Improved UV Curing of Offset Inks

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Abstract

A new photoinitiator package (PIC1) has been developed and evaluated for application and cure in an offset test ink set. The test ink containing PIC1 was compared to a process set of commercial offset inks and a set of test inks containing a commercially available oligomeric photoinitiator blend. Comparisons for lay down and resistance to IPA at SWOP density are presented.

Introduction

It is common practice in the UV curing ink industry to blend photoinitiators for the most effective performance. Typical photoinitiator blends are usually comprised of both Type I (cleavage) and Type II (abstraction) photoinitiators and can often include a tertiary amine synergist. The blending of photoinitiators has several advantages, such as cost effectiveness and, if the blend is a liquid, it also provides ease of handling and freedom from dust in the plant environment. These photoinitiator blends usually have a UV-Visible absorption spectrum, which overlaps with the emission output of a particular UV lamp, in particular the 313 and 365 nm lines. However, most photoinitiator blends lack a strong absorbance at the 365 nm line. However, those photoinitiator blends with a relatively strong absorption at 365 nm are expensive, often produce strong odors and the by-products can produce small molecule extractables, which make them unacceptable for articles such as food packaging.

Albemarle has developed a photoinitiator blend that encompasses the performance and needs required by today's UV ink formulator: such as high cure speed, high efficiency in light and dark inks and low cost in-use. The unique blend is a liquid photoinitiator combination, PIC1, which posses advantages that is free of Type I (cleavage) photoinitiators and also free of benzophenone for lower odor and migration. The low viscosity liquid has a relatively small impact on viscosity since only a small amount is required when compared to other photoinitiator blends, Table 1. A distinctive characteristic of this photoinitiator blend is a pronounced absorption at 359 nm (Figure 1), which overlaps with the 365 nm emission line of an H-bulb and also where most pigments do not reflect strongly.

Table 1. Properties of PIC1 photoinitiator blend.

Color	Dark blue/green
Viscosity (cps@25 ^{o}C)	1875
Absorption Max (nm)	248
Absorption Max (nm)	359

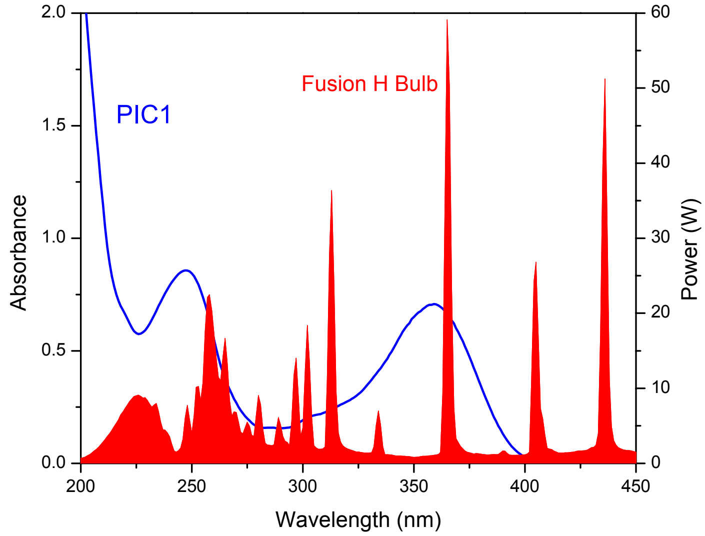

Figure 1. **UV-Vis absorption spectrum of PIC1 and output spectrum of a medium pressure mercury lamp (Fusion H bulb).**

Experimental

When evaluating a photoinitiator in offset inks, attention to the details of the formulation must be taken into account. Since the purpose of this study was to evaluate the use of a new photoinitiator and not to develop an ink, which would run on press, the raw materials were intentionally restricted to limit the variables to only the photoinitiator, as listed in Table 2. A commercial set of offset inks was used as a standard for performance parameters such as rheology, tack, misting, application and cure. Since our materials were deliberately restricted, the rheology of the standard inks in all colors could not be closely matched. However, the tack and misting were closely matched, as were the transfer properties.

In order to evaluate the photoinitiators, test inks were formulated to match the lay down (mg m^{-2}) of the standard inks at SWOP (Specifications of Weboffset Publications) density. The inks were applied onto Leneta color matching charts to remove any concern about variable ink hold-out on the substrate. These procedures assure that ink cure is evaluated as a function of the photoinitiator and not variables of application.

Test ink components were initially mixed at 60 ^{o}C and then ground on a Ross three-roll mill. Procedures for the evaluation were as follows:

1) The standard ink was applied onto the distribution roll of an IGT High Speed Inking Unit (HSIU-4) using an IGT syringe graduated in 0.01 ml units. The inking time and temperature were varied for best transfer and a calibration was made between ink volumes, lay down and color density. Blanket rolls were used as recommended for UV inks. Inks were applied to Leneta charts (Form 402C-4) using an IGT C1-5 proofer (300 newtons of printing force) and then cured. The blanket roll was weighed prior to and after application and the lay down was calculated in mg m^{-2}. Printing area was 50 mm X 210 mm.

2) Curing was performed using a Fusion UV Systems DRS-10/12 fitted with an AETEK lamp at 150 fpm (~17 mJ cm^{-2} of UVC).

3) Viscosity, thixotropy and yield stress were measured using a Rheometrics Dynamic Stress Rheometer.

4) Tack was measured at 800 fpm using a Model 106 Inkometer from Thwing-Albert Instrument Company with readings (gram meter) recorded at 240 seconds.

5) Color density was measured using an X-Rite Spectrodensitometer Model 328 with standard SWOP swatches used as a reference. Color density was less than a relative standard deviation of 3% on the proof.

6) After the evaluation of the standard ink, a test ink was prepared and formulated to match the standard so that equal lay down and equal color density was achieved.

7) A commercially available oligomeric photoinitiator blend was evaluated in the same test ink for comparison to PIC1.

8) The amount of PIC1 was varied in each color and a graphical extrapolation was made to match the IPA (isopropyl alcohol) rubs of the standard. The same procedure was used for the commercial photoinitiator.

Table 2. The raw materials used for formulating test inks.

Material	Type/Description	Supplier
KS 270	Gel vehicle	Kustom Blending, Inc
G49-6558	Cyan flush	Sun Chemical
G73-6514	Yellow flush	Sun Chemical
G19-6557	Magenta flush	Sun Chemical
SP-250	Black dispersion	Sun Chemical
Antimyst	Talc dispersion	Eastman Chemicals
MP 0609	Talc	Micro Powders, Inc
MP 28XF	Wax	Micro Powders, Inc
TMPEOTA	Monomer	UCB Chemicals Corp

Results and Discussion

Table 3 lists the formulation of the test inks prepared for the evaluation of the Albemarle PIC1 photoinitiator in cyan, yellow, magenta and black. Photoinitiator levels for Albemarle PIC1 were estimated from Figure 2. The IPA rubs of the standard inks are the horizontal lines parallel to the x-axis. The intersection of the standard lines with the % PIC curves is the estimated amounts of PIC1 used in the formulas shown in Table 3. In the case of cyan and magenta these estimated quantities were used in the evaluation but for yellow and black the quantities of PIC1 were increased to give a better surface to the ink. IPA rubs are not the only criteria in selecting the best photoinitiator or its concentration; other tests such as Sutherland may also be used. A simple thumb twist immediately after cure gives an indication of the mar resistance of the ink off press. The graphical estimation gives a good 1st pass concentration, which can be subsequently refined to optimize for properties and cost.

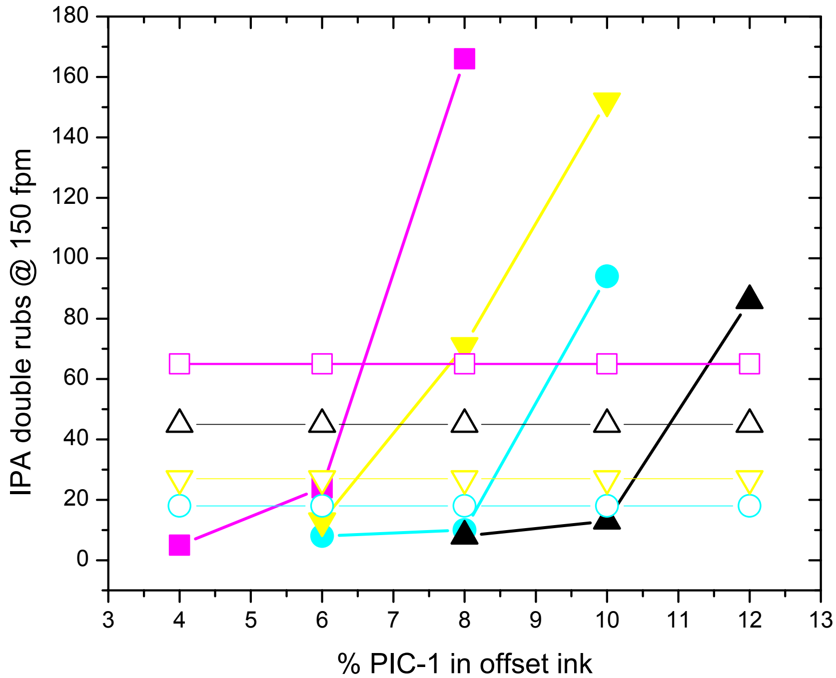

Figure 2. Isopropyl alcohol double rubs for (□) standard process magenta, (△) standard process black, (▽) standard process yellow, (O) standard process cyan, (■) magenta test ink, (▼) yellow test ink, (●) cyan test ink and (▲) black test ink.

Table 3. Test ink formulations for Albemarle PIC1.

Component	Cyan Test Ink	Yellow Test Ink	Magenta Test Ink	Black Test Ink
Sun Chemical Cyan G49-6558 flush	52.13	----	----	8.07
Sun Chemical Black SP-250 flush	----	----	----	43.00
Sun Chemical Magenta G19-6557 flush	----	----	56.67	4.60
Sun Chemical Yellow G73-6514 flush	----	56.85	----	----
KS270 Gel Vehicle	23.2	19.40	23.33	17.67
Eastman Anti-Myst	2.00	2.00	2.34	
MicroPowders 28XF	1.00	1.00	1.00	1.00
MicroPowders 0609 talc	---	---	---	3.00
TMPEOTA	13.67	13.55	10.41	11.56
Albemarle PIC1	8.00	7.20	6.25	11.10

Evaluation in Cyan

Table 4 shows results of the test inks when compared to the cyan process standard at a volume of 0.09mL. The PIC1 formulation showed slightly higher results for lay down, color density and IPA resistance when compared to the standard process cyan and the oligomeric photoinitiator. At 8.0% by weight of PIC1, the lay down was 0.89 g m^{-2} with a color density of 1.32 and yielded 72 IPA double rubs. These results show that PIC1 prints stronger than the standard process cyan and oligomeric photoinitiator. The PIC1 concentration could however be increased slightly (to 8.25%) or the ink formula could be adjusted to increase the density of the oligomeric photoinitiator to get equal IPA rubs. The standard process cyan when proofed to meet SWOP density; required 0.09 mL with a lay down of 0.82 g m^{-2} and yielded 47 IPA double rubs, but had a slight mar by thumb twist. The oligomeric photoinitiator (10.0% by weight) formulation showed higher resistance to IPA (82 double rubs), but printed considerably weaker (0.76 g m^{-2} and 1.19 color density) when compared to the cyan process standard.

Table 4. Properties of test inks (Albemarle PIC1, standard process cyan and an oligomeric photoinitiator) in cyan.

	Albemarle PIC1 (8.0%)	**Standard Process Cyan**	**Oligomeric Photoinitiator (10%)**
Volume (mL)	0.09	0.09	0.09
Lay down (g m^{-2})	0.89	0.82	0.76
*Color density	1.32	1.27	1.19
IPA double rubs	72	47	82
Thumb twist	Pass	Slight mar	Pass

*SWOP density of cyan = 1.28 $\pm$ 0.07

Evaluation in Yellow

Table 5 shows results for the evaluation for the standard process yellow, oligomeric photoinitiator and Albemarle PIC1. When proofed at 0.06 mL/0.48 g m^{-2}, the PIC1 had a color density of 0.93 with 26 double rubs required to break the continuous film at only 7.2%. The standard process yellow required 0.06 mL,/0.46 g m^{-2} to meet SWOP density with resistance of IPA at 39 double rubs. The oligomeric test ink at 0.6 mL/0.50 g m^{-2} produced a proof that failed to thumb twist and resisted only 16 IPA double rubs.

Table 5. Properties of test inks (Albemarle PIC1, standard process yellow and an oligomeric photoinitiator) in yellow.

	Albemarle PIC1 (7.2%)	**Standard Process Yellow**	**Oligomeric Photoinitiator (8.0%)**
Volume (mL)	0.06	0.06	0.06
Lay down (g m^{-2})	0.48	0.46	0.50
*Color density	0.93	0.92	0.91
IPA double rubs	26	39	16
Thumb twist	Pass	Pass	Fail

*SWOP density of cyan = 0.95 $\pm$ 0.07

Evaluation in Magenta

At 0.10 mL for the magenta test inks, PIC1 and the oligomeric photoinitiator showed significant differences to the standard process magenta as shown in Table 6. Firstly, PIC1 printed considerably stronger (1.50 color density) then the standard process magenta (1.37 color density) and oligomeric photoinitiator (1.11 color density) at 0.10 mL. The PIC1 formulation printed stronger but had approximately the same lay down as the standard process magenta, while the oligomeric photoinitiator lay down was lower at 0.87 g m^{-2}. However, at similar volumes and with differing amounts of ink transferred to the substrate, PIC1 and the oligomeric photoinitiator showed a higher resistance to IPA double rubs; when the oligomeric photoinitiator concentration was dropped to 6%, the IPA rubs were about equal to the standard (32) but there was a slight surface tack. At 6.0% PIC1 the IPA rubs were 24 but a very slight tack was noticed. The PIC1 had an excellent mar resistant surface.

Table 6. Properties of test inks (Albemarle PIC1, standard process magenta and an oligomeric photoinitiator) in magenta.

	Albemarle PIC1 (6.25%)	**Standard Process Magenta**	**Oligomeric Photoinitiator (8.0%)**
Volume (mL)	0.10	0.10	0.10
Lay down (g m^{-2})	0.96	0.94	0.87
*Color density	1.50	1.37	1.11
IPA double rubs	78	29	70
Thumb twist	Pass	Pass	Pass

*SWOP density of cyan = 1.40 ± 0.07

Evaluation in Black

In Table 7, PIC1 showed similar results to the standard process black, with similar lay down and color density. In this case, the oligomeric photoinitiator printed considerably weaker and showed inferior resistance to IPA when compared to PIC1 and the standard process black even though the lay down and density were less.

Table 7. Properties of test inks (Albemarle PIC1, standard process black and an oligomeric photoinitiator) in black.

	Albemarle PIC1 (11.10%)	**Standard Process Black**	**Oligomeric Photoinitiator (12.0%)**
Volume (mL)	0.13	0.14	0.13
Lay down (g m^{-2})	1.41	1.45	1.23
*Color density	1.58	1.62	1.43
IPA double rubs	23	25	19
Thumb twist	Pass	Pass	Fail

*SWOP density of cyan = 1.60 ± 0.07

Conclusions

The evaluation of a new photoinitiator for offset inks must take into account both cost and performance. The cost in use of the new photoinitiator is determined by the cost per process set, since different quantities are used for each color. In the case of the oligomeric photoinitiator, we saw that it greatly influenced transfer properties of the test ink so the ink would need to be reformulated to match the standard. The PIC1 inks more closely matched the standard in lay down and density. Table 8 below shows the amount (in pounds) of photoinitiator needed in a four-color process set for the two photoinitiators (PIC1 and oligomeric photoinitiator) based on the concentrations used in the above evaluation.

With this information, a decision can be made about the cost effectiveness of the new photoinitiator. Of course the actual amount of PIC1 must be determined in a specific formula and against an in-house standard, but the previous data provides a guideline for its evaluation.

Table 8. Photoinitiator (lbs) needed for a four-color process set of PIC1 and oligomeric photoinitiator.

Color	Albemarle PIC1	Oligomeric Photoinitiator
Cyan	0.08	0.10
Yellow	0.072	0.08
Magenta	0.0625	0.08
Black	0.111	0.12
Total	0.3255	0.38