UV-Curable Graphic Arts versus Industrial Inkjet Inks: A Progress Report

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It is quite well known that UV/EB technology has played a leading role in the development of coatings, adhesives and inks. Traditional ink technologies based on UV offset, litho, and flexo (as well as screen) were the main workhorses of the printing industry . More recently, UV Inkjet inks have been gaining significant traction in the printing arena, especially in the graphic arts market. Industrial printing is also definitely picking up due to the advantages of personalization and customization, line speed, environmental benefits and physical characteristics that UV brings to the end-user for their specific application[1]. The question is how to differentiate these two markets—Graphic Arts versus the Industrial Inkjet Market.

- The Graphic Arts Market is currently well established and will maintain high growth in the wide format and signage sectors. Process colored inks will generally suffice for this market while still requiring good physical characteristics, including adhesion and chemical resistance. Overall, the path to this market is through relationships with original equipment manufacturers (OEMs)—although recently the entry of the third party suppliers has limited the profits.
- The Industrial Inkjet Market, on the other hand, is enabling where demands for the fluids as well as the curved film are varied and customer specific. This requires tailored inks, as a universal ink may not be suited for all applications. Both process and spot-colored inks (including white and a clear inkjetable overcoat) are required. These inks must provide excellent adhesion to customer-specific substrates (including glass and metals) and provide excellent intercoat adhesion between the ink layers. The inks' adhesion needs to meet end-user specifications, which in many cases are very intense. In many instances a custom-built printer featuring secondary cure and in-line part fabrication, etc, are also required. This presents an opportunity for ink makers to be a part of the "Total Solution Provider."

Due to the demanding nature of the "Industrial Print Market," formulating these inks is a real challenge. This is primarily due to the stringent requirements being placed on the fluid, both in terms of viscosity and the properties these inks need to exhibit during delivery and upon cure. Thus, there exists an excellent opportunity for the Total Solution Providers to enable this important market segment as it is forecasted that by 2016 the digital industrial print market will be around € 300.9 billion (~ $418 billion, see Table 1). The wide array of printing applications listed in Table 1 demonstrates the versatility of this technology.

An attempt is made in this paper to highlight certain aspects of these two market sectors. The Industrial market segment has far more demanding and varied requirements than the traditional point-of-sale, point-of-purchase, signage-based graphic arts market segment[3]. Within the Industrial market, the ink that is good for application on glass or metal requiring abrasion and hardness may not be good for an application that may require extreme elongation and flexibility. This is especially the case for automotive applications where displays such as gauge clusters and appliqués printed on polycarbonate substrates are thermoformed and will need to be highly flexible so that the printed ink will maintain the same degree of flexibility under extreme stress and provide no sign of ink fading or cracking. Currently, UV screen inks are used in applications ensuing high elongation. However, a digital solution that exhibits similar aspects of flexibility and elongation remained elusive. This paper describes a UV digital solution to thermoformability. An attempt is also made to highlight the current challenges and features of a robust Graphic Arts ink.

Table 1

Summary of digital industrial printing revenue 2006-16 (d billion)[2]

	2006	2011	2016
Display/Signage	8.31	15.28	46.77
Textiles	9.90	16.78	108.11
Labels	2.91	7.37	51.83
Home/office	0.55	1.34	9.29
Manufacturing	0.07	0.18	2.60
Food/medical	0.00	0.01	1.54
Decoration/coating	0.01	0.21	4.46
Security	0.42	0.78	10.99
Electronics	0.02	0.41	25.02
Imagery	2.94	5.86	20.06
Other	1.33	3.72	20.23
Total	**26.46**	**51.94**	**300.90**

Source: Pira International Ltd.

Graphic Arts Ink: Challenges and Features

Apart from the challenges (such as the low viscosity, optimum surface tension, excellent shelf life, particle size and settling stability), the ink also needs to display optimum performance during jetting and good image quality, as well as indoor and outdoor weathering characteristics. Certainly, these challenges are enormous but need to be met to make a truly good graphic arts ink. This is further complicated by the fact that many end-users are also requiring performance suited to their specifications, mainly during the printing and curing process.

Although some of the needs and demands of this segment of the printing market are generally well known, original equipment manufacturers (OEMs) are now requesting more robust inks at a cheaper price. Faster production speeds with better light fastness and wider color gamut, as well as desirable ink adhesion characteristics (along with flexibility and chemical resistance) are also some of the features being highly sought. In many printing applications, the wet out of the ink during the shorter times (typically < 1000 milliseconds) is very important to minimize banding and to achieve good print quality[4]. Banding may not be a significant problem for applications involving advertising where one will see the graphics from a long distance, compared to a short distance in which banding may cause significant image distortion and affect gloss.

Another important challenge in the graphic arts market is creating inks that provide excellent opacity while still maintaining curing features that are reminiscent of the industrial market segment. This is true of a pure 100% black as well as a four-color rich black. Thus, inks that exhibit faster cure speeds, as well as maintaining adhesion and chemical resistance to banner substrates, are desirable.

Another important aspect of the printing-over-the-banner substrate is the ability to wind the prints upon cure as well as unwind them during the application process. In order to maintain this feature the ink needs to exhibit optimum coefficient of friction (COF) to aid during the winding and the unwinding of printed banners.

For instance, a robust graphic arts ink involving all four colors was applied via a drawdown over a vinyl substrate and cured using a standard mercury vapor lamp at an energy density of 150mJ/cm^2. Under these conditions, the ink exhibited very high acrylate carbon-carbon double bond conversion

Table 2

Summary of the results on the film properties of robust graphic arts inks

Testing	Cyan	Magenta	Yellow	Black
% Elongation at 50°C	72.7	78.6	70.4	51.7
FTIR, 1410 cm^{-1} peak, Top surface, Cured at 150 mJ/cm^2	99.8%	99.6%	100%	100%
Static COF, 250 mJ/cm^2, H Lamp	0.17	0.18	0.17	0.16
Kinetic COF, 250 mJ/cm^2, H Lamp	0.10	0.10	0.09	0.09
X-Hatch Adhesion over clear PVC	49	49	49	49
Chemical Resistance measured in terms of rubs over clear PVC	19	28	25	17
X-Hatch Adhesion over PC	49	49	49	49
Chemical Resistance measured in terms of rubs over PC	7	11	12	16
X-Hatch Adhesion over Vinyl	49	49	49	49
Chemical Resistance measured in terms of rubs over Vinyl	6	21	9	10

measured by considering the area of the 1410 cm^{-1} peak between the cured and the liquid ink using Fourier Transform Infrared Spectroscopy (FTIR). The cured ink showed good flexibility and chemical resistance. The flexibility of the ink was determined via % elongation at 50°C using an Instron until the failure occurred. This was either due to cracking of the ink over vinyl or as a result of a substrate failure. The chemical resistance was determined via a Methyl Ethyl Ketone (MEK) chemical rub test until an ink failure occurred. As shown in Table 2, the cured ink exhibited a very low static and kinetic COF lower than the flexible vinyl without the ink, which was typically about 0.7 and 0.37, respectively. This indicates that less force will be required to unwind the printed banner. The static and kinetic COF were determined via Instron using a 100 Newton load cell at 200.7 gram force of a square bar taped with the backside of the vinyl. The bar was allowed to slide at a rate of 100 millimeters/minute over a 5 centimeter length and the static and kinetic COF values were recorded. A blank test involving vinyl substrate was also run as a control. The ink also exhibited great adhesion over several plastic substrates quantified according to the method of ASTM D3359 where “49” refers to the best adhesion and “0” refers to the worst adhesion. Figure 1 is an example of a UV-curable four process color digital inkjet ink printed over a vinyl feedstock.

Industrial Inkjet Market

Industrial inkjet market opportunities are numerous and vary depending on end-user application. Apart from the stringent fluid requirements, it is the film properties (such as flexibility, adhesion, cure at low-energy density, including low energy consuming LEDs, higher opacity and chemical and abrasion resistance) that will have to be addressed to be successful in this marketplace. One such application involving thermoformability via a UV digital inkjet process was examined and is the subject of further discussion.

UV-curable Formable Inkjet Inks

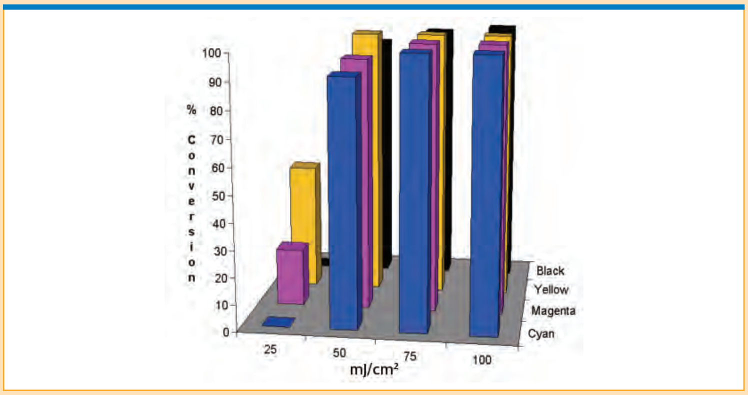
UV-curable coatings and inks are intrinsically crosslinked, similar to a thermoset system. The crosslinking makes it difficult to formulate coatings and inks that exhibit high elongation and formability. Apart from the conventional properties that these inks need to demonstrate, formable UV inkjet ink should also exhibit elongation at temperatures above the glass transition temperature (T_g) of the substrate and under vacuum. Under such conditions, the elongated ink

Figure 1

Example of a robust graphic arts ink printed over vinyl

FIGURE 2

Acrylate percent conversion based on 1410 cm^{-1} peak via FTIR



should not only retain adhesion to the substrate but also exhibit excellent ink coverage without any sign of ink fading or cracking. Furthermore, given the low viscosity of digital inks being typically below 35 cps at 25°C, there is less room to incorporate high-molecular weight, high-viscosity oligomers. This can impact the mechanical properties of the cured ink.

Currently, inks that are thermoformed are printed using a screen ink process. The viscosities of these inks are considerably higher than the digital ink. One of the problems with using screen ink is the necessity to build a wide variety of screens each time the printed image changes. The operator does not have the luxury to change the image on demand as with digital ink, making this process rather tedious.

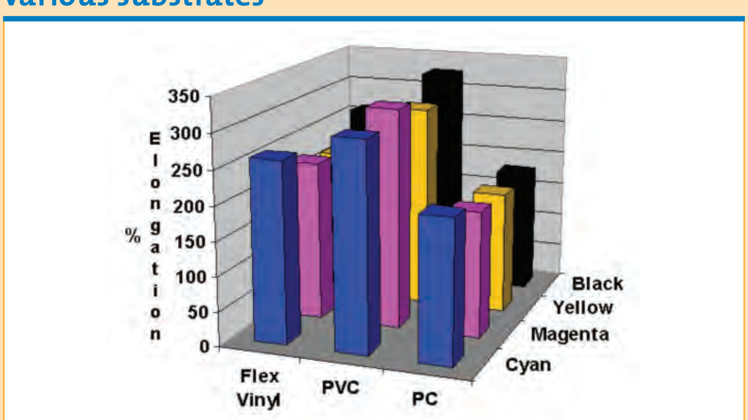
What is Flexibility?

During the forming process (which involves heat, pressure/vacuum), the cured ink over the substrate undergoes continuous elongation or stretching (at a rate similar to the rate at which the substrate is stretched) in different directions. Under such conditions, the elongated inks need to maintain uniform coverage without signs of cracking or stress-induced micro-cracking, as well as maintain adhesion under extreme elongation or stress. Screen inks used in thermoforming applications do provide these features. If digital ink is to be a viable option, it needs to provide the same degree of flexibility as the screen inks. Flexibility is also important for vehicle graphics for applications over interior/exterior signage that is typically associated with complex curves and riveted surfaces.

The onset of crosslinking in the UV/EB compositions results in a covalent bond between the growing chains causing network formation. These network structures compromise flexibility but do provide excellent abrasion resistance. Materials such s polyvinyl chloride (PVC), polypropylene (PP), polyester (PET), polycarbonate (PC) and polystyrene (PS) are thermoplastic in nature and, as a result, thermoform readily. These high-molecular weight materials do not have covalent bonds between the chains. The mechanical properties are dictated by chain entanglements and, to a large extent, depend on the non-covalent interaction between the chains. Typically, a thermoplastic material will exhibit narrow T_g. Below the T_g, the material is in the glassy state and above is in the rubbery state. Similarly, modulus below and above the T_g is higher and lower, respectively. Thermoset systems exhibit broad T_g such that the modulus is typically higher than the thermoplastic material even above the T_g, thus providing somewhat similar properties under wider temperature ranges. As a result, these types of materials have

FIGURE 3

Percent elongation of formable inks over various substrates



excellent hardness, scratch and abrasion resistance.

Requirements of Formable Inks

The requirements for formable inks are very stringent. The ink should exhibit jettable viscosity between 8 to 15 cps, between the temperatures of 40 to 55°C and a surface tension between 20 to 40 mN/m. The degree of polymerization needs to be very high, enabling chain entanglements such that the cured ink imparts excellent scuff resistance at room temperature, typical of materials exhibiting higher T_5. The ink compositions need to be 100% solids without solvent, as solvent aids flexibility due to plasticization but may pose tack, thereby increasing drying times and environmental issues. The cured ink needs to provide extreme elongation at elevated temperatures and under vacuum without cracking or color fading.

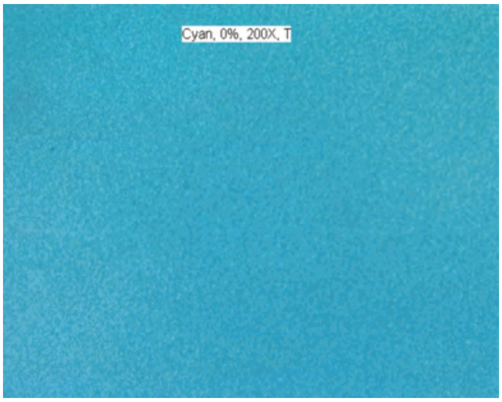
Cure Speed

Formable inks need to be mostly thermoplastic with little or no crosslinkable moieties. During cure these inks need to achieve molecular weight above the critical chain entanglement, which has a direct bearing on the physical and mechanical properties of the cured ink. Since these inks will see most of the consumer contact at room temperature, it needs to exhibit tack-free and scuff resistance at or above room temperature. This feature can only be achieved if the degree of polymerization enables high molecular weight chains, resulting in chain entanglements. The % conversion of acrylate was monitored via FTIR by determining the area under the 1410 cm^{-1} peak for both the cured and the uncured ink at various energy densities. 9-Micron coated ink was cured using a medium pressure mercury vapor lamp powered at 300 W/in, by varying the energy density between 25 to 100 mJ/cm^2 (Figure 2) to obtain acrylate conversion of > 90% at an energy density of 50 mJ/cm^2.

Figure 4

Micrograph of a non-elongated cured ink

0 %



Flexibility and Elongation

In order to exhibit thermoformability, the cured ink needs to be extremely flexible and needs to elongate under extreme conditions and above the T_g of the substrate. Although several test methods are available to gauge flexibility, a quantitative approach was taken via the Instron to obtain information on % elongation. 9-Micron cured ink over a wide variety of plastic substrates (such as flexible vinyl, PC and clear PVC), were elongated at room temperature or above the T_g of the substrate until a failure occurred. The failure mode typically depends on the substrate and the temperature at which the ink is stretched. The modes of failure are typically ink fading, ink cracking or both. The cured ink over the flexible vinyl elongated to over 230% at room temperature, at which point the substrate failure took place. However, at 50°C the ink over the flexible vinyl

Figure 5

Micrograph of an elongated ink aged over a month without micro-cracking

245 %
Day 50

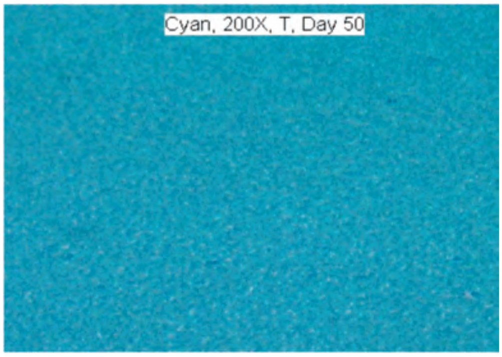
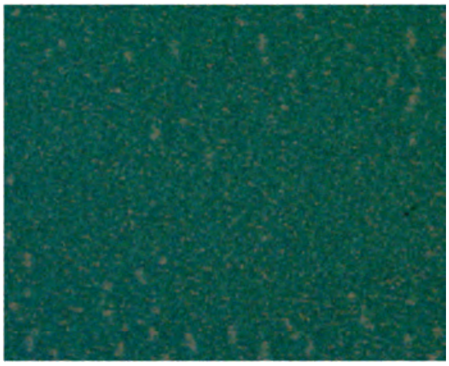


Figure 6

Micrograph of an elongated ink that exhibits micro-cracking

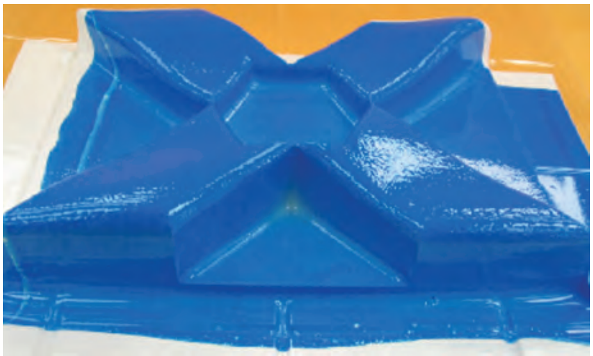


elongated to over 300% at which point the elongation was discontinued. This was also true of an ink over a clear PVC substrate, which when stretched at 75°C exhibited PVC failure before any ink failure at and above 300%. Over the polycarbonate substrate, the ink elongated to over 175% at 150°C. This is shown in Figure 3.

Upon elongation, the cured ink is under extreme stress which over time could induce micro-cracking. In order to investigate stress-induced micro-cracking, the elongated ink over the flexible vinyl substrate (before the substrate failure) was transferred over a glass slide. The stretched ink was monitored weekly for more than a month using an optical microscope to observe any signs of micro-cracking. Figures 4 and 5, is an example of Cyan ink before elongation and upon elongation, aged over a month on a glass slide. An example of micro-cracking of an ink is also shown in Figure 6. The cured ink in Figure 5 does not show any sign of micro-cracking.

Figure 7

Thermoformed cured ink drawn down over vinyl, laminated over clear PVC



Furthermore, the grainy structure of the ink is also evident, indicating well-dispersed pigment particles in the cured ink.

Thermoforming over a 3D Part

In the automotive industry, applications requiring printing and thermoforming of gauge clusters and appliqués (which are commonly back lit) are achieved by the screen process. Digital UV inks developed under the trade name HexiFlex™ are perfectly suitable for automotive applications whereby the printing over flat, plastic stock (such as PVC, PC or PS with higher ink loading) is deposited, cured and formed under heat and vacuum. As an example shown in Figure 7, a drawdown of the Cyan ink using a #6 Meyer rod over flexible vinyl was cured using a standard mercury vapor bulb at an energy density of 700mJ/cm^2. The drawdown was laminated over clear PVC and thermoformed at elevated temperature and under vacuum. Upon thermoforming, the cured digital inkjet ink exhibited high elongation, providing excellent ink coverage and no sign of cracking or loss of adhesion.

Four-process color digital inks were also printed over flexible vinyl and the prints were laminated with a clear, formable laminate to provide extended outdoor durability. The laminated prints were placed over the clear PVC and any air bubbles trapped were removed with a squeegee. The thermoformed print over the mold is shown in Figure 8. Similarly, the printed image over polystyrene containing a clear laminate was also thermoformed, exhibiting a draw of about 2.25 inches with excellent results and is shown in Figure 9. In all these examples, the digital inkjet ink showed excellent elongation and thermoformable characteristics involving uniform ink coverage and no sign of ink cracking or loss of adhesion from the substrate. The lamination adds an extra feature such as extended outdoor durability and also provides gloss enhancement to the print. The added feature makes it very attractive for applications involving fleet graphics, shrink-wraps and blister packaging.

Conclusions

There is now a trend in the high-growth graphic arts market requiring more robust inks that address different facets applicable to the printing industry. Typically, inks that provide faster print speed, versatile color gamut, higher opacity, optimum coefficient of friction, good light fastness, adhesion, flexibility and chemical resistance are being sought by the OEMs and end-users. Furthermore, the ink supplier needs to be well aware of the potential pitfalls related to image quality associated with banding, as well as meeting the cure characteristics that are more typical of lamps being used on the print carriages.

However, unlike the traditional graphic arts market, the industrial inkjet ink market sector is constantly evolving and will need new solutions in relation to inks, equipment and process characteristics. This opens a wide window for formulators and equipment designers. Although screen ink has been the method of choice for many thermoforming applications, the advent of UV inkjet thermoformable inks provides a unique opportunity to the end-user to go digital and achieve speeds and reliability far greater than ever before, while still maintaining similar features provided by the analog printing processes.

Figure 8

Thermoformed laminated printed image, printed with formable inks over vinyl and laminated over clear PVC

Figure 9

Thermoformed laminated printed image, printed with formable inks over polystyrene

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