayer). The co-reactant used in part A of the clearcoats prepared at the GCI laboratory is an anionic polyacrylate dispersion (Bayhydrol A 2542 by Bayer) containing OH-functional co-solvents/amines that react with isocyanates. The obtained FTIR results pointed out to the styrene modification of the acrylic polymer through the characteristic absorptions of styrene, appearing in the spectra at 3029, 756 and 703 cm^{-1}.

6.2.3. Activated systems

The FTIR spectra obtained for the two pack water-borne samples using acrylic and/or polyester dispersion as co-reactants do not significantly differ from the spectra recorded for

their solvent-borne counterparts. The fingerprint of HDI based polyisocyanate resins can be readily identified in the 2KWBPU spectra. For the NCP topcoats as well as for the laboratory prepared clear coats, the IR absorptions arising at 2935, 2860, 1680, 1460, 1335, 1255, 760 and 730 cm^{-1} are in accordance with HDI isocyanurate crosslinkers. Less obvious but still present is the IR band at 1630 cm^{-1} noticed for pure activators. As seen in Fig. 4, the PU system produces a broad single band centered at 1680 cm^{-1} when prepared with OH-functional PUD co-reactants. The actual absorption can be reasonably attributed to the HDI isocyanurate. The absence of the carbonyl stretching band at around 1730 cm^{-1} characteristic of the acrylic and polyester resins provides a reliable FTIR marker for identifying 2KWBPU prepared with PUD co-reactants. Concerning the clear coats involving Bayhydrol A 2542, the most intense IR bands induced by the styrene-acrylic dispersion arise at 2960, 1723, 1140, 760 and 700 cm^{-1}.

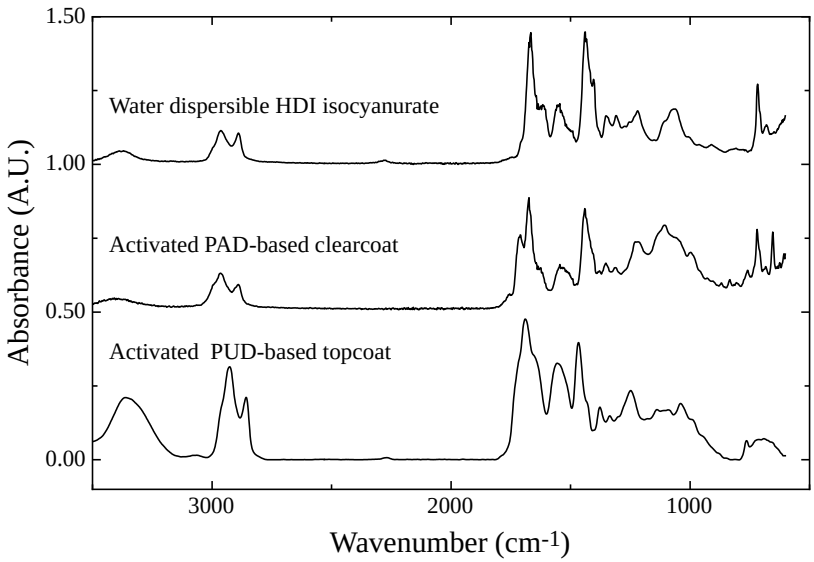

Fig. 4. FTIR spectra of two 2KWBPU coatings activated with water dispersible HDI isocyanurates, developed for conserving OPS by Calder; white topcoat (N9688A) from NCP using PU dispersion (PUD) as co-reactant and clear coat using polyacrylic dispersion (PAD) as co-reactant (Bayhydrol 2542, Bayer).

6.3. One Package Water-borne PU (1KWBPU)

The FTIR spectra of the 1K water-borne isocyanate free PU references, presented in Fig. 5 display the same salient features, which led to the identification of a urethane-nBMA copolymer in every case. Only the IR bands arising at 2930, 2860, 1640 and 1560 cm^{-1} may be reasonably attributed to the urethane linkage. Unlike, the 2K aqueous systems, there is no evidence of styrene modification. By comparing the 2K and 1K PU spectra, the most significant differences appear in the 1750-1650 cm^{-1} region. The predominant band at ca. 1680 cm^{-1}, characteristic of HDI polyisocyanates is missing in the spectra recorded for the 1K systems (Fig.5). Instead, the 1K samples produce a single strong band at around 1730 cm^{-1}. The absence of the 1680 cm^{-1} band may be explained by the non-use of separate polyisocyanate adducts as crosslinking agents, and therefore could be helpful to identify isocyanate free 1KWBPU systems.

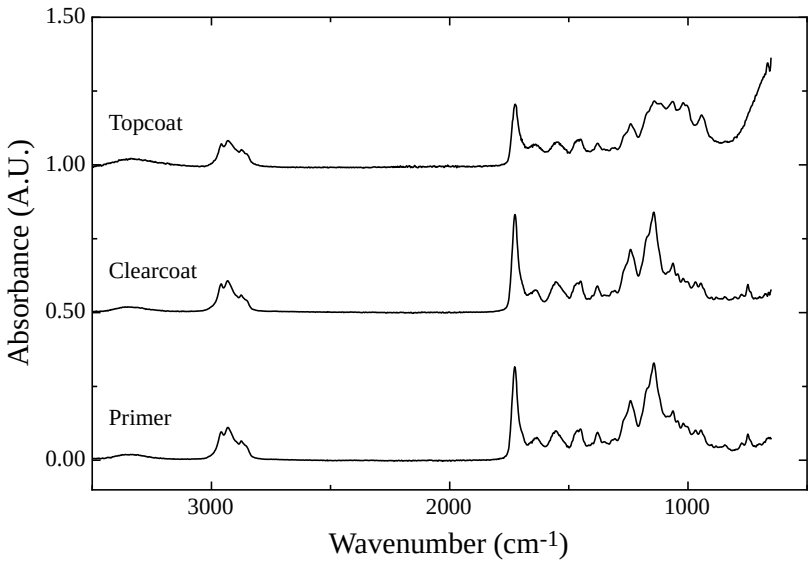

Fig. 5. FTIR spectra of 1KWBPU systems; Imron 1.2 HG-C clearcoat, Imron 1.5 Pr grey primer and Imron 1.5 ST-D direct-to-metal white topcoat. The three spectra all display a single band in the 1730-1650 cm^{-1} region.

6.4. Fluoropolymer Urethane (FPU)

All the FPU coatings collected at the GCI are solvent-based systems involving a separate use of HDI polyisocyanates as crosslinking agents. According to the information provided in the

related safety data sheet the fluorinated polymer in part A of the Fluoranar series is a 1-butanol, 4-(ethenyloxy)-polymer with chlorotrifluoroethene, (ethenyloxy)cyclohexane and ethoxyethene. In the case of the Caroflon products from PPG, the safety data sheet depicts a fluoropolymer made from a fluoroethylene vinyl ether resin (FEVE). The fluoropolymers used in the formulations of the Carboxane and the Fluorokem lines, produced by Carboline and Sherwin-Williams, are unknown.

The FTIR spectra obtained from the FPU samples, display the salient features of HDI polyisocyanurate. Similarly to the 2KWBPU systems made with PUDs (NCP topcoats), the FPU samples produce a single band of medium intensity at around 1690 cm^{-1}, corresponding to the dominant peak observed for HDI cyclic trimers. On the other hand, the FPU spectra also exhibit a very strong IR doublet band arising at 1110 and 1065 cm^{-1}. Examples of characteristic FPU spectra are given in Fig. 6. These values match with the typical F-C stretching region (1150-1000 cm^{-1}) reported for aliphatic fluoro compounds [31]. This assignment still need to be confirmed, but if it is correct the detection of the broad doublet band at 1110 and 1065 cm^{-1} would provide a valuable indicator of FPU systems.

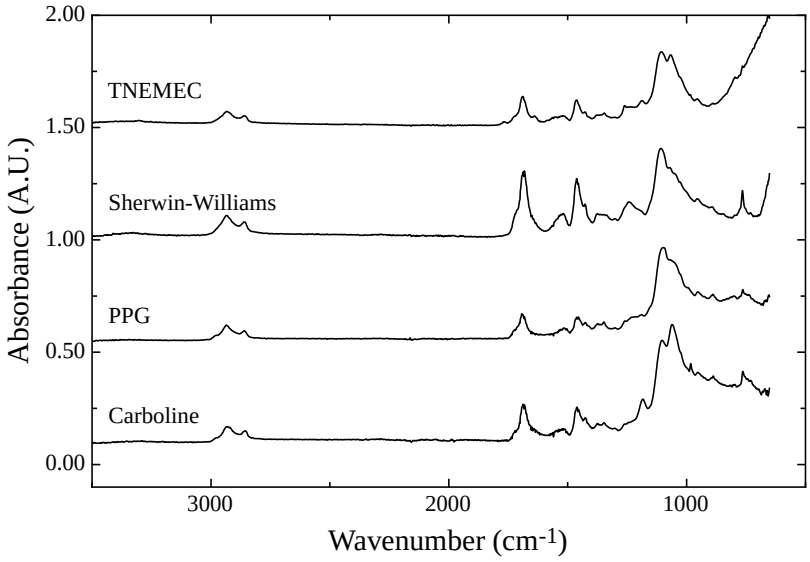

Fig. 6. FTIR spectra of four black 2KFPU topcoats from different manufacturers; Fluoranar Series 1072 by Tnemec, Fluorokem by Sherwin-Williams, Coraflon by PPG and Carboxane 950 by Carboline. All of them exhibit a strong IR double absorption at ca. 1110 and ca.1065 cm^{-1} in accordance with the typical F-C stretching region.

7. Conclusions

The ATR-FTIR study conducted on a wide range of reference materials has highlighted the relevance of this routine analytical method to discriminate certain subgroups of PU coatings. Indeed, by investigating well-known specimen it was possible to outline diagnostic FTIR features for three specific systems; FPUs, 1KWBPUs made from acrylic latexes and 2KWBPUs prepared with PU dispersions. The intense absorbance in the 1150-1000 cm^{-1} region, assigned to the F-C stretching mode, could provides a valuable marker for the identification of fluoropolymers. In the same way, aqueous systems based on PUD polyols could be identified through the detection of a single broad band centered at 1690-1680 cm^{-1}. Conversely, the investigated one component water-borne PU samples produced a single, sharp and intense band at 1735-1720 cm^{-1} in accordance with a predominant proportion of water dispersible acrylic polymers. Furthermore, the FTIR measurements performed on various activators and co-reactants emphasized the significant contribution of the polyisocyanate absorptions in the spectra of the activated two package PU systems. However, the results obtained for various unmodified and water dispersible HDI polyisocyanate activators showed that the FTIR-ATR technique does not allow the discrimination within both types.

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Competing interests

The authors declare that they have no competing interests.

Authors' Contributions

CD conceived the study and coordinated it. CD carried out the FTIR measurements and discussion of the results and drafted the manuscript. 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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