

USE OF NEW PHOTOINITIATORS IN GRAPHIC ARTS

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INTRODUCTION

More than ever, the printers of today are required to increase productivity and line speeds while simultaneously reducing their VOC's and improving the quality of their product. Utilizing energy curable technology can satisfy these tougher requirements.

The cure speed of a UV ink formulation is dependent upon many factors such as the monomer and oligomer package, the type and power of the lamp, the substrate, and of course the choice of photoinitiator or combination of photoinitiators. These reactive species are key components in any UV formula and their selection must be carefully done to obtain the intended results. Because many existing commercial photoinitiators did not fully satisfy the requirements of the formulators and end users, Lamberti has developed two novel photoinitiators to help meet the changing UV ink and OPV market needs ^{i,ii}.

While typical requirements for a photoinitiator in an OPV formulation might only include high reactivity with low post cure yellowing, the requirements for an ink formulation are far more challenging as the photoinitiators must also compete with the pigments for the absorption of the light. This typically leads to the use of photoinitiator "cocktails." These combinations of photoinitiators are carefully selected based on their individual absorption in order to produce just the right amount of both surface and through cure. One characteristic that is becoming increasingly important is the migratability of these photoinitiators from the cured ink and coating films to comply with the requirements of food packaging applicationsⁱⁱⁱ. Solving this problem could greatly increase the penetration of UV technology in graphic arts. This paper deals with the use of two new photoinitiators, in both clear OPV's and dark, heavily pigmented black and cyan inks that are suitable for both flexo and offset applications.

EXPERIMENTAL

OPV Formulations:

Clear coatings were prepared and applied on a paperboard substrate using a wire wound rod to obtain a coat weight of 6 g/m². The formulas and properties tested are below:

Clear Formulas		
	Formula 1	Formula 2
Epoxy acrylate	38.5	---
Aromatic urethane acrylate	9.9	---
Amine modified polyether acrylate	---	100
TPGDA	50.6	---
Wetting agent	1.0	---

Photoinitiators were then top added to each formula at 4% and tested. The formulas containing Esacure 1001M were also supplemented with 4% amino acrylate.

Test	Test Method
Tack Free Time (TFT)	Recorded as the fastest belt speed in which tack free films were generated.
Yellowness and Whiteness Index:	Measured using a BYK Color-Guide 45/0 (Measured at TFT minus 30%)
Gloss:	Measured using a BYK Micro-TRI-Gloss Meter (Measured at TFT minus 30%)
Odor:	Odor is tested on the cured film by a panel of 5 trained volunteers after conditioning for 60 minutes at 60°C. The rating is based on a scale of 0-5 with 0 be lowest odor.
Migration:	Migration is tested by placing 0.58 dm ² of cured film into 200 ml of 95% ethanol. Samples are then conditioned for 10 days at 40°C. Migration is then measured by a validated HPLC method.

Flexo Inks:

Flexo inks were prepared and applied on a paperboard substrate using IGT model C1 Printability Tester to obtain a film weight of 5 g/m² (~5 microns).

Flexo Ink Formulas		
	Cyan	Black
Polyester acrylate	38.1	39.3
Ethoxylated PETA	30.5	31.0
Pigment	23.3	23.3
Additive Package*	8.1	6.4

* Dispersant, wetting agent, defoamer and wax.

Photoinitiators were then top added to each formula at the levels indicated.

Test	Test Method
Through Cure:	Recorded as the fastest belt speed in which the film passes the thumb twist test
Gloss:	Measured using a BYK Micro-TRI-Gloss Meter
Solvent Resistance:	Measured as number of rubs using the reported solvent
Odor:	Odor is tested on the cured film by a panel of 5 trained volunteers after conditioning for 60 minutes at 60°C. The rating is based on a scale of 0-5 with 0 be lowest odor.

Gloss and solvent resistance tested after 12 hours.

Offset Inks:

Offset inks were prepared and applied on a paperboard substrate using IGT model C1 Printability Tester to obtain a film weight of 3 g/m² (~3 microns).

Offset Ink Formulas		
	Magenta	Cyan
Epoxy acrylate	31.0	31.0
Aromatic urethane acrylate	8.0	8.0
TMPTA	40.0	40.0
Pigment	18.0	18.0
Additive Package*	3.0	3.0

* Dispersant, wetting agent, defoamer and wax.

Photoinitiators were then top added to each formula at 3% and tested. The formulas containing Esacure 1001M were also supplemented with 2.25% Esacure EDB.

Test	Test Method
Through Cure:	Recorded as the fastest belt speed in which the film passes the thumb twist test
Gloss:	Measured using a BYK Micro-TRI-Gloss Meter
Solvent Resistance:	Measured as number of rubs using the reported solvent
Odor:	Odor is tested on the cured film by a panel of 5 trained volunteers after conditioning for 60 minutes at 60°C. The rating is based on a scale of 0-5 with 0 be lowest odor.

Gloss and solvent resistance tested after 12 hours.

Curing:

All samples were cured using a Fusion UV Curing System using a 400 W/in medium pressure Hg lamp unless noted otherwise. Experiments were carried out in both air and N₂ atmospheres.

RESULTS

OPV Formulations

Formula (1) was prepared using both Esacure 1001M (A) and Esacure ONE (B). The results of the tests performed are reported in figures 1 & 2. Curing was carried out in air and under N₂.

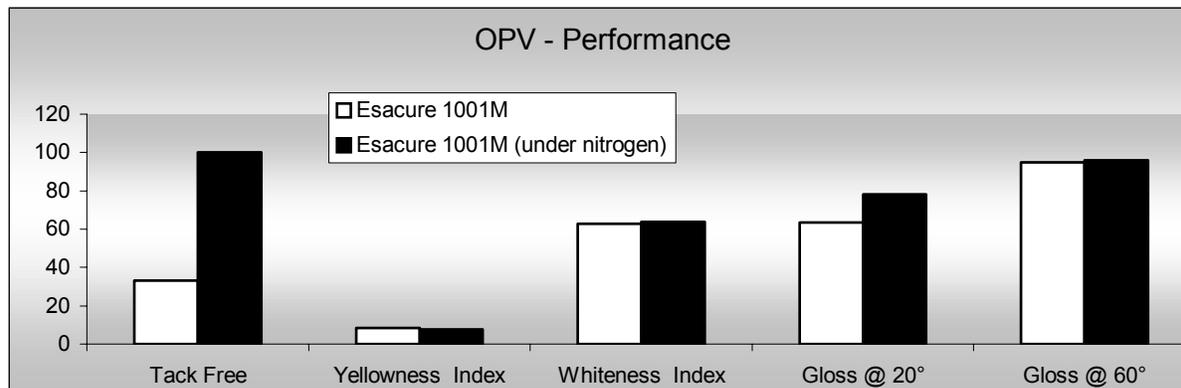


Fig.1 – OPV Performance – photoinitiator concentration 4%, formulation 1

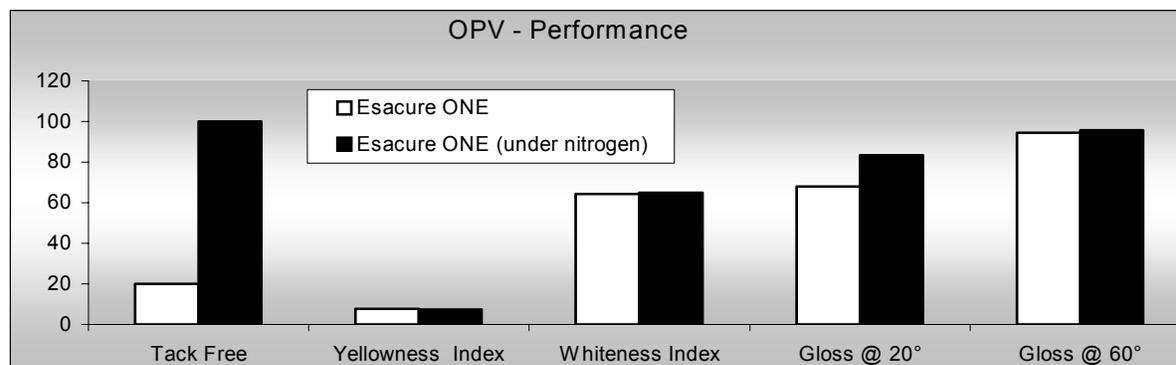


Fig.2 – OPV Performance – photoinitiator concentration 4%, formulation 1

The reactivity of Esacure 1001M is slightly better than Esacure ONE in the presence of oxygen. This is due in part to the scavenging effect of the amine on the oxygen but also because Esacure 1001M can better exploit the emission of the lamp^{iv}. Surprisingly, the formulation containing Esacure 1001M with amine has no real negative effect on post cure yellowing^v.

As expected, the absence of oxygen in the curing process strongly enhances the reactivity of both systems to allow line speeds 4 to 5 times higher than in the presence of O₂.

Migratability

Migratability refers to the release of the photoinitiator from the cured films when they are in contact with simulating fluids. In the tests conducted here, we measured the release of Esacure 1001M and Esacure ONE from the cured films produced from formulations 1 and 2 while at varying photoinitiator concentrations. In this case, the simulating fluid was a 95% ethanol solution as reported in the experimental section. The tests were conducted in both air and nitrogen atmospheres both with and without the presence of 2% amino acrylate. The results are shown in tables I and II.

Table I – Migration of Esacure 1001M (A) from cured OPV films in EtOH 95% at 40°C for 10 days.

Formulation	PI (A) Concentration	Amine Co-Initiator	Conditions	Conc. of (A) in EtOH 95% (ppb)
1	2%	None	N2 @ 15m/min	< 40
		None	Air @ 15 m/min	< 40
		2%	Air @ 15 m/min	< 40
2	2%	None	N2 @ 15m/min	< 40
		None	Air @ 15 m/min	< 40
		2%	Air @ 15 m/min	< 40

Table II – Migration of Esacure ONE (B) from cured OPV films in EtOH 95% at 40°C for 10 days.

Formulation	PI (B) Concentration	Conditions	Conc. of (B) in EtOH 95% (ppb)
1	2%	Air @ 15 m/min	< 40
	4%		< 40
	2%	N2 @ 15m/min	< 40
	4%		< 40
2	2%	Air @ 15 m/min	< 40
	4%		< 40
	2%	N2 @ 15m/min	< 40
	4%		< 40

The results show the specific migration of both photoinitiators was always below 40 ppb. Because we see such low levels of migration under such harsh conditions (EtOH 95% at 40°C for 10 days), we feel this is a strong indication for the low potential of these materials to be released from the cured films.

Odor has been evaluated as reported in the experimental part. The results are reported in table III.

Table III – Odor evaluation of Esacure 1001M (A) and Esacure ONE (B) from OPV cured films

Formulation	PI and Concentration	Condition	Odor
1	(A) at 4%	Air @ 15 m/min	0
	(B) at 4%		0

0 = no odor, 5 = very intense odor

The results clearly show that neither of the photoinitiators release any post cure odor. It is noteworthy that even though Esacure 1001M contains a sulfur atom in the structure, there is still no odor due to the photodecomposition profile of the product, which does not entail any cleavage of the C-S bond^{vi}.

FLEXO INKS

The two generic flexo formulations that were detailed in the experimental section of this paper were used for the studies of the black and cyan flexo inks. Two types of photoinitiator combinations have been considered: photoinitiators with a low potential of migration for special applications (like food packaging) and a more conventional combination to satisfy less demanding market applications.

Cyan Flexo Ink PI Packages				
	Blend 1	Blend 2	Blend 3	Blend 4
Esacure 1001M	3.5%	3.5%	3.5%	3.5%
Esacure One	----	3.0%	----	3.0%
Esacure KS 300	3.0%	----	----	----
Esacure TZT	1.0%	1.0%	3.5%	----
Esacure ITX	0.5%	0.5%	0.5%	----
Acrylated Amine	5.0%	5.0%	5.0%	3.0%

The results of the cyan flexo ink evaluations are reported in Figure 3.

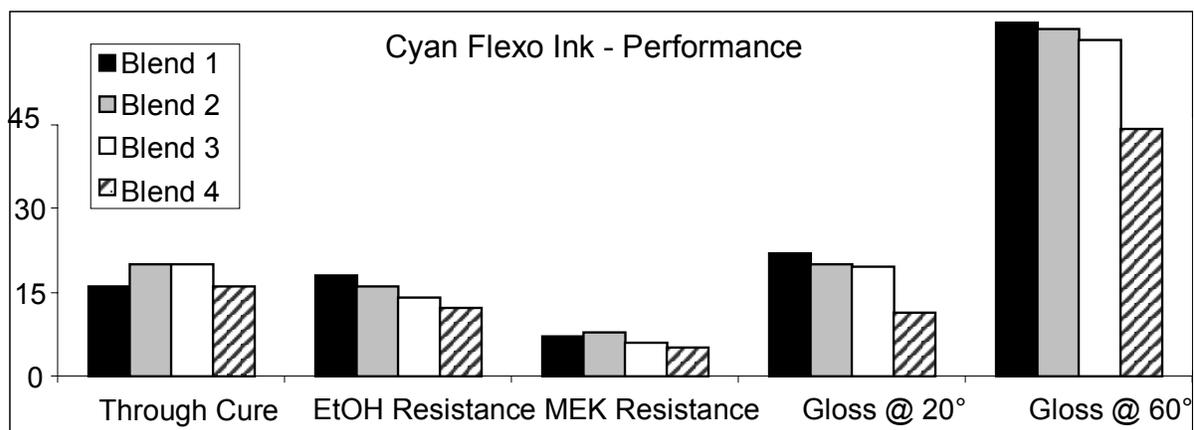


Fig.3 – Performance of different photoinitiator packages in a cyan flexo ink.

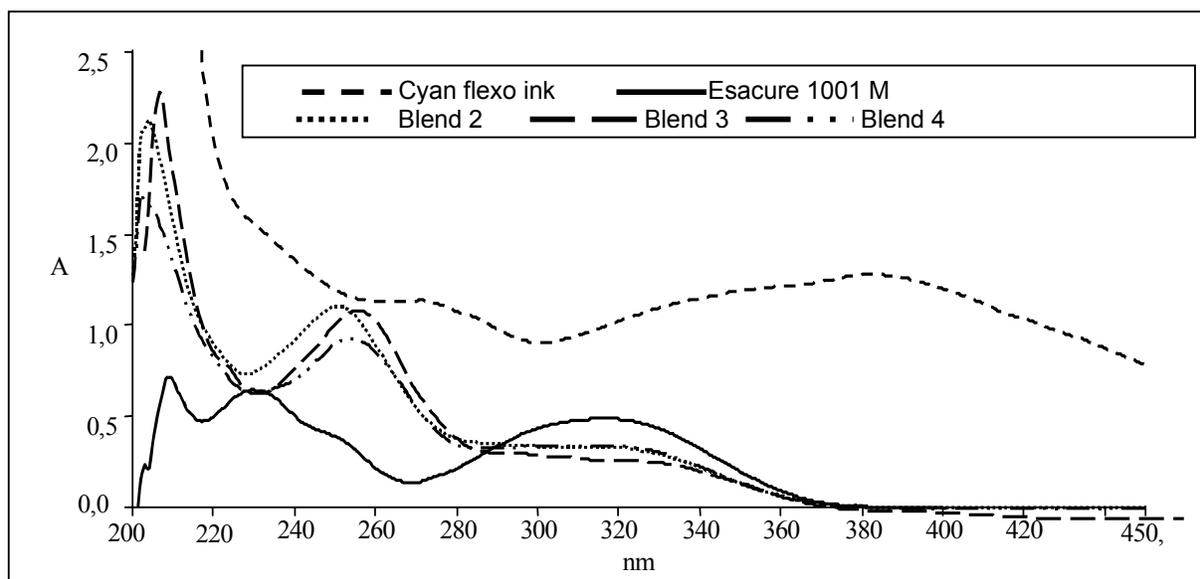


Fig.4 – Absorption spectra of: a) cyan flexo ink without PI, b) Esacure 1001M and c) blend 2,3,4

As reported in figure 3, the best performance was obtained in presence of the difunctional α -hydroxy ketone and of the eutectic mixture of benzophenone derivatives (Blend 2). The complete substitution of α -hydroxy ketone with an increase of concentration of benzophenone derivatives (Blend 3) keeps the through cure but reduces the solvent resistance. The formulation without any benzophenone derivatives (Blend 4) gives the poorest performance but would be expected to be free of migration.

The UV absorption spectra of each blend (figure 4) are very similar except for the absorption at 260 nm. It is likely that not only the absorption profile is the driving force for the performance, but also a possible synergistic effect among the photoinitiators is occurring.

Black Flexo Ink PI Packages				
	Blend XX	Blend HH	Blend JJ	Blend ZZ
Esacure 1001M	3.5%	3.5%	3.5%	3.5%
Esacure KT55	3.0%	3.0%	3.0%	----
Esacure KB1 (BDK)	3.0%	6.0%	----	----
Esacure TZT	----	----	----	3.0%
Acrylated Amine	4.0%	4.0%	4.0%	4.0%

The results of the black flexo ink evaluations are reported in Figure 5.

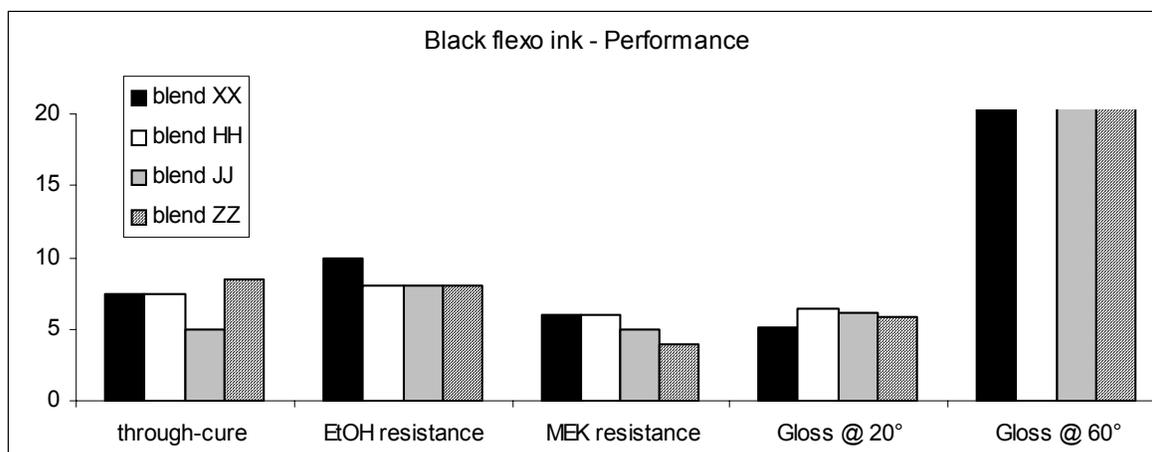


Fig. 5 – Performance of different packages of photoinitiators in a black flexo ink.

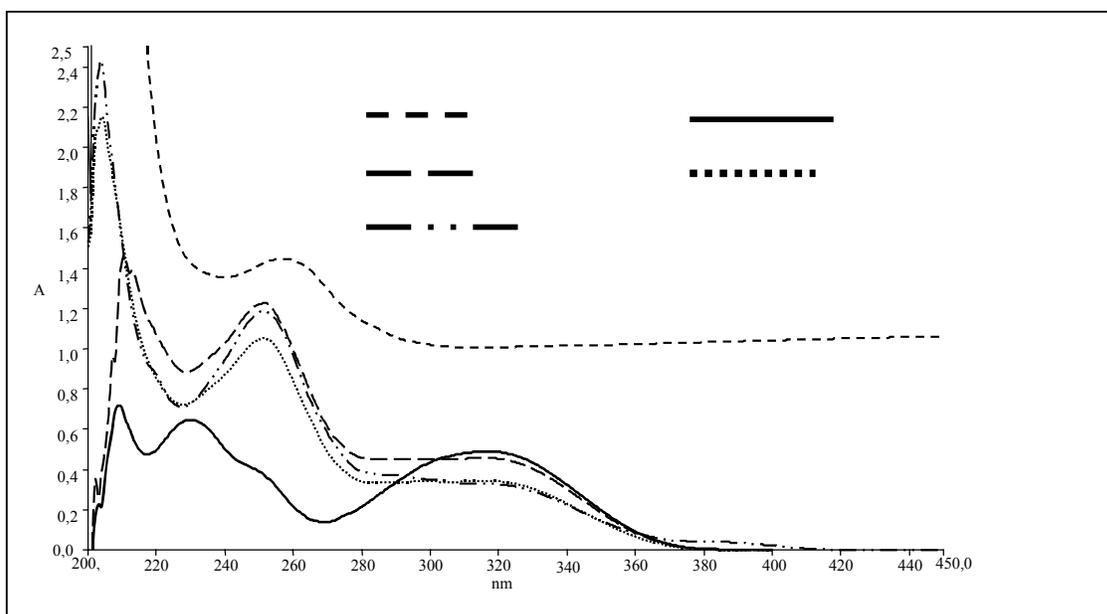


Fig.6 – Absorption spectra of: a) black flexo ink without PI, b) Esacure 1001M and c) blends XX, JJ, ZZ

Again in this case, the best performance was observed in presence of the eutectic mixture of benzophenone derivatives. To obtain a good compromise between through cure and the other characteristics, the addition of benzildimethylketal (BDK) and a α -hydroxy ketone is very helpful. It should be noted that this blend is not suitable for special applications due to the migratability of the two added components. The addition of BDK does not seem to significantly affect the UV-vis absorption profile of the blend of photoinitiators (Fig.6) however its presence does help to obtain a balanced effect of through cure and solvent resistance.

For high tech applications /special applications such as food packaging, different blends of photoinitiators are required to cure black flexo inks.

Special Black Ink PI Packages				
	Blend A	Blend B	Blend C	Blend D
Esacure 1001M	3.5%	6.0%	3.0%	3.0%
Esacure ONE		----	3.0%	6.0%
Acrylated Amine	2.5%	4.5%	3.0%	3.0%

The results are reported in figure 7.

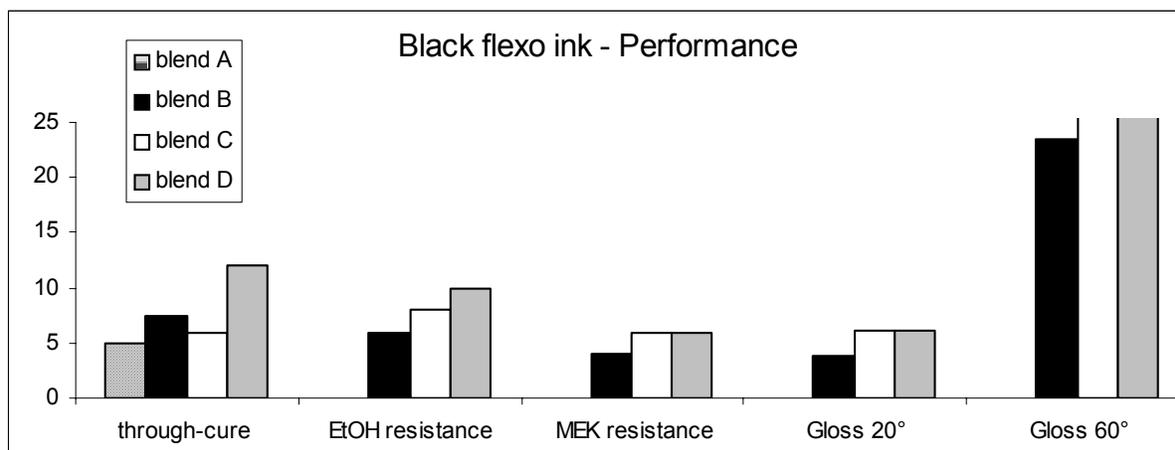


Fig.7 – Performance of different packages of photoinitiators in black flexo inks

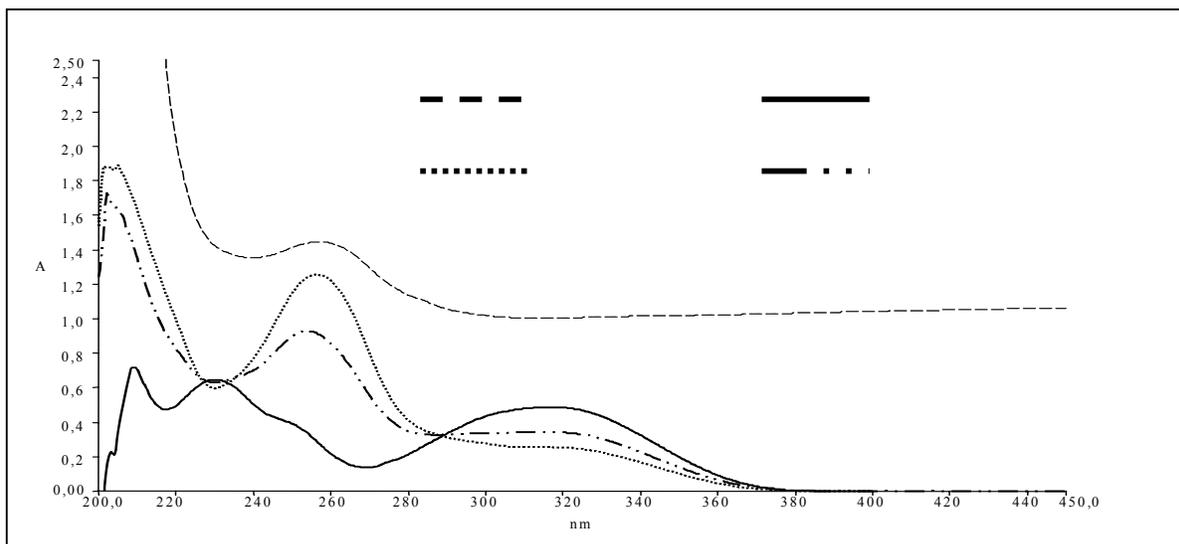


Fig.8 – Absorption spectra of: a) black flexo ink without PI, b) Esacure 1001M and c) blends C, D

In this challenging ink, Esacure 1001M in combination with an amino acrylate shows good reactivity. However, the best performance was obtained when we added the difunctional α -hydroxyketone Esacure ONE to the formula, specifically when its concentration was set at 6%. The UV spectra of this blend (fig.8) shows that not only is the absorption at high wavelengths (320 nm) important in curing black ink, but it is also necessary to have good absorption in the region of 260 nm which corresponds to the maximum absorption of Esacure ONE.

Post cure odor was measured on the flexo inks as reported in the experimental section. The results are reported in table IV.

Table IV – Odor evaluations from cured ink formulations

Ink Formulation	Photoinitiator Blend	Post Cure Odor
Cyan Flexo ink	Blend 2	1
Black Flexo ink	Blend XX	2
Black Flexo ink	Blend D	0

0 = no odor, 5 = very intense odor

The results clearly show that when only Esacure 1001M and Esacure ONE are combined in an ink formulation, no release of any significant post cure odor occurs. The presence of BDK clearly increases the post cure odor of the formulation.

OFF-SET INKS (cyan and magenta)

The generic offset formulation that was detailed in the experimental section of this paper has been used for the studies of magenta and cyan offset ink. The results obtained with these compositions are reported in figure 9.

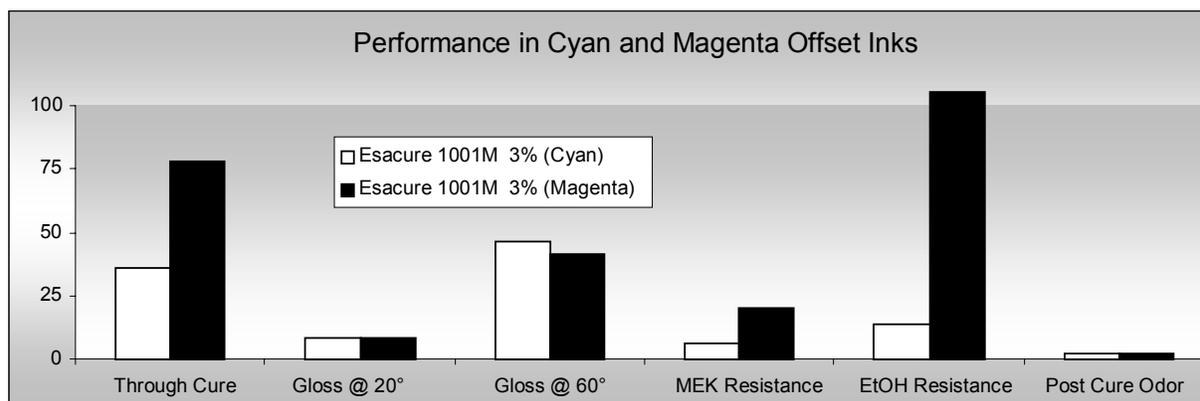


Fig. 9 – Performance of Esacure 1001M (with additional 2.25% EDB) in cyan and magenta offset inks.

The results obtained with magenta ink are more favorable than with the cyan ink and is easily explained by the difference of transmission windows between the two inks. Nevertheless, with a very difficult ink to cure such as cyan, Esacure 1001M has very good performance due to its favorable UV absorption profile. As reported above, the post cure odor of these inks is negligible due to the photodecomposition profile of Esacure 1001M.

CONCLUSIONS

The new photoinitiators Esacure 1001M and Esacure ONE show very promising results in different graphic arts applications. They can be used for OPV as well as for curing heavily pigmented ink systems.

In the pigmented formulations, blending the two photoinitiators allows us to obtain good through-cure results while meeting the other characteristics required in graphic arts applications. The combination of these photoinitiators is also suitable for high tech applications due to their low migratability. Another important advantage of these photoinitiators is the low level of post cure odor released. The relatively high molecular weight of these materials is likely the reason for their low tendency to migrate from cured films when they are in contact with even very aggressive simulating fluids such as 95% EtOH. These results can open the door to the development of formulations suitable for food packaging applications thus allowing an increased penetration of energy curing technology in graphic arts.

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