

Zero VOC Sunlight Curable Coatings

Huilei Zhang, John L. Massingill, and James T. Woo

Coatings Research Institute
Eastern Michigan University
430 W. Forest Avenue
Ypsilanti, MI 48197

Curing of one-pack epoxy coatings by exposure to visible light for a few hours would be a useful innovation for architectural, industrial, and maintenance (AIM) coatings as well as for any large objects that would be difficult to heat but easy to shine a light on.

Zero VOC, low viscosity, sunlight curable clearcoats can be formulated with cycloaliphatic epoxy compounds as well as aromatic glycidyl ethers. Cure is achieved with a cationic photoinitiator that generates a strong acid when exposed to sunlight for a couple of hours. The clearcoats had good hardness, adhesion, and solvent resistance. No cure was achieved with incandescent light or with fluorescent light, which contains only 0.1% UV light as compared to sunlight that has 5% UV light. This work indicates that zero VOC one pack clearcoat epoxy formulations for AIM applications and large objects could be cured by light racks that generate the spectrum of sunlight.

INTRODUCTION

Energy-curing is the essentially instantaneous conversion of a usually liquid, low-viscosity combination of reactive ingredients into a crosslinked, polymerized mass—a process often termed “cure”—by exposure to a radiation energy source. Crosslinking is necessary to provide the desired properties, such as chemical resistance, solvent resistance, flexibility, and adhesion. The radiation source is usually 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} Curing of one-pack coatings by exposure to visible light for a few hours would be a useful innovation for architectural, industrial, and maintenance coatings as well as for large objects that would be difficult to heat but easy to shine a light on.

Energy-cure of coatings is usually concerned with two basic types of chemistry; one type involves a free radical polymerization of compounds containing ethylenic unsaturation such as that in acrylates and unsaturated polyesters.⁵ The other type involves a cationic polymerization of epoxide resins and co-curable compounds such as vinyl ethers, polyols, glycols, and alcohols.⁶

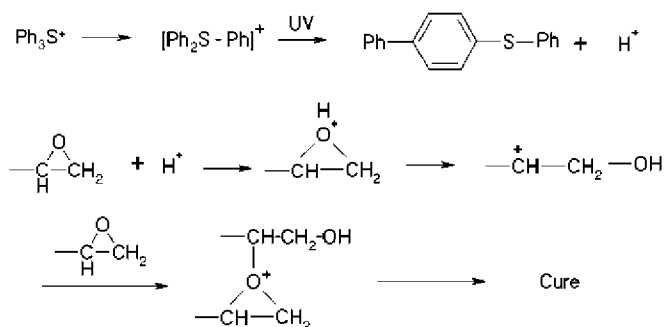
Epoxides are one of the most important and widely used classes of binders in the field of surface coatings. Their remarkable performance can be attributed to the fact that epoxides can react with a variety of functionalized compounds that contain hydroxyl, carboxyl, amino, and thiol groups. This versatility has led to a wide range of coating properties with excellent adhesion, good strength, and toughness and chemi-

cal resistance.⁷ Two major classes of epoxides, aromatic glycidyl ethers and cycloaliphatic epoxides, are used for coatings. Cycloaliphatic epoxides are more reactive in cationic UV cured systems than the aromatic glycidyl ethers and they are used commercially.^{8,9} The high reactivity of cycloaliphatic epoxides (*Figure 1*) is not only attributed to the high ring strain present in these monomers, but also to the lack of UV absorbing aromatic chromophors.¹⁰

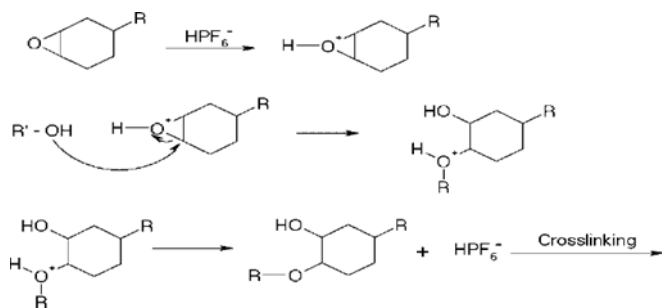
Acrylate esters are widely used in UV curable coatings. They cure through the free radical polymerization of double bonds. These formulations in the presence of photoinitiators can cure very fast, but essentially stop when the light source no longer generates new radicals. It is difficult to cure some pigmented systems since many pigments absorb and/or scatter UV radiation. Pigments 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 epoxides 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 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. This phenomenon is typically referred to as “dark” cure.¹⁴

The pioneering work of ultraviolet light initiated cationic curing of epoxides and particularly cycloaliphatic epoxides and related compounds was carried out by Crivello over two decades ago.¹⁵ Cationic curing technology involves the photolysis of onium salts and certain other light activated compounds.¹⁶ When these materials are irradiated with ultraviolet light of the proper wavelength, either Brønsted or Lewis acids are formed.¹⁷ 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,¹⁸ vinyl ethers,⁹ and other epoxides¹⁹ as shown in the following mechanism:



A typical cationic epoxy starting point formulation consists of cycloaliphatic epoxide and cationic photoinitiator. Other ingredients such as polyols and other epoxides²¹ can be added to modify properties. Rapid cationic cure is one of the advantages of cycloaliphatic epoxides over an aromatic epoxy system.^{8,9} Polyols co-react with epoxides by acting as chain transfer agents, generally improving cure speed as shown in the following mechanism¹⁸:



This communication deals with limited work done in this laboratory on light initiated cationic curing of epoxy resins using several visible light sources including sunlight, incandescent bulbs, and fluorescent bulbs.

EXPERIMENTAL

Materials

EPOXY RESINS: Cycloaliphatic epoxy ERL-4206 (vinyl cyclohexene dioxide, Epoxy 1) was supplied by Union Carbide Corp. It is listed as a carcinogen by the state of California. The structure of ERL-4206 is shown in *Figure 1*. Epoxy resin Epon[®]828 (Epoxy 2), a diglycidyl ether of bisphenol A (DGEBA), was supplied by Shell Chemical Company.

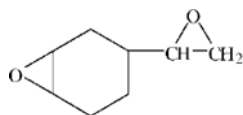
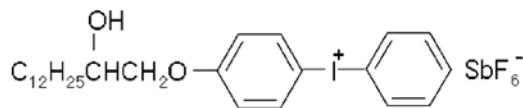


Figure 1—ERL-4206.

VISIBLE LIGHT PHOTOINITIATOR: CD-1012 (VPI-1, diaryliodonium hexafluoroantimonate, *Figure 2*)²⁰ was supplied by Sartomer.



Diaryliodonium hexafluoroantimonate (CD-1012)

Figure 2—Structure of CD-1012.

PIGMENTS: Basonyl black X- 22 liquid dye (Phenazine, C. I. Solvent Black 5) was obtained from BASF. The structure of X-22 is given in *Figure 3*.

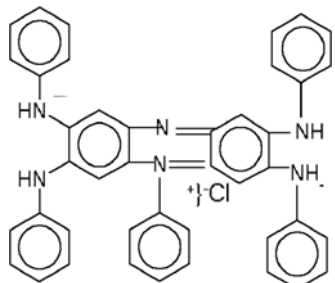


Figure 3—Structure of dye X-22.

SUBSTRATE: Iron phosphated steel panels of type R-36 I with dull matte finish were obtained from Q-panel Company.

ADDITIVES: Silicone surfactant Silwet[®]L7604 was obtained from Witco Corporation.

Testing Methods

Films were applied on the substrate with a wire wound applicator rod #3. Cured film properties were determined at least 24 hours after curing. Dry film thicknesses were determined by a Deltascope[®] MP (Helmut Fischer GmbH + Co.) from Fischer. Pencil hardness was determined by ASTM D 3363, adhesion by ASTM D 3359, and solvent resistance by ASTM D 5402.

RESULTS AND DISCUSSION

From previous work,²¹ a formulation was developed as a low VOC low viscosity UV cationic curable ink-jet ink system (*Table 1*). The dry time was one second with two passes and a total UV exposure of 576 mJ/cm².

Table 1—UV Curable Formulation with 10% Dye

Ingredients	Weight
Epoxy 1	100 g
Surfactant	0.5 g
Dye	10 g
Photoinitiator	10 g

The photoinitiator in this UV curable formula was replaced by photoinitiator VPI-1 that was thought to be active in visible light. VPI-1 is reported to offer fast UV cure speeds in epoxy, vinyl ether, and other cationically cured resin systems. It has better solubility than similar iodonium salts. A starting concentration of 2.5% VPI-1 was recommended by the supplier and it was incorporated in the formulation in *Table 1* at this level. None of the black dye formulations cured under incandescent light or under fluorescent light at ambient conditions. Nor did the formulations cure when exposed to sunlight for one summer day in Michigan. The presence of black dye appears to absorb light and prevent activation of the photoinitiator. The “dark cure” of cationic epoxy black ink (very thin films) did not overcome the pigment in thicker conventional coatings.

The clearcoat formulation in *Table 2* was evaluated to verify the postulate that black dye was absorbing activating radiation. The formulation did not cure under fluorescent light for two months. However, the formulation did cure under sunlight (*Table 3*).

Table 2—Formulation without Dye

Ingredients	Weight
Epoxy 1	100 g
Surfactant	0.5 g
VPI-1	2.5 g

Table 3—Visible Light Cure of Clearcoat Formulations

Formulations	Cure Condition	Cure Time
Epoxy1-S-VPI-1	Fluorescent light	Two months, did not cure
Epoxy1-S-VPI-1	Sunlight	Two hours

Epoxy 1 was replaced by Epoxy 2 since aromatic epoxies are often more reactive than aliphatic epoxies chemically. The

results are shown in *Table 4*. The formulations did not cure under fluorescent light for two months. The formulation did cure when exposed to sunlight for two hours.

Table 4—Visible Light Cure of Epoxy 2 Clearcoat Formulations

Formulations	Cure Condition	Cure Time
Epoxy 2-S-VPI-2	Fluorescent light	Two months, did not cure
Epoxy 2-S-VPI-2	Sunlight	Two hours
Epoxy 2 (alone)	Fluorescent light	Two months, did not cure
Epoxy 2 (alone)	Sunlight	One day, did not cure

Clearcoats made from Epoxy 1 and Epoxy 2 with VPI-1 were cured in sunlight for two hours. The cured film properties are shown in *Table 5*. A formulation containing glycerin, Epoxy 2, and VPI-1 was cured in the same way. The cured film properties are also shown in *Table 5*. Clearly, one-pack epoxy clearcoats can be cured in two hours exposure to sunlight to give excellent physical properties.

Table 5—Film Properties of Sunlight Cured Clearcoats

Sample	Film Thickness	Pencil Hardness	Adhesion	MEK rub
Epoxy 2-VPI-1	0.87	5H	B	> 200
Epoxy 2-G-VPI-1-S	0.11	6H	4B	35
Epoxy 1-VPI-1-S	0.14	6H	5B	> 200

Note: G = glycerin; S = surfactant.

To evaluate incandescent light for photoinitiation, aliphatic Epoxy 1 and aromatic Epoxy 2 formulations with VPI-1 were applied on panels and exposed at a distance of three inches to a 500 watt halogen work light for three, four, and five minutes. None of the panels cured. The longer the time, the hotter the panels became. The coatings on the panels became thin and runny without curing. The panels were stored at room temperature for two months and still did not cure.

The reason for curing in the presence of sunlight is probably the 5% UV component of sunlight. Incandescent and fluorescent lights apparently did not initiate cure because they have minuscule UV components. For instance, the UV component of fluorescent light is only 0.1%.

CONCLUSIONS

Zero VOC, low viscosity sunlight curable clearcoats can be formulated with cycloaliphatic epoxy compounds as well as aromatic glycidyl ether resin. Using a photoinitiator thought to be active in visible light, cure was achieved only under sunlight. No cure occurred in two months exposure to fluorescent or incandescent light. Apparently, VPI-1 is actually activated by the 5% UV component of sunlight. The presence of black dye inhibited cure in coatings. There did not appear to be any difference in the reactivity between Epoxy 1, an aliphatic epoxy, and Epoxy 2, an aromatic liquid epoxy, under the conditions tested.

It appears that zero VOC one pack epoxy clearcoat formulations for AIM applications as well as large objects could be cured by light racks that generate the spectrum of sunlight.

ACKNOWLEDGMENT

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

References

- Decker, C., "Photoinitiated Curing of Multifunctional Monomers," *Acta Polymer*, 45, 333 (1994).
- Hoyle, C.E. and Kinstle, J.F. (Eds.), "Radiation Curing of Polymeric Materials," *ACS Symposium Series 417*, American Chemical Society, Washington, D.C., 1990.
- Pappas, S.P. (Ed.), *Radiation Curing—Science and Technology*, Plenum Press, New York, 1992.
- Decker, C., "Photoinitiated Crosslinking Polymerization," *Prog. Polymer Sci.*, 21, No. 4, 593 (1996).
- Koleske, J.V., "Free Radical Radiation Curing," *Federation Series on Coatings Technology*, Federation of Societies for Coatings Technology, Blue Bell, PA, 1997.
- Koleske, J.V., "Cationic Radiation Curing," *Federation Series on Coatings Technology*, Federation of Societies for Coatings Technology, Blue Bell, PA, 1991.
- May, C.A., *Epoxy Resins Chemistry and Technology*, New York, 1988.
- Tokizawa, M., Okada, H., Wakabayashi, N., Kimura, T., and Fukutani, H., "Preparation and Cured Properties of Novel Cycloaliphatic Epoxy Resins," *J. Applied Polymer Sci.*, 50, No. 4, 627 (1993).
- Eaton, R.F., "Coating Crosslinking Reactions Using Cycloaliphatic Epoxides," *Paint Coat. Ind.*, 76 (June 1999).
- Paul, S., *Surface Coatings: Science and Technology*, John Wiley & Sons, 759, 1996.
- Beck, E., et al, *Proc. Conf. Radtech Asia 93*, Tokyo, p. 181, 1993.
- Rutsch, W., et al, *Proc. XXth International Conf. in Organic Coating Science and Technology*, Athens, p. 467, 1994.
- Chang, C., et al, *Proc. Radtech '98 North America Conf.*, Chicago, p. 444, 1998.
- Cunningham, W., "UV Curing of Acrylate Resins Versus Cationic Epoxies," *Adhesives Age*, 39, No. 4, 24 (1996).
- Crivello, J.V. and Lam J.H.W., *Macromolecule*, 10, 1307 (1977).
- Koleske, J.V., "Mechanical Properties of Cationic, Ultraviolet Light-Cured Cycloaliphatic Epoxide Systems," *Proc. of Radcure Europe '87*, Munich, 9-43, May 4-7, 1987.
- Crivello, J.V., "Application of Photoinitiated Cationic Polymerization in Coatings," *JOURNAL OF COATINGS TECHNOLOGY*, 63, No. 35, 793 (1991).
- Koleske, J.V., Spurr, O.K., and McCarthy, N.J., "UV-Cured Cycloaliphatic Epoxide Coatings," *Proc. 14th National SAMPE Tech. Conf.*, 249, Atlanta, 1982.
- Wicks, Z.W. Jr., Jones F.N., Pappas S.P., *Organic Coatings: Science and Technology*, Wiley, New York, pg. 262, 1994.
- Jurczak, E.A., "Photopolymerization Behavior of Cationic Photoinitiators," *Paint & Ink International* (January/February 1997).
- Zhang, H.L., Massingill, J.L., and Woo, J., "Low VOC, Low Viscosity UV Cationic Radiation Cured Ink-jet Ink System," scheduled to be printed in the June 2000 issue of the *JOURNAL OF COATINGS TECHNOLOGY*.

Short Communications

Short submissions (i.e., submissions that will not exceed three published pages) should focus on important new results that do not justify publication as a full article. The *Short Communications* section is intended to provide a forum for initial reports of new phenomena and of work in progress as well as short descriptions of interesting theoretical or experimental results of limited scope. Within the limits of scope imposed by their length, *Short Communications* must meet the same technical standards as full length Technical Articles. *Short Communications* will be subjected to peer review. The editors will endeavor to publish *Short Communications* rapidly.