# MITIGATING CHEMICALS OF CONCERN THROUGH THE USAGE OF NOVEL ENERGY CURABLE ACRYLATE TECHNOLOGY

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## ABSTRACT

Epoxy acrylates are one of the most widely used resins in energy cured inks, coatings and overprint varnishes for consumer product packaging and graphic arts. In addition to outstanding scratch and impact resistance, epoxy acrylates are known for their cost effectiveness. Bisphenol-A (BPA) as part of BADGE (Bisphenol A diglycidyl ether), one of the building blocks used for acrylated epoxy resins, has been identified as a chemical of concern. The purpose of this presentation is to review a developing chemistry with potential use as a replacement for standard Bisphenol-A containing epoxy acrylates that are in used consumer product packaging and graphic art applications.

## INTRODUCTION

Energy (UV/EB)-cured inks and coatings are well accepted in the graphics industry. Energy curing technology is recognized to offer numerous advantages over conventional technologies, such as excellent resistance properties, high printing speeds, low VOCs, high gloss, and high reactivities. Issues with possible “chemicals of concern,” including bisphenol A (BPA), have presented challenges. Allnex has focused on developing a range of forward-looking solutions that address these issues in advance of potential future legislation.

For some time, there has been a need in the food packaging industry for resins used in inks and coatings that have minimal migration properties. By considering chemical properties, toxicity profiles and the overall manufacturing processes of its products, several years ago Allnex began introducing products to address this important issue. This comprehensive approach has been extended to include the use of bio-renewable building blocks, and is now being applied to the development of a solution to address bisphenol A.

## BISPHENOL A BACKGROUND

Epoxy acrylate oligomers are widely used in energy curable coatings for overprint varnishes (OPVs), wood, metal, plastics, and lithographic and screen inks. In these applications epoxy acrylates offer a good balance between performance and cost. Films based on epoxy acrylates cure rapidly, have high gloss, high hardness, and offer good chemical, water, corrosion and scratch resistance.

One of the key components used in the preparation of epoxy acrylate oligomers, Bisphenol A diglycidyl ether (BADGE) contains small levels of BPA. While most studies to date have generally indicated that the current levels at which humans are exposed to BPA are safe, recent results obtained using new methodologies have raised some concerns about the possible effects that BPA may have on the health of the very young. The US Food and Drug Administration (FDA) has initiated additional studies to determine what, if any, regulatory actions it should take with respect to BPA in food contact applications. In Europe, BPA is currently permitted for use in food contact materials, but the human risks associated with exposure to BPA through the diet are being re-evaluated. Canada declared BPA a toxic substance in 2010.

## BPA-FREE ALTERNATIVES

There are several bisphenol A-free alternative chemistries available on the market for use in packaging and graphic arts applications, including aliphatic and aromatic urethane acrylates, polyester acrylates, and acrylated bio-based building blocks. Urethane acrylate oligomers can provide hardness, chemical and abrasion resistance and flexibility. This oligomer type typically has higher viscosities and higher costs. Polyester acrylate oligomers are lower in viscosity, provide good pigment wetting, but can also be moisture sensitive. Acrylated polyols derived from soybean and other natural oils are attractive for their bio-based content and pigment wetting properties, but have solvency issues and their ink and coating films are often too soft.

Eliminating BPA-containing products used in UV/EB energy cured inks and coatings can be a difficult task and depends greatly on the final application and performance requirements. To achieve this goal, efforts were first focused on the properties of bisphenol A and BPA diglycidyl ether that contribute to the final desirable performance properties observed in UV cured films derived from these raw materials. At the same time, taking into consideration current and future market needs, a bio-based solution was highly desired in order to address the need for alternatives to petrochemical-based products throughout the ink and coatings value chain.

## INITIAL INVESTIGATIONS

A series of bio-based experimental acrylates containing greater than 50% renewable content were prepared and then formulated with diluents and photoinitiators to produce BPA-free systems. The typical properties for one of the leading candidates are shown in Table 1; and a comparison of the cured properties of this experimental oligomer versus an industry standard BPA oligomer is presented in Table 2.

**Table 1. Typical Properties of an Experimental Bio-based Aliphatic Diacrylate**

| | |
|---|---|
| Dynamic Viscosity, cP @ 25C | ~ 450 |
| Density, g/ml @25°C | 1.26 |
| Color, Gardner | 1-2 |

**Table 2. Typical Tensile Properties for Films of a BPA Epoxy Acrylate and an Experimental Bio-Based Oligomer**

| Properties | BPA Epoxy Acrylate | Bio Based Oligomer |
|---|---|---|
| Tensile strength (MPa) (*) | 70 | 12 |
| Tensile elongation (%) (**) | 4 | <1 |
| Young's Modulus, (MPa) (**) | 2200 | 3150 |
| Tg (by DMTA- max tan δ) (°C) | 130 | 162 |
| Shrinkage (%) (**) | 6.2 | 8.4 |

(*)Measured on an 80μ EB cured film. Measurement methods: Tg (by DMTA- max tg δ): ASTM E1640 ; Tensile strength, tensile elongation, Young's Modulus: ASTM D638-61T and ISO 527-1;

(**) Shrinkage: estimated from the density change between the liquid and the cured solid state l

Initially, the bio-based oligomer was evaluated in a basic coating formulation. The control for this testing was an industry standard BPA epoxy diacrylate, diluted with 25% TPGDA. To achieve an appropriate viscosity, additional monomer was added to the control formulation. The results, shown in Table 3, indicate the minimum energy dosage required for cure was lowest for the experimental system. The hardness and mechanical properties for the bio-based coating were similar to the BPA based system.

**Table 3: Comparison of the properties of BPA-based and Bio-based coatings**

| | **BPA Epoxy Diacrylate Coating** | **Bio-based Oligomer Coating** |
|---|---|---|
| BPA epoxy diacrylate (contains 25% TPGDA) | 70 | |
| Bio-based aliphatic oligomer | | 100 |
| TPGDA | 30 | |
| ADDITOL BCPK | 5 | 5 |
| TPGDA, % | 47.5 | 0 |
| Viscosity, cP @ 25°C | 760 | 400 |
| Min cure dose, J/cm$^2$ | 0.794 | 0.269 |
| Pendulum Hardness, sec | 340 | 357 |
| Young’s Modulus, MPa | 2215 | 2271 |
| Elongation, % | 4.4 | 0.2 |

Curing Conditions: - 10µ on white paper - curing with 80W UV lamp.
(Source: Collette Moulaert – Allnex TS&D)

Next, the performance of the bio-based oligomer in a hardcoat formulation for plastic was compared to a hardcoat formulation containing either a hexafunctional aliphatic urethane or a tetrafunctional polyester. The fast cure, excellent hardness and solvent resistance were key performance characteristics for selecting the urethane acrylate. The polyester acrylate was chosen for its low viscosity, chemical resistance and relative hardness and chemical resistance. The complete results are given in Table 5.

**Table 4. Hardcoat Formulations for Plastics**

| | **A** | **B** | **C** |
|---|---|---|---|
| Urethane Acrylate, 6f | 66 | | |
| Polyester Acrylate, 4f | | 66 | |
| Bio-based Aliphatic Acrylate, 2f | | | 66 |
| Monomer, difunctional | 30 | 30 | 30 |
| Flow Additive | 0.5 | 0.5 | 0.5 |
| Photoinitiator | 4 | 4 | 4 |

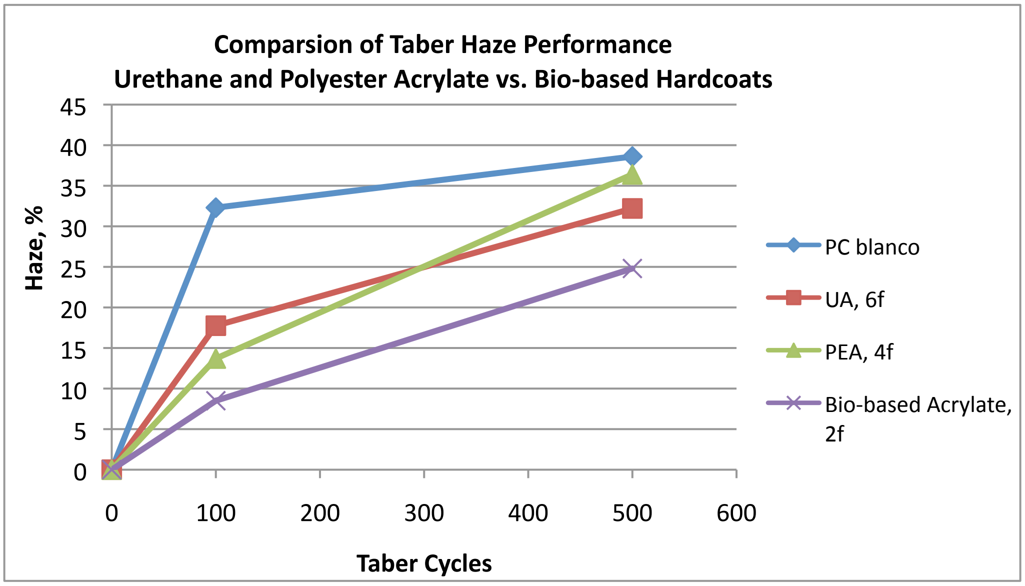
**Table 5. Comparison of Urethane/Polyester Acrylate and Bio-based Hardcoats Formulations on Plastic**

| | Urethane Acrylate, 6f | Polyester Acrylate, 4f | Bio-Based Oligomer |
|---|---|---|---|
| **Viscosity, cP @ 25°C** | 628 | 82 | 53 |
| **Appearance** | | | |
| **on Leneta paper** | ok | ok | ok |
| **on PC sheet** | ok | ok | ok |
| **Cross Hatch Adhesion (0=good, 5=bad)** | 0 | 0 | 0 |
| **Pencil hardness** | 2B | 3B | 3B |
| **Stains (1=bad,5=good)** | | | |
| **coffee (4%,16h)** | 5 | 1 | 5 |
| **mustard (16h)** | 5 | 1 | 5 |
| **N70 black marker (xh)** | 5 | 4 | 5 |
| **Steel wool, 10 DR (5=good, 1=bad)** | | | |
| **on Leneta paper** | 5 | 1 | 3 |
| **on PC sheet** | 3 | 1 | 3 |
| **100 DR Steel wool (scratch)** | | | |
| **on Leneta paper** | 5 | 1 | 3 |
| **on PC sheet** | 3 | 1 | 3 |
| **Taber haze (abrasion)** | | | |
| **100 cycles** | | | |
| **sample 1** | 18 | 13.4 | 8.6 |
| **sample 2** | 17.5 | 13.9 | 8.3 |
| **500 cycles** | | | |
| **sample 1** | 32.6 | 38.7 | 26.1 |
| **sample 2** | 31.8 | 34.1 | 23.6 |

The resins were diluted 30% in hexanediol diacrylate and formulated with Additol CPK as the photoinitiator and Modaflow 9200 for flow and leveling. The coatings were cured at 10 m/min with a 120 W/cm Hg lamp at a coating weight of10 g/cm² on a 250 micron polycarbonate sheet.

As can be seen in Table 5, the bio-based formulation again had a viscosity lower than either the urethane acrylate or polyester acrylate based hardcoats. Overall, the experimental hardcoat had performance fairly comparable to the urethane system and better than the polyester acrylate system. Both the urethane and the bio based hardcoats exhibited good resistance to stain, scratch and abrasion. With the Taber haze abrasion testing, the bio based oligomer system had the best performance at 100 and 500 cycles (Figure 1). However, the steel wool resistance and pencil hardness were slightly lower for the bio-based hardcoat.

**Figure 1.**



## BIO-BASED CHEMISTRY IN OVERPRINT VARNISH APPLICATIONS

The performance of the bio-based aliphatic acrylate was also evaluated in an OPV. For this testing the controls were a BPA epoxy diacrylate diluted with 25% TPGDA and a modified BPA epoxy diacrylate. Additional monomer was added to both epoxy acrylate formulas and amine synergist and photoinitiator added to all formulations.

**Table 6. OPV formulations with BPA Epoxy Acrylates and Bio Based Oligomer**

| | **OPV 1** | **OPV 2** | **OPV 3** |
|---|---|---|---|
| BPA epoxy diacrylate<br>(contains 25% TPGDA) | 24 | | |
| Modified BPA epoxy diacrylate | | 52 | |
| Bio based oligomer | | | 80 |
| Diluting acrylate, tetrafunctional | 56 | | |
| Monomer, difunctional | | 28 | |
| Amine synergist | 15 | 15 | 15 |
| Photoinitiator | 5 | 5 | 5 |

OPV viscosity: 500 cP (+/- 20 cP) at 25°C

Compared to the epoxy acrylate systems tested, the bio-based oligomer system exhibited improved surface cure (Figure 2) and superior solvent resistance as measured using acetone double rubs (Figure 3).

**Figure 2.**

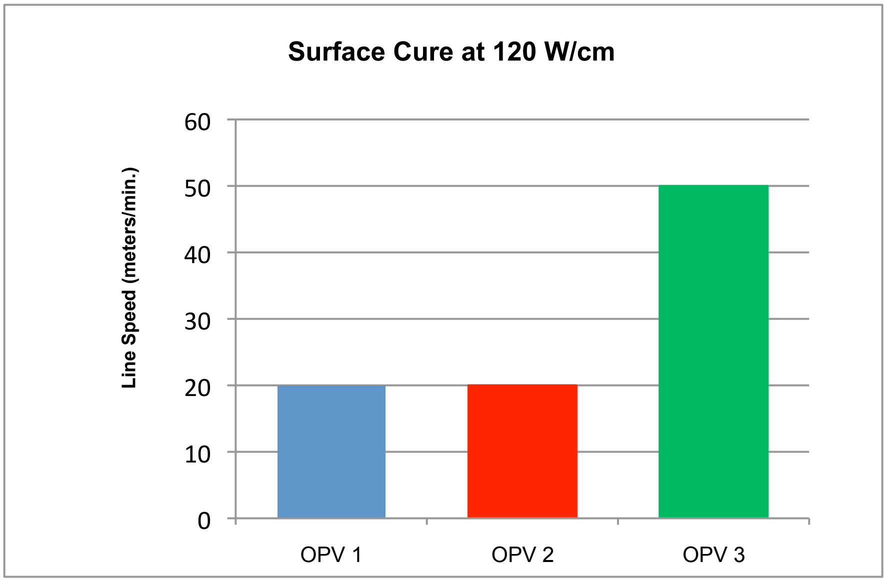
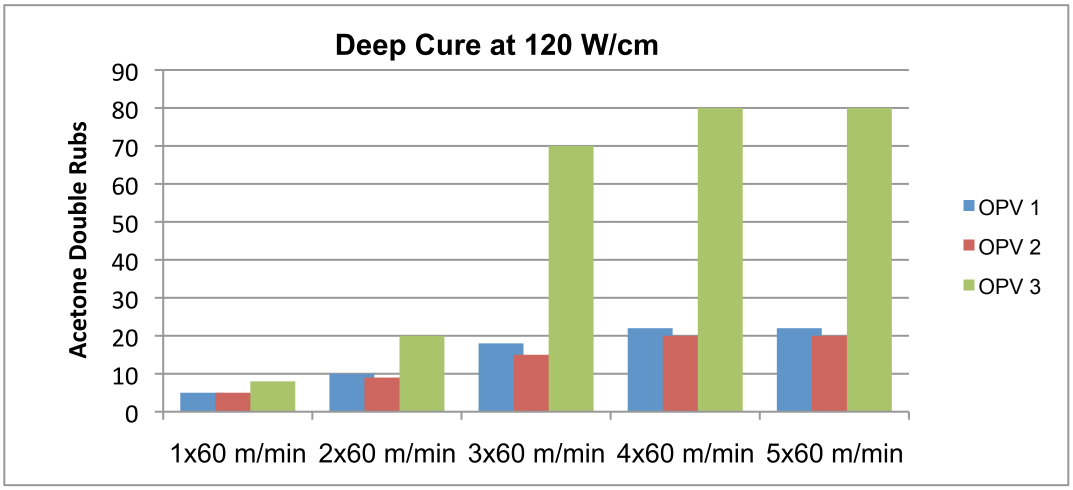


**Figure 3.**



## Bio Based Oligomer in Lithographic and Flexographic Inks

Given the positive performance observed in the hardcoat and OPV testing, the bio-based oligomer was next evaluated in lithographic and flexographic inks. For the litho ink evaluation the experimental oligomer was compared to a tetrafunctional polyester acrylate commonly used in UV offset applications. To achieve a suitable milling viscosity, the experimental oligomer was first blended with 20% of a hexafunctional polyester acrylate. Pigments used in the dispersions were Clariant process color pigments PY13 Permanent Yellow GR, PR57:1 Permanent Rubine

L5B-01 and PB15:3 PV Fast® Blue BG. During the milling process the bio based oligomer/polyester acrylate kicked out of the pigment dispersions after three mill passes. Overall the experimental oligomer/polyester acrylate dispersions exhibited poor pigment wetting capabilities. More testing must be completed in order to prove out the potential for the bio based oligomer in lithographic applications.

In the flexo ink evaluation the performance of bio-based aliphatic acrylate was compared to a modified epoxy acrylate in a black ink (Table 7). Again, to achieve an appropriate milling viscosity, a hexafunctional polyester acrylate was used in conjunction with the experimental oligomer. Testing included rheology, optical density, gloss and surface cure. Results indicated the experimental ink exhibited comparable surface cure and optical density as the control but a higher gloss. The bio-based aliphatic acrylate black ink also exhibited more Newtonian like rheology.

All testing of the pigment wetting capability of the experimental oligomer was completed at the Graphic Arts Application Laboratory of Clariant Corporation in Charlotte, NC.

**Table 7. Formulations and Performance Properties of Black Flexo Inks Made with Modified Epoxy Acrylate and the Bio-based Aliphatic Diacrylate**

| | Control | Experimental |
|---|---|---|
| Modified Epoxy Diacrylate | 24.3 | |
| Hexafunctional Polyester acrylate | | 9 |
| Bio-based aliphatic acrylate | | 15.3 |
| Stabilizer solution | 0.45 | 0.45 |
| Pigment wetting additive | 2.25 | 2.25 |
| Black pigment | 16 | 16 |
| Bio-based aliphatic acrylate | | 34 |
| Diluting acrylate, multifunctional | 10 | |
| Diluting acrylate, multifunctional | 36 | |
| Trifunctional monomer | | 12 |
| Photoinitiator | 5 | 5 |
| Photoinitiator | 3 | 3 |
| Photoinitiator | 1 | 1 |
| | | |
| Viscosity at 2.5 s-1 @ 25°C | 1320 | 1230 |
| Viscosity at 2500 s-1 | 760 | 950 |
| Shortness Index (2.5/2500) | 1.8 | 1.3 |
| Flow after 30 sec (cm) | 23 | 19 |
| Optical Density at 1.2 g/m² | 1.82 | 1.76 |
| Gloss 60° at 1.2 g/m² | 65 | 69 |
| Cure speed 120W/cm - m/min | 70 | 70 |

Inks were applied to 3nt-4 regular bond natural white coated Leneta.

Due to the initial promising performance in UV Flexo inks, additional testing of the bio-based oligomer was conducted. In this testing, another commonly used, low viscosity tetrafunctional polyester acrylate was selected as a comparative reference (Table 8).

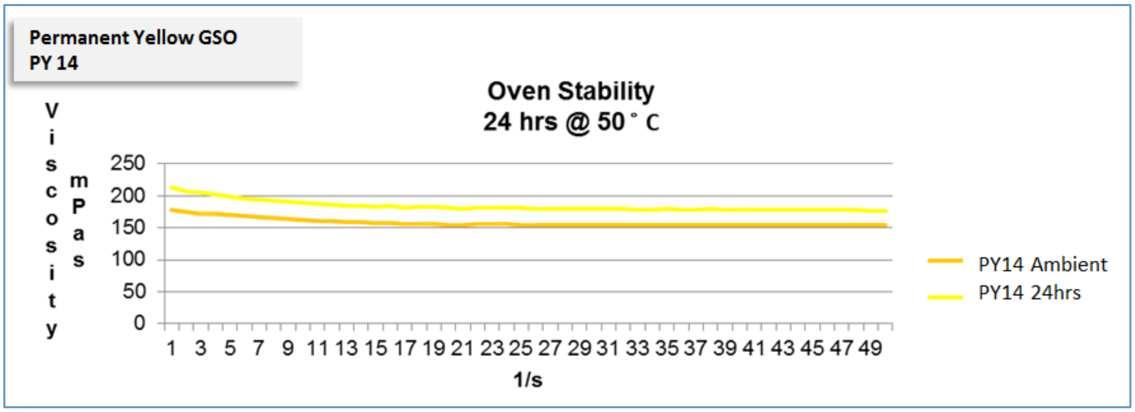
**Table 8 Dispersion and Ink Formulations for UV Flexo Inks** **(prepared at Clariant Corporation)**

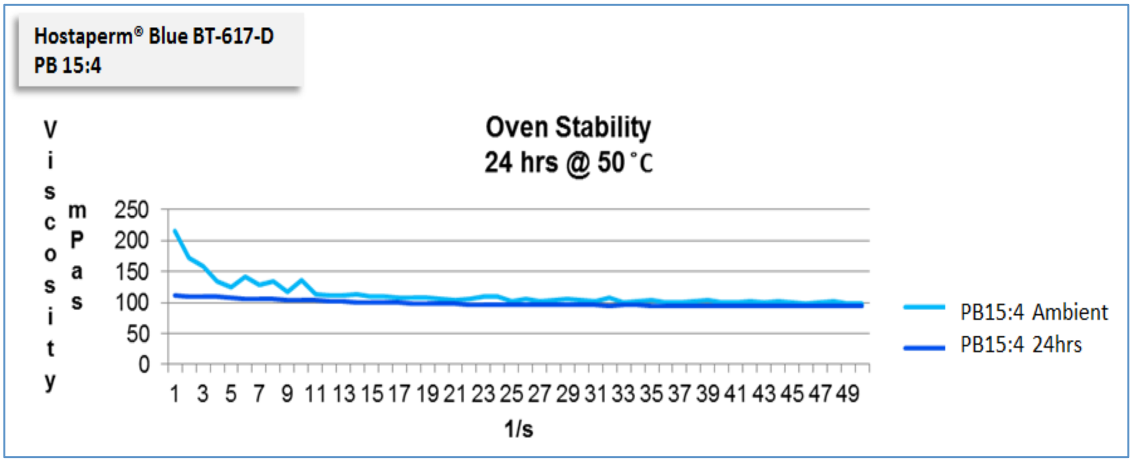
| **Pigment Dispersion** | |
|---|---|
| NPG Monomer | 58% |
| Pigment wetting additive | 10% |
| Pigment wetting additive (for yellow only) | 1.5% |
| Stabilizer | 2.0% |
| Pigment | 30% |

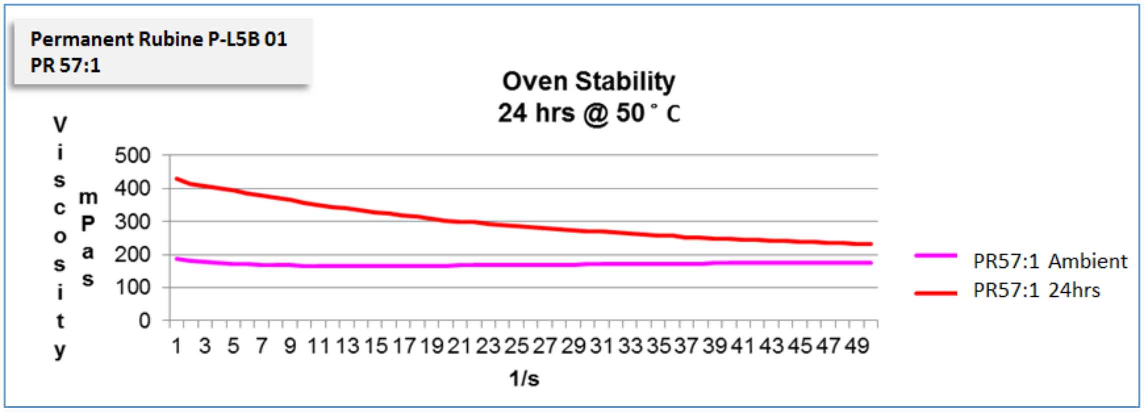
| **Ink** | |
|---|---|
| Dispersion | 50% |
| Hexafunctional Polyester Acrylate **OR** Bio-based aliphatic oligomer | 40% |
| Photoinitiator | 10% |

The bio-based oligomer was found to be fitting as a flexo pigment dispersion letdown oligomer. The dispersions had very stable viscosities (Figure 4) and exhibited minimal shear thinning properties. The experimental ink formulation exhibited an excellent cure response with strong color densities and high glosses observed for all pigments tested. Also observed was a viscosity sensitivity with the bio based oligomer when used with rubine pigments. Additional work is underway to determine the cause of this sensitivity.

**Figure 4. Viscosity stability of Flexo Inks made with Bio Base Aliphatic Acrylate**







## POSITIVE OUTLOOK

Performance results of the bio based aliphatic oligomer in various coatings and flexo inks are very encouraging. Clearly, this type of oligomer has the potential to serve as an important renewable raw material in a variety of energy curable ink, overprint varnish and coating applications. The low viscosity and high reactivity performance characteristics of the bio-based diacrylate suggest that it may not only be an appropriate replacement for BPA epoxy acrylates, but it may also be suitable in a variety of other ink and coating applications.

Further studies are underway to determine the bio based aliphatic oligomer's performance in UV inkjet and UV gravure applications, where its low viscosity, shear stability and high reactivity, coupled with its capacity for building reduced diluent content inks, are of great interest in a variety of consumer product packaging and graphic art applications.

## CONCLUSIONS

The consumer product packaging and graphic arts industries are facing numerous challenges with respect for the need to eliminate possible chemicals of concern. Advances in energy curing technology are helping overcome these key challenges in printing and coating applications. With new BPA-free resin technology based on renewable raw materials, customers in various market segments will also be prepared to replace BPA-containing formulations with high-performing alternatives.

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