UV Ink Jet-Development of Unique Raw Materials

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Abstract

The development of heated piezo print heads for Ink Jet Applications has expanded the range of raw materials that can be utilized in the formulation of UV curable inks. While higher jetting temperatures increases the range of monomers and oligomers that can be successfully formulated, ink instability also increases. With increased viscosity and gel particle formation, head reliability decreases.

A new range of monomers has been developed which demonstrate a remarkable increase in thermal stability. These materials are specifically designed to have low viscosity and fast cure at jetting temperatures up to 100 Deg C.

Sartomer continues to expand their work in developing the line of dendrimers and specialty oligomers previously reported at NIP18 in San Diego. Polyester acrylates, based on dendrimer technology, exhibit low viscosity at room temperature, as well as improved cure speeds, essential elements of a UV ink jet formulation. Improved outdoor weatherability has become important for may ink jet applications. New urethane oligomers, with low viscosity profiles, have been developed which demonstrate excellent gloss retention and low yellowing.

Introduction

UV curable ink jet printing is a rapidly developing area of digital imaging for industrial applications. The advantages of UV curing now recognized in coatings, adhesives and other types of inks are becoming available to the ink jet market. These advantages include no VOC emissions, fast cure, low energy requirements, superior physical properties and the ability to adhere to wide range of substrates.

Ink jet printing presents some unique challenges to the suppliers of radiation curable raw materials in terms of achieving in the same molecule the liquid properties needed for jet-ability and drop formation and the print and film properties required after curing.

Liquid properties:	Cured properties:
Low Viscosity	Scratch/Abrasion Resistance
Low Volatility	Adhesion to Substrates
Friendly EH&S Profile	Hardness
Good Droplet Formation	Flexibility
Formulation Stability	Good Color Density
Fast Cure	Sharpness of Image

UV curable formulations typically consist of mixtures of acrylated monomers and oligomers. The monomer's role is to reduce viscosity, provide cross-linking and contribute some physical properties. The oligomer provides the bulk of the physical properties of the final cured film and in the case of inks, stabilizes the pigment dispersion. The common epoxy acrylate, urethane acrylate, polyester acrylate, acrylated acrylic or other oligomers usually used in UV curable formulations are of too high viscosity to be used at any more than a few percent concentration in an ink jet formulation. In most cases this is not enough to achieve desirable physical properties.

Unique Monomers

The primary components of an UV ink jet ink are reactive diluents or functional monomers. The proper monomer selection is important in order to achieve:

- Newtonian flow characteristics
- Low viscosity
- Cure speed
- Adhesion
- Pigment wetting or grinding characteristics

However, the traditional acrylate monomers used in screen printing or in flexographic applications lacked some key performance properties.

Issue 1: Thermal Stability

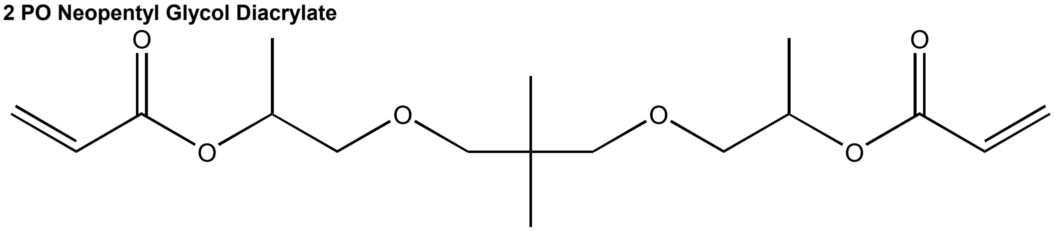
Early UV ink jet formulations utilized low viscosity monofunctional acrylate monomers since the final ink viscosity was targeted at 4-6 cps at room temperature. While the viscosity was achieved, the performance of the ink suffered due to poor cure speeds and adhesion.

The development of heated piezo print heads permitted the use of higher viscosity raw materials. As a result, monomers with higher functionality and film forming properties are now commonly used. In particular, difunctional materials, such as SR 9003 (2M PO NPGDA), are key reactive diluents.

At temperatures above 50°C, UV Inks that are formulated for ink jet experience some stability issues. This is seen by the formation of microgels in the in the ink. While filtration can remove these particles, Sartomer has sought to address the issue thru the development of functional monomers that exhibit higher temperature stability. The new materials, designated as IJ grade, exhibit temperature stability up to 100°C.

SR 9003IJ and SR 508IJ (DPGDA) were the first two materials developed exclusively for UV Inkjet formulations.

SR9003IJ
2 PO Neopentyl Glycol Diacrylate



SR508IJ
Dipropylene Glycol Diacrylate

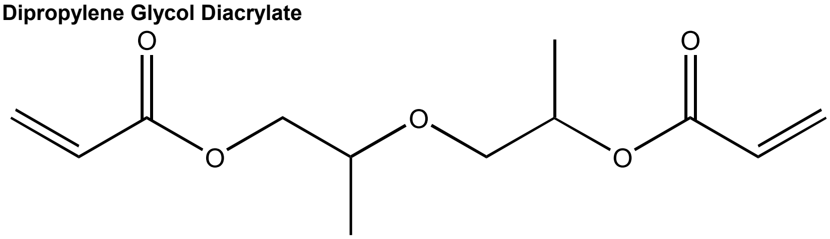


Figure 1. Ink Jet Grade Monomers

Table 1: Physical Properties of Ink Jet Grade Materials

	SR508IJ	SR9003IJ
Viscosity (cps, 25°C)	10	15
Specific Gravity (g/cm3)	1.052	1.005
Static Surface Tension (D/cm, 25°C)	32.8	32.0
Refractive Index (25°C)	1.4502	1.4464
Color (APHA)	40	35
Tg of Homopolymer (°C, by DSC)	104	32

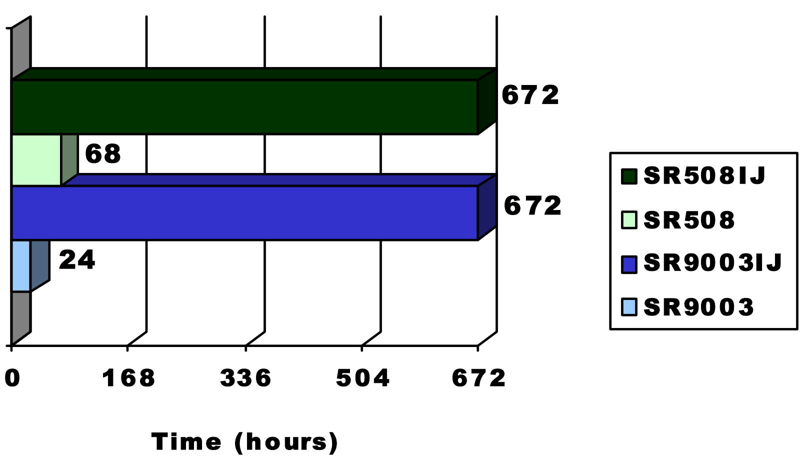


Figure 2. Time Before Gellation at 100°C- 100% Monomer Formulation

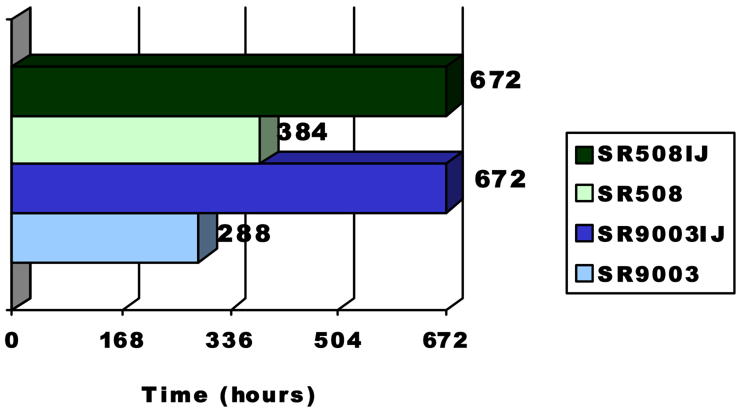


Figure 3. Time Before Gellation at 100°C- Ink Formulation

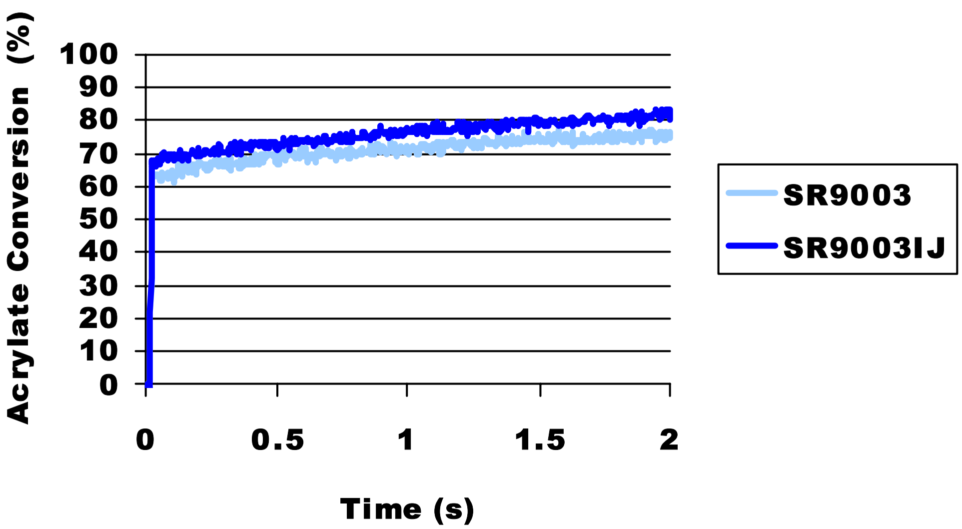


Figure 4. Reactivity by Real Time FTIR

At room temperature, these difunctional monomers exhibit the desired properties for inkjet formulations: low viscosity, good cure speeds and pigment compatibility. However, standard grades of these materials displayed poor thermal stability. Even when formulated into an ink, the instability of the traditional monomers was evident.

By modifying the processing conditions, Sartomer has been able to improve significantly the thermal stability of these two materials. As shown in Figure 3, the Inkjet Grade materials did not develop gel particles even after 600 hrs at 100°C. Additionally, the improved stability was achieved without impacting the cure rates of the materials (Figure 4).

Table 2: New Monomers for UV Ink Jet

	SR531	PRO6622	PRO7149
Acronym	CTFA	TMCHA	DOGDA
Functionality	1	1	2
Viscosity (cps, 25° C)	15	4	370
Specific Gravity (g/cm3)	1.091	0.928	1.159
Static Surface Tension (D/cm, 25° C)	33.1	23.7	28.4
Refractive Index (25° C)	1.4634	1.4517	1.4677
Color (APHA)	100	40	30
Tg (˚C, by DSC)	10	67	87
Elongation (%, by Instron)	98	2	2
Weight Loss (%, 4hrs, 80° C, by TGA)	47.0	100.0	1.7

Issue 2: Adhesion to Plastic

Since UV Ink Jet ink formulations must be in the 20 cps range at jetting temperature, standard film forming monomers and oligomers cannot be utilized. As a result, adhesion t o plastic can be an issue. Traditional formulations have utilized monofunctional acrylates, such as SR 506 (IBOA) and SR 531 (CTFA), to improve the adhesion of the inks. However, the use of monofunctional materials can reduce the rate of cure.

A wider range of monomers have been developed by Sartomer that exhibit improved cure speeds and adhesion to plastic substrates. These physical properties of these materials are summarized in Table 2.

PRO 7149 (DOGDA) is the newest monomer designed for UV ink jet applications. This material is a difunctional version of SR 531 (CTFA). While the viscosity of the material is relatively high, PRO 7149 has a surface tension of 28.5 D/cm. This property allows the monomer to be an effective film former on low energy plastics, such as HDPE. In addition, it’s cure rates are comparable to higher functional materials. PRO 6622 (3,3,5 TMCHA) is a new monofunctional monomer that has the lowest viscosity profile (4 cps) of any commercial materials available. In addition to the low viscosity, PRO 6622 has improved surface cure compared to SR 506 (IBOA) with a slightly lower Tg.

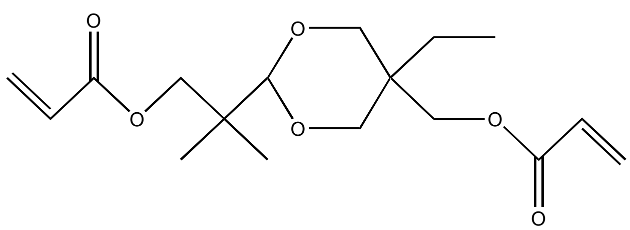


Figure 5. Sartomer PRO 7149 DOGDA- Dioxaneglycol Diacrylate

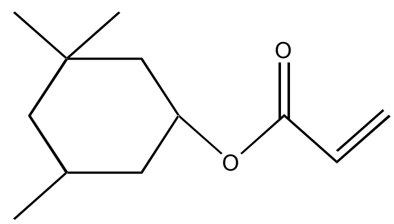


Figure 6. Sartomer PRO 6622 3,3,5 TMCHA- 3,3,5 Trimethylcyclohexyl Acrylate

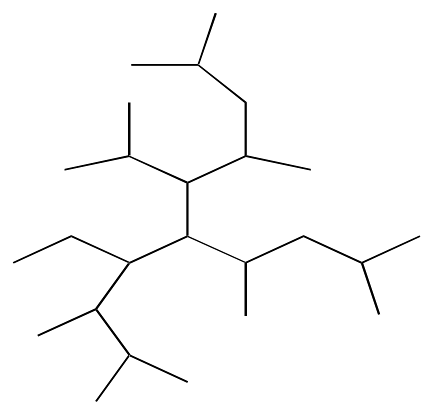


Figure 7. Dendrimer Structure

Unique Oligomers

Hyperbranched Materials

Acrylates based on dendritic or hyperranched molecules offer the potential to meet the conflicting demands of UV curable ink jet printing. In particular the compact more-or-less spherical shape results in a lack of chain entanglements and low hydrodynamic volume leading to low viscosity while the high concentration of acrylate groups provides attractive physical properties.

Hyperbranched Acrylate Feature	Resulting Final Property
Spherical Shape	Low Viscosity Low Shrinkage Jetability
High Functionality	High Reactivity Fast Cure Hardness Scratch Resistance Chemical Resistance
High Molecular Weight	Water Resistance Pigment Dispersion

Sartomer Company has prepared acrylates of commercially available hyperbranched polyester polyols containing sixteen hydroxy end groups using standard acrylation methods. The extent of end group conversion to acrylates can be easily varied over a wide range, but to get the maximum advantage of the hyperbranched structure the conversion should be as high as possible.

For ease of handling the hyperbranched acrylates are blended with multifunctional acrylate monomers. Table 4 shows how the viscosity of the hyperbranched polyester acrylate blended with an acrylate monomer – propoxylated neopentyl glycol diacrylate (2PONPGDA) - compared to viscosities of conventional radiation curable oligomers blended with the same monomer. The effect of the compact structure of the hyperbranched acrylate on blend viscosity is clear.

Table 3: Commercial Dendrimers for Ink Jet

	CN2300	CN2301	CN2302
Viscosity (cps, 25° C)	600	3500	350
Specific Gravity (g/cm3)	1.10	1.16	1.13
Static Surface Tension (D/cm, 25° C)	32.6	38.4	37.8
Refractive Index (25° C)	1.463	1.476	1.474
Color (APHA)	200	200	100
Average Functionality	7	8	15
Shrinkage (%)	9.0 ± 0.3	8.1 ± 0.4	9.0 ± 0.5

Table 4: Viscosity of Hyperbranched Polyester Acrylate vs. Conventional Acrylate Oligomers in Monomer Blends.

	# of Acrylate Groups	Functional Group Equivalent Weight	Viscosity in 50% 2PONPGDA @ Temp.
Hyperbranched Polyester Acrylate	14	157	200 @ 25°C
Conventional Polyester Acrylate	2	1300	1500 @ 75°C
Urethane Acrylate	3	375	10,000 @ 25°C
Epoxy Acrylate	2	250	1500 @ 25°C

Viscosity of Hyperbranched

The speed at which UV cured ink jet printing can currently be done is limited by the cure speed of the inks being used. There is a need for raw materials that can boost the maximum cure speed of ink formulations to the limit attainable by current equipment designs. The rate at which acrylate monomers and oligomers cure depends mainly on functionality. The high concentration of reactive end groups in hyperbranched acrylate oligomers makes them effective cure-speed enhancers. The effect is especially evident in formulations containing low viscosity, relatively slow curing mono- and di-functional monomers.

As expected cured films prepared from hyperbranched polyester acrylate/monomer blends show excellent physical properties including hardness, strength, flexibility, abrasion resistance and chemical resistance. More surprisingly the films show relatively low shrinkage upon cure. Low shrinkage upon cure is usually associated with low functionality/high molecular weight materials. Higher functionality typically results in higher shrinkage. Low shrinkage upon cure is a desirable property as it often can be correlated with good adhesion to substrates. As shown in Table 5 the shrinkage of hyperbranched polyester acrylate/monomer blends is actually lower than that of the low functionality monomers used in the blends.

Table 5: Shrinkage Upon Cure of Hyperbranched Polyester Acrylates vs. Lower Functionality Monomers

	% Shrinkage
Hyperbranched Polyester Acrylate Blended 50% in 2PONPGDA	9
100% 2PONPGDA	11
Hyperbranched Polyester Acrylate Blended 50% in 3EOTMPTA[7]	8
100% 3EOTMPTA	11.5

Weatherable Oligomers

One of the applications of UV Curable Ink Jet is in outdoor advertising, such as billboards and vehicle wraps. Aliphatic urethane acrylates have traditionally demonstrated good weathering resistance (ref). However, the high viscosity of these materials make it difficult to successfully formulate a jettable ink. As indicated in Table 6, there is a wide range of specialty urethane acrylates that could be utilized in UV ink jet. These materials have viscosities ranging from 350-1600 cps at 60°C.

Of particular interest is a new product, CN 991, difunctional urethane acrylates. CN 991 shows moderate flexibility.but is highly resilient. Films made with this oligomer demonstrate high strength. CN 9001, a material that is thermoformable, shows excellent flexibility and adhesion to many plastics. While the viscosity of CN 9001 is very high, it is jet-able at elevated temperatures when formulated with low viscosity monomers. CN 2920 is a 20% cut of the CN 9001 in difunctional monomer. The viscosity of this oligomer blend is 3000 cps at 60°C.

In order to demonstrate the weatherability of these oligomers, cold roll steel panels with e-coat primer and white basecoat were coated with the neat oligomer with 3% type I photoinitiator (Luciirin TPO from BASF) Each blend was used as a clearcoat and was then applied to the panels. The coating thickness was between 35 and 45 microns. Two 600 W/inch lamps (an H bulb and V bulb from Fusion) were used to cure the formulations. A minimium of three replicates for each tested oligomer have been cured and put in the accelerated weathering tester and a minimum of three other replicates were tested outdoors.

The QSUN 3100 with Xenon lamps was used with a daylight filter. The standard ASTM D6695-01 or SAE J1960 procedures were utilized. In addition, the panels were evaluated in QTRAC in Arizona using SAE J 1961-02 procedures. Gloss retention and Yellowness Index were measured.

According to Q-Lab, the total UV (or TUV) is the radian dosage of light with a wavelength shorter than 385 nm, expressed in J/m2. 970 MJ/m2 of TUV correspond approximately to 75% of the TUV obtainable after a year exposure on QTRAC racks in Arizona. Figures 5-6 relate the YI of these new oligomers. The initial photoyellowing and the YI decrease are mainly due to the PI residues and photoproducts formed during the curing process (ref). This initial photoyellowing and bleaching can be reduced by using a PI, like Sarcure SR 1130 (Sartomer) with better yellowing characteristics. This has been previously reported on by Schaeffer, et.al. (reference). After the initial bleaching, a YI change of less than 0.5 units for the tested oligomers is considered a very good result.

Figure 8 shows the 20 degree gloss retention of panels exposed in the outdoor accelerated testers. Clearly, the addition of monomer to the CN 9001 improves the gloss retention. However, the CN 991 exhibits the best retention over time.

Table 6: Weatherable Oligomers Suitable for Ink Jet

	CN929	CN968	CN991	CN 9001	CN9006
Functionality	3	6	2	2	6
Viscosity (cps, 60° C)	400	350	660	46500	1600
Specific Gravity (g/cm3)	1.114	1.200	1.132	1.007	1.174
Refractive Index (25° C)	1.5010	1.4933	1.4882	1.4971	1.4895
Elongation (%)	62	1	79	143	1
1% Modulus (psi)	7100	485000	19400	11240	350000
Tensile Strength (psi)	1970	11000	5380	3300	8520
Tg (° C, by DSC)	43	145	27	24	132

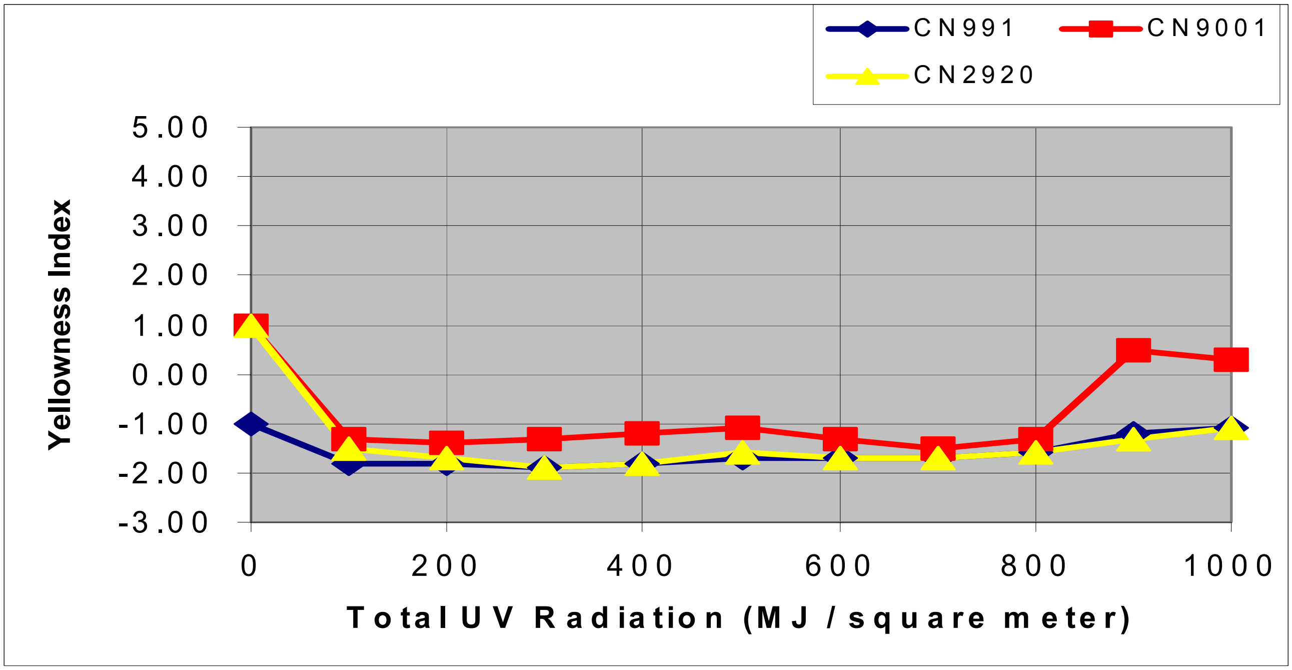


Figure 8. Yellowing Index- QTRAC

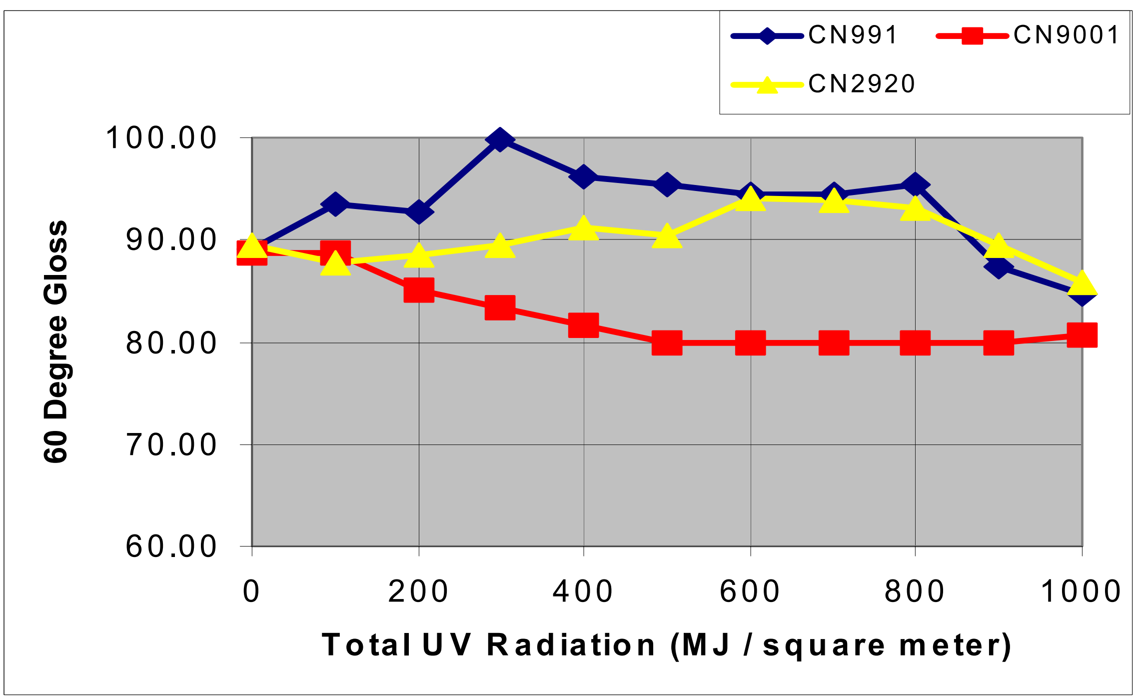


Figure 9. Gloss Retention QTRAC

Conclusions

Sartomer Company has introduced a wide range of monomers and oligomers designed for UV Curable ink jet applications. The new monomers show improved thermal stability, an important property in applications where a heated piezo head is being utilized. In addition, new mono and difunctional acrylates have been designed to provide improved adhesion to plastic with increased cure speeds.

Dendritic or hyperbranched acrylates offer many attractive attributes as raw materials for UV cured ink jet printing. Among these are low viscosity, fast cure speed, low shrinkage and good cured physical properties. There are now a range of hyperbranched materials with functionality up to 15.

New weatherable oligomers have been developed for outdoor applications. CN 991 and CN 2520 show the best gloss retention and yellowing index in QTRAC tests. When formulated, these materials have viscosity profiles that permit them to be jetted thru a heated head.

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Author Biography

James Goodrich earned his B.S. in Chemistry and a minor in Polymer Science from the Pennsylvania State University in 2000. Currently he is a Senior Applications Chemist for Sartomer Company, Inc. located in Exton, PA. James' work is concentrated on the UV/EB ink market with a focus on design and application of new energy-curable raw materials for the paste, liquid, and digital markets.