Low VOC, Low Viscosity UV Cationic Radiation-Cured Ink-Jet Ink System

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Ink-jet inks need to be very low in viscosity to transport the ink through the jet nozzle as well as for drop formation and integrity. The objective of this project was to demonstrate UV-cured systems for ink-jet inks and coatings with zero volatile organic compounds and very low viscosity. Cycloaliphatic epoxy systems were selected as binders of choice for this project due to their low viscosity and ability to be cured using UV-cationic photoinitiators. UV-curable coatings and inks with zero VOC and less than 10 cPs viscosities were formulated using exempt solvent acetone and vinyl cyclohexene diepoxide. UV-curable inks with up to 10% black dye were formulated. Rapid cure was achieved through the use of aryl sulfonium salts of hexafluorophosphoric acid. The presence of dye inhibited the reaction, but adequate cure of dyed formulations was achieved by increasing the concentration of the photoinitiator.

INTRODUCTION

The use of zero VOC coatings is growing as more finishers see them as the solution to their VOC compliance challenges. The purpose of this work was to demonstrate zero VOC ink-jet inks with less than 10 cPs viscosities. This low viscosity is important not only to transport the ink through the jet nozzle, but also for drop formation and integrity. Ink-jet inks need to dry quickly to prevent smearing and allow high speed production of labels and other printed materials.

Energy cure (UV/EB cure) is essentially an instantaneous conversion of a usually liquid, low viscosity material combined with other reactive ingredients into a crosslinked, polymerized mass by exposure to a radiation energy source. Crosslinking is necessary to obtain the desired properties, such as chemical resistance, solvent resistance, flexibility, and adhesion. The radiation source is typically an ultraviolet light or an electron beam.[1] Radiation-cured systems have wide and growing acceptance in the coating, ink, adhesive, and sealant areas because of high performance characteristics, desirable environmental considerations, low energy requirements, and small space requirements.[2-4]

Energy cure of coatings is usually concerned with two basic types of chemistry. The dominant technology uses free radical polymerization of ethylenic unsaturation, such as acrylates, unsaturated polyesters, and polyenes/thiol.[5] The other type involves a cationic mechanism and deals with onium salts and polymerization of epoxy resins and co-curable compounds, such as vinyl ethers, polyols, glycols, and alcohols.[6]

Epoxides are one of the more important and widely used classes of binders in the field of surface coatings. Their remarkable applications can be attributed to the fact that epoxides can react with a variety of functionalized compounds that contain hydroxyl, carboxyl, amino, and thiol groups. This versatility has led to a wide range of coating properties with excellent adhesion, good strength, toughness, and chemical resistance.[7] Two major classes of epoxides, glycidyl ethers and aliphatic oxiranes are used for coatings. Cycloaliphatic epoxides are more reactive in cationic UV-cured systems than the aromatic glycidyl ethers, and they are used commercially.[8,19] The high reactivity of cycloaliphatic epoxies (*Figure* 1) is not only attributed to the high ring strain present in these monomers, but also to the lack of UV aromatic chromophors.[9]

Acrylate esters are widely used in UV-curable coatings. They cure through the free radical polymerization

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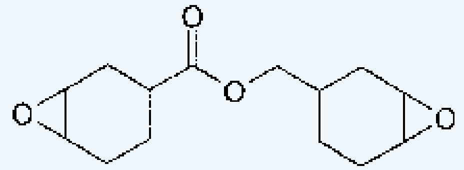


Figure 1—Structure of 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate.

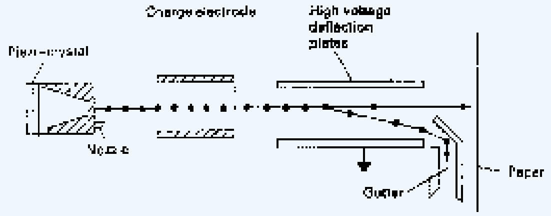
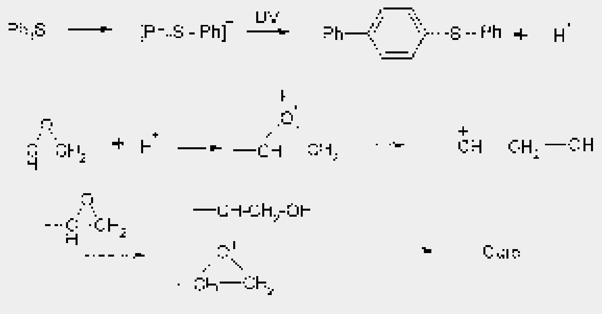


Figure 2—Continuous ink jet print system.

of double bonds. In general, the vehicle consists of acrylate terminated oligomers and acrylate monomers. The monomers range from mono- to multi-functional. Most common commercial systems are mixtures of mono-, di-, and tri-functional acrylates. The monomers are also called reactive diluents. The multifunctional oligomers contribute to a high rate of crosslinking and, in large measure, control the properties of the final coating properties such as abrasion resistance, flexibility, and adhesion. Their viscosity is too high alone and low molecular weight acrylate, solvents, heat, etc., are required to reduce viscosity for application. These formulations with the presence of photointiators can cure very fast, but essentially stop when the light source no longer generates new radicals. It is difficult to do this in a pigmented system since many pigments absorb and/or scatter UV radiation. They generally inhibit UV curing to some degree.[10] Other investigators have shown that free radical formulations that are white pigmented and color pigmented can be cured by selecting the proper photoinitiator and/or photoinitiator combinations.[11-13]

On the other hand, cycloaliphatic epoxies are generally low in viscosity. They cure through the epoxide functionality with the use of cationic photoinitiators, such as onium salts of very strong acids. The initiator continues to be active after the light source is off. This phenomenon is typically referred to as “dark” cure.[14] The acid initiator generated from the photoinitiator continues to be active after UV curing and so conversion of reactants and crosslinking continues in the absence of UV light.

Ultraviolet light initiated cationic curing of epoxides, and particularly cycloaliphatic epoxides and related compounds, is a relatively new technology introduced about a decade ago.[15] It involves onium salt photoinitiators prepared by relatively old chemistry but applied in a unique manner. Cationic curing technology involves the photolysis of onium salts and certain other light activated compounds. When these materials are irradiated with ultraviolet light of the proper wavelength, either Brønsted or Lewis acids are formed.[16] These strong acids cause rapid polymerization of cycloaliphatic epoxides and copolymerization with other epoxides and hydroxyl compounds such as glycols, polyols, other active alcohol hydrogen-containing compounds,[20] and vinyl ethers[17] (*Scheme* 1).



Scheme 1

A typical cationic epoxy starting point formulation consists of a cycloaliphatic epoxide and a cationic photoinitiator. Other ingredients such as polyols and other epoxides[18] can be added to modify properties. Upon exposure to UV light, the cationic photoinitiator generates a superacid. This superacid is an initiator for rapid cationic polymerization of epoxides and for reaction of epoxides with hydroxyls. Rapid cure is one of the advantages of cycloaliphatic epoxides over aromatic epoxy sytems.[8,19] Polyols co-react with epoxides by acting as chain transfer agents, generally improving cure speed.[20]

Ink-Jet Ink

Ink-jet printing is based on the generation of very small droplets and directing them very rapidly to paper and other surfaces. There are many different types of ink-jet devices. Jaffe and Mills reviewed printing technologies for computer systems and categorized ink-jet printers on the basis of their drop formation mechanisms and system components.[21,22] Generally, ink-jet technology is classified into two main groups: (1) continuous-stream (CS) and (2) drop-on-demand (DOD).

Continuous ink-jet technology can be divided into three different mechanisms, all of which are driven by piezo technology. The three main technologies are: (1) hertz, (2) binary deflection, and (3) multiple deflection.[23]

In the continuous jet process, a high frequency voltage is applied to an electrically responsive crystal that is

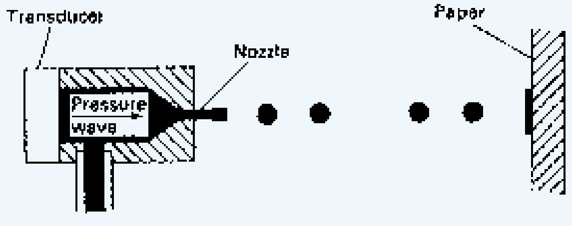


Figure 3—Drop-on-demand system.

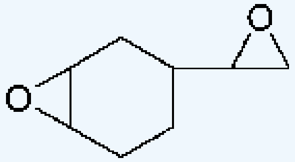


Figure 4—Structure of vinyl cyclohexane dioxide.

in contact with the ink. By applying pressure pulses at a suitable frequency, a stream of uniformly sized and spaced droplets is generated. If these droplets are directed to a surface that is moving, a line of dots is created (*Figure* 2).[24]

Drop-on-demand ink-jet technology essentially can be divided into two major types of systems: (1) thermal ink-jet and (2) piezo DOD. Examples of thermal ink-jet technology is the Hewlett–Packard printing technology used in both home and office, as well as in the wide format and industrial addressing markets. Thermal ink-jet inks typically have a viscosity of less than 5 cPs. Piezo DOD technology is widely used in the ink-jet, or digital, printing industry. The only piezo DOD technology well known to everyone can be found in the Epson printers. The other piezo DOD technologies have been developed by industry.[23] The piezo DOD technology can use water, solvent, hot melt, and UV-curable inks with viscosity ranges from 10–25 cPs, making this technology very versatile.

In the DOD system, pressure is applied to ink to generate droplets when needed. There is usually an array of nozzles, each controlled to generate a droplet as required. This system is simpler since no electrostatic charge is generated in the droplet and no deflection and recovery is necessary (*Figure* 3).[24]

Generally, ink-jet inks can be described by their intrinsic properties, their performance in printers, and the ink-substrate interactions. A suitable ink must meet rigid requirements in physical properties, such as viscosity and surface tension, to be operable in ink-jet devices. The ink must be compatible with printer materials, with no corrosion of metal parts and no interaction with organic components; it must not clog the orifice, but must be fast drying on paper; and it must be stable under various environmental conditions. In addition, no chemical reactions or biological growth should occur during storage. When applied to the substrate, such as paper, plastic, or metal, the ink must have good wettability and be fast drying. It is also desirable to have a permanent and sharp image on substrates. Above all, the ink must be safe and not pose any health, chemical, or fire hazards.

From the chemical standpoint, there are water-based dye inks, pigment dispersion inks, solvent-based inks, heterogeneous inks,[25,26] and many state-of-the-art inks.[27-31] Pigment inks are not very popular in ink-jet practice, because nozzle clogging can result from the particles. Solvent-based inks have to face the problems of solvent recovery, VOC, solvent odor, fire hazard, and/or toxicity.[23]

Ink-jet inks are very low in viscosity—1-10 centipoise, but preferably 1-5 centipoise.[24] The low viscosity is important not only for transport of the ink through the nozzle but also for drop formation and integrity. Zero VOC, low viscosity systems for ink-jet inks are described that can be used with UV-cured ink-jet ink technology.

EXPERIMENTAL

Materials

Epoxy Resins: Cyracure™ cycloaliphatic epoxides ERL-4221, UVR-6105, UVR-6110 (different viscosity versions of 3,4-epoxycychohexylmethyl-3,4-epoxycyclohexane carboxylate (*Figure* 1)), ERL-4206 (vinyl cyclohexene dioxide (*Figure* 4)), UVR-6128 (bis-(3,4-epoxycyclohexyl) adipate (*Figure* 5), UVR-6216 (1,2-epoxyhexadecane), and UVR-6100 (mixed cycloaliphatic epoxides) were sup-

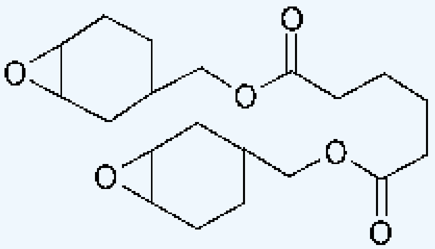


Figure 5—Structure of UVR-6128.

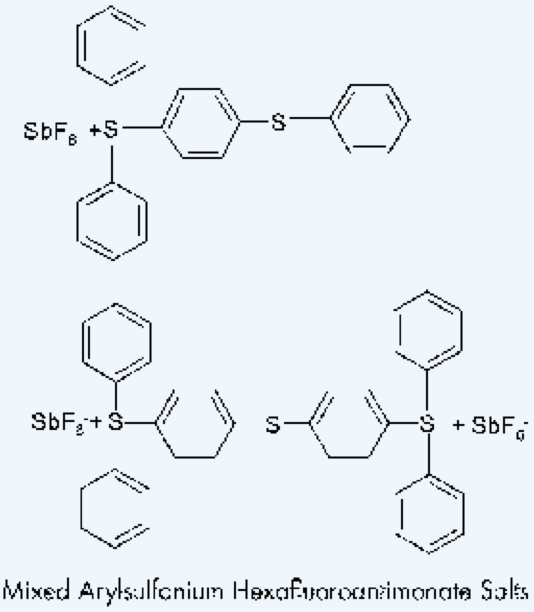


Figure 6—Structure of UVI-6974 and UVI-6976.

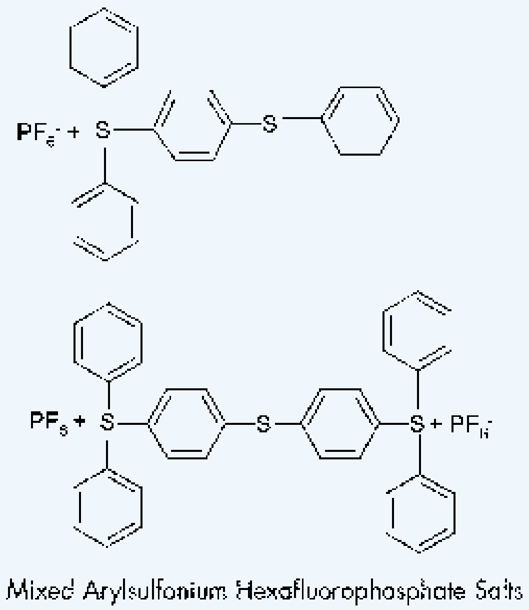


Figure 7—Structure of UVI-6990 and UVI-6992.

plied by Union Carbide Corp. Epoxy resin Epon® 828, a diglycidyl ether of bisphenol A (DGEBA), was supplied by Shell Chemical Co.

Polyols: Tone® polyol 0301 (a caprolactone triol, hydroxyl equivalent weight (HEW 98 ~ 103)), and Tone® polyol 0201 (di-functional polyol) were supplied by Union Carbide Corp.

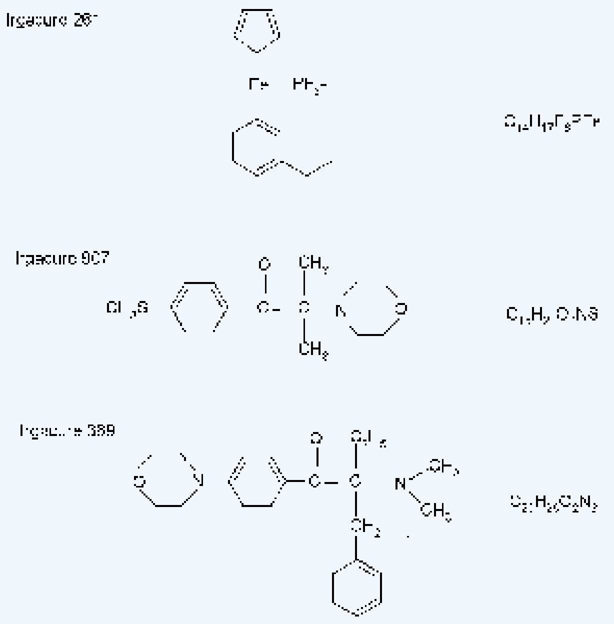


Figure 8—Structure of Irgacure 261, 907, and 369.

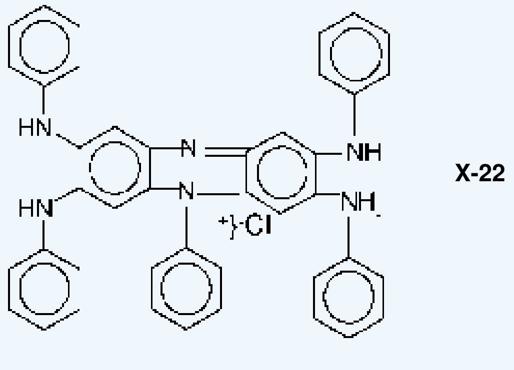


Figure 9—Structure of X-22.

Cationic Photoinitiators: Cyracure photoinitiators UVI-6974 (mixed triarylsulfonium hexafluoroantimonate salts), UVI-6990 (mixed triarylsulfonium hexafluoroantimonate salts), UVI-6992 (aryl sulfonium salt), and UVI-6976 (aryl sulfonium salt) were supplied by Union Carbide Corp. The structures of these photoinitiators are shown in *Figures* 6 and 7.[32,34] Photoinitiators Irgacure® 261, 907, and 369 (*Figure* 8) were obtained from Ciba Specialty Chemicals, Inc.

Pigments: Basonyl® black X-22 liquid (phenazine, C. I. Solet black) and Dye Neopen® black X-55 (Colour Index solvent black 29) were supplied from BASF. The structures are shown in *Figures* 9 and 10.

Substrate: Curing on coated paper #60 and metal panels appeared to be identical. For convenience, iron phosphated steel panels of type R-36 I with dull matte finish, obtained from Q-Panel Co., were used in this study.

Additives: Silicone surfactant Silwet® L-7604 from Witco Corp. was used in all of the evaluations.

Testing Methods

Viscosity Measurement: The viscosity was measured with a Brookfield viscometer (Model DVII) at room temperature (25°C). For most material, we used spindle #31 at 3.0, 6.0, and 12.0 rpm. The units are centipoise (cPs). Because the viscosities of ink-jet inks are relatively low, usually less than 10 cPs, an ultra-low adaptor was used to provide better measurement accuracy in this range. The adapter consists of a large cylindrical spindle that is

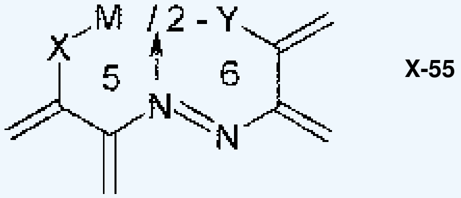


Figure 10—Structure of X-55.

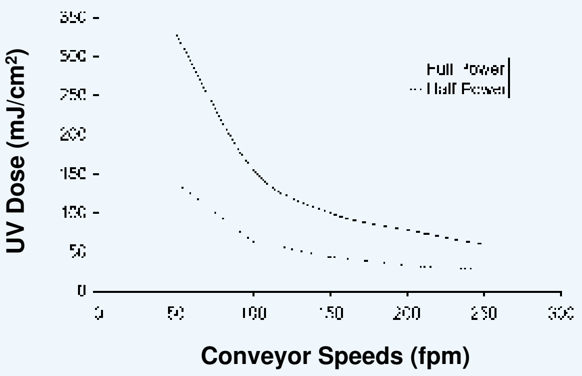


Figure 11—UV dose vs. belt speed.

rotated within the walls of a tube containing an ink sample. It has four rotational speeds—60, 30, 12, and 6 rpm (spindle # 00). At least three measurements are taken for each ink, and the average value is reported. The standard deviation of the measurement is about 0.04 cPs.

Film Properties Measurement: Films were applied on the substrate with a No. 3 wire-wound applicator rod. For thick films, a square-blade drawdown applicator was used. Cured film properties were determined at least 24 hr after curing. Dry film thickness was determined with a Deltascope® MP (Helmut Fischer GmbH + Co.) from Fisher. Pencil hardness was determined according to ASTM D 3363. Adhesion was determined according to ASTM D 3359. Solvent resistance was determined according to ASTM D 5402.

Photocure: Films were cured using a UV-curing conveyor from the Radiant Products Co. The conveyor speed was adjusted from 50 to 250 fpm. The reported UV dose was determined with a compact radiometer from UV Process Supply Inc. The radiometer was placed on the conveyor with the "expose" side up and conveyed through the UV-light box. Radiation dosage was measured in joules/sq. cm. The relationship between UV-light dose and conveyor belt speed is shown in *Figure* 11. Curing is slower at high speeds because the ink receives smaller doses of energy. For full and half UV light, the energy received by the coating goes down proportionately as the conveyor speed goes up.

Table 1—Viscosity of a Series of Cycloaliphatic Epoxies and Polyols (25°C)

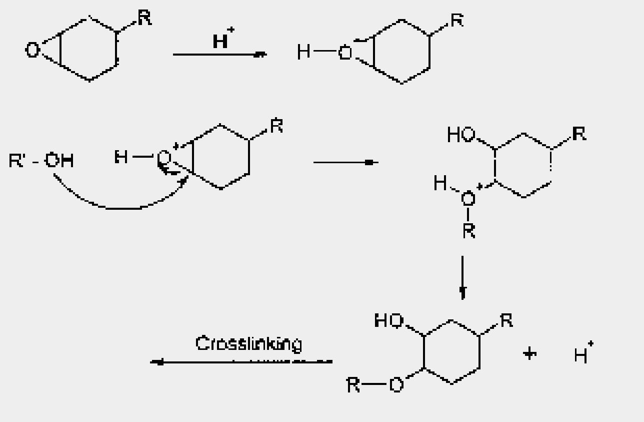
Name	3.0 rpm	6.0 rpm	12.0 rpm
UVR 6105	439.9	359.9	339.9
UVR 6100	230.0	150.0	115.0
UVR 6110	629.9	589.9	549.9
UVR 6216	170.0	85.0	22.5
UVR 6128	1180	1030	969.8
ERL 4221	559.9	519.9	484.9
ERL 4206	30.0	10.0	2.5
Tone® Polyol 0201	729.8	514.9	467.4
Tone® Polyol 0301	2400	2230	2072
Glycerol	874.8	918.6	906.7

Table 2—General Purpose Starting Formulation

Ingredient	Weight	Description
Cyracure®UVR-6110	70.4 g	Epoxide
Tone® Polyol 0301	25.1 g	Polyol
Cyracure®UVI-6974	4.0 g	Photoinitiator
Silwet® L-7604	0.5 g	Silicone surfactant

RESULTS AND DISCUSSION

The viscosity of a series of cycloaliphatic epoxy resins and polyols selected for this study are shown in *Table* 1. All of the resins have a viscosity greater than 25 cPs at the highest shear rate except vinyl cyclohexene dioxide (VCD) and 1,2-epoxyhexadecane. Addition of polyol to a cycloaliphatic epoxy formula increases flexibility and



Scheme 2

Table 3—Cycloaliphatic Epoxide Based UV-Curable Formulations with Viscosity and Dry Times

	A	B	C	D	E	F
Epoxide used	UVR-6110	UVR-6105	UVR-6100	UVR-6216	ERL-4221	ERL-4206
EEW	131 ~ 143	130 ~ 135	130 ~ 140	240 ~ 280	131 ~ 143	70 ~ 74
Weight of epoxy, g	35.2	35.2	35.2	35.2	35.2	35.2
Polyol 0301, g	12.6	12.6	12.6	7.2	12.6	24.7
UVI 6974, g	2	2	2	2	2	2
L-7604 , g	0.3	0.3	0.3	0.3	0.3	0.3
Viscosity, 12 rpm	502	385	225	23	535	58
Dry time, sec						
4 mil	20	10	10	n/c[a]	20	30
2 mil	10	10	10	n/c[a]	10	20

R value = 2
(a) n/c= no cure, a mono-functional epoxy

Table 4—Dry Times and Film Properties of UV-Curable Formulations (50 fpm conveyor speed)

Dry Times and Film Properties	A	B	C	E	F
Dry time (sec)	20	10	10	20	30
Measured film thickness (mil)	1.5	1.9	1.42	1.9	2.1
Pencil hardness	F	F	2H	F	2H
Adhesion	B	0	B	0	2B
MEK rub	190	> 200	90	> 200	> 200
Dry time (sec)	10	10	10	10	20
Measured film thickness (mil)	0.53	0.7	0.59	0.68	0.81
Pencil hardness	H	H	2H	2H	2H
Adhesion	0	2B	4B	4B	B
MEK rub	60	190	40	150	> 200

Table 5—UV-Curable Low Viscosity Formulation

Ingredients	Weight
ERL-4206	35.2 g
Polyol-0301	24.7 g
UVI-6974	2 g
L-7604	0.3 g
Viscosity, 25°C, 12 rpm, cPs	58

Table 6—Dry Times and Dry Film Properties of UV-Curable Formulations with ERL-4206

Conveyor Speed	50 fpm	100 fpm	150 fpm	200 fpm
Dry time	30 sec.	40 sec.	No cure	No cure
Film thickness (measured)	2.1	1.8	—	—
Pencil hardness	2H	2H	—	—
Adhesion	B	0	—	—
MEK rub	> 200	> 200	—	—
Dry time	20 sec.	25 sec.	45 sec.	60 sec.
Film thickness (measured)	0.81	0.72	0.57	0.63
Pencil hardness	2H	2H	2H	2H
Adhesion	B	B	0	0
MEK rub	> 200	> 200	> 200	> 200

Table 7—Viscosity of "General Formulation with Vinyl Cyclohexene Dioxide" with Different Acetone % (25°C)

Acetone %	0%	10%	20%	30%	40%
60.0 rpm	EEEE	EEEE	6.1	3.5	2.2
30.0 rpm	EEEE	13.8	6.7	3.8	2.5
12.0 rpm	37.3	15.5	6.8	2.8	1.4
6.0 rpm	37.8	14.4	7.7	5.6	3.2
3.0 rpm	43.6	8.4	9.8	5.4	7.2

Note: EEEE – Data was unreadable

Table 8—Effect of Acetone on Dry Time and Film Properties

Acetone %	0%	10%	20%	30%	40%
Dry time (sec)	30	33	35	40	55
Film thickness	0.76	0.69	0.64	0.58	0.3
Pencil hardness	2H	2H	2H	2H	2H
Adhesion	B	B	2B	3B	4B
MEK rub	> 200	> 200	> 200	> 200	> 200

Table 9—Formulation with Black Dye

Ingredients	Weight
ERL-4206	100 g
UVI-6992	4 g
L-7604	0.5 g
Dye X 22 or X 55	4 g

Table 10—Dry Time Test

Sample	Dry Time
ES – 6992 (no dye)	1 sec
ES – 6992 – X 22	No cure immediately, but cured next day
ES – 6992 – X 55	No cure immediately, but cured next day

Note: ES – mixture of epoxy resin (ERL-4206) and surfactant (L-7604)

Table 11—Black Formulation with Different Photoinitiators

Ingredients	Weight
ERL 4206	100 g
OSI 7604	0.5 g
Dye X 22	4g
Photoinitiator	4g

Table 12—Dry Times of Black Formulation with Different Photoinitiators

Sample	Pass Number	UV Dose	Dry Time
ES 6992 (no dye)	1	184.1	1 sec
ESD-6992	1	184.1	4 sec
ESD- 6992	2	368.2	3 sec
ESD-6992	3	552.3	1 sec
ESD-6990	1	184.1	2′30′′
ESD-6990	2	368.2	10 sec
ESD-6990	3	552.3	1 sec
ESD-6974	1	184.1	> 5 min
ESD-6974	2	368.2	40 sec
ESD-6974	3	552.3	10 sec
ESD-261	3	552.3	Cured next day
ESD-907	3	552.3	Not tack free after 24 hr
ESD-369	3	552.3	Not tackier after 24 hr

Table 13—Film Properties of Black Formulations

Sample	Conveyor Speed × Pass Number	Film thickness	Adhesion	Pencil Hardness	Sward Hardness	MEK Rub
ES-6992	80 × 1	0.38	5B	6H	84	> 200
ESD-6992	80 × 1	0.19	5B	6H	78	> 200
ESD-6992	80 × 2	0.17	5B	6H	73	> 200
ESD-6992	80 × 3	0.13	5B	6H	86	> 200
ESD-6990	80 × 1	0.16	5B	6H	93	> 200
ESD-6990	80 × 2	0.17	5B	6H	76	> 200
ESD-6990	80 × 3	0.16	5B	6H	85	> 200
ESD-6974	80 × 1	0.15	5B	6H	77	> 200
ESD-6974	80 × 2	0.12	5B	6H	76	> 200
ESD-6974	80 × 3	0.17	5B	6H	73	> 200
ESD-261	80 × 3	0.11	5B	6H	41	> 200

accelerates the curing rate. Reaction *Scheme* 2 shows the nucleophilic attack of the oxirane ring by polyol in the presence of acid.[35] The ratio of epoxide equivalents to hydroxyl equivalents (the R value) is an important factor affecting properties when formulating with polyols. Compositions with lower R value (more hydroxyl equivalents) are typically more flexible and softer.

$$R = \frac{\text{Epoxide Equivalents}}{\text{Hydroxyl Equivalents}} = \frac{\text{g Epoxides/Epoxy Equivalent Wt}}{\text{g Polyol/Hydroxyl Equivalent Wt}}$$

The starting formulation (*Table* 2) for UV-curable coatings and inks is based on the general purpose formulations of the supplier.[32,34] The R value needs to be between 1.5 and 10 for good coating physical properties, according to the supplier. Most of the formulations shown by the supplier are at R=2. The formulations used in our initial survey, their viscosities, and their dry times are shown in *Table* 3. These formulations were cured at 250 mJ/cm^2 (50 fpm) at both 2 and 4 mil thickness. The dry time and film properties of the formulations are shown in *Table* 4. The dry time reported is the tack free time after exit from the UV-light chamber. As expected, the mono-functional 1,2-epoxyhexadecane formulation did not cure to a usable film.

From *Table* 4, it appears that coating thickness affects cure speed and film properties, with thicker films curing slower to softer films with worse adhesion. Formulation F with VCD had the lowest viscosity and best overall properties. Hence, ERL-4206 was chosen for formulating a low viscosity UV-cured system for an ink-jet ink.

Low viscosity compositions with VCD and polyol were formulated as shown in *Table* 5. This 58 cPs formulation was cured at different conveyor speeds and different film thicknesses. The results are shown in *Table* 6. Again, the data shows that thick films cure slower than thin films, and that coating adhesion is affected by conveyor speed. The higher the speed, the poorer is the adhesion. With the higher speed, there is less UV exposure, therefore less cure. However, pencil hardness and solvent resistance were apparently not affected by conveyor speed. The viscosity of the VCD formulation in *Table* 5 was reduced by adding up to 40% exempt solvent acetone. The viscosity of these diluted formulations is shown in *Table* 7. The addition of acetone lowered the viscosity of the ink-jet formulation to the desired range. Addition of acetone to the formulations increases dry time and causes instability due to its low boiling point. The effect of the concentration of acetone on dry time and film properties at an exposure of 250 mJ/cm^2 (50 fpm) is shown in *Table* 8.

We investigated the effect of pigment or dye on this UV-cured system. Due to difficulty in obtaining a low viscosity and stable black pigment dispersion, we used black dyes in our UV-curable formulas. The formulation with black dye is shown in *Table* 9.

Coatings were cured at 100 fpm, with UV-irradiation of 153 mJ/cm^2. The dry time data is shown in *Table* 10. It is apparent that black dye can inhibit cure speed. The inhibition of cure could result from the fact that the dye behaves like pigments, which are known to inhibit cure.[10] They are basic and could interact with the acidic

Table 14—Dry Time Test of Formulation with Different Percentage of Dye at Different UV Dose

Sample	Pass Number[a]	UV Dose (mJ/cm^2)	Dry Time
ES 6992 – no dye	1	276.7	1 sec
ES 6992 – 4% dye	1	276.7	15 sec
ES 6992 – 4% dye	2	553.4	1 sec
ES 6992 – 6% dye	3	831.1	Cured next day
ES 6992 – 8% dye	3	831.1	Cured next day
ES 6992 – 10% dye	3	831.1	Cured next day

(a) Note:The number of passes through the UV irradiation system ES 6992 – Mixture of ERL-4206, L-7604, and UVI-6992.

Table 15—Viscosity with Different Percentage of Dye at 25°C (cPs)

Sample	60 RPM	30 RPM	12 RPM
ERL-4206	7.7	7.7	7.6
ES 6992 – 4% dye	8.7	9.0	8.5
ES 6992 – 6% dye	8.5	8.9	8.2
ES 6992 – 10% dye	8.3	8.8	8.0

Table 16—Dry Time with Different Levels of Photoinitiator at 10% Dye

Sample	Pass Number[a]	UV Dose	Dry Time
ESD 6992 4%	3	865.2	Cured in two hours
ESD 6992 6%	4	1153.6	Cured in two hours
ESD 6992 8%	3	865.2	7 sec
ESD 6992 10%	2	576.8	1 sec

(a) Note: EDS – mixture of ERL 4206, surfactant, and dye X-22 photoinitiator and/or the photoinitiator photolytic products and decrease the actual amount of photoinitiator present. The shelf life of the X55 formulation was less than 24 hr, due to the presence of –NH– in the X55, which would react with cycloaliphatic epoxy as a curing agent.[36] Although dye X22 has –NH–, it is sterically hindered, and there was no reaction at room temperature for months as evidenced by the absence of viscosity change. Dye X22 was selected for further studies.

The effects of different photoinitiators on the colored system (four percent dye) were investigated using the formulation shown in *Table* 11. The panels were passed through the UV-irradiation system multiple times, at 80 fpm to give a UV dose of 184 mJ/cm^2 per pass. The results of dry time tests are shown in *Table* 12. The film property tests are shown in *Table* 13. Photoinitiator 6992 gave the fastest cure speeds. The effect of dye concentration (4 to 10%) on cure speed using this photoinitiator was investigated (*Table* 14). Very slow cure was obtained for six percent and higher levels of dye, even at an exposure level of 800 mJ/cm^2. Increasing the level of dye does not seem to affect viscosity significantly (*Table* 15).

Cationic inks require more photoinitiator than clears, because dyes absorb and scatter UV light to reduce the effective UV dose on the monomers. Basic photoinitiators react with the acidic photoinitiator and reduce its effective concentration. The effect of photoinitiator concentration was evaluated using VCD with 10% dye and up to 10% photoinitiator. When the concentration of the photoinitiator was increased to 10%, the dry time was very fast with a dose of 575 mJ/cm^2 in two passes (*Table* 16).

CONCLUSION

UV-curable inks with 10% black dyestuff were formulated with zero VOC and less than 10 cPs viscosity using vinyl cyclohexene diepoxide. Rapid cure was achieved through the use of cationic photoinitiators, which generate a strong acid, by UV irradiation of aryl sulfonium salts of hexaflouroantimonic and hexafluorophosphoric acids. The photoinitiator UVR 6992, a mixture of triarylsulfonium hexafluorophosphate salts, has low odor and worked well in the low viscosity cationic UV-cured formulations. The presence of dye inhibited the cure, but adequate cure of dyed formulations was achieved by increasing the concentration of the photoinitiator.

ACKNOWLEDGEMENT

The authors wish to acknowledge the financial support from the National Science Foundation Industry/University Cooperative Research Center in Coatings.

References

(1) Decker, C., "Photoinitiated Curing of Multifunctional Monomers," *Acta Polym.*, 45, 333 (1994).
(2) Hoyle, C.E. and Kinstle, J.F. (Eds.), "Radiation Curing of Polymeric Materials," *ACS Symp. Series 417*, American Chemical Society, Washington, D.C., 1990.
(3) Pappas, S.P. (Ed.), *Radiation Curing-Science and Technology*, Plenum Press, New York, 1992.
(4) Decker, C., "Photoinitiated Crosslinking Polymerization," *Prog. Polym. Sci.*, 21, No. 4, 593 (1996).
(5) Koleske, J.V., "Free Radical Radiation Curing," *Federation Series on Coatings Technology*, Federation of Societies for Coatings Technology, Blue Bell, PA, 1997.
(6) Koleske, J.V., "Cationic Radiation Curing," *Federation Series on Coatings Technology*, Federation of Societies for Coatings Technology, Blue Bell, PA, 1991.
(7) May, C.A., *Epoxy Resins Chemistry & Technology*, New York, 1988.
(8) Tokizawa, M., Okada, H., Wakabayashi, N., Kimura, T., and Fukutani, H., "Preparation and Cured Properties of Novel Cycloaliphatic Epoxy Resins," *J. Appl. Polym. Sci.*, 50, No. 4, 627 (1993).
(9) Swaraj, P., *Surface Coatings: Science & Technology*, John Wiley and Sons, 759, 1996.
(10) Pappas, S.P. and Wicks, Z.W. Jr., in *UV Curing Science and Technology,* Vol. I, Pappas, S.P. (Ed.), Technology Marketing Corp., Norwalk, CT, p. 78, 1978.
(11) Beck, E. et al., *J. Proc. Conf. Radtech Asia 93*, Tokyo, Japan, p. 181, 1993.
(12) Rutsch, W. et al., *Proc. 20th International Conf. in Org. Coat. Sci. and Techn.*, Athens, Greece, p. 467, 1994.
(13) Chang, C. et al., *Proc. Radtech '98*, North America Conf., Chicago, IL, p. 444, 1998.
(14) Cunningham, W., "UV Curing of Acrylate Resins Versus Cationic Epoxies," *Adhesives Age*, 39, No. 4, 24 (1996).
(15) Koleske, J.V., "Mechanical Properties of Cationic, Ultraviolet Light-Cured Cycloaliphatic Epoxide Systems," *Proc. of Radcure Europe '87*, Munich, 9-43, 1987.
(16) Crivello, J.V., "Application of Photoinitiated Cationic Polymerization in Coatings," JOURNAL OF COATINGS TECHNOLOGY, *63*, No. 35, 793 (1991).
(17) Wicks, Z.W. Jr., Jones, F.N., and Pappas, S.P., *Organic Coatings: Science and Technology*, Wiley and Sons, New York, 262, 1994.
(18) Raghavachar, R., Sarnecki, G., Baghdachi, J.A., and Massingill, J.L., "Cationic UV-Cured Coatings Using Epoxidized Soybean Oil," *RadTech Report*, 12, No. 5, 36 (1998).
(19) Eaton, R.F., "Coating Crosslinking Reactions Using Cycloaliphatic Epoxides," *Paint Coat. Ind.*, 76 (June 1999).
(20) Koleske, J.V., Spurr, O.K., and McCarthy, N.J., "UV-Cured Cycloaliphatic Epoxide Coatings," *Proc. 14th National SAMPE Tech. Conf.*, Atlanta, 249, 1982.
(21) Jaffe, A.B. and Mills, R.N., "Color Hard Copy for Computer Displays," *Proc. Soc. Info. Display*, 24: 219, 1983.
(22) Keene, A.G., "Ink Jet Printing Technologies, Products and Applications," *Electronic Imaging '89, Advanced Printing of Paper Summaries*, 1, 55, 1989.
(23) Le, H.P., "Progress and Trends in Ink Printing Technology," *Journal IS&T*, 42, No. 1, 49 (1998).
(24) Fishman, D.H., "Ink Jet Technology," *American Ink Maker*, 75, No. 6, 36 (1997).
(25) Lin, A.R., "Heterologous Ink Jet Composition," U.S. Patent 4,386,961 (1983).
(26) Cooke, T.M., Lin, A.R., Whitfield, R.G., and Hock, A., "Ink Jet Ink Formulation for Reduced Start-Up Problems," U.S. Patent 4,400,215 (1984).
(27) Sambucetti, C.J., "Magnetic Ink for Jet Printing," *IEEE Trans. Magn.*, MAG-16: 346, (1980).
(28) Yao, Y., "Ink Composition for Ink Jet Recording," U.S. Patent 4,246,154 (1981).
(29) Wong, R., Hair, M.L., and Croucher, M.D., "Sterically Stabilized Polymer Colloids and Their Use as Ink-Jet Inks," *J. Imaging Technol.*, 14, 129 (1988).
(30) Croucher, M.D. and Hair, M.L., "Design Criteria and Future Directions in Ink-jet Ink Technology," *Ind. Eng. Chem. Res.*, 28, 1712 (1989).
(31) Lepessant, J.P. and Tantot, G., "High Stability Printing Liquid, Intended More Particularly for Printing by Ink-Jet," U.S. Patent 4,409,039 (1983).
(32) Union Carbide Bulletin, "Cyracure® Cycloaliphatic Epoxides Cationic UV-Cure," UC-958, 1997.
(33) Union Carbide Bulletin, "Cycloaliphatic Epoxide Systems," UC-1640, 1999.
(34) Union Carbide Bulletin, "Cyracure® Cycloaliphatic Epoxides Cationic UV-Cure," UC-958, 1999.
(35) Swaraj, P., *Surface Coatings: Science & Technology*, John Wiley and Sons, 761, 1996.
(36) Wicks, Z.W. Jr., Jones, F.N., and Pappas, S.P., *Organic Coatings: Science and Technology*, Wiley and Sons, New York, 214, 1999.