Effect of Amine Synergists on the EB-Curing Properties of Acrylate-Based Coatings

By Stephen C. Lapin, Ph.D., and Zach S. Geiger

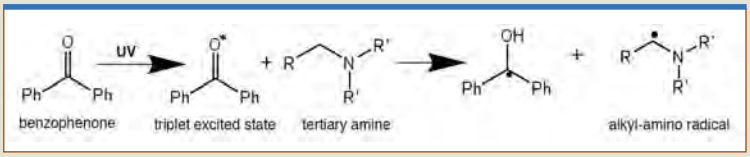
Amine synergists are widely used in UV-curable, acrylate-based coating formulations. They are often used together with Norrish Type II photoinitiators such as benzophenone. The tertiary amine function provides an active hydrogen donor sight for the excited triplet state of the photoinitiator. This produces a very reactive alkyl-amino, free radical (Equation 1), which subsequently initiates the polymerization of acrylate-functional monomer and oligomer components of the formulation.

Another important function of tertiary amines in UV-curable coatings is to reduce oxygen inhibition. Oxygen which diffuses into the surface of a coating quickly reacts with growing free-radical chains and converts them into unreactive peroxy radicals. Tertiary amines react with peroxy radicals converting them to reactive alkyl-amino radicals, thereby reducing the effects of oxygen on curing (Equation 2).[1,2]

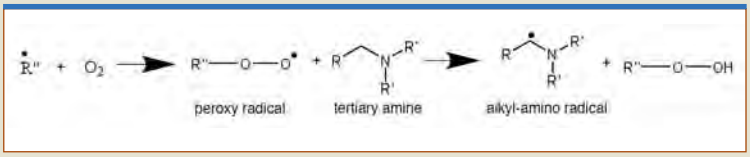
A wide range of different types of amine synergists are used in UV-curable coatings. The simplest materials are low-molecular weight tertiary amine compounds such as triethanol amine or methyl diethanol amine. These compounds can be very effective in combination with Type II initiators and also for reducing the effects of oxygen inhibition. Disadvantages of these compounds include potential migration and blushing of residual amines. These free amines are also known to react with certain pigments that can result in fading of the corresponding printed ink colors. These compounds are also somewhat hydroscopic, which can be a problem in lithographic inks where hydrophobic ink properties are critical to the lithographic imaging process. Amino-benzoate compounds—including the ethyl ester of dimethylamino benzoate (EDB) and the 2-ethylhexyl ester of dimethylaminio benzoate (EHA)—are commonly used in lithographic inks because they have more hydrophobic properties.[2]

Another class of amine synergists is acrylated amines. These are formed by the Michael addition of secondary amines to acrylate-functional groups

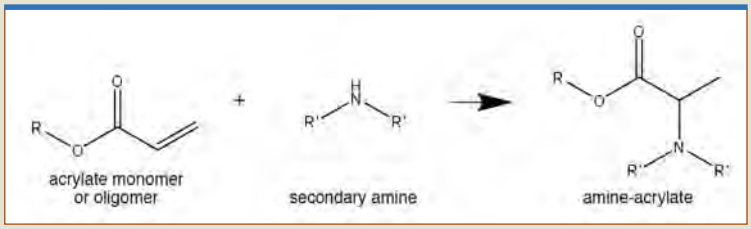
Equation 1



Equation 2



EQUATION 3



(Equation 3). Secondary amines can be combined in this manner with a large variety of different multifunctional-acrylate monomers and oligomers. Depending on the stoichiometry, a large variety of compounds can be produced which have both acrylate and amine functionality.[4] The presence of an acrylate group on an amine synergist will allow it to react into the polymer matrix and reduce the potential for migration. Other oligomeric compounds with multiple tertiary amine functional groups are also known and used in low-migration ink and coating formulations.[2,3]

Although the use of amine synergists are well known in UV-coating formulations, they are not commonly used in electron beam (EB)-curable coatings. Acrylate-based EB coatings cure without added photoinitiators so amine synergists are not needed to initiate polymerization. EB curing is almost always conducted under an inert atmosphere so the use of amines may not be considered beneficial for reducing oxygen inhibition. The purpose of this study is to evaluate potential benefits of using amine synergists in EB-curable coatings.

Experimental Methods

Commercial raw materials were used. Coating formulations were prepared by blending raw materials to give homogeneous mixtures. The coatings were applied to BYK paperboard test cards using a number 6 wire-wound rod which gave a coating weight of about 10 g/m^2. The coatings were cured using a BroadBeam EP Series EB system operating at 150 kV. Samples were attached to a fiberglass carrier web moving at 15 m/minute. Four layers of paper towel were wrapped on the round end of a 1 kg ball-peen hammer. Surface cure was evaluated after 10 back-and-forth strokes of the dry paper towel surface on the coating under the weight of the hammer. Through-cure was evaluated by the same test using paper towel layers that were saturated with methyl ethyl ketone (MEK). The effect of dry and MEK rubs on the coatings were ranked on the following scale:

0 – No cure/compete removal of coating

1 – Tacky coating/severe smudging

2 – Significant effect from rub test

3 – Slight effect from rub test

4 – Minimal noticeable effect from rub test

5 – Complete cure/no visible effect from rub test

Results and Discussion

The base coating formulation for testing was a simple mixture of 60% trimethylol propane triacrylate monomer (TMPTA), and 40% bisphenol-A expoxy acrylate oligomer (Ebecryl 3700, Cytec). The amine synergists that were studied are shown in Table 1. The synergists include a free amine A; acrylated amine

TABLE 1

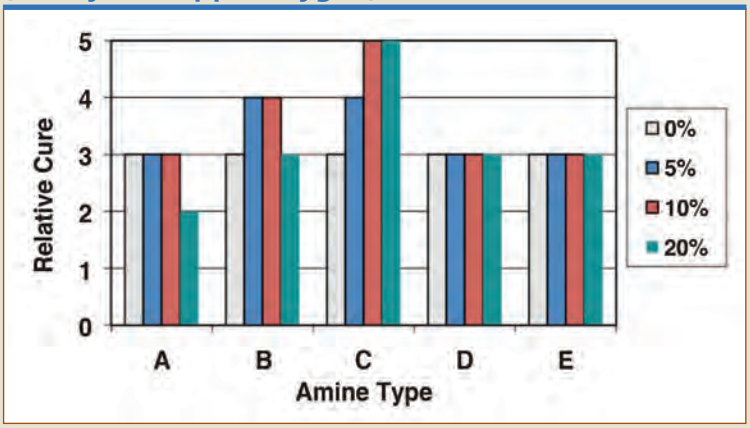
Amine synergists for EB-curing evaluation

	Description	Amine functionality	Acrylate functionality	Molecular weight	Weight per amine	Weight per acrylate
A	Triethanol amine	1	0	135	135	NA
B	Triethanol amine zirconate	4	0	627*	157*	NA
C	Acrylated amine	2	0	430	215	NA
D	Acrylated amine	1	2.5	500	500	200
E	Amine-modified epoxy acrylate	unknown	2	>1000	unknown	>500

*Theoretical based on a complex of four equivalents of triethanol anime per equivalent of zirconium

FIGURE 1

Effect of amine synergist on surface cure (10 kGy, <200 ppm oxygen)



with no remaining acrylate functionality C; acrylated amine with both amine and acrylate functionality D; and an amine modified oligomer E. An amine zirconate complex B was also tested.

The four monomeric synergists A, B, C and D were relatively low-viscosity liquids and were evaluated at levels of 5, 10 and 20% replacing a corresponding amount of TMPTA in the base formulation. The oligomeric synergist E was used to replace unmodified epoxy acrylate oligomer in the formulations also at levels of 5, 10 and 20%.

The first set of tests involved looking at cure-dose response under well-inerted (<200 ppm oxygen) conditions. When a cure dose of 20 to 30 kGy was used, all formulations (with and without amines) showed good surface-cure and through-cure properties (5 rating after both dry and MEK rub testing). Differentiation of curing properties was only observed by reducing the EB dose to 10 kGy. The effect of the amines on the surface cure (dry rub test) is shown in Figure 1. The results show that the amines had relatively small impact on surface cure under these conditions. Slightly better surface cure was observed with the amine acrylate C. These results are not unexpected. Under good inerting conditions, good surface cure is expected and the amines would not be expected to have much effect.

The effect of amines on through-cure (MEK rub test) under the low-dose (10 kGy) cure conditions is shown in Figure 2. The results were quite dramatic. In the absence of amine, through-cure was very poor at this low dose and the coating is easily removed by the MEK. All of the amines greatly improved the curing (MEK resistance). The amine acrylate D at 5 and 10% levels in the formulation improved curing to the point where it was unaffected by the MEK rubs. It is interesting that amine C actually shows a decrease in the rub resistance at the highest level (20%). This may be due to the fact that this amine does not have acrylate functionality, and the excess amine may lower crosslinking and plasticize the coating.

The large improvement in through-cure at low dose levels is likely due to the tertiary amines functioning as chain-transfer agents. A highly crosslinked network forms as a result of the curing process. This can trap growing radical chains and limit the overall conversion of acrylate groups. Tertiary amines can donate a hydrogen atom that regenerates a mobile alkyl-amino radical that results in increased conversion of the monomer and oligomer components.

The second part of this study involved looking at EB-curing properties under partial-inerting conditions. A constant EB dose of 30 kGy was used for this part of the study. Partial inerting was achieved

FIGURE 2

Effect of amine synergists on through-cure (10 kGy, <200 ppm oxygen)

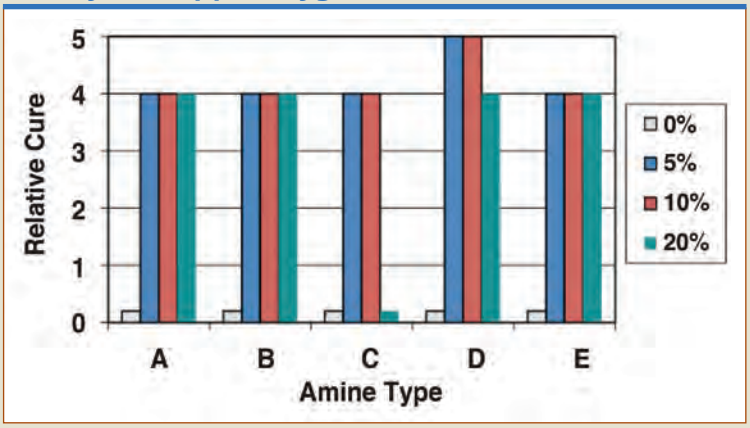
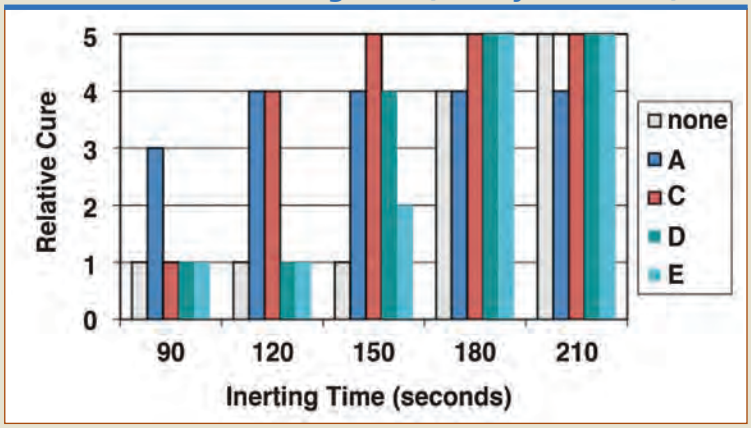


FIGURE 3

Effect of amine synergists (10% level) on surface cure as a function of inerting time (30 kGy cure dose)

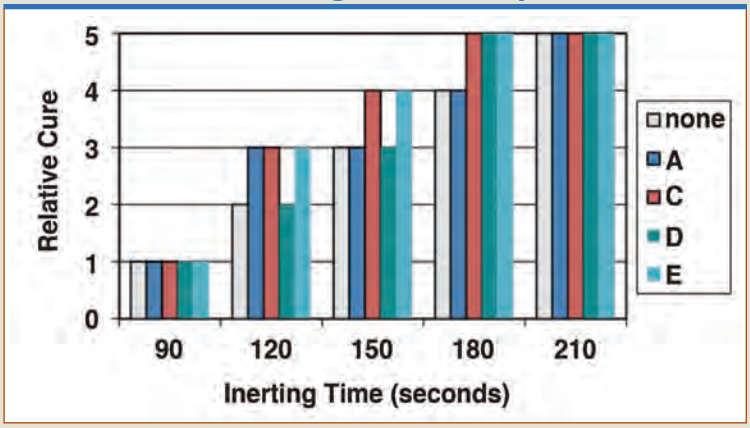


by starting the EB system with the reaction chamber in an air atmosphere. A nitrogen purge was then started at a low flow rate of 18 scfm. Coating samples were then irradiated at 30-second intervals while continuing the purge. This produced an oxygen concentration gradient that decreased with increasing purge time. The actual oxygen concentration at the time of irradiation could not be measured due to the lag time in the response of the electrochemical oxygen sensor used in the EB system.

Figure 3 shows the surface cure (dry rub test) as a function of inerting time for coatings containing amines A, C, D and E at a 10% concentration (amine B was not used due to gelation problems). In the absence of amine, the critical time for coating surface cure is after about 150 to 180 seconds of nitrogen purging. The surface cure is improved at earlier times relative to the base coating for all of the amines. This shows that the addition of amines gives more effective surface cure at higher oxygen concentrations.

FIGURE 4

Effect of amine synergists (10% level) on through-cure as a function of inerting time (30 kGy cure dose)



Triethanol amine A appeared to be the most effective at improving surface cure while the oligomeric amine E was the least effective.

Figure 4 shows the effect of amine addition on through-cure (MEK rub test) as function of inerting time. The amines did appear to give a slight improvement in curing at shorter purge times (higher oxygen levels), but the effects are not as pronounced as the surface-curing effects (compare Figures 3 and 4). The impact of oxygen inhibition on though-cure is highly dependent on coating thickness. Oxygen inhibition will affect the full cross section of very thin (less than about 5 microns) coatings and will mainly affect the surface curing of thicker coatings (more than about 15 microns). This is determined by the rate of oxygen diffusion into the coating during curing.

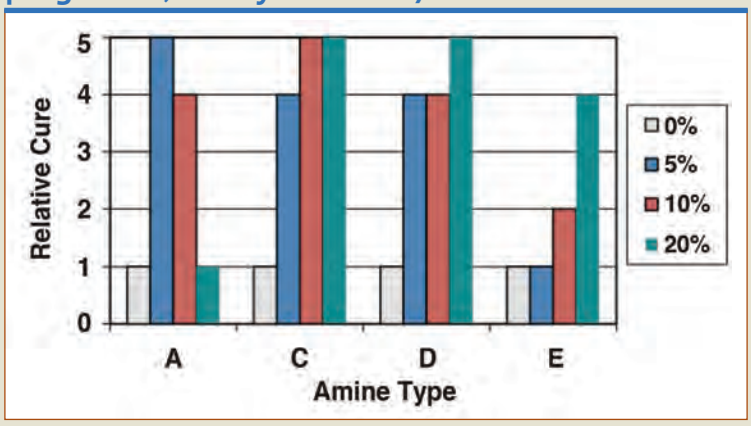
In order to get a view of the effect of amine concentration on reducing oxygen inhibition, surface cure is plotted in Figure 5 for 150 seconds of inerting time, which is a representative partially inerted condition. The results indicate that the optimal amine concentration for surface curing at elevated oxygen levels is different for each amine. In the case of the triethanol amine A, the maximum effect was observed at 5%. Higher concentrations of A adversely affected the surface cure. This could be due to residual amine that may migrate to the surface following EB curing at 30 kGy. With acrylated amines C and D, there seems to be little additional benefit to concentrations above about 10%. In the case of the oligomeric amine E, higher concentrations were beneficial which could be due to a lower relative amine concentration in this synergist.

Conclusions

Good through-cure was achieved in the presence of amine synergists

FIGURE 5

Effect of amine synergist concentration on surface cure under partial inerting conditions (150 seconds purge time, 30 kGy cure dose)



at cure doses as low as 10 kGy under well-inerted conditions. The potential consequences of this curing enhancement are interesting. Commercial EB-converting applications often run at high speeds. Modern EB systems are well-suited to high-speed applications and can deliver a typical 30 kGy cure dose at 400 m/min. There are some applications such as commercial publication printing where even higher speeds are desirable. It is possible to use multiple EB units in series to deliver the desired cure dose at very high speeds. This results in high capital cost and a large space requirement on the process line. If the required cure dose can be reduced to 10 kGy, then speeds up to 1,200 m/min may be possible with a single EB unit. Another possible benefit of low-cure dose levels may be in cases where EB-induced degradation of the substrate is a concern. If EB curing can be achieved at 10 kGy, there may be little concern with most substrates at this level.

Good surface cure was achieved in the presence of amine synergists under partial-inerting conditions at typical (30 kGy) cure dose levels. The potential consequences of this reduced oxygen inhibition are interesting. Typical curing of acrylate-based inks and coatings require oxygen levels below about 200 ppm. In high-speed web applications, a boundary layer of air is carried into the EB reaction chamber along with the web. Large volumes of high-purity nitrogen must be directed onto the web and into the reaction chamber to reduce oxygen levels. The operating cost associated with the nitrogen supply is often greater than the electrical power costs to generate the electron beam. Reduced oxygen inhibition with amine synergists could potentially result in good curing at higher oxygen levels, thus allowing lower volumes of nitrogen to be used.

Even in cases where dose levels and oxygen levels remain at established levels, formulations containing amine synergists could result in a more robust cured product under a wider range of production conditions.

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—Stephen C. Lapin, Ph.D., is an applications specialist, Broadbeam, and Zach S. Geiger is an intern at PCT Engineered Systems LLC in Davenport, Iowa.

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