

New Developments in Cationic Curing Flexo Inks

Antoine Carroy, Dow Deutschland GmbH, D-77836 Rheinmuenster, Germany

Introduction

The main established uses of ultraviolet light initiated, cationically-cured systems are as clear coatings for various metal packaging applications and as over-print varnishes and inks for plastic substrates coating applications. Cationic UV-cured systems based on cycloaliphatic-diepoxides are also being used more and more in applications, such as electronics ⁽¹⁾, stereolithography ⁽²⁾ and composites ⁽³⁾, where the curing of much thicker sections is involved. There has been a considerable amount of work dedicated to the development of new materials for cationic UV-curing systems over the recent years. These materials include both photoinitiators and cationically reactive compounds, whose characteristics and performances will help address the issues or limitations associated with the currently available products. As a result of their capacity to enable the development of coatings and inks, which can meet more stringent end-use requirements, they will contribute to the expansion and use of cationic UV-curing systems.

The specific features of cationic UV-curing technology, e.g. the post-cure reaction that leads to high degree of conversion, thus low level of migration, the excellent adhesion to a variety of plastic or aluminum foils and the superior mechanical properties, make it particularly attractive for the formulation of UV-curing flexographic inks. The present paper will report on the performance of one of the recently developed type of sulfonium salts as cationic photo-initiator in model formula of flexographic inks.

A- New raw materials for cationic UV-curing systems

Cationic photo-initiators

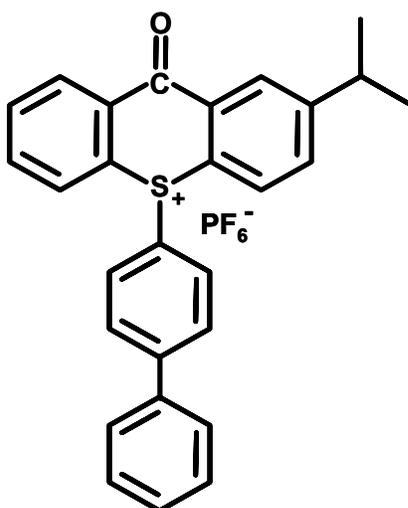
Several bis-substituted diaryl-iodonium salts have been introduced on the market, some of them being already registered and commercialized. Although these salts exhibit a lower UV absorptivity than the standard triarylsulfonium salts, they offer the big advantage of being indirectly activated by a range of photo-sensitizers through a trans-esterification process. Thioxanthone and recently developed anthracene derivatives, but also certain free radical photoinitiators, such as hydroxyalkylphenone photoinitiators, have been found to be efficient photosensitizers for the diaryliodonium salts ⁽⁴⁾. By artificially expanding the photocure response of diaryliodonium salts into the UV-B and UV-A regions, the combination of these cationic photoinitiators with above-mentioned photosensitizers constitute particularly attractive photoinitiator systems for curing pigmented systems. Some of these diaryliodonium have a tendency to form low levels of odorous by products which make them less attractive for food packaging applications, unless some process steps, e.g. post-baking or hot air exposure can help getting rid of the volatile compounds.

Several developments have been carried out to come up with new types of sulfonium salts, where the incorporation of cyclic structures into the molecule results in reducing dramatically the number of cleavage by-products from the photolysis, as well as the toxicity of these by-products. One important class of these new sulfonium salts is constituted by the alkylphenacyl-sulfonium salts ⁽⁵⁾, but no product of this class has been commercialized as yet. One particular type of sulfonium salt that contains cyclic structures is currently being

introduced on the market by Lamberti. Its interesting characteristics and performance will be reported shortly ⁽⁶⁾.

Another class of cyclic sulfonium salts has been presented ⁽⁷⁾ at the last Conference organized by RadTech Europe; some structures from this category of cationic photoinitiators look particularly interesting. These salts are thioxanthonium salts, which are actually obtained by means of a commercially viable route consisting of selectively oxidizing thioxanthenes to the sulfoxide. We have focused our attention on the most promising structure identified and made pre-commercial so far, which is presented on Figure 1.

Figure 1: 10-biphenyl-4-yl-2-isopropyl-9-oxo-9H-thioxanthen-10 ium-hexafluorophosphate or “so-called “Meerkat” photoinitiator.



As this has been proven by experimentation and reported ⁽⁷⁾, only two by-products can be generated from the photolysis of this cationic photoinitiator, which will be referred to as “**BPITX-PF₆**” in the rest of the paper: these by-products are isopropyl-thioxanthenone and biphenyl. The latter is actually an anti-fungicide food additive commonly used on citrus fruits; it is known as food additive “E-230” in Europe and “ASP-129” in the USA.

Reactive compounds

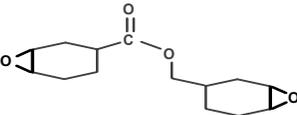
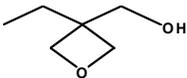
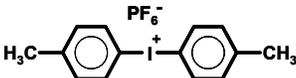
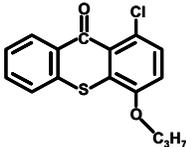
Several cationically-curing compounds have recently been developed. These include oxetane derivatives, in particular bis-[[1-ethyl-(3-oxetanyl)]-methyl]-ether, which exhibits very nice synergistic curing performance in combination with cycloaliphatic-diepoxide ⁽⁸⁾. New cycloaliphatic-diepoxides have also been recently developed; one of these has been found ⁽⁹⁾ to provide excellent toughness to typical cationic UV-curing metal coatings; another one was developed to provide higher curing rate than the standard cycloaliphatic-diepoxide (ECC) and has been found to also provide excellent adhesion to a variety of difficult metal substrates.

B- EXPERIMENTAL

Formulation ingredients:

Table I shows the reactive components used in the formulations. The primary component of the formulas is the 3,4-Epoxy-cyclohexylmethyl-3',4'-epoxy-cyclohexane-carboxylate (**ECC**). 3-ethyl-3-hydroxymethyl-oxetane (**EHMO**) is used primarily as reactive diluent for ECC, but also as a source of hydroxyl. The commercial solid form of ditoluyliodonium-hexafluorophosphate (**DTI-PF₆**) is used as cationic photoinitiator in the reference ink formula together with chloropropoxy-thioxanthone (**CPTX**) as photosensitizer.

Table I: Materials used in the formulations.

Notation	Structure
ECC (a)	
EHMO (b)	
DTI-PF ₆ (c)	
CPTX (d)	

(a): CYRACURE UVR-6105 Cycloaliphatic Epoxide Resin (Dow)
 (b): CYRACURE UVR-6000 Oxetane Diluent (Dow)
 (c): C-440 (IGM)
 (c): Speedcure CPTX (Lambson)

The pigments used in the inks are the following:

- (i)- 1 yellow pigment: **Yellow** = Sunbrite Yellow 13 / 275-0049 (Sun Chemical);
- (ii)- 1 cyan pigment: **Blue** = Irgalite Blue GLVO (Ciba Specialties);
- (iii)- 1 black pigment: **Black** = Special Black 250 (Degussa).

The following acrylic copolymer is used as leveling additive (“**Lev-Add**”) in the inks: Byk-361 (Byk Chemie).

The inks have been prepared as follows: for all the ink formula, the amount of ECC was mixed together with 10wt.% of EHMO (same level in all the inks) before adding the solid photoinitiators or/and photosensitizer. In the case of the iodonium salt, 2 wt.% of DTI-PF₆ was used together with 0.5 wt.% of CPTX. The sulfonium salt BPITX-PF₆ was used at a level of 4 wt.% as a solid. The mixture was never warmed up to facilitate the dissolution of these solid materials; only 4 wt.% of propylene-carbonate (“PropCarb”) was added to help the dissolution, except when the photoinitiator was previously dissolved into propylene-carbonate. The agitation (at room temperature) was maintained until a clear solution was obtained. The pigment was then added to the solution, mixed and finally grinded by means of a triple-roll-mill.

Inks application and testing

- Inks were applied onto soft (annealed) aluminum (50 μm thick) by the draw-down technique, using the “K-bar” (or wire rod) #0 to evaluate properties at a thickness of approximately 4 μm . The surface of the substrate was cleaned with iso-propyl-alcohol and air-dried prior to application. Coated substrates were then placed on a conveyor belt running under an UV unit at a speed that could be adjusted from 10 up to 200 m/min. The UV curing unit used throughout this study consisted of one standard microwave powered lamp “F-450” from Fusion UV Systems, which is fitted with an H-bulb operated at approx. 120 W/cm.
- The curing of the inks was assessed by applying a thumb twist pressure on the ink as soon as it was exiting the UV unit. The maximum conveyor belt speed at which the ink was not affected by the thumb twist was recorded as the cure rate (expressed in m/min.) of the coating or the ink.
- Whenever it is reported, the UV dose (mJ/cm^2) was measured by means of a "CON-TROL-CURE[®] Compact Radiometer" from UV Process Supply (USA).
- The MEK (2-butanone) resistance was determined the usual way by rubbing (with minimum pressure) the surface of the cured coating or ink with cotton swabs impregnated with MEK until the film was affected and started to be removed. It was expressed as the number of “double-rubs” required getting to this point, with a maximum of 100 double-rubs. Generally, this MEK resistance test was carried out at various times following the exposure of the film to UV light in order to follow up the progression of the so-called dark cure process.

C- RESULTS AND DISCUSSION

The performance of the new cationic photoinitiator “BPITX-PF₆” has been evaluated in various colored low viscosity inks.

Performance in yellow inks

The solid BPITX-PF₆ sulfonium salt was found to be very difficult to dissolve in the ECC/EHMO(10%)/PropCarb (4%) mixture at ambient temperature. Although most but not all the salt was dissolved in the mixture after several hours of mixing, it was decided to go ahead with the pigment grinding operation, thinking that the grinding would complete the dissolution, or at least the fine dispersion, of the photoinitiator in the ink.

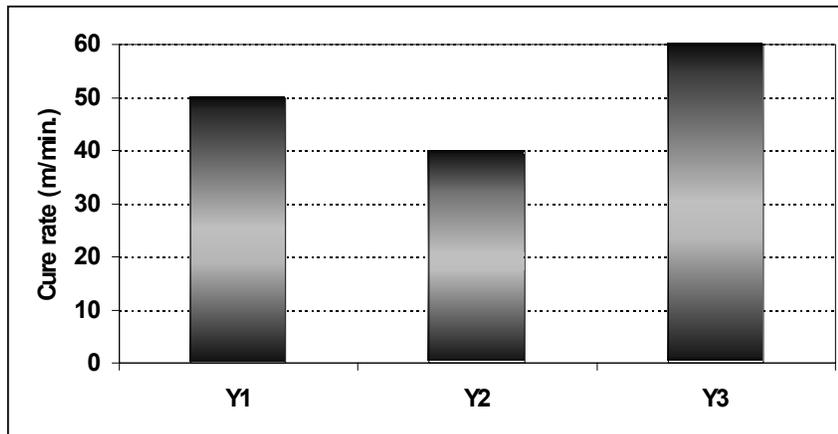
As a consequence, we decided to try to incorporate this photoinitiator as a solution into the formulation. We used propylene-carbonate to dissolve it, but did not try to heat the solution since we had no information about the heat stability of this photoinitiator. We found out that a clear solution of BPITX-PF₆ could be obtained at ambient temperature at only 23 wt.% solids in propylene-carbonate. Although the solids content was low, we nevertheless used this solution to prepare the yellow ink Y3.

Table I: Cationic UV-curable yellow inks formula

Ingredients	Formula Y1	Formula Y2	Formula Y3
ECC	70.0	66.5	57.1
EHMO	10.0	10.0	10.0
Yellow	15.0	15.0	15.0
DTI-PF ₆	2.0		
CPTX	0.5		
BPITX-PF ₆		4.0	
BPITX-PF ₆ solution (23% in Prop.Carb.)			17.4
PropCarb	2.0	4.0	
Level. Add.	0.5	0.5	0.5

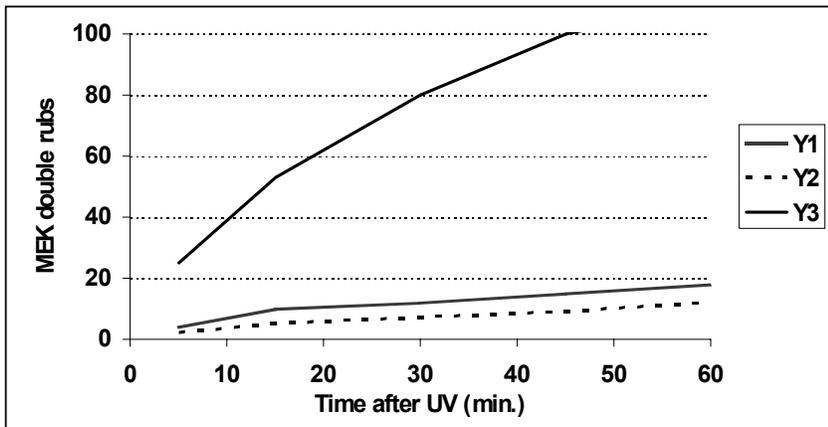
The cure rates of the ink formula detailed in Table I are shown on the graph of Figure 2.

Figure 2: Cure rate of the cationic yellow inks formula



The results of Figure 2 show that the reactivity achieved with the new sulfonium salt are highly dependent on how well the product is dissolved in the binder of the ink. In addition they show that it can lead to higher cure rate than the reference photoinitiator system when it is properly dispersed in the ink. As this is clearly illustrated by the results of Figure 3, this new sulfonium salt exhibits a very high reactivity in the ink when it is very well dissolved; in this condition, it exhibits a significantly higher efficiency than the reference photoinitiator system.

Figure 3: Evolution of the cross-linking of the cationic yellow inks formula cured under 1 H-bulb (120 W/cm) at a belt speed of 50 m/min. (95 mJ/cm²).



Performance in the blue and black inks

On the basis of the results obtained for the yellow inks, we decided to carry out a similar evaluation of the photoinitiators in the blue and black inks. Using the selected blue and black pigments respectively, in replacement (same level) of the yellow pigment, we prepared the ink formula “B1” and “Bk1” similar to the reference formula “Y1” and ink formula “B2” and “Bk3” similar to the test formula “Y3”.

The results achieved in terms of cure rate and evolution of the cross-linking (MEK resistance) are reported on the graphs of the Figures 4 and 5 respectively.

Similarly to what was observed in the yellow inks, the new cationic photoinitiator “BPITX-PF₆” leads to higher reactivity than the sensitized iodonium salt, which was selected as a reference in this study. Higher cure rates have been recorded in both the blue and black inks. A better cross-linking shortly after UV exposure is also achieved with this new photoinitiator, although the difference is more significant with the blue pigment rather than with the black pigment.

In addition, it was visually noticeable that the cured films obtained with the inks “Y3”, “B2” and “Bk2” exhibited higher color strength and also higher gloss. It is not clear, at this point in time, whether this should be attributed to the better reactivity and polymerization of the film, or to the better dispersion of the pigment resulting from the higher concentration of propylene-carbonate.

Figure 4: Cure rate of the cationic blue and black inks formula

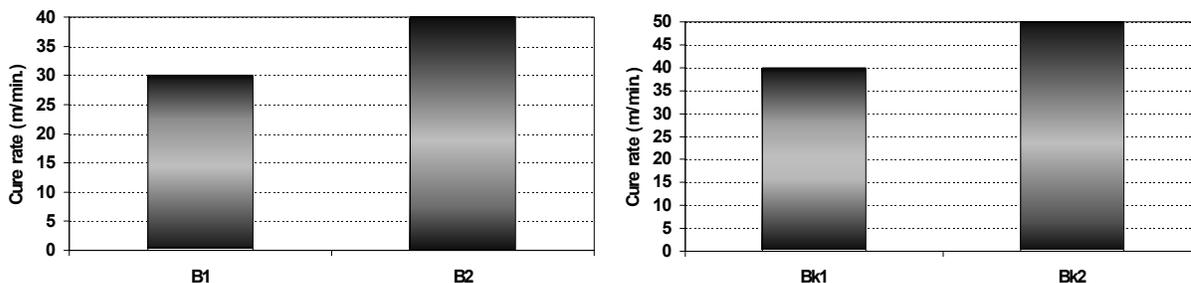
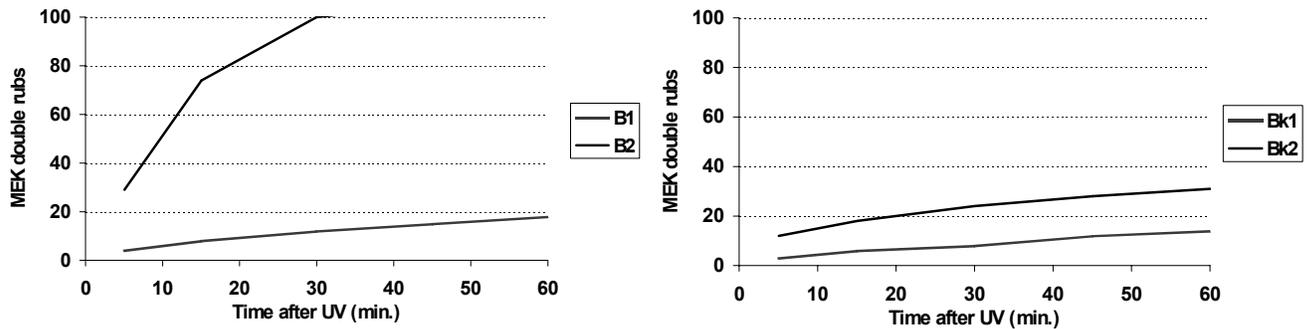


Figure 5: Evolution of the cross-linking of the cationic blue and black inks formula cured under 1 H-bulb (120 W/cm) at a belt speed of 40 m/min. (120 mJ/cm²).



Solubility of “BPITX-PF₆”

Other attempts of putting this material into solution have been carried out because it was not satisfactory from a formulation standpoint to use the low solids content solution of BPITX-PF6 in propylene-carbonate, which we know from past experience will remain in the cured film as propylene-carbonate, at least most of it.

The new cationic photoinitiator “BPITX-PF₆” is actually highly heat-stable; we therefore took advantage of this feature to prepare solution of this material in various media. The following combinations have been identified to give stable clear solution of the product at ambient temperature:

- 10 BPITX-PF6 / 5 PropCarb / 85 ECC; solution heated and mixed at 70-75°C.
- 20 BPITX-PF6 / 25 PropCarb / 55 ECC; solution heated and mixed at 75-80°C.

Depending on how much propylene-carbonate could be tolerated, these combinations constitute examples of solutions that will make easier the incorporation of the photoinitiator into an ink formulation, while making sure it is well dissolved without adding too much of non-reactive diluent.

SUMMARY

This study confirms that the new thioxanthonium salt “BPITX-PF6” exhibits better performance in curing model cationic flexo inks based on cycloaliphatic-diepoxides, as compared to a photo-sensitized iodonium salt used as a reference system. Faster cure rates and significantly higher cross-linking can be achieved in inks with this new cationic photoinitiator. In addition, the facts that no odor was detected in the experiments, and that its photolysis can lead to the release of only 2 well-known by-products, make this material a very attractive cationic photoinitiator, especially for very sensitive applications, such as the decoration of food packaging. Results from our investigation show that it is essential that it is perfectly dissolved into the binder to get the highest curing efficiency. The poor solubility of this material at ambient temperature is somewhat compensated by its high heat stability, which allow the use of heat to put it into solution. A couple of combinations have been identified to make stable solutions of this new cationic photoinitiator into cationically-reactive materials, such as the standard cycloaliphatic-diepoxide “ECC”.

This new material is a nice addition to the range of cationic photoinitiators that are now available to the formulators. There are now several commercially available molecules, as well as some developmental structures, in the family of iodonium salts that offer the advantage of being easily sensitized, and another interesting cyclic sulfonium salt⁽⁶⁾ will soon be commercially available. All together, these products will contribute to further expand the use of cationic UV-curing systems, especially into pigmented coatings and inks.

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