

A NOVEL DI-FUNCTIONAL HIGH MOLECULAR WEIGHT CO-INITIATOR

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INTRODUCTION

Co-initiators are a critical component of many UV curable formulations, especially in printing inks and thin film weight coatings for their activities as oxygen scavengers and as hydrogen donors when combined with type II photoinitiators.

Both UV curable inks and OPV's play a large role in the development of various types of food packaging materials. One of the critical issues regarding food packaging applications is the potential migration of the ink and coating components, including both the photoinitiators and the co-initiators into the foodstuff. The migration of the photoinitiators has been largely overcome by the development of di-functional photoinitiators, while co-initiators have remained a matter of risk for their migration characteristics. For this purpose we have developed a novel di-functional high molecular weight amine co-initiator. It is characterized by high reactivity, low yellowing and low odor properties. This novel co-initiator also shows very low migration tendencies in a variety of simulating fluids upon curing into a film. The combination of this new di-functional co-initiator along with existing di-functional photoinitiators offer new solutions for the use of UV curable technology in food packaging applications.

The UV spectrum is reported in figure 1 and its trade name is Esacure A-198 (I).

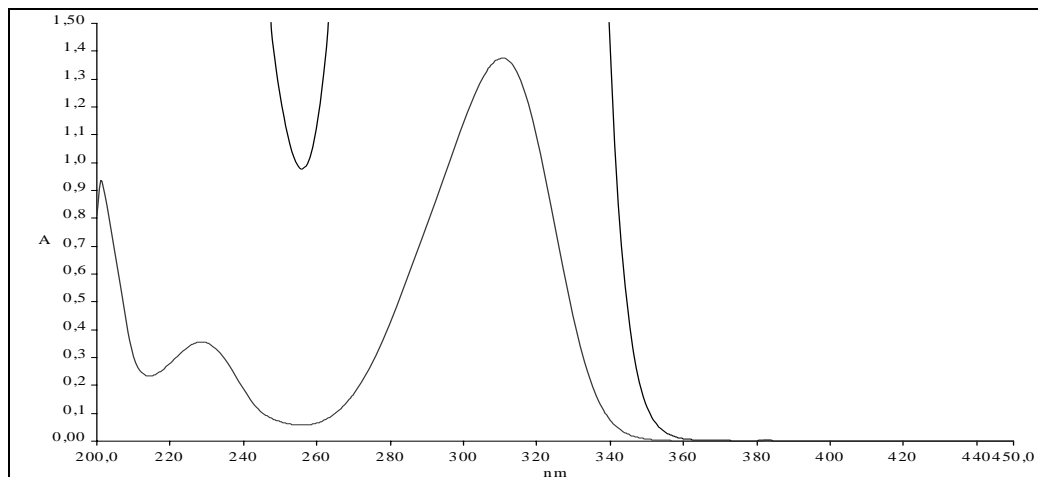


Figure 1. UV spectrum of the di-functional co-initiator Esacure A-198 (I)

EXPERIMENTAL

OPV Formulation

Clear coatings were prepared and applied on a paperboard substrate using a wire wound rod to obtain a coat weight of 12 g/m². The base formula is listed below:

Clear Base Formula	
Epoxy acrylate	40
TMPTA	30
GPTA	30

Formula 1:

Photoinitiator Esacure TZT (V) was top added to the clear base formula at 5%. We then supplemented the formula with 7% of A-198 (I), Esacure EDB (II) and Esacure EHA (III) as co-initiators for performance comparisons.

Test

Tack-free time (TFT) was recorded as the fastest belt speed in which tack free films were generated. Yellowness and whiteness index were measured using a BYK Color-guide 45/0. Solvent resistance was measured as the number of rubs using the reported solvents. Odor was tested on the cured film by a panel of 5 trained volunteers after conditioning at 60°C for 60 min. The rating is based on a scale of 0 to 5 with 0 being lowest in odor. For odor testing, the coatings were cured at TFT minus 30%. All samples were conditioned for 12 hours at room temperature in the dark before the testing.

Migration

Migration is tested by placing 0.58 dm² of cured film into 200 ml of a simulating fluid such as: 95% ethanol or 10% ethanol. Samples are then conditioned for 10 days at 40°C. Specific migration is then measured by a validated HPLC method. All samples were cured using a Fusion UV system apparatus equipped with a 300 W/in H-bulb in air.

Offset Inks

Offset ink formulations (lab and industrial) were applied onto a paperboard substrate using an IGT Reprotest model C1 Printability Tester to obtain a film weight of 3 g/m² (3μ). Through-cure (THC) is recorded as the fastest belt speed in which the film passes the thumb twist test. Solvent resistance was measured as number of rubs using the reported solvents (at THC minus 30%). Gloss at 20° and 60° were measured by a BYK Micro-TRI-Gloss meter (at THC minus 30%). All samples were conditioned for 12 hours at room temperature in the dark before testing. The lab cyan offset ink formula is listed below while the industrial formulas (cyan, magenta and black) must remain undisclosed.

Lab UV Cyan Offset Ink Formula	
Epoxy acrylate	31.0
Aromatic urethane acrylate	8.0
TMPTA	40.8
Pigment	18.0
Additive Package	2.2

Esacure 1001M (IV) was added to the formula at 3% and the samples were then supplemented with 3% of A-198 (I), EDB (II) or EHA (III) as co-initiators for performance comparisons.

Curing

All samples were cured using a Fusion UV system apparatus equipped with a 400 W/in H-bulb in air.

RESULTS

OPV formulation

Formula 1 was a blend containing photoinitiator (V) at 5% with the three different co-initiators (I), (II) or (III) at 7%. The results of the tests performed are reported in figures 2 and 3.

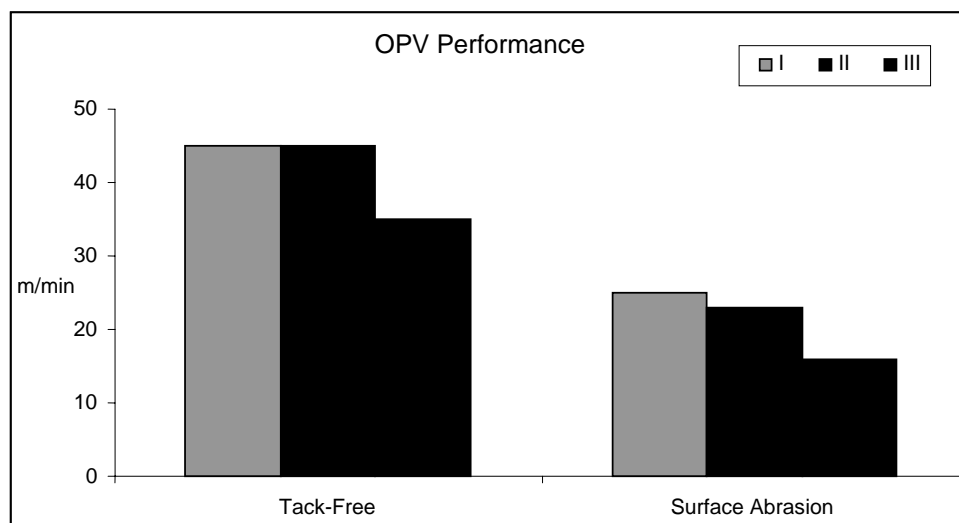


Figure 2. TFT and surface abrasion performance comparisons of (I) vs. (II) vs. (III) in formula 1

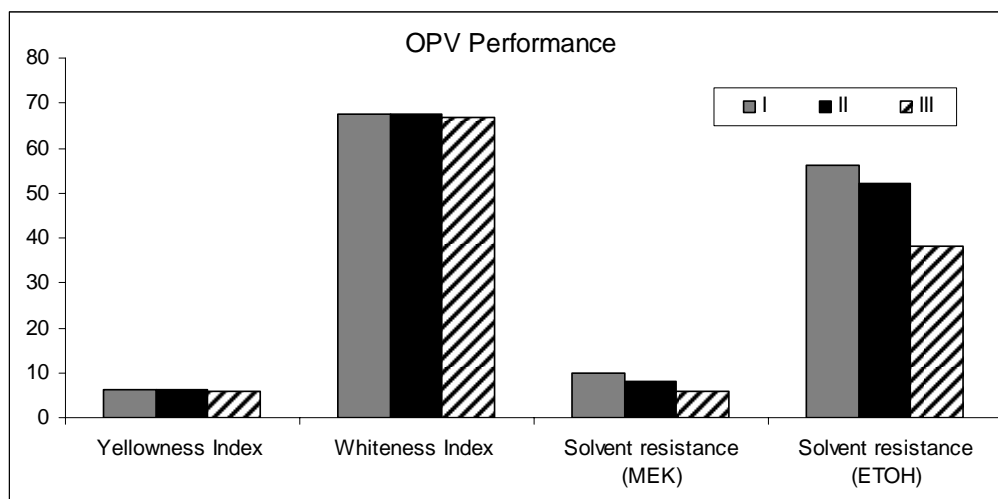


Figure 3. Yellowness and whiteness index along with solvent resistance comparisons of (I) vs. (II) and (III) in formula 1.

The new di-functional co-initiator (I) provides similar solvent resistance to (II) but clearly better than (III) as demonstrated in figure 3. The color stability is also comparable to those of (II) and

(III). These results clearly show that (I) provides very good physical properties and could easily be incorporated into commercial OPV applications.

Odor was also evaluated as reported in the experimental part. The results are reported in table 1.

Formula 1		
Initiators	Conditions	Odor
(I + IV)	Air @ TFC 30% minus	0
(II + IV)	Air @ TFC 30% minus	2
(III + IV)	Air @ TFC 30% minus	0

Table 1. Post cure odor comparison of (I), (II) & (III) in formula 1

The results clearly show that when (I+IV) are combined in a clear formulation, no significant release of post cure odor occurs.

Offset inks

Two generic formulations, one lab and one industrial, were used for the reactivity and migratability testing of cyan offset inks. Three different photoinitiator combinations were compared in the lab offset ink and two in the industrial ink. They all included 3% of the di-functional photoinitiator (IV) due to its low potential for migration in special applications such as food packaging along with 3% of each of the different co-initiators (I), (II) & (III).

The UV absorption spectra of each final UV Cyan lab offset ink is also represented in figure 5 while the results of all the performance testing are shown in figures 6 & 7.

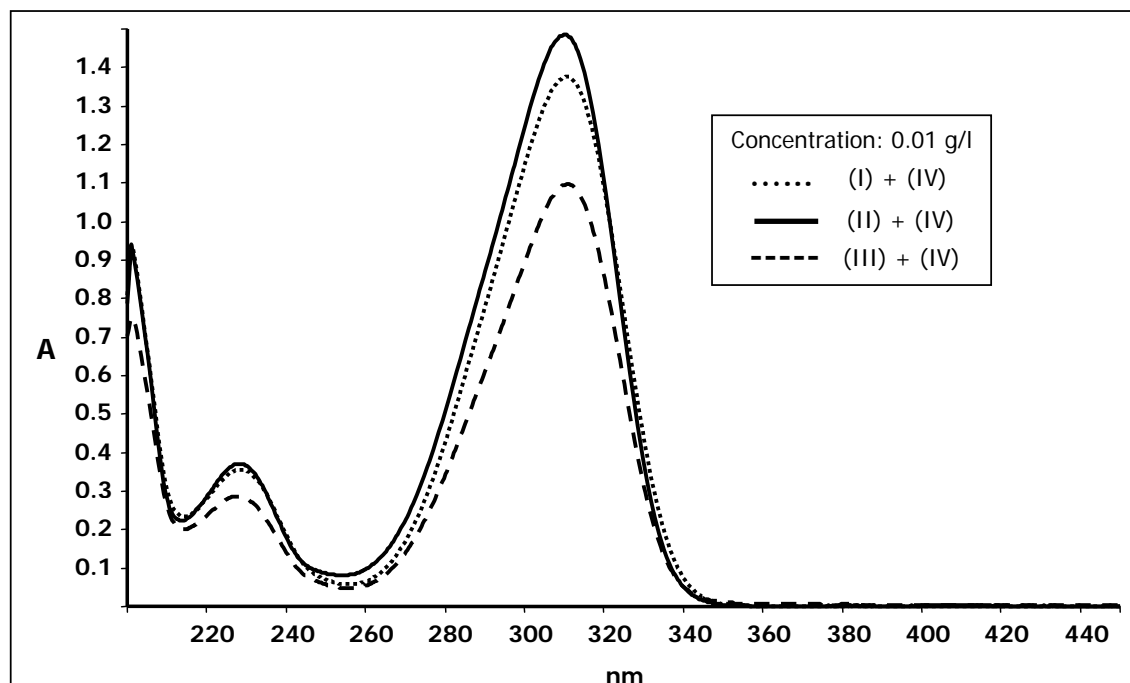


Figure 5. Absorption spectra of blend (I + IV) compared to (II + IV) and (III + IV) in a lab UV Cyan offset ink.

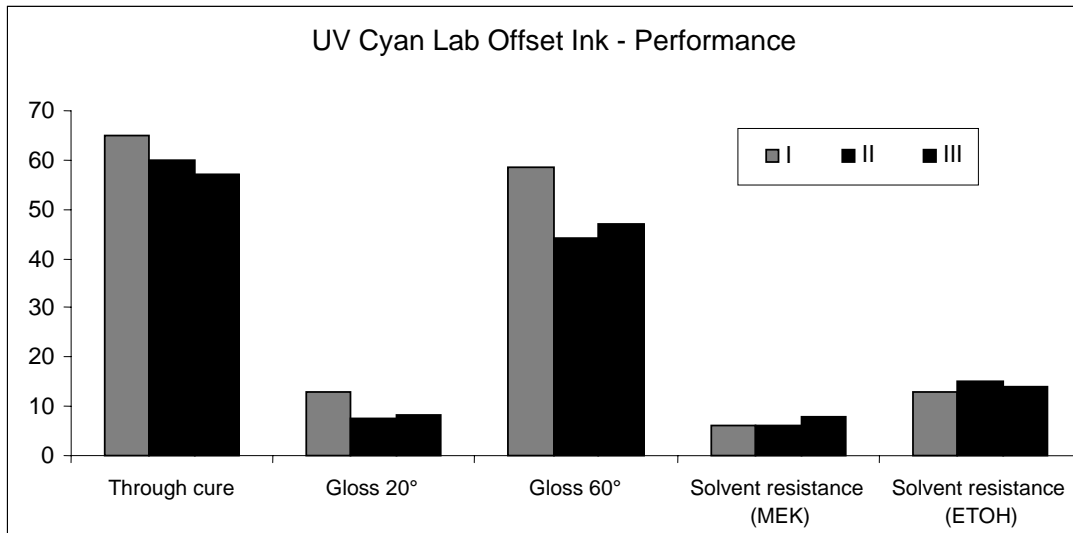


Figure 6. Performance of (I) in comparison with (II) and (III) in cyan lab offset ink.

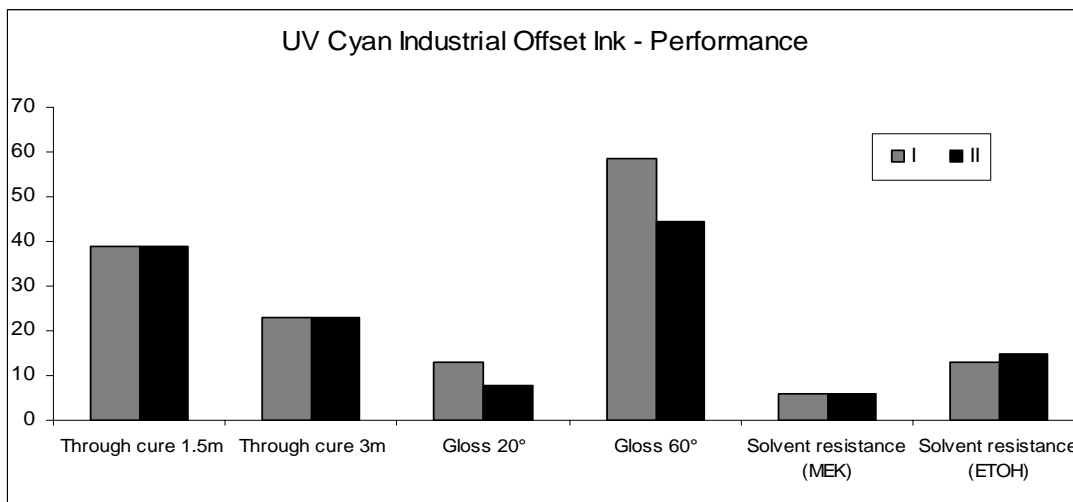


Figure 7. Performance comparison of (I) versus (II) in an industrial UV Cyan offset ink.

Migration

Migration refers to the release of the photoinitiator and/or co-initiator from the cured ink when in indirect contact with simulating fluids. In the tests conducted here, we measured the release of the photoinitiator and various co-initiators of the cured cyan lab offset ink films in reverse side conditions. Reverse side conditions are as follows: The surface of the cured ink is pressed onto a substrate for 10 days at room temperature under a pressure of 4 lbs/in². In this case, the simulating fluids were a 10% and 95% ethanol solution as reported in the experimental section. The results are shown in table 4 and 5.

UV Cyan Lab. Offset Ink			
Ethanol 95%	Co-initiator	Concentration of co-initiators (ppb)	Concentration of photoinitiator (IV) (ppb)
15m/min	(I) 3%	<25	<25
	(II) 3%	390	<25
	(III) 3%	290	<25
30m/min	(I) 3%	<25	<25
	(II) 3%	417	<25
	(III) 3%	510	<25

Table 4. Specific migration comparison of (I), (II) & (III) along with (IV) from the cured cyan lab offset ink in 95% ethanol solution at 40°C for 10 days

UV Cyan Industrial Offset Ink			
10m/min	Condition	Concentration of co-initiators (ppb)	Concentration of photoinitiator (IV) (ppb)
Ethanol 95%	(I) 3%	<25	<25
	(II) 3%	264	<25
Ethanol 10%	(I) 3%	<25	<25
	(II) 3%	247	<25

Table 5. Specific migration comparison of (I) & (II) along with (IV) from cured UV cyan industrial offset ink film in 10% and 95% EtOH solutions at 40°C for 10 days

Magenta and Black Offset inks

Undisclosed industrial offset ink formulations were used to demonstrate the performance characteristics of A-198 (I) versus EDB (II). The results obtained with these compositions are reported in figures 8 and 9.

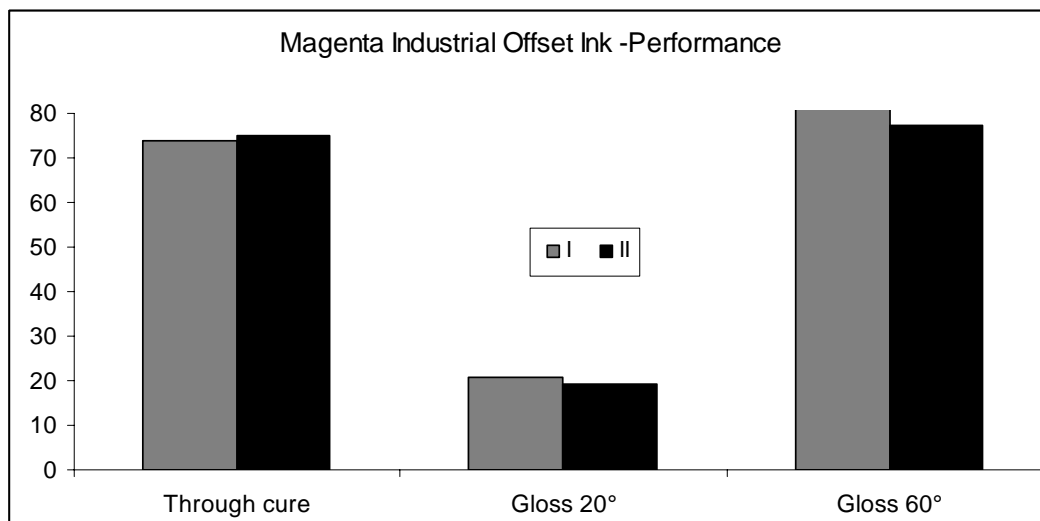


Figure 8. Performance of (I) in comparison with (II) in a magenta industrial offset ink. Photoinitiator (IV) concentration 3%.

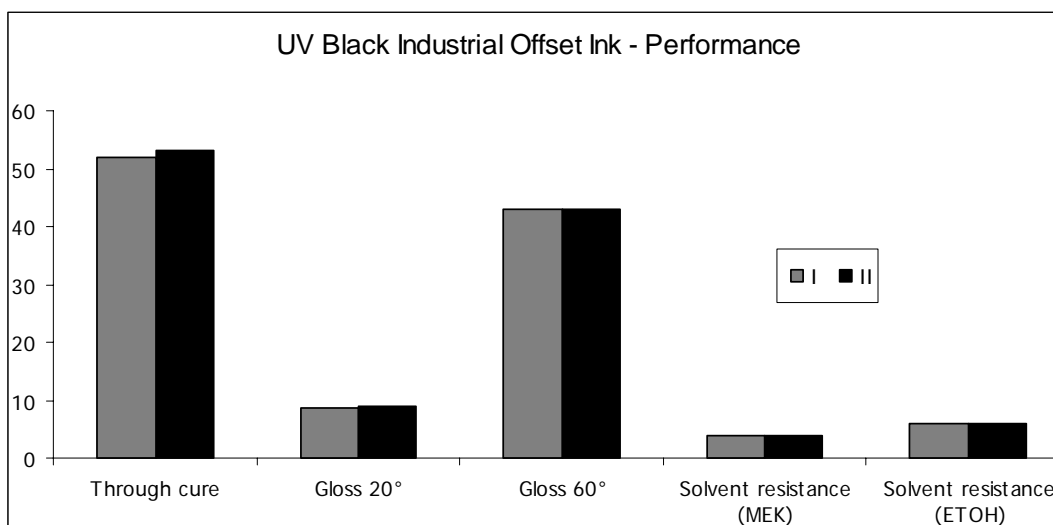


Figure 9. Performance of (I) in comparison with (II) in a black industrial offset ink. Photoinitiator (IV) concentration 3%.

The results clearly show that when (I+IV) are combined in an ink formulation, results consistent with commercially available inks are readily obtained.

CONCLUSIONS

The new co- initiator A-198 (I) shows a very interesting flexibility in different applications within graphic arts. It can be used in OPV applications as well as in curing pigmented printing inks. These experiments also show that A-198 is another advancement in UV cure technology. The combination of this novel di-functional co-initiator and di-functional photoinitiator (IV) is suitable for high tech applications due to their low migratability. The relatively high molecular weight of (I) is likely responsible for its low tendency to migrate from the cured films even when tested with very aggressive simulating fluids such as 95% EtOH. These results can open the door to the development of UV curable formulations suitable for food packaging applications, allowing an increase of the penetration of energy curing technology into that market.

ACKNOWLEDGMENTS

Thanks are due to Dr. T. Crolla and her staff for the analytical support in migration studies. Thanks are also due to Emilio Cremona and Loredana Alessi for the analytical support in UV-Vis spectroscopy studies and application evaluations.

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