

A New Class of Tertiary Amines

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Novel tertiary amines have been shown to be effective synergists/coinitiators for use in type II photoinitiating systems such as benzophenone. These innovative tertiary amines will be shown to be comparable to, or surpass, the performance of traditional amine synergists in performance evaluations, as well as to overcome the limitations.

Introduction

Tertiary amines have been widely used in conjunction with type II photoinitiating systems; they act as a cosynergist/coinitiator to initiate the free

can have adverse effects. Residual amounts of free-amines in cured films can migrate to either the surface or the interface, leading to post-cure problems. Migration to the surface can cause blushing or sweating on over-print varnishes, while migration to the interface can show discoloration, fading, bleeding or burn-out of sensitive pigments.

- Amine acrylate adducts are secondary amines reacted with an acrylate monomer to yield amine functionality in an effort to overcome some of the adverse properties of free-amines. The amount of amine functionality can be controlled by the ratio of secondary amine reacted with acrylate. Similar to free-amines, amine acrylate adducts provide for good through-cure, contribute to overcoming oxygen inhibition, but do not blush in high humidity. However, they are higher in cost, can discolor sensitive pigments and must be used in the range of 8-12% to be effective.
- Amine acrylates are made by the reaction of an amine and a multi-functional acrylate in such a ratio to yield an oligomeric compound. Unlike free-amines, amine acrylates do not blush or discolor sensitive pigments. However, they are high in cost, can cause skin burns and must be used in the range of 12-20% to be effective.

Though these three types of amine synergists have beneficial attributes, they do have certain drawbacks, which can be improved upon. Therefore, it would be advantageous to have amine

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Traditional tertiary amines can be placed into three categories:

- Free-amines (ethanolamines), which are low in cost and effective at relatively low concentrations (4-6%). While these amines give excellent through-cure and contribute to overcoming the effects of oxygen inhibition, they

TABLE 1

Photo-DSC peak exotherms for mixtures of benzophenone (5%) and various amine synergists (5%) to initiate the polymerization of HDDA, TRPGDA and TMPEOTA. Light intensity of a medium-pressure mercury lamp (full arc) was 50 mW cm⁻² in N₂.

Amine Synergists	Exotherm (mW) in HDDA	Exotherm (mW) in TRPGDA	Exotherm (mW) in TMPEOTA
AS-1	63	74	117
MDEA	65	76	118
Amine A	51	65	94
Amine B	54	67	98
AS-3	69	75	118
Amine C	50	62	115

synergists that possess all the performance qualities of the traditional tertiary amine while overcoming the deleterious effects. An innovative class of liquid aliphatic tertiary amines based on patent-pending technology, which is focused on meeting the performance requirements of today's formulators, have been developed.

Experimental

The materials used in these performance evaluations were obtained and used as received without further purification. Ebecryl 3720-TP25, TMPEOTA, TRPGDA and HDDA were obtained from UCB Chemicals Corporation. Methyldiethanolamine (MDEA), benzophenone (BP), hydroquinone monomethylether (MEHQ) and methylethylketone (MEK) were obtained from Aldrich. DC-57 and FC-430 were obtained from Dow Corning and 3M. FirstCure® HMPP (2-hydroxy-2-dimethyl-1-phenylpropane-1-one) was obtained from Albemarle Corporation.

Photo-DSC (differential scanning calorimetry) was performed using a Perkin-Elmer DSC-7 with modifications, including the addition of quartz

windows in the sample head cover and a 450W medium-pressure mercury lamp, mounted above the sample head. Light intensities of the full arc of a medium-pressure mercury lamp were approximately 50 mW cm⁻², with lower light intensities attained by using neutral density filters or by changing the distance between the lamp and the sample cells. The sample cell chamber was purged with N₂ at 25°C for 2.5 minutes prior to polymerization. Data was acquired using the supplied Pyris software from Perkin-Elmer.

Viscosities of the formulations were measured using a Brookfield LV viscometer at 25°C after they were mixed and allowed to set for 24 hours. The formulations were applied to Leneta charts (Form 5C) using a No. 3 wire round rod and cured under a Fusion H bulb at 145 fpm (35 mJ cm⁻¹ UVC). The final cured films were evaluated for these performance parameters.

- Blush resistance was determined by exposing freshly cured coatings in a 95% relative humidity chamber at 95°F for 24 hours. The exposed coatings were then visually examined

for blushing over the black section of the Leneta chart.

- Pigment discoloration was evaluated by making proofs with Reflex Blue and Rhodamine Red on a Little Joe press, using offset sheet-fed inks applied to SBS board. The proofs were allowed to dry until unmarred by a thumb twist. The proofs were then overcoated with the UV coatings at 145 fpm. The freshly cured proofs were placed in between glass plates, and the edges were sealed with tape to simulate conditions in a stack. The plates were placed into a 50°C circulating air oven for 72 hours and rated visually for discoloration. An uncoated proof was included as a control.
- Methylethylketone (MEK) double rubs were performed on the cured films three minutes after exposure.
- Yellowness index was measured using a BYK-Gardner colorimeter.
- Gloss was determined at 60° using a BYK-Gardner Tri-Gloss meter.
- Extractions were performed for 10 hours by MEK in a Soxhlet extractor on films cured at 75 fpm with a Fusion H bulb.

TABLE 2

Viscosity and appearance of comparative amine synergists

Amine Synergists	Viscosity (cps) at 25°C	Appearance
AS-1	8-10	Clear liquid
MDEA	35	Yellow liquid
AS-3	8-10	Clear liquid
Amine A	20	Yellow liquid
Amine B	30	Yellow liquid
Amine C	1,200	Viscous yellow liquid

Results and Discussion

Photo-DSC

Photo-DSC experiments were performed in order to compare the relative efficiency of two liquid aliphatic amines tertiary amines (AS-1

and AS-3) to the traditional amines on a per-weight basis. Photo-DSC peak exotherm data is presented, which can be correlated to the conversion of double-bonds from the acrylate functionality. Mixtures consisted of 5%

of comparative amine, 5% benzophenone and 90% monomer. The comparative amines to be evaluated are: MDEA is the free-amine, Amine A and Amine B are amine acrylate adducts, and Amine C is an acrylated amine.

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TABLE 3

Composition and viscosities of test formulations for AS-1, AS-3, MDEA, and Amines A, B and C

Material	AS-1	AS-3	MDEA	Amines A	Amines B	Amines C
Ebecryl 3720TP25	41.50	41.50	39.43	37.50	39.50	27.67
Benzophenone	6.00	6.00	6.00	6.00	6.00	6.00
"FirstCure" HMPP	0.50	0.50	0.50	0.50	0.50	0.50
AS-1	2.50					
AS-3		2.00				
MDEA			5.50			
Amine A				10.0		
Amine B					11.0	
Amine C						15.00
DC-57	0.50	0.50	0.50	0.50	0.50	0.50
FC-430	0.10	0.10	0.10	0.10	0.10	0.10
MEHQ	0.02	0.02	0.02	0.02	0.02	0.02
Monomer mix*	48.88	49.38	47.95	45.38	42.38	50.21
Total Weight	100.0	100.0	100.0	100.0	100.0	100.0
Viscosity (cps) @ 25°C	158	168	165	163	167	170

* For dilution, a monomer mixture of approximately 31% TMPEOTA and 69% TRPGDA was used in all formulas for a constant monomer cost and diluency.

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FIGURE 1

Optimal concentration of AS-1 and AS-3 was determined by MEK double rubs. Formulations were applied to Leneta charts, Form 5C, by a No. 3 wire.

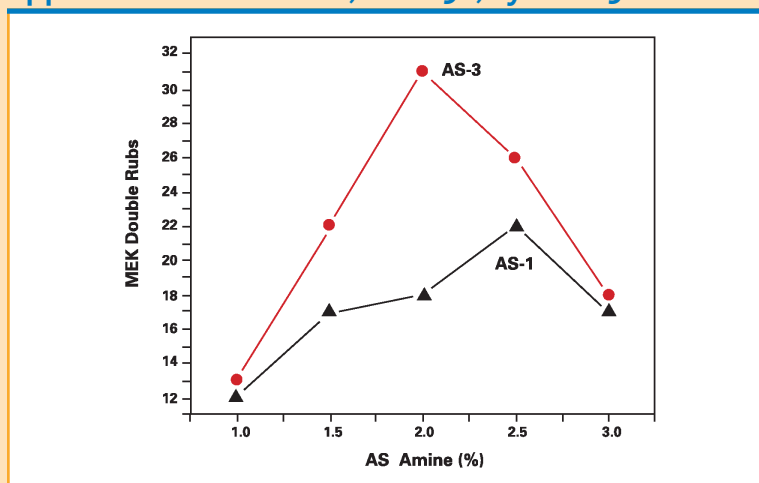
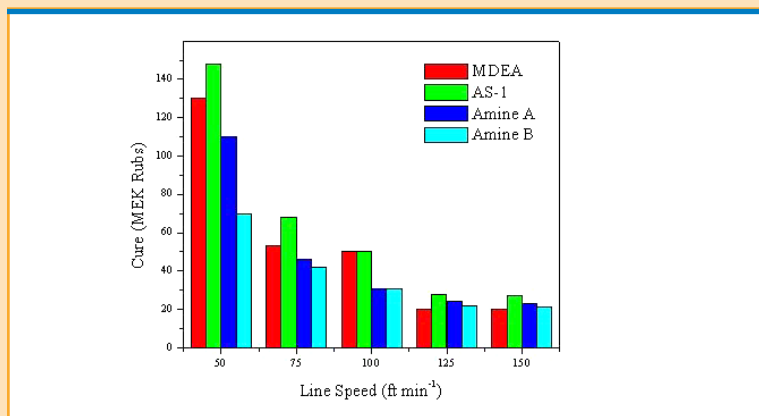


FIGURE 2

Cure comparison for AS-1 amine and traditional free amine and amine acrylate adducts, MDEA, Amine A and Amine B



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Table 1 summarizes the results obtained. In HDDA, maximum peak exotherms for AS-1 is comparable to MDEA, Amine A and Amine B, while AS-3 shows a marked increase over Amine C. In TRPGDA, maximum peak exotherms for the AS amines are comparable to MDEA, Amine A, B and C.

In TMPEOTA, AS-1 is comparable to MDEA and surpasses the peak exotherms attained with Amine A and B. Peak exotherm data shows that AS-3 and Amine C give similar results.

Formulations

A typical over-print varnish formulation was chosen as the vehicle for the performance evaluations.

Viscosities of the amines to be compared were in the range of 10 to 1,200 cps, with the AS amines having the lowest viscosity (8-10 cps) and Amine C (1,200 cps) having the highest, as shown in Table 2. The comparative amines were incorporated at optimal concentrations, and the formulation viscosities were adjusted within a range of 155 to 170 cps, as shown in Table 3.

Optimal Concentrations of AS Series Amines

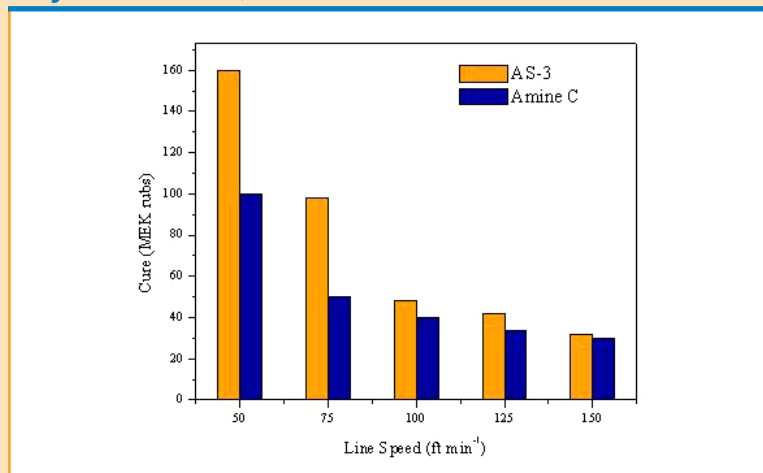
A determination of the optimal concentration of the comparative amines was performed with the results for the AS amines shown. As with all amines participating in an electron transfer reaction with a type II photoinitiator, an optimal concentration will be observed. The concentration of each AS was varied in the test formula from 1% to 3%. The results are shown in Figure 1. The composition of each variation was adjusted to retain constant viscosity. From the results, it was determined that the optimum concentration of AS-1 was at 2.0%, while AS-3 was most effective at 2.5%.

Line Curing

Line curing data was acquired at 145 fpm on a Fusion UV DRS-120 with an H bulb. It was shown that AS amines fall into two comparative performance groupings with the traditional amine synergists. Figure 2 shows cure vs. line speed of the formulations (Table 3) in performance matches. Line speeds used for the performance evaluations were 50, 75, 100, 125 and 150 fpm. In Figure 2, when AS-1 was incorporated (2.5%) and compared to Amine A (10%) and Amine B (11%), AS-1 showed a dramatically superior cure. In Figure 3, when AS-3 (2%) is compared to Amine C (15%), the cure is comparable. In all cases where an AS amine is used in place of a traditional amine synergist, the AS amines produced cure results that were comparable to or superior.

FIGURE 3

Cure comparison for AS-3 amine and traditional acrylated amine, Amine C



Performance Evaluations

The results for the comparative evaluation of the AS amines and the commercial amine synergists are shown in Tables 4 and 5. The AS amines fall into two performance categories (shown in Figures 2 and 3).

- AS-1 is comparable to MDEA, Amine A and Amine B.
- AS-3 is comparable to Amine C. As shown in Table 4, AS-1 compares to and exceeds the performance obtained for MDEA, and Amines A and B. AS-1 was used at 2.5% to attain equal or superior performance to 5.5% MDEA, 10% Amine A and 11% of Amine B. Since only a relatively small percentage of AS-1 is required,

this gives some latitude to adjust the formulation for performance and cost. The remaining percentage can be substituted with a higher loading of oligomers to give better properties, or the monomer can be substituted with a lower-cost monomer to reduce the cost of the final formulation. The performance evaluation for AS-1 vs. MDEA, Amine A and Amine B are summarized (and shown in Table 4):

- AS-1 and Amine B do not blush like MDEA and Amine A.
- In pigment discolorations in both Rhodamine Red and Reflex Blue, only AS-1 did not have an adverse effect on the sensitive pigments where MDEA showed severe fading and Amine A and Amine B showed moderate to slight fading and discoloration.
- Solvent-resistance evaluations show that AS-1 and MDEA were comparable, while Amine A and Amine B both performed significantly less.
- Yellowness data was acquired following cure and shows that AS-1 “yellows” less than MDEA, Amine A and Amine B.

TABLE 4

Performance evaluations for AS-1

Evaluation	AS-1 (2.5%)	MDEA (5.5%)	Amine A (10%)	Amine B (11%)
Blush	None	Severe	None	Slight
Pigment Discoloration (Reflex Blue)	None	Severe fade	Moderate and spotty fade	Moderate and spotty fade
Pigment Discoloration (Rhodamine Red)	None	Severe fade	Moderate and spotty fade	Slight, and spotty fade
Solvent Resistance (MEK double rubs)	24	24	12	20
Yellowness Index	5.01	5.93	6.02	5.98
Gloss (60o)	95.7	96.1	95.1	96.5
MEK Extraction (% weight loss)	7.52	7.69	10.38	12.62

TABLE 5

Performance evaluation of AS-3

Evaluation	AS-3 (2%)	Amine C (15%)
Blush	None	None
Pigment Discoloration (Relfex Blue)	None	Slight, spotty discolor and fade
Pigment Discoloration (Rhodamine Red)	None	Moderate fade
Solvent Resistance (MEK double rubs)	25	22
Yellowness Index	4.77	5.82
Gloss (60°)	96.0	95.7
MEK Extraction (% weight loss)	4.55	5.29

- Gloss measurements were comparable for AS-1 and MDEA, Amine A and Amine B.
- Extraction by MEK showed that AS-1 performs similarly to MDEA and significantly better than Amines A and B.

As shown in Table 5, AS-3 is comparable to and exceeds the performance obtained for Amine C. AS-3 was used at 2% to attain equal or superior performance of 15% of Amine C. Since only a relatively small percentage of AS-3 is required, the remaining percentage can be substituted with a higher loading of oligomers to give better properties. In this case, the monomer can be substituted with a lower-cost monomer to reduce the cost of the final formulation. AS-3 is also a good choice for formulations requiring low viscosity, such as gravure-applied coatings. The performance evaluations for AS-3 vs. Amine C are summarized (and shown in Table 5).

- AS-3 and Amine C did not show any blushing.
- In pigment discolorations for both Rhodamine Red and Reflex Blue,

only AS-3 did not have an adverse effect on the sensitive pigments. Amine C showed moderate to slight fading and discoloration.

- Solvent resistance showed that AS-3 and Amine C were comparable.
- Yellowness data was acquired following cure and showed that AS-3 yellows less than Amine C.
- Gloss measurements were comparable for AS-3 and Amine C.
- Extraction by MEK showed that AS-3 performs similarly to Amine C.

Conclusions

Two novel tertiary amines have been shown to be comparable to the traditional amine synergists without some of the limiting effects. Photo-DSC data show that the relative efficiency of these two liquid aliphatic amines are comparable to and surpass the maximum peak exotherm obtained by the traditional free-amines, amine acrylate adducts and acrylated amines. It was shown in performance evaluations that the AS amines did not blush or discolor sensitive pigments, while performing comparably to the traditional amines at a fraction of the

concentration, giving the formulator latitude to design a better formulation. ■

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