Polyurethane coatings used in twentieth century outdoor painted sculptures. Part I: comparative study of various systems by means of ATR-FTIR spectroscopy

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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.

Background

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 (outdoor painted sculptures). The examination of case studies reported in literature confirmed this predominance [2, 3]. Indeed, many outdoor artworks from the late twentieth 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. The FTIR spectra of the PU reference materials discussed in this paper will enrich the IRUG spectral database, subject to approval.
**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.

**Isocyanates**

The synthesis of urethane polymers is based on the isocyanate reactions. Isocyanates are highly reactive chemicals containing the functional group \(-\text{N}==\text{C}==\text{O}\). 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].

**Polyls**

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 polyls. Along with the hydroxyl groups, polyls may contain other functionalities such as ester, ether, amide, and acrylic. Polyls with low functionality form linear PUs while polyls of high functionality give crosslinked polymers. In addition, polyls with low molecular weight produce rigid PU with a high concentration of urethane groups in the polymer chain [7]. Polyester and acrylic polyls are conventional coractants, employed for tailoring high performance PU coatings. Such polyls contain ester and/or acrylic and hydroxyl groups in their backbone. Note that the acrylic polyls, 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].
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-borne coatings. 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 twentieth century, DuPont, Sherwin-Williams Co., PPG Industries Inc., Akzo Nobel Coatings Inc., Bayer AG and BASF Corporation dominated the worldwide PU industry.

Subgroups of PU coatings

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 polysiocyanates (–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 polysiocyanate resins. Two pack systems can only be used as two component coatings. The poly-addition process starts directly after mixing Part A and B and the curing process may be completed at ambient temperature. The concentration of polysiocyanates, 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.

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 twentieth 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].

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].

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.

Experimental

PU reference materials
The GCI reference collection contains 137 PU coatings from various manufacturers, namely Dupont, PPG, Akzo, BASE, 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.

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 single bounce diamond crystal (refractive index 2.4). 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. The FTIR results discussed in this paper were used without applying any spectral data treatment. For a better characterization of the activated and/or cured PU coatings, pure polyisocyanate resins and co-reactants involved in the preparation of the corresponding systems were analyzed individually in the same experimental conditions. In this paper, the FTIR results obtained from the 2KSBPU, FPU, 2KWBPU and 1KWBPU samples will be discussed separately.

Results and discussion
Two package solvent-borne PU (2KSBPU)  
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 [22–24] 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].

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 CH₃ 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 (CH₃ 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.

Co-reactants
In this section samples of unactivated co-reactants included in part A of Imron 2.1, Imron 5.0 and Aircraft 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, 1136 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 styrene 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
| Artist                  | OPS                        | Trade names                          | Coating type | Samplex | Color |
|------------------------|----------------------------|--------------------------------------|--------------|---------|-------|
| 2KSBPU                 |                            |                                      |              |         |       |
| 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 633-3-7      | 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           | *Gandy dancer'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              | n/a                        | 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       | Bk    |
| G. Hume                | Back of Snowman (ink)      | BASF/Glasur® 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                 |                            |                                      |              |         |       |
| A. Calder              | *Jousters* (1963)          | NCP®/2KWBPU                         | T           | 9       | W, Bk, Rd, Yel |
| A. Calder              | *Four Arches* (1975)       | 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                 | 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                  | n/a                        | PPG/Coralflon® ADS Intermix         | T           | 1       | Bk    |
| T. Smith               | n/a                        |                                      |              |         |       |
FTIR data reported for acrylics made of nBMA homopolymer [29].

**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 *Spiny Top* [3].

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.

### Two package water-born PU (2KWBPU)

#### 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 polyisocyanurate resin (Bayhydur 303, Bayer).

Actually, the FTIR fingerprints obtained for the investigated water dispersible and regular polyisocyanate 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$^{-1}$.

### 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 [22–24]

| Imron$^{®}$ FG1333™ | NCP$^{®}$ H2OB | HDI isocyanurate | Intensity | Band assignment |
|---------------------|----------------|-----------------|-----------|----------------|
| 3330                | 3330           | 3330            | m         | Secondary urethane $\text{N}=$H stretch/NH bonded/N–H stretching vibration band |
| 2930                | 2930           | 2936            | m         | $\nu_a$ CH$_2$          |
| 2860                | 2860           | 2856            | m         | $\nu_s$ CH$_2$          |
| 2270                | 2270           | 2263            | m         | Isocyanate asymmetric $\text{N}=$C=O stretch/NCO out of phase |
| 1765                | 1765           | 1765            | w         | Free C=O stretch       |
| 1680                | 1680           | 1680            | vs        | $\text{H}=$ bond $\text{C}=$O stretch/tertiary urethane $\text{C}=$O/C=O bonded |
| 1630                | 1630           | 1627            | m         | Carbonyl groups in urea bonds ($\text{C}=$O) |
| 1565                | 1565           | 1574            | m         | Secondary amide RCOND($\text{N}$)      |
| 1515                | 1515           | 1513            | sh        | $\delta$-NH and $\nu$ C–N |
| 1455                | 1455           | 1455            | vs        | $\delta$-CH$_2$        |
| 1425                | 1425           | 1425            | s         | $\delta$ OH            |
| 1375                | 1375           | 1375            | m         | $\delta$–C(=O)         |
| 1330                | 1330           | 1334            | m         | $\text{NCO}$ in phase/CH$_2$ |
| 1250                | 1250           | 1248            | m         | $\nu$(=)C–O–C stretch/Urethane C–O stretch |
| 1155                | 1145           | 1155            | w         | $\nu$ (C–N–C)         |
| 1091                | 1089           | 1090            | w         | $\nu$ C–O–C            |
| 865                 | 865            | 865             | w         | $\nu$ C–N–C            |
| 765                 | 765            | 765             | s         | C–N skel str            |
| 730                 | 730            | 730             | m         | CH$_2$ in phase rock   |

$\nu_a$ asymmetric stretch, $\nu_s$ symmetric stretch, $\delta$ deformation

### Fig. 2

FTIR spectra of Imron$^{®}$ FG1333, NCP H2OB and HDI polyisocyanurate resin (Bayhydur 303 supplied by Bayer) recorded in the same conditions.
**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\(^{-1}\).

**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\(^{-1}\).

**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.

**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 chlorotrifluoroethylene, (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\(^{-1}\) in accordance with the typical F–C stretching region.
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; FPU, 1KWBPU made from acrylic latexes and 2KWBPU prepared with PU dispersions. An overview of the characteristic FTIR features outlined for the studied PU systems is given in Table 3. The intense absorbance in the 1150–1000 cm⁻¹ region, assigned to the F–C stretching mode, could provide 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 features outlined for the studied PU systems is given in Table 3. The intense absorbance in the 1150–1000 cm⁻¹ region, assigned to the F–C stretching mode, could provide 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.

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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Competing interests
The authors declare that they have no competing interests.

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Table 3  Characteristic FTIR features outlined for the 2KSBPU, 2KWBPU (based on PUDs), 1KWBPU and 2KFPU reference samples used in this study

| 2KSBPU | 2KWBPU | 1KWBPU | 2KFPU | Attribution |
|--------|--------|--------|--------|-------------|
| 2940–2930 (m) | 2940–2930 (m) | 2940–2930 (m) | 2940–2930 (m) | Urethane |
| 2860–2855 (m) | 2860–2855 (m) | 2860–2855 (m) | 2860–2855 (m) | Urethane |
| 1735–1720 (s) | abs. | 1735–1720 (vs) | abs. | Polyester and/or acrylic polymer |
| 1690–1680 (vs) | 1690–1680 (abs) | 1690–1680 (vs) | 1690–1680 (s) | HDI isocyanurate |
| 1640–1630 (v) | 1640–1630 (m) | 1640–1630 (m) | 1640–1630 (m) | Urethane |
| 1575–1565 (m) | 1575–1565 (m) | 1575–1565 (m) | 1575–1565 (m) | Urethane |
| 1455–1450 (s) | abs. | 1455–1450 (s) | 1455–1450 (m) | HDI isocyanurate |
| abs. | abs. | abs. | 1110 (vs) | Fluorinated polymer |
| abs. | abs. | abs. | 1065 (vs) | Fluorinated polymer |
| 765–760 (s) | 765–760 (s) | 765–760 (m) | 765–760 (m) | HDI isocyanurate |
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