Advances in UV/EB Chemistry and Printing Technology

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Abstract

UV and EB curing have been expanding at an unprecedented rate over the last several years. This technology is already well established in publishing (coatings for magazine covers) and, especially, packaging areas of the Graphic Art industry. Traditional acrylate based products have been dominated most of these applications since this technology was first introduced in the late 60's. The latest trends in free radical polymerization of acrylates in respect to Graphic Art are low odor products; improved lithographic properties of UV/EB offset inks and coatings with stable gloss. Cationically curable cycloaliphatic epoxy based products are finding application in the areas where advanced physical properties and adhesion to plastics are required. Water based UV/EB curable products have recently been introduced to the market place. These monomer free systems offer very low odor and performance characteristics of typical 100% solid energy curable products at a lower film thickness. One of the benefits of monomer free products is almost negligible skin irritation, some times associated with acrylate monomers. Novel chemistry and enhanced properties of traditional acrylates have led to development of liquid energy curable inks for packaging. Recently introduced UV flexographic printing has already demonstrated superior printability (reproduction of gray scale), faster press speeds and outstanding physical properties required for various packaging applications.

Introduction

Chemistry of ultra violet (UV) and electron beam (EB) inks and coatings has been changing over the last several years in order to adapt to the rapid evolution of the printing technology and the aggressive penetration into previously inaccessible segments of the market. While free radical chemistry of the UV/EB lithographic inks remains the same to a large extent, emerging liquid ink and coating applications have stimulated the introduction of some novel approaches to formulation. In this paper, we would like to present some of the new trends in formulation of energy curable products as well as their applications.

Energy Curable Lithographic Inks

UV/EB lithographic inks are very well established on the market today. Their major benefits are good physical and chemical resistance properties that are achieved immediately after curing. This allows for the converting of folding cartons in-line without damaging a printed image (scratches, flaking off etc.), something that is hardly achievable with conventional oil based lithographic inks.

It has always been a challenge to formulate energy curable lithographic inks with acrylate monomers and oligomers as "building blocks" due to their polar nature. Higher polarity leads to the formation of a relatively stable emulsion and poor "release" of fountain solution on the plate. This may cause plate toning which forces a pressman to raise water setting. Water trapped in the ink affects the ink transfer and narrows the so called "water window" or ability to sustain print density with excessive amount of water. A number of novel acrylated oligomers with lower polarity have recently been introduced for this application. Fatty acid modified polyesters and, recently, epoxy acrylates are recommended for improved lithographic performance of the energy curable offset inks.

A novel approach has been demonstrated with the introduction of "hybrid inks". The hybrid inks represent an attempt to improve drying of conventional sheet-fed inks, that suffer from so called "dry back" or reduction of initial print gloss of an in-line applied UV overprint varnish (OPV). This phenomenon is especially noticeable over the higher coverage print areas. UV coating applied over still wet ink film can be visualized as a rigid polymeric layer sitting on the top of a continuously changing its volume liquid base. The change is a result of both loss of some ink components (oil) and the polymerization process. Highly cross-linked UV coatings do not have the required flexibility to adjust to the changes in the ink's topography. This results in deterioration of gloss proportionally to the variations in the ink coverage. In other words, gloss changes vary throughout the print.

The plot below represents the statistical analysis of gloss distribution over the print job produced on a Komori press with two conventional and two hybrid sets of inks. In this test, a four-color print job was coated with UV OPV in-line without intermediate cure. Measurements were performed in 7 different locations representing different ink coverage. Locations 1 through 4 represent heavy ink coverage (up to 400% trapping) while locations 4 through 7 are areas with medium and light coverage.

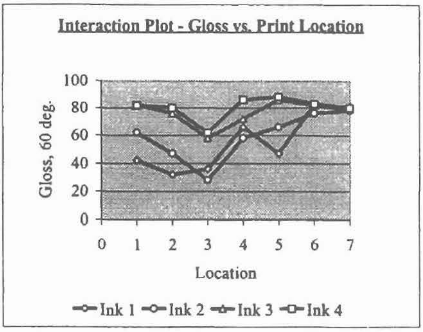


Figure1

Conventional oil based sets of inks (1 and 2) have large gloss fluctuations while hybrid sets (3 and 4) demonstrate more uniform gloss throughout the print. If additional UV lamps are used to cure inks before over-printing with UV coating (between some printing stations or just before coater), gloss variations become negligible. UV curable components combined with conventional materials in the hybrid inks accelerate drying under UV exposure, therefore, reducing "dry back".

Liquid Energy Curable Inks and Coatings

Liquid ink technology has become an area of great interest after the introduction of UV flexographic inks several years ago. The success of UV flexo demonstrated the versatility of these products and the benefits they can offer in virtually any area of printing and converting. On the other hand, these new applications have exposed some limitations of existing energy curable products that had to be overcome in order to replace conventional inks and coatings.

Two groups of technical requirements are typically taken into consideration when decision about printing method selection has to be made. They are print quality and physical properties of the print. While a ratio of their importance varies depending on application, a system that scores the highest in both categories has a good chance to succeed. If we are to name the most common requirements in both groups, then the following list can be compiled:

Print Quality:

- Solid ink lay
- Gray Scale reproduction

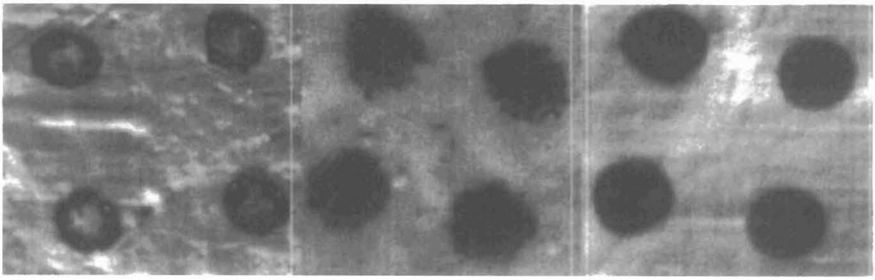
Physical properties:

- Cure speed
- Low odor
- Adhesion
- Abrasion and chemical resistance

Some aspects of print quality in UV flexo printing have been discussed before [1,2]. It has been shown that exceptional print quality can be achieved by selecting appropriate anilox roller and manipulating press settings. Inherently good dot structure has been the most attractive feature of the UV flexo printing attributed to higher viscosity of the UV ink. While being liquid in nature, UV flexo inks can produce the large variations of dot size depending on press settings. For example, an excessive printing pressure that is set to improve the solid ink lay can upset the proper balance of the gray scale. Therefore, the optimization of the printing press conditions that can produce both balanced gray scale and uniform, pinhole free solids is very important for the success of this technology.

Low spreading of the UV flexo inks leads to an exceptional dot structure in the printed image. Typical microphotographs of the water-based flexo, lithographic offset and UV flexo inks printed on the same type of recycled board show clear differences in the shape of the individual dots (Figure 2).

Dot Structure of Different Printing Processes over Non-Coated Board



Water Based Flexo Inks *Offset Inks* *UV Flexo Inks*

Figure 1

Water based flexographic inks tend to have mottled or uneven ink lay within the dot area, especially at higher press speeds. Different drying of the water based inks in the middle and at the perimeter of the ink droplet causes viscosity and surface tension gradients within the printed dot [3]. As a result, water based dots may have lighter and darker areas.

Offset dots are much more uniform than water based flexo dots because ink transfer is achieved primarily through adhesive forces which are relatively uniform throughout the dot area. Spreading on the printed surface is rather limited in this case due to very high viscosity of the ink. The dots have a slightly uneven contour reflecting micro roughness of the paper substrate.

The UV flexo ink produces uniform dots with a circular contour. Its viscosity is low enough to allow equal spreading in all directions, and the ink does not dry until it is exposed to UV light. After that, instantaneous polymerization "freezes" the ink, preventing it from further spreading. UV flexo inks are generally stronger than conventional water based flexo inks and are printed with finer anilox rollers. Similar print densities are produced with thinner ink film and a lower thickness gradient from the center to the contour of the dot. These factors also contribute to the uniformity of the ink lay.

Consistency of print quality is an other important factor in the selection of a printing method. One of the problems associated with solvent-based flexo or gravure printing is poor ink transfer at higher press speeds. It is usually more pronounced at highlights of the print image. Yuri Bery, had proposed a mechanism of ink transfer in gravure printing [4] based on his measurements of "flushing skin temperature" on the surface of the gravure cylinder. This temperature can be as high as 200 °C at 2 m/sec press speed (400 ft/min). Excessive overheating is a result of friction between doctor blade and gravure cylinder. This, in turn, leads to loss of solvent and an increase in ink viscosity, especially in shallow cells of highlights. Contemporary flexographic printing today is not much different from gravure in this respect. Most of the presses are equipped with enclosed doctor blade systems, which use not one but two steel doctor blades and presses are routinely run at 800-1000 fpm. Additionally, ceramic anilox rollers do not dissipate heat generated from friction as well as chrome coated copper based gravure cylinders. All these factors lead us to believe that a very high "flushing skin temperature" may also be responsible for the high-speed transfer problem in the case of solvent-based flexographic inks. On the contrary, viscosity of 100% UV flexo inks will remain unchanged or, possibly lower depending on the temperature gradient.

In order to confirm this field observation, UV flexo cyan ink was printed on the Chesnut flexo press using banded anilox roller with engravings varying from 280 to 800 lines/inch and press speed gradually increasing from 100 to 900 fpm. Ink transfer identified by the print density does not change with the increase of press speed even at the 800 lines/inch band, which represents the most shallow anilox cells.

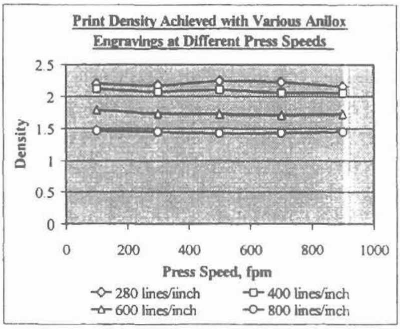


Figure 3

Chemistry of Energy Curable Inks and Coatings

Physical properties of the ink film are for the most part determined by the ink chemistry. Typical UV and EB curable compositions follow the polymerization scheme presented below.

Free radical polymerization of acrylates under UV and EB irradiation is well known and widely used in printing. In first instance, photoinitiators added to a mixture of acrylate functional oligomers and monomers produce free radicals under UV exposure. Free radicals "attack" double bonds of acrylates starting rapid polymerization of the mixture.

Free Radical UV:

Acrylate Ester/PI →UV → PI• →Initiation → Propagation/Chain Transfer→ Polymer

In the case of EB irradiation, the presence of photoinitiators is not required. Electrons "attack" double bonds directly and through a series of events lead to a fast cross-linking of the mixture. Free radical polymerization is inhibited by oxygen. This is especially noticeable on the ink or coating surface that is exposed to oxygen of the air to the greatest extent. While in UV curing an effect of oxygen can be offset by the presence of electron donors such as amines, EB curing requires inerting, i.e. application of a nitrogen blanket that reduces concentration of oxygen below the 200 ppm level.

Free Radical EB and UV/EB:

Acrylate Ester/PI →EB → R• → Initiation → Propagation → Polymer

While free radical polymerization is a very rapid process, resulting polymer network leads to the shrinkage of the ink film. In most cases, higher functionality acrylates needed for very fast curing (0.03 sec on some central impression flexo presses) may induce excessive shrinkage and the loss of adhesion on plastic substrates. Cross-linking of free radical inks depends on color because pigments have different absorption in the UV zone. Some pigments (blue, black) interfere with curing by absorbing a large portion of UV energy and, and therefore, reducing concentration of photogenerated radicals.

The electron beam is comparatively "color blind" and degree of cure, generally, does not depend on the pigment. EB web offset does not require inter-station curing. EB litho inks are tack rated and get cured all together at the end, quite often with EB curable OPV applied in-line. EB alone cannot be used for curing free radical liquid inks that are not tack rated and required inter-station UV curing. However UV/EB combination can improve adhesion due to the deep penetration of electrons capable of additional cross-linking between UV cured ink film and plastic substrate. Since inks are already cured before entering an EB unit, and EB is used to enhance physical properties of the ink film, oxygen does not have its effect on the surface cure.

UV curable cationic inks have been recently introduced on the market place. Cationic polymerization of epoxides requires presence of acid generatingIt has been reported photoinitiators and follows the scheme bellow:

UV Cationic:

Epoxide/PI $\rightarrow$ *UV* $\rightarrow$ H^+ $\rightarrow$ *Propagation/Chain Transfer* $\rightarrow$ *Polymer*

Cycloaliphatic epoxides and vinyl ethers typically used in cationic inks offer very good adhesion on most plastic films. Other benefits of the cationic polymerization is a post cure effect attributed to the presence of photo-generated protons in cured ink film that can reach remaining non-reacted epoxy groups long after initial UV exposure. While initial cure of the cationic inks also depends on color, final cross-linking density (typically after 24 hours) is color independent due to post cure effect. Some other positive features of cationic inks are low odor, the ability to dissipate static electricity, and lack of shrinkage. The latter is very important for label printing because any curling resulting from a stress introduced by the ink shrinkage has a negative effect on the process of automotive label application.

Water based Energy Curable Systems:

Low molecular weight components present in energy curable inks and coatings may limit the use of these products in some packaging applications. For example, excessive amount of monomers required for viscosity adjustment has a negative effect on the cure speed and adhesion of the UV curable liquid inks. Also, they can contribute to a residual odor of the final package. It has been reported [5-6] that water, to some extent can replace the low molecular weight monomers in UV/EB formulations. While a polymerization scheme does not change in this case, water removal is required in order to produce completely cured ink film.

Water based free radical system (UV/EB):

Acrylate Ester/(PI)/H_2O →UV/EB → PI• → H_2O↑ → Initiation →Propagation/ Chain transfer/Polymerization

Water-based energy curable systems can be formulated as hetero-phase (emulsions or colloidal dispersions) or mono-phase (water-soluble) compositions. In the first case, acrylate functional materials are added to emulsified acrylic polymer while a photo-initiator (PI) can be introduced into continuous water phase (water soluble PI) or directly into the polymer/acrylate mixture (oleofilic PI). Interpenetrated network of acrylic polymer and cross-linked acrylate is formed after drying following by UV curing.

Another approach is to use solutions of the hydroxyl functional pre-polymers such as polyurethane, epoxy, polyester or polyether acrylates in water. These systems reportedly demonstrate excellent surface cure. In all cases, water containing photo-curable compositions may have many positive attributes of conventional water-based systems, while physical properties of the cured film are very similar to those of 100% solid UV curable systems. Water is an excellent viscosity reducer and its presence makes it easier to formulate photocurable systems for applications that require very low viscosity (wood coatings, ink-jet printing). At the same time, UV cross-linking leads to formation of films with excellent physical properties, unachievable in most cases with the conventional water based systems.

Deinking of Energy Curable Inks and Coatings

A different mechanism of cure raises some questions about the effect that energy curable inks and coatings may have on paper recyclability. In order to answer this question, RadTech International initiated a study conducted by Beloit Co[7]. . In this work, several ink-coating combinations (conventional, EV and EB) were subjected to pulping and deinking, i.e. flotation and cleaning, and in some cases dispersion and washing. The study focused on the two most important parameters characterizing deinking performance:

- Efficiency of ink/coating removal from pulp;
- Brightness (light reflectance)

A matrix below represents a scope of tested ink/coating combinations and the summary of deinking results (the paper base was a bleached kraft in all cases):

Visible Ink Specks in Pulp, % (>50 micron)

Inks	**Coatings**			
	Water Based	*Catalytic Water Based*	*UV*	*EB*
Comventional Offset	L/1.73 (3.94)*	K/2.93	J/1.36	-
UV Offset	I/1.02	-	H/2.17	-
EB Offset	-	-	-	G/4.16
Water Based Flexo	F/0.63	-	D/11.70	-
Heatset	C/4.59	B/6.48	A/6.86	-

* Repeat

While the combination of water-based flexo inks and coating (F) had the lowest speck count, UV offset inks demonstrated very good deinking results with both water based (I) and UV (J) overprint coatings. Overall, energy curable materials did not appear to be significantly worse than typical conventional inks and coatings.

While all tested materials could be recycled for low-grade board, better quality paper products require higher brightness and, therefore, additional flotation of the pulp. Comparative brightness of the tested samples before and after flotation is summarized in the table below. With the exception of water based inks, additional floatation led to increased pulp brightness. Low brightness numbers yielded by water based ink samples are attributed to the excess of very small ink particles, probably below 50 micron, that are not visible as specs but can affect pulp brightness. The EB ink/EB coating combination demonstrated especially high removal efficiency as compared to other tested samples.

Overall, this study demonstrated that energy curable products can be used for the recycling of paper, and in some situations, can offer benefits of easy removal and high pulp brightness.

Brightness Profile Before and After Flotation

Inks	Coatings			
	Water Based	*Catalytic Water Based*	*UV*	*EB*
Comventional Offset	70⇒78	73⇒82	75⇒80	-
UV Offset	76⇒85	-	76⇒83	-
EB Offset	-	-	-	77⇒82
Water Based Flexo	24⇒43	-	30⇒24	-
Heatset	57⇒80	66⇒78	63⇒81	-

Acknowledgments

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