

New Raw materials for cationic UV/EB curing

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UV/EB cationic curing is an alternative radiation curing technology circumventing some of the free radical polymerisation disadvantages like air inhibition and poor adhesion on difficult substrates. Nowadays a number of new commercial photoinitiators, monomers and co-resins suitable for such systems are available. It can be mentioned for example trimethylolpropane oxetane (TMPO) as a non irritant highly reactive diluent as well as new oligomeric photoinitiators.

In this paper, we present a number of new polyols like hyperbranched polyester polyols acting as chain transfer crosslinkers and flexibilisers as main function. But they bring also other benefits like improved adhesion and rheology of different inks. These benefits are highlighted using different substrates and ink formulations.

General

The cationic photoinduced polymerisation of epoxides and oxetanes is an alternative technology to the well established free radical radiation curing of acrylates. The particular photo-crosslinking mechanism of cationic systems offers a number of advantages and addresses the major drawbacks associated to acrylate systems (beside the common environmental and productivity advantages of the radiation curing technology):

- outstanding adhesion to a variety of substrates (metals, plastics, glass and ceramics)
- very good dimensional stability (low shrinkage)
- low viscosity
- excellent toughness
- no air inhibition and high curing rates under air
- formable coatings
- post cure effect beneficial for reaching full cure and optimum properties

In contrast to radical initiated polymerisation of acrylates, the cationic photopolymerisation¹ is a ring opening polymerisation process of oxiranes and/or oxetanes initiated by strong protonic acid generated by the photolysis of diaryliodonium² or triarylsulfonium³ salts. Photosensitisers like thioxanthone and anthracene derivatives as well as free radical photoinitiators can be used to enhance the activity of the onium salt. The living character of the polymerisation will continue to develop after radiation exposure, providing a beneficial post cure effect for shadows areas. This effect can be enhanced by a thermal treatment. The ring opening mechanism results in a low shrinkage and the resulting outstanding adhesion on many substrates is one of the main features of cationic systems over free radical polymerisation. Furthermore, the oxonium ion and the carbocation are inactive towards the oxygen which allows high curing speed under air.

The main components of cationic formulations for coatings and inks applications are typically cycloaliphatic epoxide based resins like the 3,4- epoxy cyclohexyl methyl-3,4 epoxy cyclohexane carboxylate as the main resin and trimethylolpropane oxetane (TMPO) as the reactive diluent.

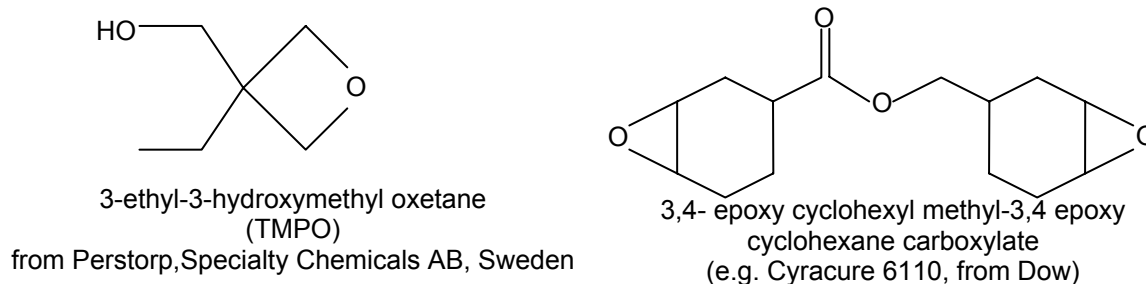


Figure 1. 3-ethyl-3-hydroxymethyl oxetane and 3,4- epoxy cyclohexyl methyl-3,4 epoxy

The ring opening of the epoxide and/or the oxetane can be accompanied by crosslinking with hydroxyl functional compounds like caprolactone polyols, polyether polyols or polyester polyols. These polyols act as chain transfer crosslinkers and flexibilisers^{4,5} and they can be used in concentration up to 30wt% for general purpose coating applications.

A number of other components can be used to fine tune the end properties of the coatings and ink like conventional DGEBA epoxides, Novolac resins, epoxidized oils, epoxidized polybutadiene and others. The cationic polymerisation of epoxides and oxetanes can be combined with free radical polymerisation of acrylate systems to built interpenetrating polymer networks (IPNs)⁶.

Three main issues are associated with cationic curing:

- a. Base contamination: the cationic polymerisation can be altered by the presence of alkaline compounds like amines, urethanes, basic pigments or fillers. The right choice of additives, substrates and primers is therefore recommended.
- b. Moisture inhibition: water can act as a chain transfer and it terminates the polymerisation. It is therefore desirable to have a proper humidity and environmental control during the overall process and handling.
- c. Heat has a strong impact on the photo-polymerisation rate and a slight increase of the temperature of the formulation before the UV exposure (for example by IR) may have a strong effect on improving curing speed⁴ (and vice-versa). A post thermal treatment (by IR or oven) can be useful for accelerating the living polymerisation in order to achieve faster the optimal coating properties.

These factors need to be taken into account in order to obtain optimal and reproducible process and coating properties.

Applications

When a desired performance like adhesion on difficult substrate, a high dimensional stability or any other of above mentioned properties is a top requirement, UV/EB cationic systems are a preferred choice over free radical UV/EB systems. It can be mentioned in particular the following applications

- Graphic Arts
 - Overprint varnishes on difficult substrates like metal and TPO (thermoplastic polyolefins) for packaging applications
 - UV screen inks (clear and pigmented primers for metals like for can coating, glass and plastics)
 - UV flexo inks (food packaging)
 - UV inkjet
- Industrial Coatings
 - Coil coating (formable metal)
 - Plastic coating
- Adhesives
 - UV laminated adhesives
 - UV structural adhesives
 - UV pressure sensitive adhesives
- UV/EB silicone release coatings
- Composites
- Electronics (dielectric coatings for electronic metal parts, insulators, encapsulation)
- Rapid Prototyping and Modelling (RPM) (high dimensional stability)
- Holographic storage media

Recent new raw materials⁷

There has been in the recent years, enormous progress on new commercially available raw materials for cationic UV/EB curing. Among them, it can be noticed new photoinitiators as for example thioxanthonium salts (Omnicat 550, IGM, NL), an odor and benzene free photoinitiator, particularly suited for food packaging applications.

New cycloaliphatic epoxides demonstrating superior toughness are as well available.

Materials and equipment

The cycloaliphatic epoxide, UVR6110 was received from DOW and used as main component of the formulations, and the diaryliodonium salt Irgacure 250 from CIBA, Switzerland as photoinitiator. ITX (isopropyl thioxanthone, lambson, UK) was used as sensitiser.

Trimethylolpropane oxetane, TMPO

Trimethylolpropane oxetane (TMPO) is a clear colourless non skin irritant reactive diluent which combines increased reactivity with very good diluting power of cycloaliphatic epoxide.

Table 1. TMPO characteristics

	Hydroxyl functionality	Nominal hydroxyl and epoxy equivalent weight (resp. HEW and EEW)	Molecular Weight (Mw, g/mol)	Viscosity (mPas, 23°C)
TMPO	1	116	116	25

Advantages of TMPO

TMPO is a very effective reactive diluent for cycloaliphatic epoxide like the Cyracure UVR 6110. It can improve the curing speed by almost a factor 2 when using 15 parts for the same photoinitiator concentration as illustrated in figure 3.

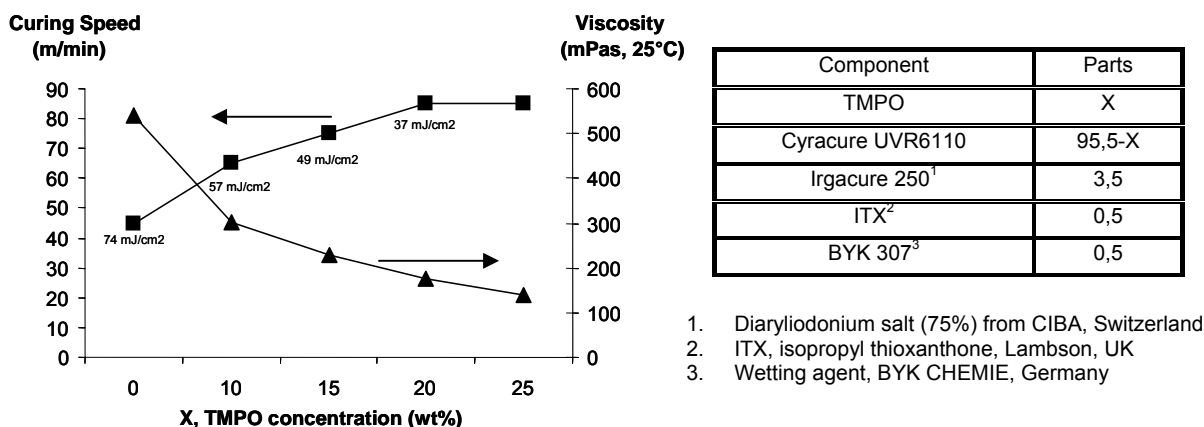


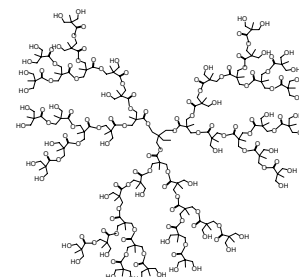
Figure 2. Maximum curing speed (m/min) for nail scratch free and viscosity (mPas) as a function of TMPO content. Curing conditions: 1 pass under a 160W/cm Hg lamp (12 µm film on aluminium substrate)

Dendritic polyester polyols

The dendritic polyester polyols presented here are a new family of aliphatic polyester polyols of high functionality (≥ 6) and relatively low viscosity. Several grades are commercially available.

Table 2. Characteristics of the dendritic polyester polyols and illustration

Aliphatic Dendritic Polyester Polyols				
	Hydroxyl functionality	Hydroxyl Equivalent weight	Molecular Weight (Mw, g/mol)	Viscosity (mPas, 23°C)
Boltorn® H2004	6	530	3200	16000
Boltorn® H2003	12	200	2500	1000 (60°C)



Like many aliphatic polyols, the dendritic polyesters act as chain transfer crosslinkers and flexibilisers with substantial benefits like:

- better chemical resistance
- increased toughness
- improved rheological behaviour of pigmented systems for a better ink transfer

Overprint varnishes (OPV's) for metal and plastics

Several formulations suitable for roller coater are presented in the table 3, together with some coating properties. The formulation 2 contains 15wt% of TMPO and the formulations 3 further 10wt% of the hexafunctional dendritic polyester polyol.

Table 3. Formulation and properties of OPV's suitable for both metal and plastic substrates
(The following coating properties were evaluated for a 12 µm thick coating cured with 2 pass at 70m/min under a 160W/cm Hg lamp (UV dose approximately 100 mJ/cm²) and conditioned for 24 hours at 23°C, RH50%, the substrates are specified)

	Formulation 1	Formulation 2	Formulation 3
Cyracure UVR6110	95,5	80,5	70,5
TMPO	-	15	15
Boltorn® H2004	-	-	10
Irgacure 250	3,5	3,5	3,5
ITX	0,5	0,5	0,5
BYK 307	0,5	0,5	0,5
Total	100	100	100
R value	-	5,7	4,4
Viscosity (mPas, 25°C, cone&plate)	520	230	275
Maximum curing rate (m/min) for nail scratch free for one pass under a 160 W/cm Hg lamp	45	75	75
Water resistance 24hrs (glass) scale 0 to 5, 5 best	2	3	5
Acetone 2 min (glass) scale 0 to 5, 5 best	0	1	5
Pendulum hardness, König.s (glass)	165	215	212
Adhesion on glass, Al and Steel, crosshatch 0-5, 0 best	0	0	0
Adhesion on PE crosshatch 0-5, 0 best	1	0	0
Bend test 180 degrees (PE)	fail	fail	pass

All formulations exhibited an excellent adhesion on various substrates like aluminium, steel, glass and polyethylene. The combination of the dendritic polyester polyol and TMPO (formulation 3) exhibited excellent curing rates at lower viscosity compared to the reference formulation 1, together with an increase in flexibility, hardness and chemical resistance.

UV screen white based coats for can coatings

The cationic UV systems are very attractive to be used as primers for difficult substrates like aluminium or polyolefins. In this section are presented two basic formulations suitable for this application.

Table 4. UV white based coat formulations and coating properties

Component	Formulation 1	Formulation 2
TMPO	14,5	10
Cyracure UVR6110	30,7	28,2
Boltorn® H2003	-	7
Irgacure 250	5	5
ITX	0,5	0,5
Irgacure 2959 ¹	0,5	0,5
Byk P104S ²	0,8	0,8
TiO ₂ (Kronos 2300)	48	48
Total	100	100
Viscosity (mPas, 25°C, 500s ⁻¹)	0,6	1,3
Viscosity ratio at 25°C $\eta(1,7s^{-1})/\eta(500s^{-1})$	2,7	1,5
Max Curing speed in m/min (nail scratch free), 2 pass under a 160W/Cm Hg lamp (UV dose, mJ/cm ²) ³	45 (130)	40 (170)
12µm thick opaque white primer on aluminum plates cured with 3 pass at 30 m/min under a 160W/cm Hg lamp (UV dose approximately 300mJ/cm ²) followed by post baking at 180°C for 4 minutes ³		
MEK double rubs	>200	>200
Pendulum hardness (König.s)	188	145
Bend test 180 degrees	Fail	Pass
Adhesion (crosshatch 0-5, 0 best)	0	0
Gloss 20°	66,9	62,9
Gloss 60°	90,1	89,9

Acetone 5 min	OK	OK
Water resistance ² 4hrs	OK	OK

1. 4-(2-hydroxyethoxy)-phenyl-(hydroxyl-2-methylpropyl)-ketone, Ciba, Switzerland

2. Dispersing agent, BYK CHEMIE, Germany

3: A gallium doped lamp or microwave excitation F-V bulb is recommended to further enhanced the UV curing speed of such white based coats⁸

Irgacure 2959 was used to further enhance the reactivity of the system as demonstrated previously⁹.

TMPO is an effective reactive diluent in order to achieve adequate viscosity for screen printing. Boltorn® H2003 has the advantage to improve the flexibility of the coating, allowing better formability. Furthermore, it improves the rheological behaviour of the ink as indicated by the lower ratio of viscosity between low and high shear rate (indicative of a more Newtonian behaviour). This improved rheological behaviour can result in a better ink transfer and levelling at high speed. It can be noticed that both formulations exhibit an excellent adhesion on polyolefin (PE) and they can be used as a white based opaque primer for TPO's.

UV flexographic inks

The low viscosity, good adhesion on difficult substrates like polyolefins, together with the high curing speed under air make cationic UV systems a preferred choice UV/EB flexo inks for packaging applications based on difficult substrates like non swellable polyolefins (PE, PP, OPP).

Both formulations presented in figure 3 offered excellent curing rates under air and tack free surfaces can be obtained with UV doses as low as 30mJ/cm² using a H bulb. An excellent adhesion on aluminium and PE was obtained.

	Form. 1	Form. 2
	◆	■
Cyracure UVR6110	52,5	58
TMPO	15	20,5
Boltorn® H2004	11	-
Dispersing agent	1	1
Blue pigment (Sunfast® 15:3)	14	14
Irgacure 250	5,5	5,5
ITX	0,5	0,5
Irgacure 2959	0,5	0,5
Reactivity m/min (1 pass 160W/cm,	90	100

H bulb, in air)		
Adhesion on PE and Al	0	0
(0 to 5, 0 best)		
Viscosity (25°C, mPas, 500s ⁻¹)	620	500
Viscosity ratio at 25°C	6,1	22,6
$\eta(1,7s^{-1})/\eta(500s^{-1})$		

Boltorn[®] H2004 enhanced the rheological behaviour of the ink towards a Newtonian behaviour. This was particularly true in case of the blue pigment Sunfast[®] 15:3 (Sunchemical) with a significant reduction of the pseudoplastic behaviour of the ink as illustrated in figure 3. This better rheological behaviour can improve the ink transfer and quality of the print at high speed.

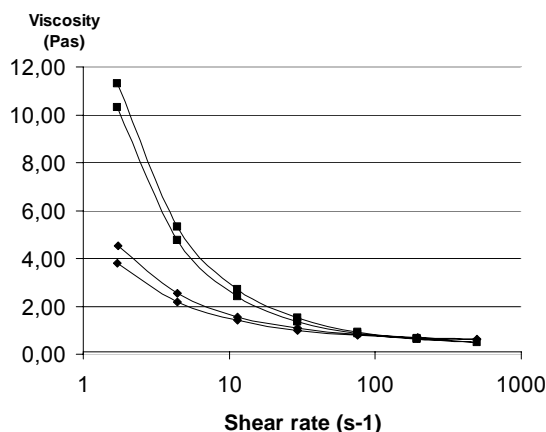


Figure 3. Effect of Boltorn[®] H2004 on the rheological behaviour of the UV flexo inks and curing (applied with Echocel hand proofer with anilox roller 750 cells/inch)

Conclusions

- TMPO is a very efficient non irritant reactive diluent, combining economical and technical advantages as increased productivity for cationic UV/EB systems (up to two times higher curing speed at constant photoinitiator concentration can be obtained). A recommend epoxy/hydroxyl ratio is 3 to 4 for an optimum combination of properties.
- The dendritic polyester polyols further enhance the chemical resistance and mechanical properties of the cationic UV clear coats and inks and improve the rheological behaviour of pigmented systems for a better ink transfer

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