

## Deformulating a Polymeric Ink Recipe by GPC-IR Technology

### INTRODUCTION

Conductive ink pastes are usually formulated with complex polymer systems and filled with highly engineered silver particles. Typically screenprinted on flexible polyester or polyimide films, they are used to make conductive flexible circuitry such as membrane switches. These ink polymer systems must have the following properties:

- Strong adhesion to the substrate
- Flexibility and rubber-like elasticity
- High load level of silver particles to form conductive patterns
- Ability to disperse silver fillers
- Resistance to processing needs

Various polymer systems have been developed along with unique silver particle engineering technologies to meet these various end-use properties. Particular attention has been given to improving the flexibility of the cured ink film while maintaining its conductivity under the ASTM F1683 stress test (Crease Test/ folding cycle with rolling weight). A commercially available Flexible Conductive Ink formulation has proven to be far superior to its competition as demonstrated by its ability to withstand 20 folding test cycles which is five times better than other leading brands. One can only assume that this superiority comes from a unique polymer system combined with a special additive package.

Deformulating the polymer system will give access to the formulation design and confirm the presence of a special additive package. Typical deformulation tools, such as FTIR, GPC, and DSC, only give access to limited information due to the complexity of the polymer system. The coupling of GPC and Infrared Spectroscopy better suits deformulation needs by separating complex mixtures and identifying the components of these mixtures at once. This application note will demonstrate the use of the DiscovIR-LC for the deformulation of the Flexible Conductive Ink and uncover the polymer/ additive package conferring flexibility and conductivity.

### EXPERIMENTAL

#### Materials

A silver-filled ink paste sample was obtained from Foxconn's electronics processing line and an analytical procedure was developed in Spectra Analysis' analytical lab using the DiscovIR-LC GPC-IR hyphenated technology.

#### Ink Sample Preparation

The ink paste was dissolved in THF and the silver fillers were allowed to settle overnight. The top layer was collected and then filtered through 0.45 µm PTFE disk filter into a standard LC vial before GPC injection. The polymer concentration was ~ 5 mg/ml (~0.5%).

#### GPC Conditions

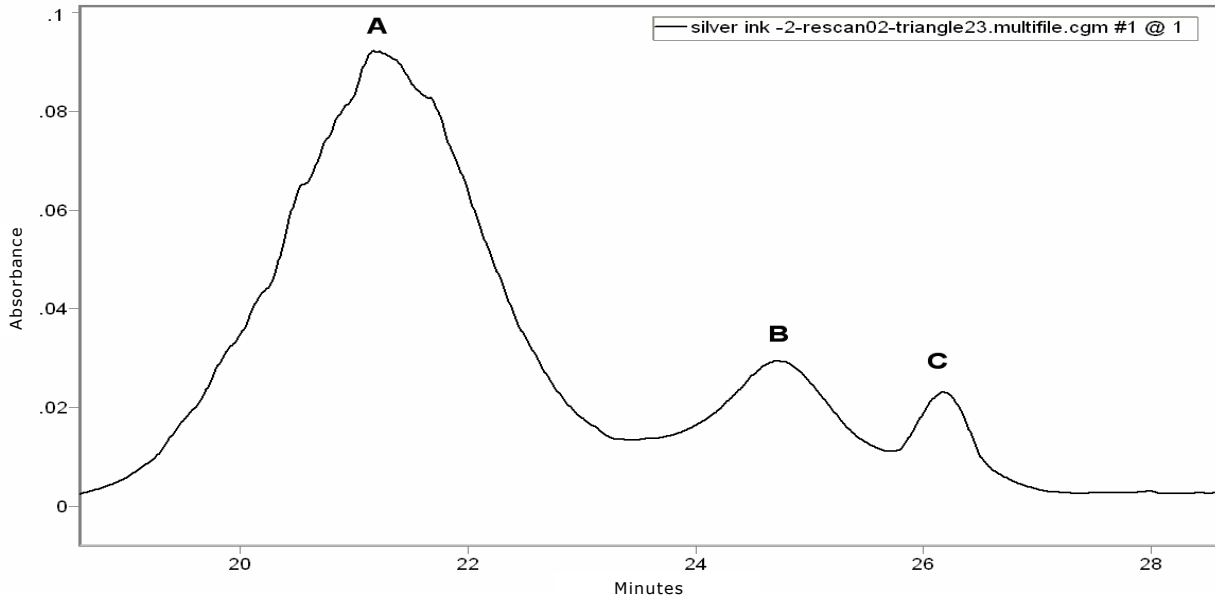
LC System: Agilent 1200  
 Column: 2 x Jordigel DVB Mixed Bed, 25 x 1cm ID  
 Mobile Phase: THF at 1.0 ml/min flow rate  
 Injection Volume: 60 µL

#### FTIR Detection

DiscovIR-LC solvent-removing,  
 direct-deposition solid phase FTIR  
 Nebulizer Power: 7 W  
 Cyclone Temperature: 130°C  
 Carrier Gas: 250 cc/min  
 Condenser Temperature: 15°C  
 Disk Temperature: -10°C  
 Disk Speed: 12 mm/min  
 IR Detector Resolution: 8 cm<sup>-1</sup>

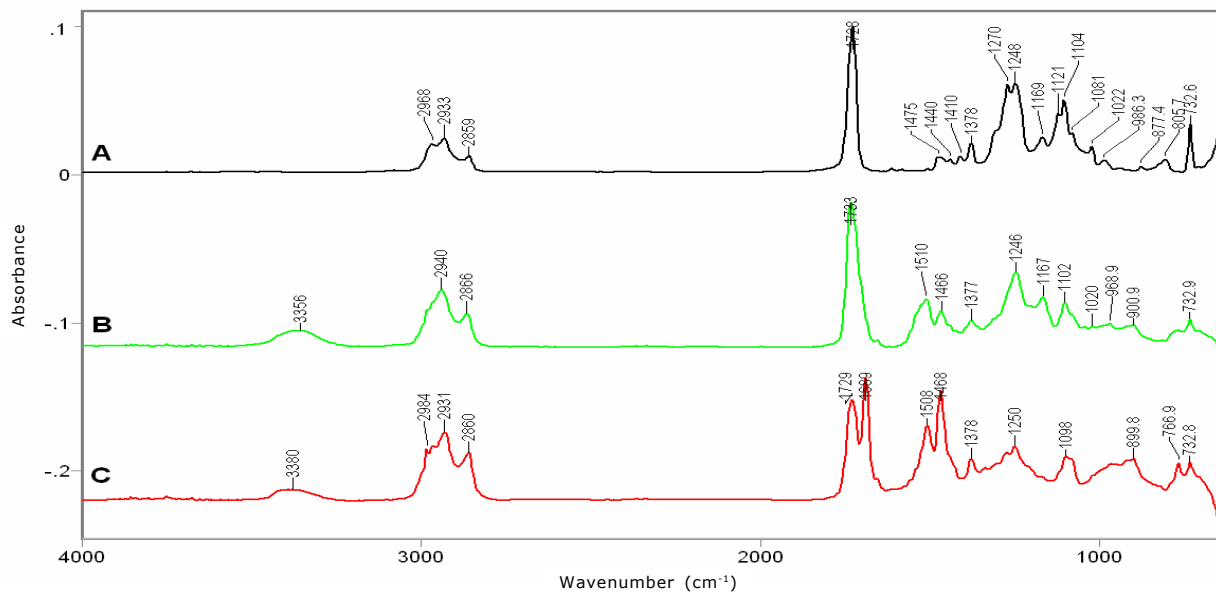
## RESULTS

Figure 1 (below) shows infrared chromatogram of the polymer solution from the silver ink paste generated by the GPC-IR detector. The trace is a display of maximum band absorbance over the whole mid-IR range showing three components A, B and C from high MW to low MW corresponding to GPC elution times.



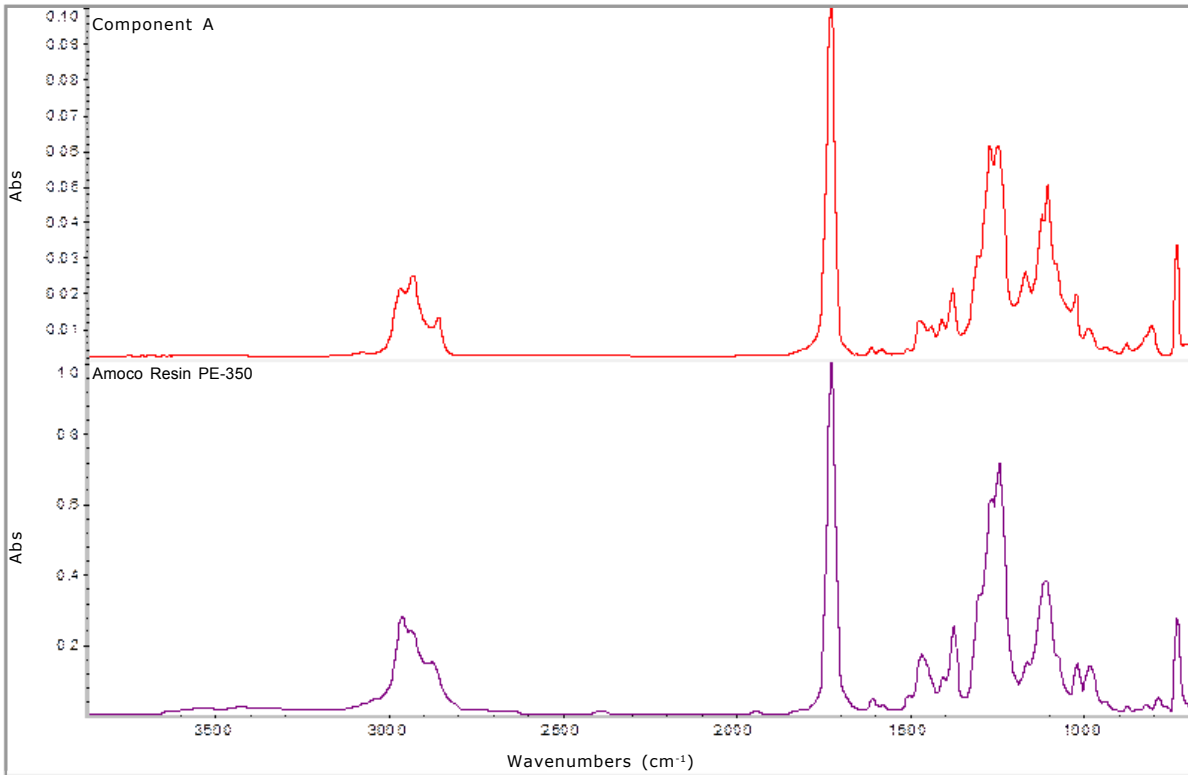
**Figure 1** - Maximum Band Chromatogram of the Polymer Solution from the Conductive Ink

Figure 2 (below) is the stacked IR spectra of each component at its MWD peak maximum. The three snapshot IR spectra were compared against a commercially available IR database to identify Components A, B and C. The commercial IR libraries used in the ink deformation were from Thermo Fisher Scientific, Inc. (81 Wyman Street, Waltham, MA 02454) and Fiveash Data Management, Inc. (211 Vista Road, Madison, WI 53726) and enabled the identification of polymers, copolymers, additives, impurities, degradants and many organic compounds.



**Figure 2** - IR Spectra of Polymer Components A, B and C at their MWD Peak Maxima

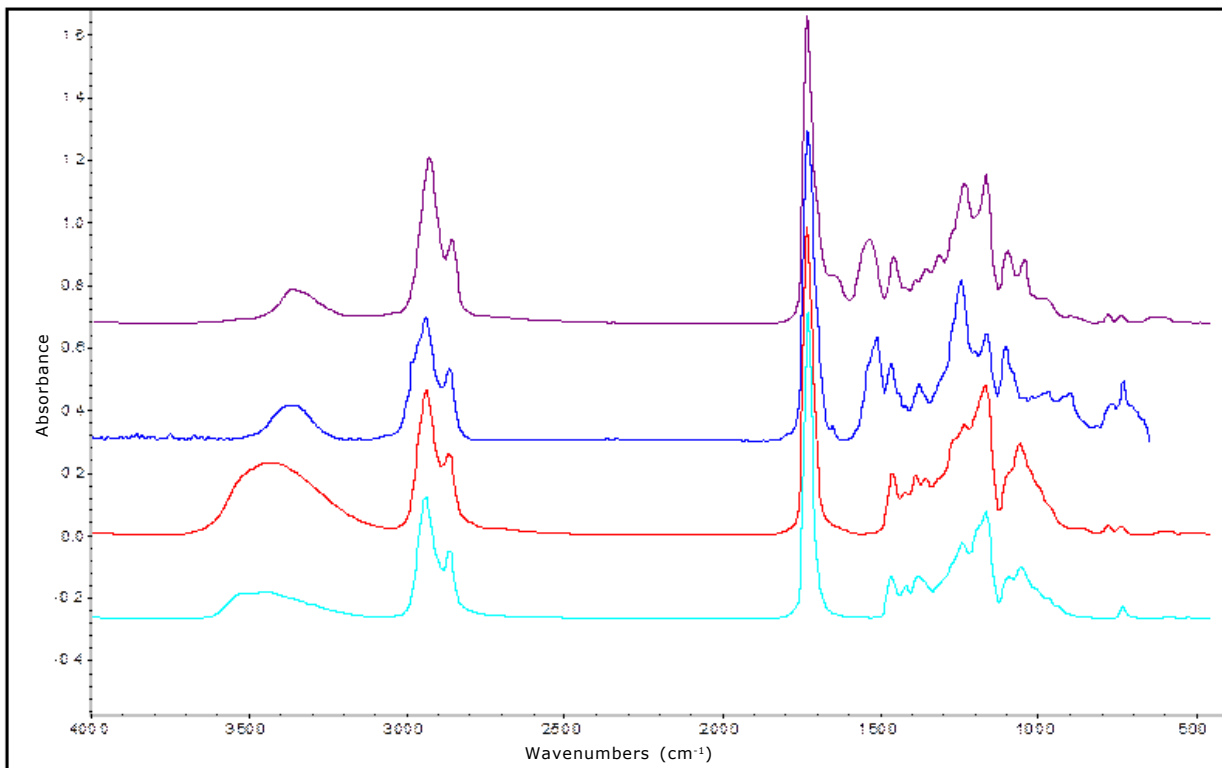
Figure 3 (below) shows the IR spectrum (red) of Polymer A and its top match (purple) with 96.6% match rate (100% indicating a perfect match). The IR database search identified Polymer A (red) as aliphatic polyester (purple) with the specific supplier information (Amoco Resin PE-350) available from the Coatings Technology Library. The next two matches with 95.6-96.0% high match rates also led to the same identification - aliphatic polyester, but from different manufacturers.



| <u>Match Order</u> | <u>Index</u> | <u>%Match</u> | <u>Compound Name</u> | <u>Library</u>      |
|--------------------|--------------|---------------|----------------------|---------------------|
| 1                  | 434          | 96.63         | Amoco Resin PE-350   | Coatings Technology |
| 2                  | 450          | 95.96         | Dynapol LH-812       | Coatings Technology |
| 3                  | 467          | 95.65         | Vitel VPE-222F       | Coatings Technology |
| 4                  | 443          | 95.06         | Dynapol L-411        | Coatings Technology |
| 5                  | 466          | 94.45         | Vitel PE-200         | Coatings Technology |

**Figure 3** - The commercial IR database search identified Polymer A (red) as Aliphatic Polyester (purple) with the specific supplier information available from the Coatings Technology Library

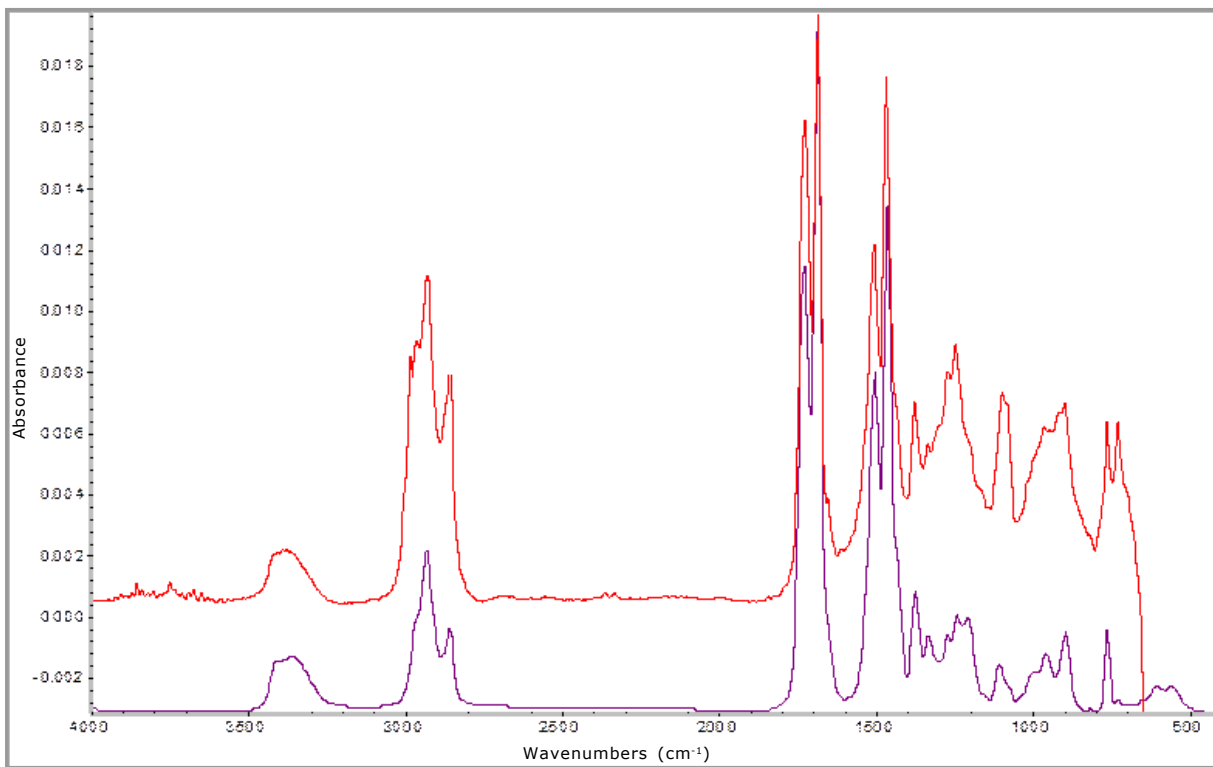
Figure 4 (below) shows the IR spectrum (blue) of Polymer B and its three top matches (purple, red and aqua) from the IR libraries. The IR database search identified Polymer B (blue) as aliphatic polyurethane (purple) with the specific supplier information (product brand and number) available from the Coatings Technology Library. The next two matches (87.3-87.5% match rates) led to different polymers: polyester polyol (red) and polycaprolactone (aqua) with broad IR absorbance across 3000-3600  $\text{cm}^{-1}$  range from their OH functional groups. The relatively narrow IR bands around 3300-3500  $\text{cm}^{-1}$  from both Polymer B (blue) and the top match (purple) confirmed the NH functional group from their polyurethane nature, excluding the second and third match. Polymer B was identified as Spensol L-53, now called UROTUF L-53, manufactured by Reichhold Chemicals, Inc.



| Match Order | Index | %Match | Compound Name                     | Library             |
|-------------|-------|--------|-----------------------------------|---------------------|
| 1           | 503   | 88.13  | Spensol L-53<br>(now UROTUF L-53) | Coatings Technology |
| 2           | 949   | 87.51  | Polyester Polyol 0305             | Coatings Technology |
| 3           | 424   | 87.33  | Polycaprolactone                  | Coatings Technology |
| 4           | 944   | 87.29  | Polyester Polyol 0200             | Coatings Technology |
| 5           | 212   | 86.86  | UCAR Cyracure UVR-6351            | Coatings Technology |

**Figure 4** - The commercial IR database search identified Polymer B (blue) as Aliphatic Polyurethane (purple) with the supplier information available from the Coatings Technology Library

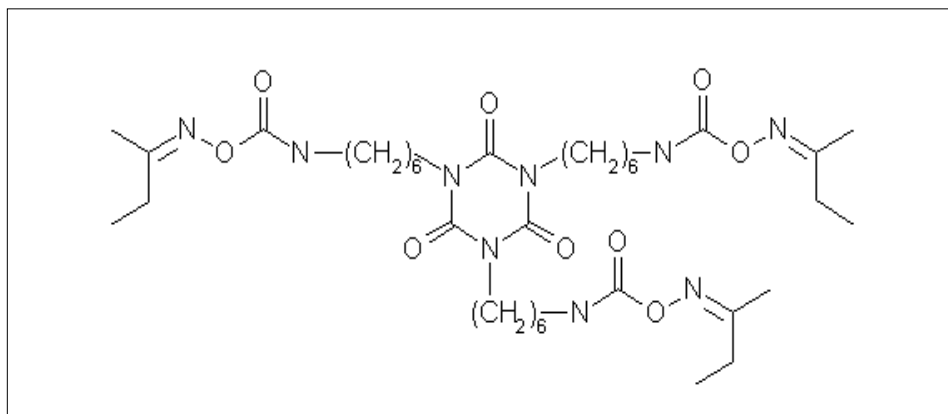
Figure 5 (below) shows the IR spectrum (red) of Component C and its top match (purple) with 92.7% match rate from the IR libraries. The next four matches can be easily excluded due to their low match rates (62.0-65.3%). The IR database search clearly identified Component C (red) as Desmodur LS-2800, a cross-linking agent manufactured by Bayer Material Science.



| <u>Match Order</u> | <u>Index</u> | <u>%Match</u> | <u>Compound Name</u>                                  | <u>Library</u>      |
|--------------------|--------------|---------------|---|---------------------|
| 1                  | 834          | 92.47         | Desmodur LS-2800                                      | Coatings Technology |
| 2                  | 3249         | 65.30         | Caffeine; 1,3,7-Trimethylxanthine                     | Coatings Technology |
| 3                  | 9302         | 64.76         | Monophenylbutazone                                    | Coatings Technology |
| 4                  | 615          | 62.15         | Betulinic Acid;<br>3-Hydroxylup-20(29)-en-28-oic Acid | Coatings Technology |
| 5                  | 860          | 62.05         | Spenlite M-27   | Coatings Technology |

**Figure 5** - Commercial IR database search identified Component C (red) as Desmodur LS-2800 Cross-Linker (purple) with the supplier information available from the Coatings Technology Library

Figure 6 (below) displays the chemical structure of the identified additive: ketoxime blocked HDI trimer with CAS #93919-05-2 and low molar mass at 766 g/mol. Component C is a latent cross-linker which is stable at ambient temperature during the ink manufacturing, ink storage and screenprinting operation but will de-block at >130°C during the thermal curing to generate tri-functional isocyanate for cross-linking with NH or OH functional groups from other components in the ink formulation.



**Figure 6** - Chemical structure of Additive C identified by GPC-IR as Latent Cross-Linking Agent: Ketoxime Blocked HDI Trimer (CAS #93919-05-2) manufactured by Bayer Material Science

## CONCLUSIONS

GPC-IR hyphenated technology separated the complex polymer mixture from the silver ink paste and identified three components and their specific suppliers by IR database search.

- (1) Polymer A was identified as an aliphatic polyester resin from Amoco (there are similar products from Evonik Degussa and Bostik) with high MW and broad MW distribution. This polymer is very flexible with very strong adhesion to flexible polyester or polyimide films.
- (2) Polymer B was identified as an aliphatic polyurethane Spensol L-53 (now UROTUF L-53) from Reichhold Chemicals, Inc. with medium MW and narrow MW distribution. This polymer is very elastomeric and highly flexible, and can be cross-linked with tri-functional isocyanate additives.
- (3) Component C was identified as the latent cross-linking agent Desmodur LS-2800 manufactured by Bayer Material Science.
- (4) Additive C (blocked HDI trimer) is stable at room temperature but will de-block during the curing at 150°C to generate tri-isocyanate which will then cross-link with polyurethane (Polymer B) to form strong, flexible and elastomeric 3D network. The latter may form a unique interpenetrating polymer network (IPN) with the flexible Polymer A that holds all the silver particles in place to form conductive circuitry paths, even under many cycles of harsh folding.

This rapid deformation was made possible because of the GPC-IR ability to capture infrared spectral information (full FTIR range) for GPC separated components. By comparison against references, the characteristic IR bands serve to indicate the chemical structure of the monomers and small molecules (additives) present. A GPC-IR instrument, such as the DiscovIR-LC, enables formulators to gain an insight on the intellectual property and marketing competitiveness of rival companies.

## HOW IT WORKS

For more information on how GPC-IR works, please see article published in LC-GC, *Polymer Characterization by Combined Chromatography-Infrared Spectroscopy*, on our website, [www.spectra-analysis.com](http://www.spectra-analysis.com), under the Applications tab, Copolymers.