

Cationic UV Cure on Polyolefins

David James, Pia Appelkvist, Eva Gustavsson, Perstorp Specialty Chemicals AB, Sweden

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 acting as chain transfer crosslinkers and flexibilizers as main function. But they also bring 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):

- Better adhesion on difficult substrates (metals, plastics, glass, ceramics)
 - Lower shrinkage thanks to the ring opening polymerization
 - Chemical anchoring groups are formed and/or present in the polymer network for chemical bonding with the substrate
- Living polymerization
 - Post-UV cure shape forming is easily achievable (expandable or shrinkable systems)
 - Full cure can be obtained, beneficial for developing low migrating systems
- High curing speed under air (no air inhibition)
- Lower odor
- Better toughness
- Lower viscosity
- Withstand sterilization
- Good barrier and electrical 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.

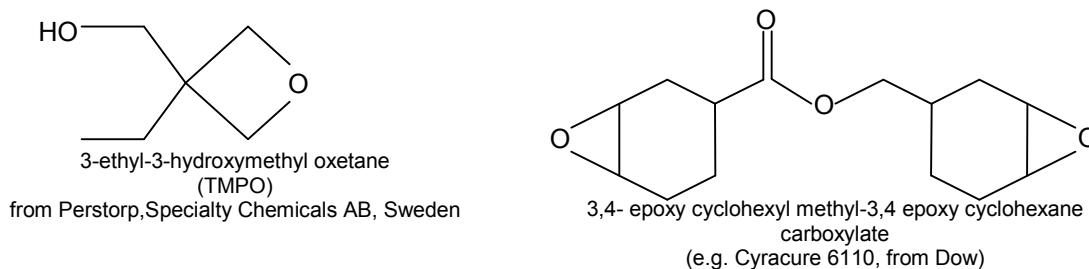


Figure 1. 3-ethyl-3-hydroxymethyl oxetane and 3,4- epoxy cyclohexyl methyl-3,4 epoxy

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 build interpenetrating polymer networks (IPNs)⁶.

Three main issues are associated with cationic curing:

- 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 important.
- 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.
- 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 the optimal coating properties faster.

These factors need to be taken into account in order to obtain an optimal, robust 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 oligomeric thioxanthonium salts (Omnicat 650, IGM, NL), an odor and benzene free photoinitiator with low migration, particularly suited for food packaging applications.

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 3,4- epoxy cyclohexyl methyl-3,4 epoxy. 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.

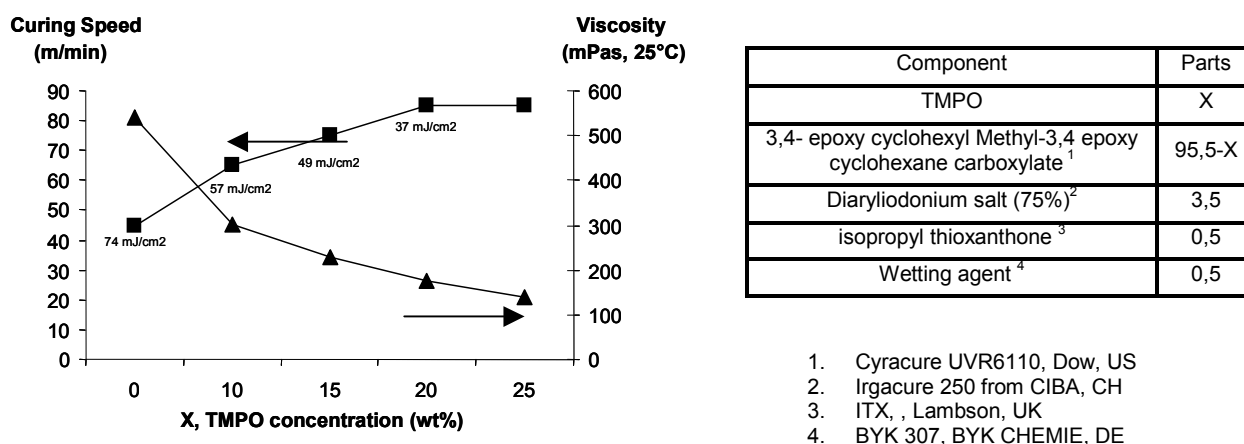


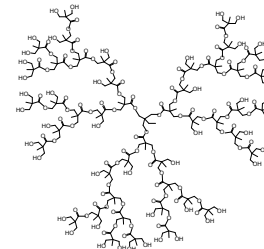
Figure 2. Maximum curing speed (m/min) for nail scratch free and viscosity (mPas) as a function of TMPO content. Curing conditions: 1 pass under a 160W/cm Hg lamp (12 μ m film on aluminium substrate)

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 plastics

As starting point formulation suitable for roller coater is presented in the table 3, together with some coating properties and compared with a free radical formulation based on conventional acrylates.

Table 3. Formulation and properties of OPV's suitable for plastic substrates

(The following coating properties were evaluated for a 6µm thick coating cured with 2 pass at 30m/min under a 80W/cm Hg lamp -UV dose approximately 100 mJ/cm²- and conditioned for 24 hours at 23°C, RH50%, the substrates are specified)

	Reference free radical	Formulation 1
3,4- epoxy cyclohexyl Methyl-3,4 epoxy cyclohexane carboxylate ¹		69,5
TMPO		15
Boltorn® H2004		10
Triarylsulfonium salt (UVI6992 ¹)		4,5
isopropylthioxanthone		0,5
BYK 307 ⁴		0,5
Epoxy acrylate (EB3701 ²)	26,7	
GPTA ²	35	
TPGDA ²	30	
Irgacure 500 ³	6	
Amine synergist P115 ²	2	
BYK307 ⁴	0,3	
Total	100	100
R value	-	4,1
Viscosity (mPas, 25°C, plate/plate)	200	170
Maximum curing speed (m/min) for nail scratch free for one pass under a 80 W/cm Hg lamp	20	30
Corresponding UV dose (mJ/cm ²)	73	47
Adhesion crosshatch 0-5, 0 best		
PE	1	0
PP	2	0
OPP	3	0
Erichsen flexibility mm (6µm thick coating on Al, 2 weeks after UV cure)	2,4	>6
Shrinkage (%) (picnometry)	10,2	6,8

1. UVR6110, Dow, US

2. CYTEC, US

3. Ciba, CH

4. Byk Chemie, DE

As shown in table 3, the cationic varnish offers a number of benefits compared to the free radical formulation:

- less photoinitiator is required and better curing speed can still be achieved: despite the cationic polymerization rate is known to be slower than the free radical polymerization of acrylates, as no air inhibition takes place, a higher belt speed can be achieved
- lower shrinkage is obtained (approximately 30% less) thanks to the ring opening polymerization
- a perfect adhesion on all tested polyolefins, without the need for a fresh corona treatment while being required and not very efficient for the free radical formulation: the lower shrinkage and the formation of hydroxyl groups is beneficial for improving the adhesion
- a much better flexibility is obtained thanks to the polyol component of the cationic formulation

UV flexographic inks

Several cationic flexographic formulations were prepared and compared with a free radical flexo ink reference as shown in table 4.

Table 4. Formulation and properties of flexographic inks suitable for plastic substrates (the inks were applied with Anilox Hand roller of 700 cells/inch and cured with 1 pass at 10m/min under a 80W/cm H bulb, corresponding to a UV dose of 150 mJ/cm²)

	Reference free radical	Formulation 1	Formulation 2
3,4- epoxy cyclohexyl Methyl-3,4 epoxy cyclohexane carboxylate (UVR6110) ¹		54	54
TMPO		12	12
Caprolactone triol (TONE305 ¹)		10	-
Boltorn® H2004		-	10
Thioxanthonium salt in propylene glycol (Omnicat 550 (62% in propylene carbonate) ²		8	8
BYK307 ³		0,3	0,3
Solsperse 5000:39000 ⁴		0,3:1,4	0,3:1,4
Sunfast Blue 15:3 ⁵		14	14
Polyester tetraacrylate (EB657 ⁶)	18		
HDDA ⁶	9,2		
EB40 ⁶	49,3		
Photoinitiator package ⁷	7,7		
Solsperse 5000:39000 ⁴	0,3:1,4		
Sunfast Blue 15:3 ⁵	14,1		
Total	100	100	100
Viscosity (mPas, 25°C, 369s-1)	620	660	720
Shortness index ($\eta(2,5s-1)/\eta(2500)s-1$)	18	22	13
Maximum curing speed (m/min) for nail scratch free for one pass under a 80 W/cm Hg lamp	25	30	37
Corresponding UV dose (mJ/cm ²)	60	44	36
Adhesion crosshatch 0-5, 0 best			
PE	1	0	0
PP	4	0	0
OPP	5	0	0
Through cure (ethanol double rubs after 24 hrs)	22	14	16

1. Dow, US 2. IGM Resins, NL 3. BYK Chemie, DE 4. Lubrizol, UK 5. Sunchemical US 6. CYTEC, US 7. (ITX:EDB:Irgacure184:Irgacure 369:Irgacure 819)

As in the case of the varnishes, the cationic formulations are far superior to the free radical in terms of adhesion. The cationic formulations have excellent adhesion as shown in the figure 3 on PE, PP and OPP (results without fresh corona treatment for the cationic formulation, with fresh corona treatment for the free radical formulation).

All three formulations exhibit a similar viscosity suitable for flexo printing (in a range from 620 to 720 mPas) but they strongly differ in rheological profile: the free radical and the cationic formulation 1 based on a caprolactone triol exhibit rather high shortness index, illustrating a strong pseudoplastic behaviour. The formulation 2 using Boltorn® H2004 is much lower in shortness index. This improved rheological behaviour is believed to be due to the higher molecular weight (yet a low solution viscosity thanks to its dendritic shape) and wetting characteristic of the hyperbranched polymer. This lower

shortness index is beneficial for better ink transfer, especially at high speed, resulting in better printing quality.

Furthermore the hyperbranched polyester polyol gives better curing speed than the caprolactone polyol, thanks to its higher molecular weight and higher functionality.

The benefits of the hyperbranched polyol in terms of rheological profile of the ink were as well investigated with other pigments as shown in figure 4 by comparing ink formulations with and without Boltorn® H2004. It shows that a decrease by a factor 2 of the shortness index can be achieved when adding Boltorn® H2004 to the formulation.

Figure 3. Tape test on the flexo inks cured with a UV dose of $150\text{mJ}/\text{cm}^2$, comparison between the cationic formulations (top) and free radical reference (bottom) on PE (left) and OPP (right). The black marks shows where the tape test has been done.

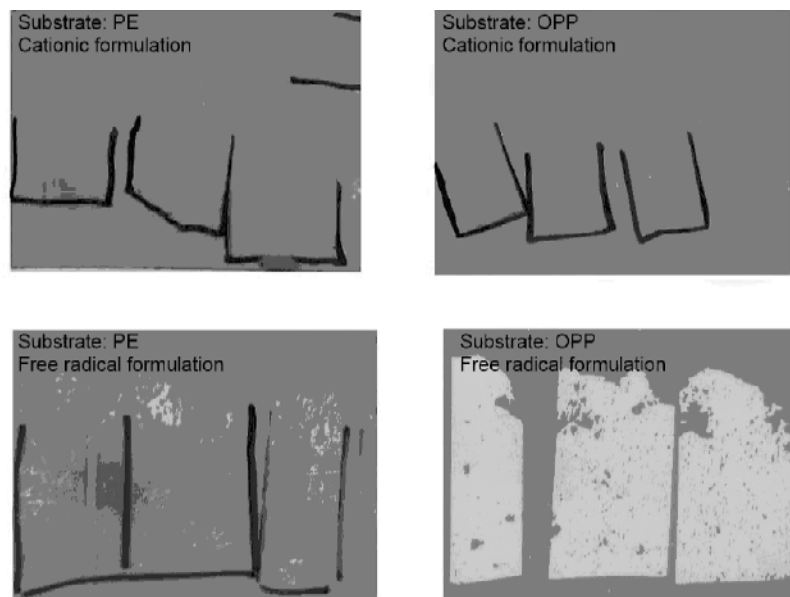
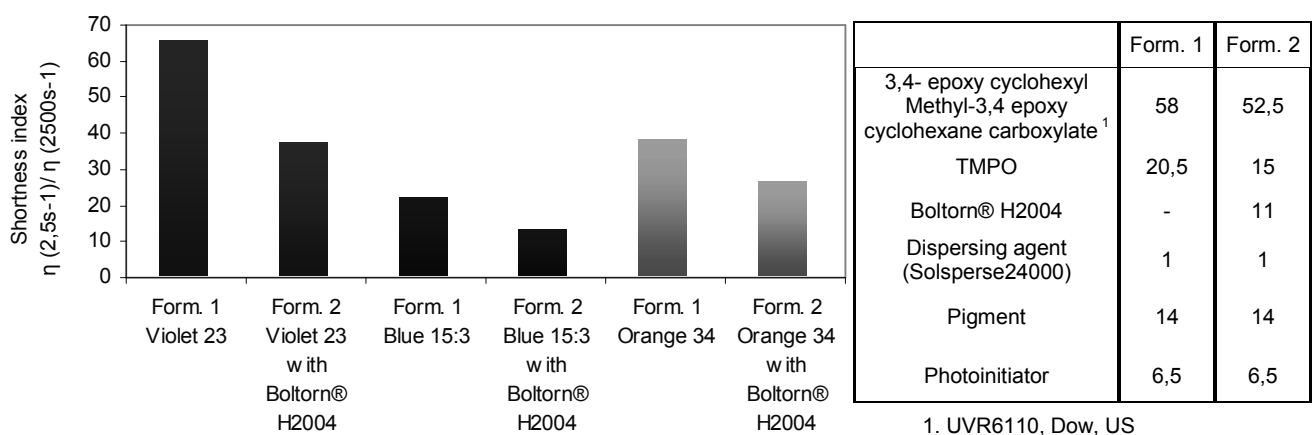


Figure 4. Effect of Boltorn® H2004 in a flexo formulation on the shortness index for 3 pigments (Violet 23, Blue 15:3 and Orange 34)



Conclusion

Cationic UV/EB offers largely superior performance over free radical UV/EB systems like a better adhesion on difficult substrate such polyolefins (PE, PP, OPP), together with fast cure (no air inhibition) and high flexibility. An excellent adhesion is achieved even without fresh corona treatment as required for free radical UV curing.

TMPO, a non-mutagenic/non skin irritant reactive diluent and performance enhancer of cycloaliphatic epoxides improves reactivity. Dendritic polyester polyols such as Boltorn® H2004 provide better rheological behavior for a better printing quality and superior curing speed of inks compared to other polyols such as caprolactone polyols.

The new raw materials nowadays available can further extend the use and acceptance of cationic UV/EB in the graphic arts industry.

References

1. Radiation curing in Polymer Science and Technology, J.P. Fouassier, J.F. Rabek, Elsevier Applied Science, London, 1993
2. J.V. Crivello, J.H Lam J. Polym- Sci. Polym. Chem Ed. 1978, 16, 563
3. J.V Crivello,, in "Development in polymer photochemistry" Vol. 2, Applied Science Publishers, Barking, UK, 1981
4. J.V Crivello, D.A. Conlon, D.R. Olson "Effect of polyols as chain transfer agent and flexibilizers in photoinitiated cationic photopolymerisation", Journal of radiation curing, 3-9, October 1986
5. H. A. Nash, H.J Doktor, D.C Webster "Effect of addition of polyol on cure kinetics and viscoelastic properties of UV curable coating formulations containing cycloaliphatic epoxide and oxetane", Polymer preprint, 44 (1), 121-122, 2003
6. C. Decker, T. N Thi Viet, D. weber-Koehl "UV radiation curing of acrylate/epoxide systems", Polymer 42 (1), 5531-5541, 2001
7. A. Carry "Recent materials for cationic UV curing and their use in cationic UV flexo inks", 29th Munich adhesive and Finishing Symposium, 2004
8. J.L. Birbaum, S. Ilg, "A new onium Salt for cationic curing of white pigmented epoxy formulations", Radtech Europe 2001, Basel
9. A. Carroy "Advances in cationic curing of cyclo-epoxide systems", Radtech Europe 2001, Basel