Deformulating UV Coating System by LC-IR Technology

This application note describes the use of coupled LC-IR to identify the polymer components, monomers and additives in a coating formulation by IR database search and also to find their specific raw material suppliers. During a 35-minute HPLC separation, solid phase IR spectra of each polymer component is obtained in real-time! IR spectra from any part of the HPLC chromatogram can be examined and library searched for component identification. The rapid identification of multiple polymer components in the coating formula gave significant insight to the formulation design that delivers the unique end-use properties. The same techniques described herein can be applied to various polymer mixtures in Coatings, Adhesives, Inks, Sealants, Elastomers, Plastics, Rubbers and Composites for competitive analysis, IP protection and analytical troubleshooting.

INTRODUCTION

Paint and coatings are used almost everywhere in protecting and decorating buildings, architecture, bridges, cars, aircrafts, ships, machinery, etc. Various substrates such as wood, metal, plastic, paper and glass can be coated by spraying, rolling, dipping, etc., then followed by drying and curing by air, heat or radiation (UV, IR). The paint and coatings are usually formulated from different polymer systems with solvent or water media and loaded with pigment, filler and various additive packages to achieve various end-use properties for protection, appearance and durability:

- Polymer Resins: acrylate, epoxy, silicone, polyurethane, etc.
- Media: various solvents and/or water
- Modifiers: toughening agent, cross-linking agent
- Fillers: pigment, colorant
- Additives: antioxidant, UV stabilizer, corrosion inhibitor, etc.

Traditional paint formulations involve lots of solvents which are hazardous and not very environmentally friendly. In the last couple of decades, many new formulation technologies have been developed to minimize the use of solvents, such as water-borne paint, powder coating, high solid paint and UV curable coating. The UV coating can be formulated with various acrylate monomers which are liquid at room temperature and have minimal need of solvent as a media. Polymeric or oligomeric acrylates (e.g. polyurethane acrylate) are commonly added to the UV coating formula to improve end-use properties such as anti-abrasion, chemical and impact resistance.

Due to the vast number of existing coating formulations and the continued effort of new formulation development to meet regulatory requirement and application demand, there is routine need to deformulate the coating systems for competitive analysis, IP protection and analytical troubleshooting. The LC-IR coupled system separates the complex coating formula by GPC or HPLC and acquires IR spectra every half second through all the separated components, and then identifies them by IR spectral database search. This application note will demonstrate the use of the DiscovIR-LC for the deformulation of a UV curable coating by HPLC separation and will identify the major ingredients and minor peaks by commercial IR library search and online IR database search.

EXPERIMENTAL

Coating Sample Preparation
100 mg of the coating sample was dissolved in 10ml methanol and the solution was filtered through 0.45 mm PTFE filter before HPLC injection. The sample concentration was ~ 10 mg/ml (1.0%).

HPLC Conditions
HPLC System: Agilent 1200
Column: Eclipse XDB-C18, 4.6 x 150mm
Mobile Phase: A & B at 1.0 ml/min flow rate
Solvent A: Water with 0.1% formic acid

Solvent B: Methanol with 0.1% formic acid
Gradient: %B linear ramp from 1% to 95% in 0-30 minutes, hold at 95%B from 30-40 minutes
Injection Volume: 75µl

FTIR Detection
DiscovIR-LC solvent-removing, direct-deposition, solid-phase FTIR
Nebulizer Power: 18W
Cyclone Temperature: 180°C
Carrier Gas: 200 cc/min
Condenser Temperature: -5°C
Disk Temperature: -10°C
Disk Speed: 3 mm/min
IR Detector Resolution: 8 cm^{-1}

RESULTS AND DISCUSSIONS

Figure 1 (below) shows an infrared chromatogram of the UV coating sample after the HPLC separation equipped with the DiscovIR-LC detector. The trace is a display of maximum band absorbance over the whole mid-IR range showing three major Components (A, B and D) and four minor Peaks (C, E, F and G).

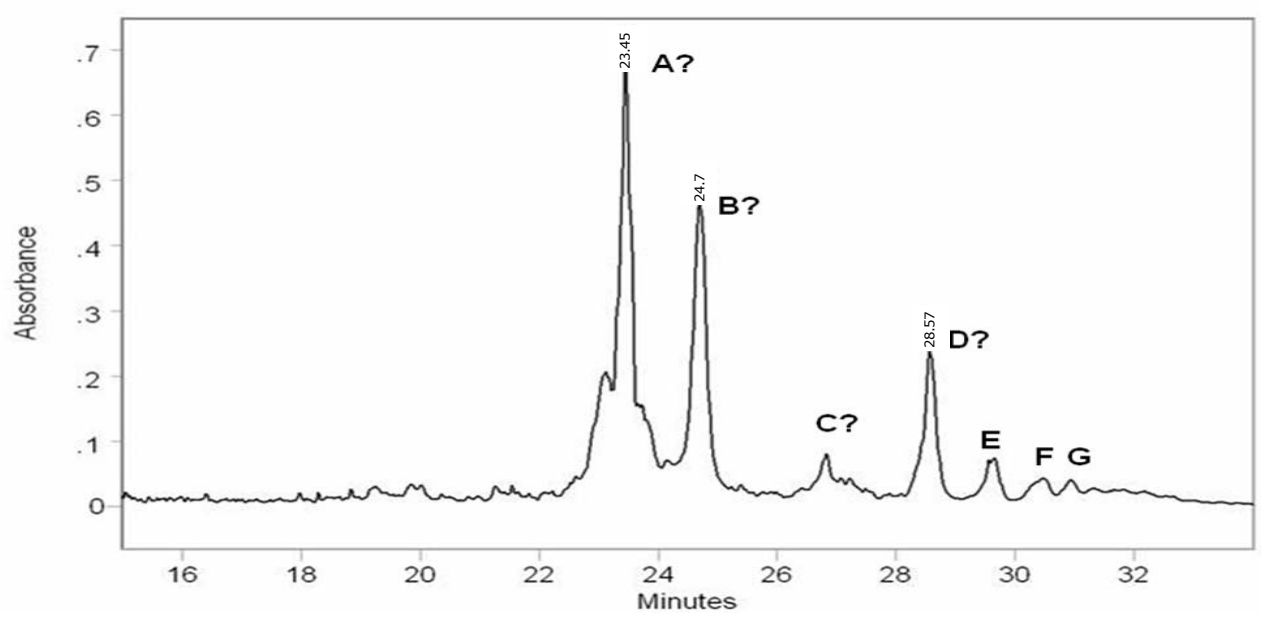
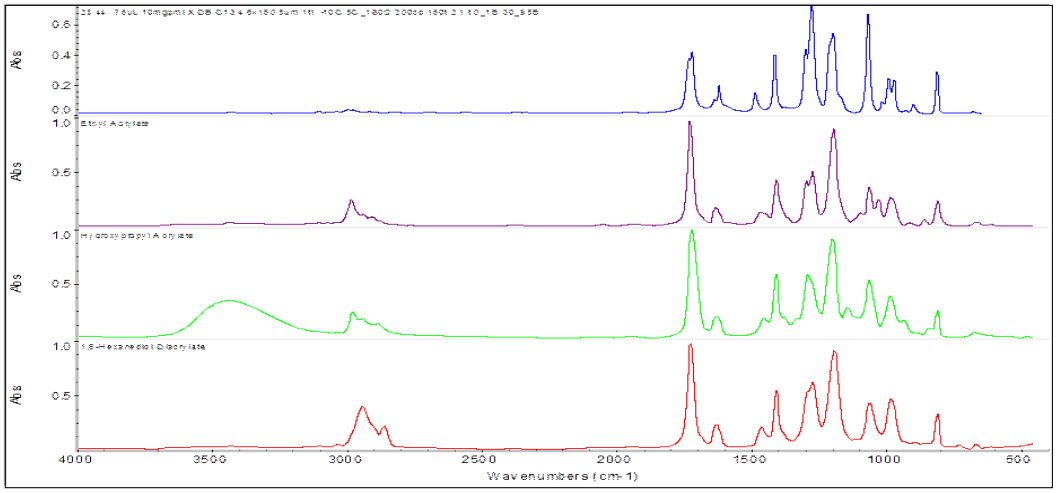


Figure 1 - Maximum Band Chromatogram of the UV Coating Sample by HPLC-IR

The DiscovIR-LC detector collects full mid-IR spectrum every half second. The snapshot IR spectrum at the apex of each component peak was used for IR database search to identify those components in the coating formula. All commercial transmission IR libraries, online IR search services and in-house IR databases can be used to identify various polymers, copolymers, additives, impurities, degradants and many organic compounds. The commercial IR libraries used in the coating deformulation were from Thermo Fisher Scientific, Inc. (81 Wyman Street, Waltham, MA 02454) and Fiveash Data Management, Inc. (211 Vista Road, Madison, WI 53726). The online IR library search was used to identify the minor components in the UV coating from the www.FTIRsearch.com website that has a large IR database (about 71000 IR spectra) to match against.

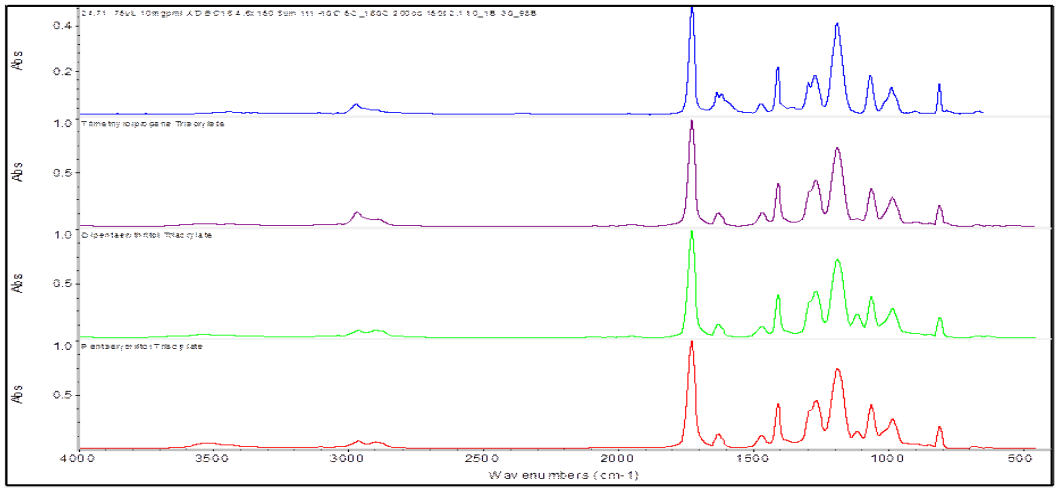
Figure 2 (below) shows the IR spectrum (blue) of Component A at its apex (23.45 min.) and its top three matches (purple, green and red) from the IR library search. The IR database search identified the Component A (blue) as Ethyl Acrylate (purple) from the Coating Technology Library (Thermo Scientific).



Match Order	Index	%Match	Compound Name	Library
1	707	71.09	Ethyl Acrylate	Coatings Technology
2	724	69.15	Hydroxypropyl Acrylate	Coatings Technology
3	750	68.43	1,6-Hexanediol Diacrylate	Coatings Technology

Figure 2 - The Commercial IR Database Search Identified the Unknown Component A (blue) as Ethyl Acrylate (purple) from the Coating Technology Library

Figure 3 (below) shows the IR spectrum (Blue) of Component B at its apex (24.70 min.) and its top three matches (purple, green and red) from the IR library search. The IR database search identified the Component B (blue) as Trimethylolpropane Triacrylate (purple) from the Coating Technology Library (Thermo Scientific).



Match Order	Index	%Match	Compound Name	Library
1	754	97.86	Trimethylolpropane Triacrylate	Coatings Technology
2	759	95.98	Dipentaerythritol Triacrylate	Coatings Technology
3	757	95.24	Pentaerythritol Triacrylate	Coatings Technology

Figure 3 - The Commercial IR Database Search Identified the Unknown Component B (blue) as Trimethylolpropane Triacrylate (purple) from the Coating Technology Library

Figure 4 (below) is the screenshot of the online IR library search at www.FTIRsearch.com for the minor Peak C. It shows the IR spectrum (red) of the Peak C at its apex (26.77 min.) overlaid with the top match (blue). The online IR database search identified the Peak C (red) as Pentaerythritol Triacrylate (blue).

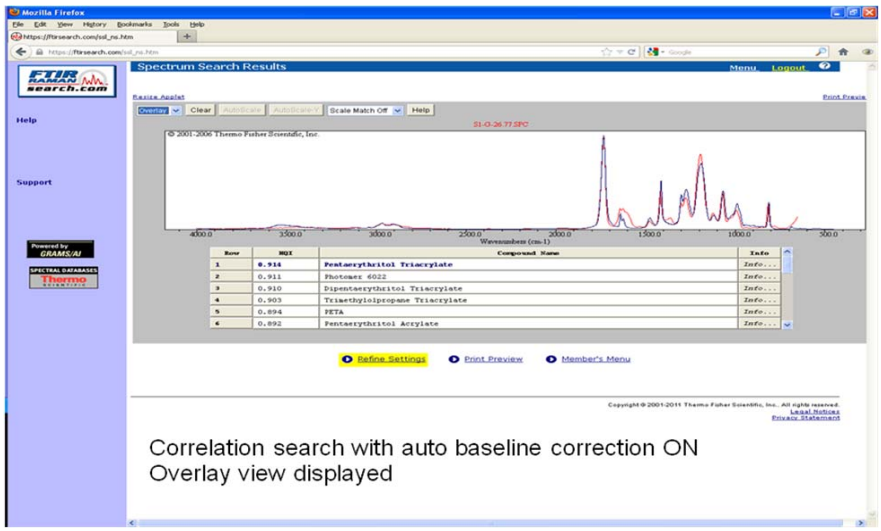
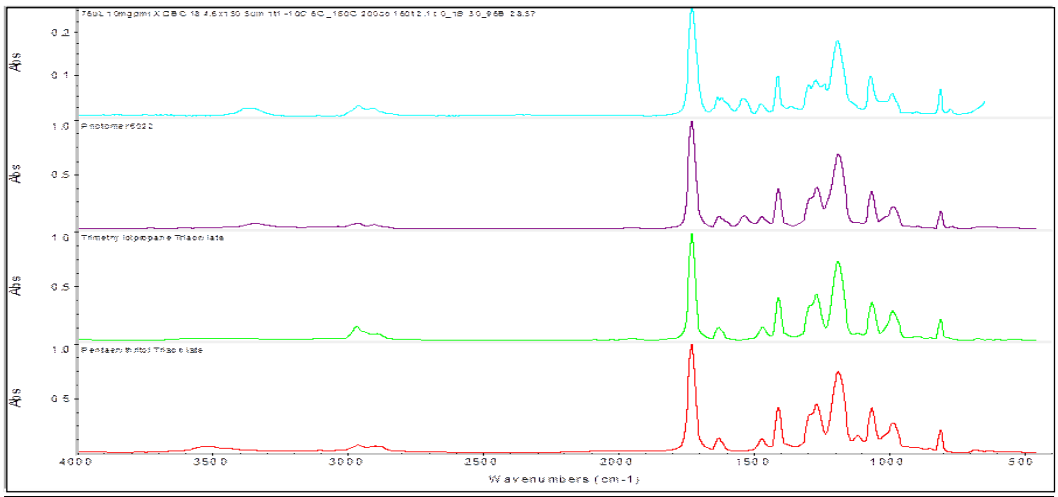


Figure 4 - The Online IR Library Search at www.FTIRsearch.com (screenshot) Identified the Peak C (red) as Pentaerythritol Triacrylate (blue)

Figure 5 (below) shows the IR spectrum (aqua) of Component D at its apex (28.57 min.) and its top three matches from the commercial IR database search. The second (green) and third (red) matches do not have the IR bands at 1530 cm^{-1} and around 3400 cm^{-1}, and can be easily excluded. The best match (purple) with 94.88% match rate shows both IR bands matching up with the Component D (aqua) for its polyurethane feature. The IR database search clearly identified the Component D as Photomer 6022: a Hexafunctional Aromatic Urethane Acrylate Oligomer manufactured by Cognis Corp. (Coatings and Inks Division). The addition of urethane copolymer in the coating formula can improve the scratch and abrasion resistance of the coating film after UV curing.



Match Order	Index	%Match	Compound Name	Library
1	807	94.88	Photomer 6022 (Urethane Acrylate Oligomer)	Coatings Technology
2	754	93.56	Trimethylolpropane Triacrylate	Coatings Technology
3	757	93.44	Pentaerythritol Triacrylate	Coatings Technology

Figure 5 - The Commercial IR Database Search Identified the Unknown Component D (aqua) as Photomer 6022 (Urethane Acrylate Oligomer, purple) with the Supplier Information Available from the Coating Technology Library

Figure 6 (below) is the screenshot of the online IR library search at www.FTIRsearch.com for the minor Peak E. It shows the IR spectrum (red) of the Peak E at its apex (29.51 min.) overlaid with the top three matches (purple, green and blue). The online IR database search identified the Peak E (red) as Photomer 6022 (purple), same as the major Component D (Urethane Acrylate Oligomer).

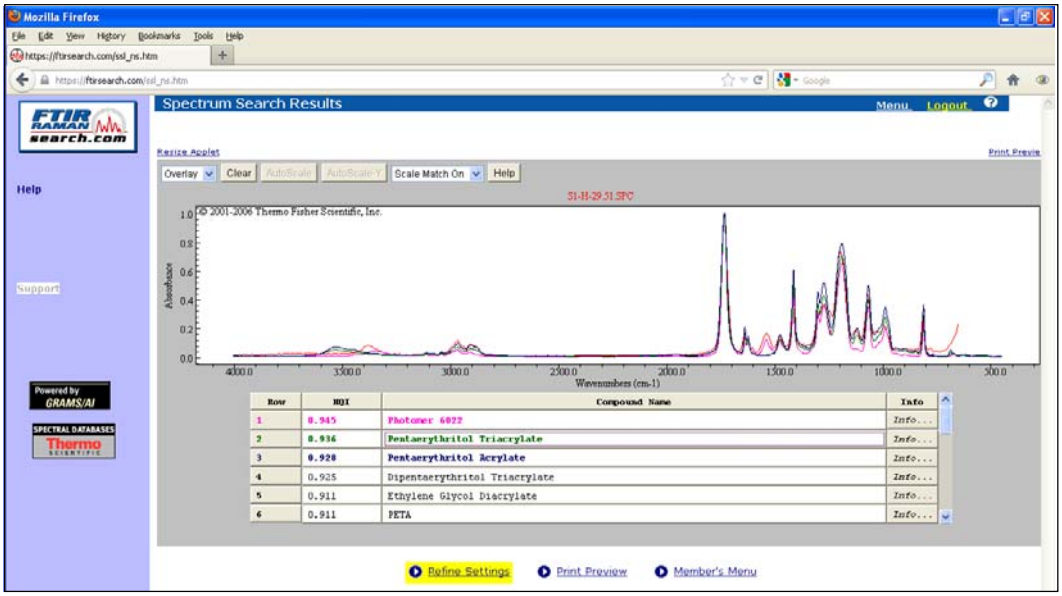


Figure 6 - The Online Library IR Search at www.FTIRsearch.com (screenshot) Identified the Peak E (red) as Photomer 6022 (Urethane Acrylate Oligomer, purple)

Figure 7 (below) is the screenshot of the online IR library search at www.FTIRsearch.com for the minor Peak F. It shows the IR spectrum (red) of the Peak F at its apex (30.50 min.) stacked with the top two matches (blue and purple). The online IR database search also identified the Peak F (red) as Photomer 6022 (blue), same as the major Component D (Urethane Acrylate Oligomer).

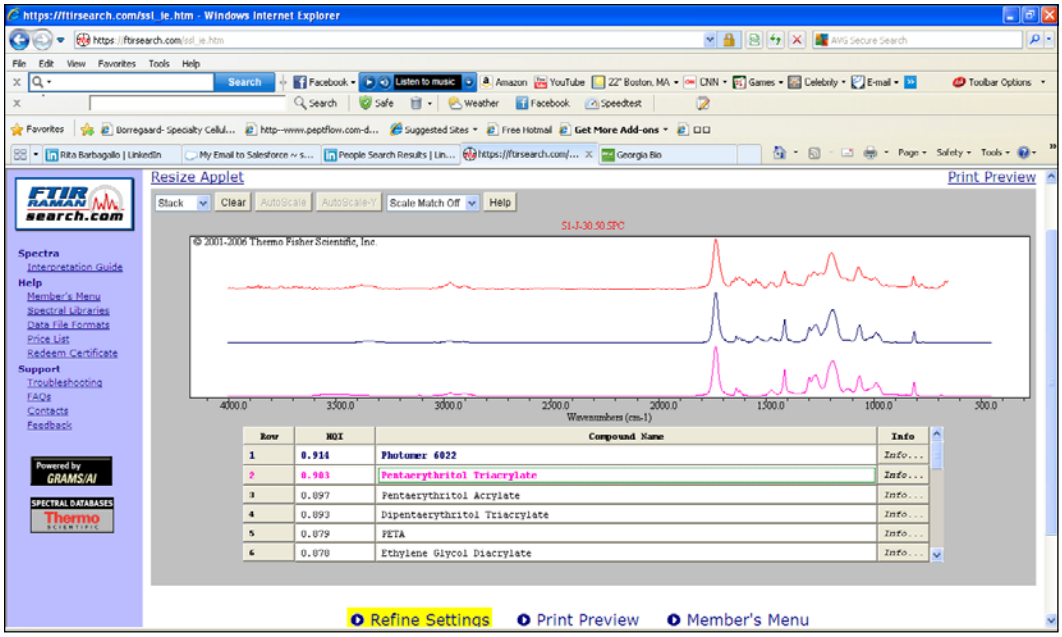


Figure 7 - The Online IR Library Search at www.FTIRsearch.com Identified the Peak F (red) as Photomer 6022 (Urethane Acrylate Oligomer, blue)

The three minor Components E, F and G were all identified as Photomer 6022 as the top match from the online IR database search. Figure 8 (below) is the overlay of the IR spectra of the major component D and the three minor components (E, F and G) eluted right after Component D. They all look very similar except the small differences around 1650 cm^{-1} region. This may well indicate that the minor components (E, F and G) might be from the same raw material as the major component D with only small variations (e.g. function groups, functionality numbers, oligomer levels).

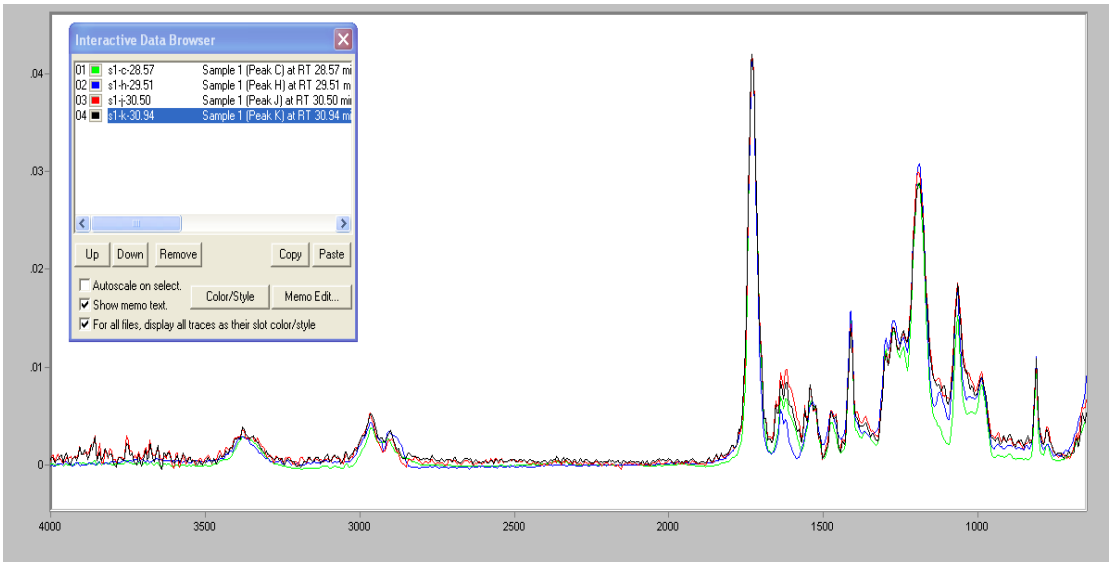


Figure 8 - IR Spectrum Overlay of Components D (green), E (blue), F (red) and G (black) -- All Identified as Photomer 6022 with Only Small Spectral Differences

CONCLUSIONS

LC-IR hyphenated technology separated the complex coating mixture and identified three major components and four minor peaks by commercial IR database search and online IR library search.

(1) Component A was identified as Ethyl Acrylate
(2) Component B was identified as Trimethylolpropane Triacrylate
(3) Peak C was identified as Pentaerythritol Triacrylate
(4) Component D was identified as Photomer 6022: a Hexafunctional Aromatic Urethane Acrylate Oligomer manufactured by Cognis Corp. (Coatings and Inks Division)
(5) Peak E was also identified as Photomer 6022: Urethane Acrylate Oligomer
(6) Peak F was also identified as Photomer 6022: Urethane Acrylate Oligomer

This rapid deformulation was made possible because of the LC-IR ability to capture infrared spectral information (full mid-IR range) for the HPLC separated components. By IR spectrum search against the available IR databases and libraries, the characteristic IR bands serve to identify the chemical structure of the polymer components and small molecules (additives) present in the complex mixtures. An LC-IR instrument, such as the DiscovIR-LC, enables formulators to gain insight into the intellectual property and marketing competitiveness of rival companies.

HOW IT WORKS

For more information on how LC-IR works, please see article: James L. Dwyer and Ming Zhou, "Polymer Characterization by Combined Chromatography-Infrared Spectroscopy," *International Journal of Spectroscopy*, vol. 2011, Article ID 694645,13 pages, 2011 at http://downloads.hindawi.com/journals/ijs/2011/694645.pdf or visit our website, www.spectra-analysis.com.