UV LED SURFACE CURING

Jennifer McClung, Tong Wang, PhD and Steven Cappelle, PhD, discuss how to solve the issue of surface cure in overprint varnishes when using LED curing technologies

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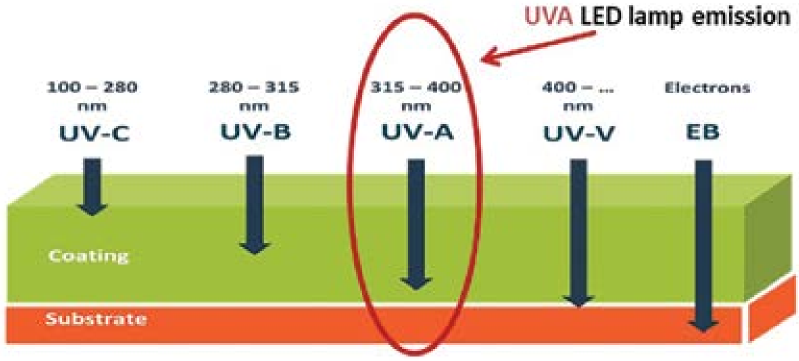

Figure 1: The correlation between light wavelength and penetration depth

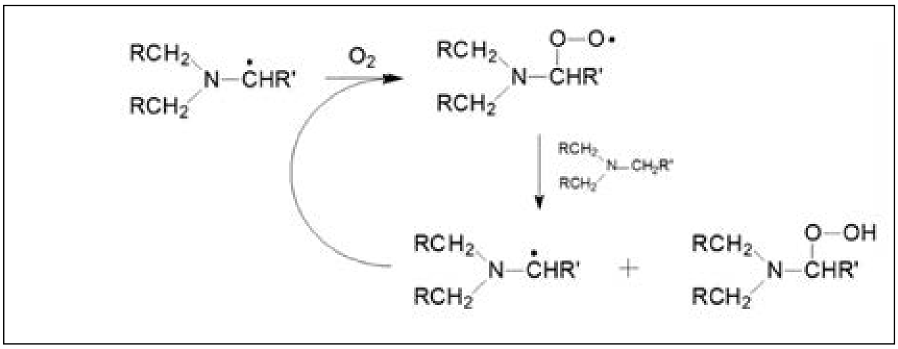

Figure 2: Reaction mechanism of an amine with oxygen

The lack of surface cure in thin coating layers due to oxygen inhibition is a common issue when curing by LED. To overcome these issues, reactive chemicals are used to ensure the surface of the coating layer is cured, generally by providing an abstractable hydrogen. Amino acrylates are a common reactive chemical used to address the lack of surface cure of the coating layer. Multiple amino acrylates were evaluated for their ability to increase surface cure and compared to one another along with an industry standard, which will be discussed here. While amino acrylates are commonly used, LED booster-type materials are another avenue to provide the surface cure that is needed, while ensuring that all regulatory needs are met. Multiple LED booster-type materials have been developed recently to be used in a variety of applications. These materials will be evaluated and compared to one another along with an industry standard. These materials provide the added benefit of a low migration material that helps ensure the increasingly rigorous needs of the packaging market are met.

INTRODUCTION

As the market continues to move towards more use of UV LED lamps to cure materials, there will be a greater focus on solving the issue with surface cure of coating layers. The use of LED lamps provides myriad benefits, including no ozone emissions, instant on-and-off of lamps, etc., that make it a trend that will continue to grow in the coatings industry. However, while UV LED has some fantastic benefits, it also has some disadvantages, the biggest of which is the inability to fully cure the surface because of oxygen inhibition. Due to the fact that the atmosphere contains 21% oxygen, the surface of coating layers is exposed to a large amount of oxygen that can quench the excited state of photoinitiators, limiting the surface cure of the coating.

> *"Multiple LED booster-type materials have been developed for a variety of applications"*

The chief reason that LED curing has such a difficult time with surface curing is the lack of short wavelengths. Surface cure is dependent on short wavelength light to ensure a complete cure of the layer. **Figure 1** shows the differences in wavelength penetration for UV light. For mercury lamps, it is possible to use the entire spectrum, which allows for complete curing of the coating layer. UV LED lamps are currently available in 365nm, 395nm and 405nm, which provides a large amount of through cure (UVA) but no short (UVC) or medium wavelength (UVB) light. Along with the lack of short wavelength light and oxygen inhibition there is the lower power output of commercially available lamps. A lower amount of power output leads to fewer radicals being generated, which again cannot overcome the oxygen inhibition. When you couple these three issues together, they work in combination to negatively impact the overall surface cure of the material, resulting in a tacky and uncured film.

There are multiple physical and chemical approaches that can be used to avoid oxygen inhibition and improve the overall surface cure of thin coating layers. The most common is the use of amino acrylates. There are easily-abstractable hydrogens on the carbon atoms that are at the alpha position to the nitrogen molecule of the amine. There are also multiple hydrogens on each molecule. These available abstractable hydrogens can also react with the peroxy radicals as shown in **Figure 2**. The acrylate functionality allows the material to be crosslinked into the overall acrylate matrix,

Properties	Value
Acrylate functionality	2
Gardner color	< 1
Viscosity at 25°C (cP)	~ 450
Molecular weight(g/mol)	1300
Usage level (%)	5-20

Table 1: Properties of EBECRYL LED 03

Components	OPV-A1	OPV-A2	OPV-B1	OPV-B2	OPV-C1	OPV-C2
EBECRYL 3720-TM40	37	37	37	37	37	37
TMPEOTA	50	40	50	40	53	42
EBECRYL LED 03	-	15	-	15	-	15
TPO-L	13	8				
TPO			13	8		
BAPO					10	6
Total	100	100	100	100	100	100
△b	5.3	4.5	6.7	4.8	8.4	4.5

Table 2: Process steps for the manufacture of multilayer modular flooring

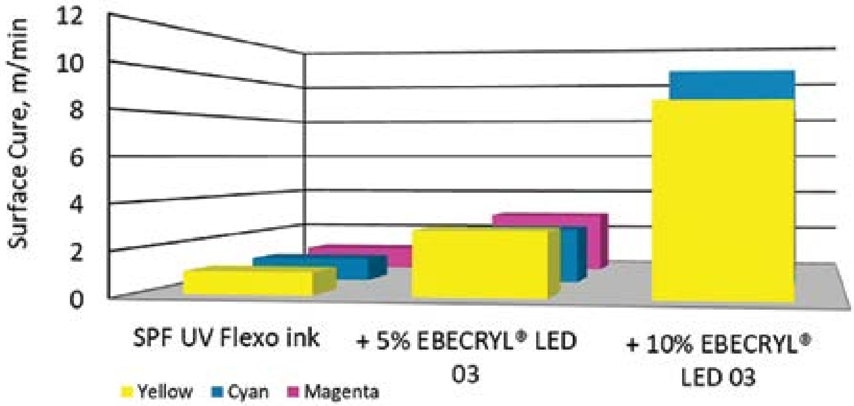

Figure 3: Surface reactivity of yellow, cyan and magenta flexo inks

Properties	EDB	Reference polymeric amino benzoate	EBECRYL LED 04
Acrylate functionality	0	2	6
Appearance	White solid	Pale yellow liquid	Clear liquid
Viscosity at 25°C (cP)	/	~ 1400	~ 17, 500
Amine content (%)	7.3	3.8	2.7

Table 4: Characteristics of EDB, reference polymeric amino benzoate and LED 04

	No amine synergist	EDB	Polymeric Amino benzoate	EBECRYL LED 04
Resin mix (EBECRYL 870/EBECRYL 1608 50/50)	46.5	46.5	46.5	46.5
Talc	6	6	6	6
Pigment(cyan 15:3)	17	17	17	17
Stabiliser solution	1	1	1	1
TPO-L/ITX (80/20)	10	10	10	10
Amine synergist	-	2.5	7.5	7.5
Resin mix	11	10.5	5	1.5
OTA-480	8.5	6.5	7.0	10.5
Total	100	100	100	100
Viscosity at 2.5 /s (cP)	78,600	88,100	78, 000	82,100
Viscosity at 100 /s (cP)	35,800	41,800	35,000	34,600
SI (2.5/100)	2.2	2.1	2.2	2.4

Table 5: Litho ink formulations with various amine synergists

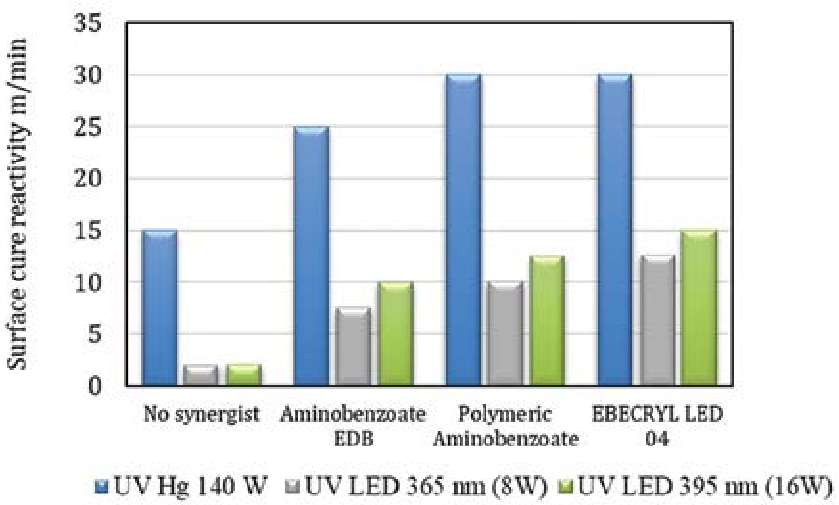

Figure 4: Surface cure speed of various litho inks cured by Hg or LED lamps

Components	Control	A	B
EBECRYL 452	24.2	22.7	21.2
NPG(PO)2DA	24.2	22.7	21.2
PETIA	24.2	22.7	21.1
EBECRYL LED03	-	4.5	9.1
Pigment	18.1	18.1	18.1
TPO-L/DETX (50/50)	5.4	5.4	5.4
Wetting & dispersing additive	3.4	3.4	3.4
Defoamer additive	0.5	0.5	0.5
Total	100.0	100.0	100.0
Viscosity at 1.1 /s (cP)	803	1410	1370
Viscosity at 2500 /s (cP)	439	573	712
Shortness, 1.1/2500	1.8	2.5	1.9

Table 3: Flexo ink formulations with or without EBECRYL LED 03

which greatly reduces the risk of migration. This article will discuss three amino acrylates which have been evaluated for their ability to reduce oxygen inhibition and help increase overall surface cure. Their characteristics and applications in overprint varnishes (OPVs), flexo inks and litho inks will be evaluated and discussed.

EBECRYL LED03 FOR OPV AND FLEXO INK APPLICATIONS

EBECRYL LED 03 is an amino acrylate from Allnex that is suitable for overprint varnishes, flexo and inkjet ink applications. The characteristics of EBECRYL LED 03 are shown in **Table 1**. The material is low-colour, low-odour and has low viscosity. Due to its ability to be crosslinked into the matrix, providing a low incidence of migration, along with its Swiss and Nestlé [global standard] compliance, this material is suitable for food packaging applications. The dosage of these materials is typically 5–20% in the total formulation.

Various OPV formulations with different types of photoinitiators were prepared to achieve similar viscosities, as shown in **Table 2**. The addition of 15% EBECRYL LED 03 is seen in some of the formulations, so that a direct comparison can be made between different formulations. The formulations were applied to black and white Leneta charts [free from optical brighteners that can affect instrumental colour measurements] with a target thickness of ~5 microns. The materials were then cured under 395nm LED at 70fpm, yielding a supplied energy density of around 760mJ/cm^2. The distance between the substrate and the lamp was about 1cm. To evaluate the surface cure of the material, the surface was gently swiped with a wooden stick and then observed for any presence of marring. The yellowing index of the films was reported as the △b value measured with a BYK Spectroguide Sphere.

The results indicate that with the addition of 15% EBECRYL LED 03, there can be a definitive reduction in the amount of photoinitiator used without a negative impact on the curing speed. Generally, the colour of the coating layer is decreased with a lower amount of photoinitiator in the formulation.

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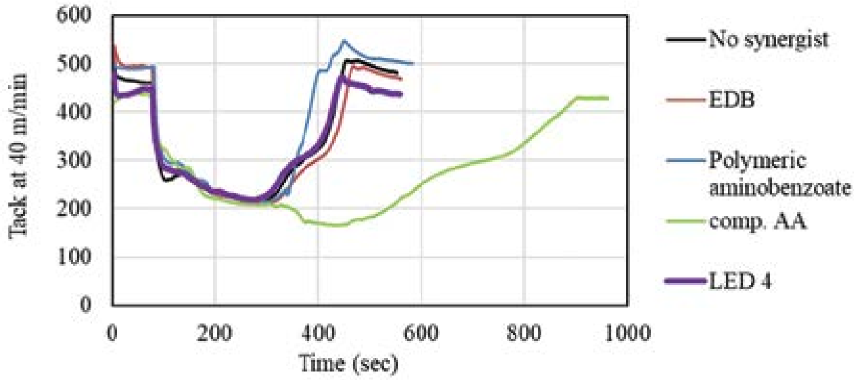

Figure 5: Hydroscope testing of litho inks

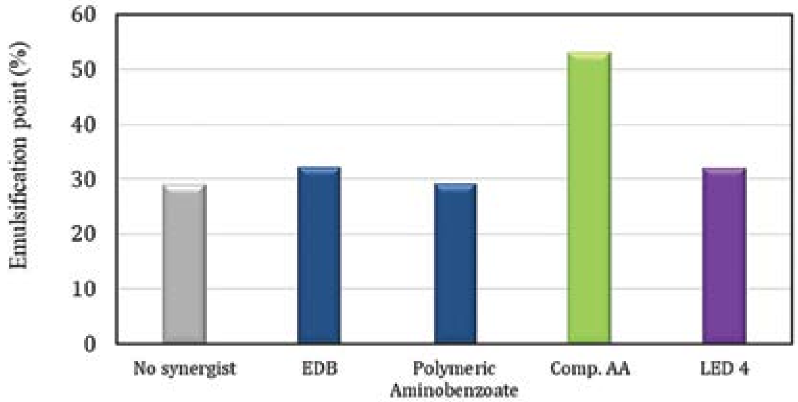

Figure 6: Emulsification point of litho inks

This is beneficial because a decreased amount of photoinitiator can lower both the colour and the cost of the coating layer, along with minimising the risk of photoinitiator migration.

"Surface cure is completely dependent on short wavelength light"

The flexo inks were prepared according to the formulations shown in **Table 3**. The material was added at 4–10% to the overall formulations. The viscosity of the inks was evaluated at both a low (1/s) and high (2500/s) shear rate. The shortness index was determined by evaluating the ratio of the viscosities at both the low and high shear. Newtonian fluids [which have a viscosity that is affected only by changes in temperature or pressure] have a shortness value that is equal to one, as the viscosity of the materials should not alter with changes to the shear rate. Therefore, the closer to one the ratio is, the more Newtonian the ink will be. A more Newtonian behaviour will lead to better performance of the ink on the press. With similar shortness indices between the different inks, this shows very little change to the overall rheology of the ink formulations with the addition of EBECRYL LED 03.

Three colours of inks were prepared, based on the formulations in **Figure 3**, applied to the substrate and subsequently cured under a 395nm LED. The speed of the surface cure was compared between the three different formulations. As shown at the bottom of **Figure 3**, the surface reactivity was much improved through the addition of EBECRYL LED 03 in each colour. A higher degree of surface reactivity is achieved when using a higher level of EBECRYL LED 03.

EBECRYL LED 04 FOR LITHO INK APPLICATION

In the past, amino benzoates, such as Ethyl-4-(dimethylamino)benzoate (EDB) have been used in litho inks due to the fact that they are more reactive than simple tertiary amines. EDB is also hydrophobic [repels water], so it works well for litho applications where the ink-water balance is critical. Recently, this material was reclassified as a reprotoxin 1B under REACH [registration, evaluation, authorisation and restriction of chemicals] regulations. The development of EBECRYL LED 04 was targeted to be an offset to replace EDB. EBECRYL LED 04 is a hexafunctional acrylate, which allows it to be cured into the acrylate matrix. The ability to be crosslinked into the system allows for a decreased likelihood of migration. The addition of its compliance with both the Swiss and Nestlé lists, makes it a perfect match for food packaging. **Table 4** exhibits the features of EDB, EBECRYL LED 04 and another reference polymeric amino benzoate product.

The formulations used are available in **Table 5**. EDB, a reference polymeric amino benzoate and EBECRYL LED 04 were used in the formulations, at varying amounts, to ensure a comparable amine content for each coating. The viscosities were evaluated at both high and low shear conditions along with the shortness index for each formulation. These formulations show similar low shortness indices, indicating the addition of the amine synergist has little impact on ink rheology. All inks were printed onto Leneta charts and cured using not only mercury lamps, but also both 365nm and 395nm LED lamps. The minimum speed needed to adequately cure the surface was evaluated; the data is shown in **Figure 4**. The curing of the surface of the film was improved significantly with the addition of amine synergists. This improvement can be seen not only in the mercury cured samples, but also the UV LED cured materials. The use of polymeric materials or EBECRYL LED 04 in the formulation can further improve the surface cure speed when compared with only EDB.

"Generally, the colour of the coating layer is decreased with a lower amount of photoinitiator in the formulation"

The ink-water balance of litho inks is integral to achieving a good print quality.

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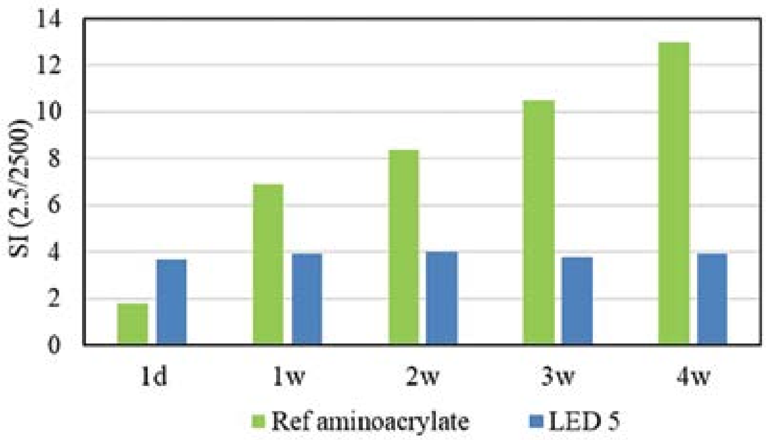

Figure 7: Shortness index of flexo inks with reference amino acrylate or LED 05 as a function of storage time

Properties	Value
Acrylate functionality	6
Appearance	Clear liquid
Viscosity at 25°C(cP)	~ 7,500
Amine content (mg KOH/g)	95

Table 6: Features of EBECRLY LED05

Pigment paste*	
Polyester acrylate (4f)	60
Stabiliser	1
Pigment red 57:1	35
Dispersing agent	4
Total	100

Table 7: Preparation of pigment paste

Components	Flexo ink
Pigment paste*	46
NPG(PO)2DA	18
PETIA	18
PI (DETX/TPO-L) (50/50)	8
EBECRYL LED05	10
Viscosity at 2.5 s^{-1} (cP)	4,070
Viscosity at 2500 s^{-1} (cP)	1,100
SI (2.5/2500)	3.7
Surface cure speed(m/min) (395 nm LED, 16 W/inch)	7

Table 8: Flexo ink with EBECRYL LED05

If the overall ink is too hydrophilic [readily absorbs water], it will pick up a large amount of water and cause ink to migrate to the non-image area of the printing plate. This can cause the print to lose optical density

> *"Use of some amine synergists can cause a drastic increase in viscosity with time"*

and dot gain, both of which lead to differences in colour. Furthermore, if the ink is too hydrophobic, the emulsification process does not happen, leading to uneven inks. Litho inks have to maintain a good ink-water balance to ensure that they can be emulsified with water to stablish a fine and stable emulsion. This fine emulsion allows the ink to transfer correctly to the blanket and then be precisely printed on the substrate. To evaluate inks, more specifically ink-water balance, a hydroscope is used to determine the total formulation. This technique is used to monitor the tack as a function of emulsification. This tool meters water into an ink at a constant speed, and measures the tack value with time. As the water comes into contact with the ink, the tack value will continuously decrease and eventually reach a plateau with more water. After the water stops, the tack value will recover to its original level.

Figure 5 contains the hydroscope results of multiple litho inks. In order to establish the influence of amino acrylates on ink-water balance, it is imperative to include a comparative amino acrylate in the study. In comparison with the control formulation, which contains no amine synergist, the tack values for almost all of the inks are comparative. Each ink, minus the

Figure 8: Flow of flexo ink with reference amino acrylate or LED 05 (left: one day storage at RT; right: four week storage at RT)

comparative amino acrylate, shows a decrease to the same plateau level and then an equivalent recovery. This data is indicative that the addition of these materials does not have a negative impact on the ink-water balance of the final formulation. The comparative amino acrylate does not show the same performance. This particular amino acrylate reaches a much lower plateau than its counterparts and also takes a much longer time to recover. This lack of performance is due to the fact that the material is more hydrophilic, causing the ink to absorb a larger amount of water, negatively impacting the ink-water balance of the formulation. The emulsification point of the material can also be determined through hydroscope testing. A higher emulsification point is indicative of a higher degree of water absorption, pointing to a more hydrophilic material. **Figure 6** confirms the higher emulsion point of the comparative amino acrylate, while the other materials have similar values.

EBECRYL LED05 FOR FLEXO INK

The stability of inks is incredibly important, especially for flexo inks, where low viscosity is critical to performance. The use of some amine synergists can cause a drastic increase in viscosity over time. It is speculated that there is an interaction between the amine and the surface treatment of particular pigments that are used. Allnex developed EBECRYL LED 05 specifically to address a lack of ink stability in flexo inks. This material has the added advantage of being a low migration material (characteristics in **Table 6**).

Flexo inks with 10% of EBECRYL LED 05 were prepared based on the formulations in **Tables 7 and 8**. To ensure better performance than the reference amino acrylate, a formulation was made with a reference material as well. The viscosities of the inks were evaluated at both low (2.5/s) and high (2500/s) shear rate and measured over time. These values were used to calculate the shortness indices. **Figure 7** displays the shortness index for the two inks over a period of time. Initially the reference amino acrylate has a lower shortness index, showing a more Newtonian behaviour in comparison with the EBECRYL LED 05 formulation. During the storage of the inks, however, there is a distinct increase in the shortness index of the reference amino acrylate formulation. From this data, a direct correlation can be made to the instability of the ink. The EBECRYL LED 05 material, on the other hand, maintains a low shortness index with very little change over time. **Figure 8** confirms the instability of the ink by showing the ink flow on a flow plate. The drastic difference between the flow of the reference amino acrylate ink and the material made with EBECRYL LED 05 confirms the increased stability of the final product.

CONCLUSION

With the continued increase in the use of UV LED lamps for curing of coatings, there is a need to create products that increase surface cure to meet the demands of the packaging and coatings industry. Three LED booster materials were evaluated and show a large degree of promise for this market. EBECRYL LED 03 proves to be a perfect match for OPVs along with flexo and inkjet inks. EBECRYL LED 04 has proven to be an excellent partner for litho inks, due to its hydrophobic nature; it can be used to achieve a higher degree of surface cure without sacrificing the ink-water balance properties. EBECRYL LED 05 was designed to meet the high demands of flexo ink formulations, combining an increased stability over conventional materials with the ability to

> *"These materials are primed for success in the UV LED curing space"*

increase surface cure. All three of these materials are listed on both the Swiss and Nestlé food packaging standards lists, and show marked improvements over conventional materials with regard to migration possibilities. These materials are primed for success in the UV LED curing space, whether in conventional packaging markets or the newest consumer electronics applications. ■

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