UV-Curable Inkjet Inks Revolutionize Industrial Printing

By S.E. Edison

Digital inkjet printing has escaped the traditional confines of the graphic arts market and exploded into the realm of industrial applications. Digital printing enables the customization and personalization of printed products that today's consumer demands, quickly and efficiently. The materials that may be digitally printed are limited only by the imagination of the formulators, equipment manufacturers and business leaders. UV-curable inkjet inks are particularly well suited to the industrial arena. Their instantaneous curing allows for in-line processing on industrial presses and they typically exhibit better durability and abrasion resistance than solvent or aqueous inks. Additionally, they are compatible with a wide range of substrates. Also, their environmental impact is less significant than aqueous or solvent inks, as there is no solvent handling or recovery involved, and they enjoy a lower energy cost of drying, especially when compared with water-based inks.

UV-curable inkjet inks are particularly well suited to the industrial arena.

Industrial inkjet printing, although still a fairly new concept, is penetrating the printing market rather aggressively. The total value of the entire global printing market is approximately € 467 billion and projected to increase to € 553 billion in 2010. Inkjet printing is expected to swell from 3.2% of all print in 2005 to 4.4% of all print in 2010. The UV-inkjet market segment is still relatively new (€ 374 million, 0.08% of the print market in 2005), but is forecasted to show steady growth over the next five years.

Table 1 lists the market segments that UV-inkjet inks participate in, as well as their expected average CAGR (compound annual growth rate). The packaging portion (corrugated, flexible material, cartons, etc.) is expected to show the greatest amount of growth as more and more companies customize their packaging to target specific demographics. One facet of the packaging market that UV inkjet has been slow to penetrate is the food packaging segment, as small molecules such as photoinitiators can migrate to the surface of the print and be extracted, making these inks non-FDA approved for food contact applications. Electron beam curing may be used to circumvent this problem by using formulas that do not contain photoinitiators, thus providing the benefits of UV inks while still being acceptable for food contact. Electron beam-curing units have become much less cost-prohibitive in recent years and also more lightweight, making them a feasible curing alternative in many respects. An alternate method to make UV-curable inks FDA approved is to use oligomeric photoinitiators, thus networking them into the cured film and preventing them from being extracted. The "Other Industrial"

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TABLE 1

UV inkjet markets, 2005 and 2010 (€ million)

	2005	2010	Av. CAGR 2005-2010 (%)
Packaging	34.9	1209.1	103
Signage	318.8	3423.7	61
Textiles	5.3	48.4	56
Other Industrial	15	345.7	87.5
Total	**373.9**	**5,026.8**	**68**

Source: Pira International

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category includes things like decorative prints on various items, as well as functional prints where the ink serves more than just an aesthetic purpose such as printed electronics and 3-D printing. This category is fairly wide open and new possibilities are constantly emerging.

Similarities and Differences Between the Industrial and Graphic Arts Inkjet Markets

The graphic arts market is quite mature. Although new hardware is continually being introduced by OEMs to improve the printing and curing speeds and better, more robust inks are constantly being released, the needs and demands of the segment are generally well known. There will always be an interest in faster production speeds, better light fastness, wider color gamuts, adhesion to difficult substrates and lower costs. In this market the substrates are typically various low-surface energy polyolefins and plastics, such as PVC, polypropylene, polyethylene, polycarbonate, polyethylene terephlatate, and vinyl as well as some paper stock. Also, the path to market for ink manufacturers is relatively well established. Typically, the ink manufacturer works closely with the printer OEM, printhead manufacturer, and the lamp supplier to fine-tune the ink for that particular press. The ink supplier sells directly to the OEM, who then repackages and resells to the end-user at a slightly higher price. This makes penetration into the graphic arts market rather difficult, as alliances between OEMs and ink suppliers tend to be both strong and long lasting. Another approach to this market is to sell the ink directly to the end-user as a third party ink. While this is a direct approach that allows more players to participate in the market, it ultimately drives down the overall ink price and is therefore not supported by the OEMs or printhead manufacturers.

The industrial market is a new and continuously evolving beast that differs in many ways from the graphic arts market. The demands are different for each industrial application, so inksets must be custom formulated for various substrates and end uses. The substrates used in the industrial inkjet market are many and varied, from metals to glass to formable plastics and beyond. These printed materials will be used for many applications other than signage and decoration, hence the need for robust inksets. Also, off-the-shelf printers that were designed to deposit one inkset onto flat stock generally do not work for industrial printing. Many of the objects printed for the industrial market are 3-D, requiring sensors to guide the printheads over the surface.

In addition, the curing properties for a significant amount of the inks developed for industrial applications are different than the standard graphic arts inks, requiring UV bulbs with different spectral outputs, as well as some thermal curing capabilities (for example an IR lamp could be used in-line to aid in curing). These equipment and ink requirements make it impossible to make an industrial printer and inkset to fit every need. This impacts the market path as well, since specialty integrators must be enlisted to design the equipment on a per customer basis. In this market, third party inks are less of an option, due to the required customization. Generally, the ink will be fine tuned in parallel with equipment development, similar to the OEM/ink partner relationship for the graphic arts market, but on a more individual basis.

Challenges to the Ink Formulator

As inkjet printing begins to enable more and more industrial printing processes, inkjet formulators are faced with increasing challenges. While digital inkjet will probably never completely replace traditional printing techniques such as screen-printing, it will over take many print processes in the future, provided the digital ink properties can match or exceed those of the existing inks.

One market that is exploring digital UV-inkjet printing, as an exciting new process technique is the automotive industry, for things like gauge clusters and appliqués. Many gauge clusters are printed on polycarbonate and appliqués often consist of flexible vinyl, so initial adhesion is usually not a problem, even for standard off-the-shelf graphic art inks. However, the adhesion and appearance must be maintained even after harsh exposure to the elements. The inks need to have the opacity of the screen inks, particularly if the gauge clusters are backlit. Digital UV-inkjet inks are typically fairly translucent, so the

FIGURE 1

Elongation of a UV-curable digital inkjet Ink "A," side-view

Drawn down on a flat sheet of PVC, then thermoformed

pigment loading must be increased, which can slow the cure speed. As a result, the photoinitiator package must be adjusted to compensate.

Another challenge for this industry is the rigorous light fastness requirements for automotive components, particularly for exterior appliqués, which must have the same light fastness as the paint and require a minimum of two years of outside panel testing in Florida and Arizona with virtually no discernable change in color or gloss. Choosing automotive grade pigments and using HALs (hindered amine light stabilizers) and UVAs (ultraviolet absorbers) can help achieve this. Of course, adding UVAs can considerably slow down the cure speed, as their function is to absorb light that could be used for curing the film. Another possibility is to apply an overcoat to the print to protect the appearance. This overcoat may be inkjetted or applied via screen or spray coat in a separate (but potentially in-line) process.

FIGURE 2

Elongation of a UV-curable digital inkjet Ink "A," top-view

Drawn down on a flat sheet of PVC, then thermoformed

UV-curable inks and coatings are generally more durable than solvent or water borne coatings; however, inkjet inks require a very small particle size (less than 1 micron absolute for optimum jetting performance), which also negatively impacts the overall weatherability (and opacity) of the coating. Yet another hindrance to using digital inkjet to replace screen-printing in this market is the requirement of spot-colors, which often cannot be achieved with four process colors (CMYK) and sometimes is not obtainable even with a hexachrome inkset (CMYK + orange, violet, and/or green). This necessitates the use of specific pigments and can be a time consuming process for the end user to swap many different colored inks into the printer. However, this too will be overcome as various pigment choices and blends constantly expand the color space accessible from process colors.

Examples of Inks Designed for Industrial Applications

Applications where the printed image is thermoformed is one area of printing that has traditionally been dominated by screen. This type of post-forming is used often in the automotive industry. The ink must be able to withstand drastic stretching of up to >300% elongation without displaying cracking and while maintaining adhesion and opacity. UV-curable inkjet inks are inherently rather brittle due to the crosslinked network that results from polymerization. This property is not easily overcome for digital inkjet inks, due to the viscosity requirements imposed by the printhead. The viscosity must be approximately 8-14 cps at the jetting temperature (many printheads have the ability to be heated, some as much as 70°C). This limits the formulator's choice of high-molecular weight oligomers with low-glass transition temperatures (Tg) that would give the cured film more elasticity. The ability to lower crosslink density without compromising cure speed and physical properties while still maintaining a crack-free finish after thermoforming is a real challenge to the formulator. However, it is also important to monitor the abrasion and solvent resistance of the coating, as lowering the crosslink density will lower the films durability.

The inks used in this study were HexiJet™ inks. Figures 1 and 2 show examples of the elongation properties of UV-curable inkjet ink "A." These inks were drawn down with a #6 Meyer rod on PVC and cured using a standard mercury vapor bulb at a dose of 700 mJ/cm^2. The samples were then thermoformed. The digital inkjet ink showed excellent elongation with no cracking. This is useful for many applications, such as fleet graphics for vehicles.

Adhesion to many difficult substrates is another challenge for formulators targeting the industrial arena. Traditional,

FIGURE 3

UV-curable digital inkjet Ink "B" printed on glass

free-radical-based acrylate chemistry is often unsuited for substrates such as glass or metal. One approach is to use cationic chemistries to allow adhesion to many substrates. Figure 3 shows an example of a UV-curable digital inkjet ink "B" print on glass. This image passed a crosshatch adhesion tape test using 610 tape with 100% adhesion.

An important feature for both the industrial and graphic arts market is faster cure speeds for improved productivity. Drop on demand (DOD) piezoelectric printheads are being developed with ever increasing print speeds; however, curing speed often remains the critical factor. The combination of low-viscosity acrylate oligomers, monomers, and specific photoinitiator blends can dramatically increase cure speed and give excellent cured film properties.

The difference in cure speed for some standard free-radical inks and a specially formulated fast-curing inkset Ink "C" was measured. Films of each ink were prepared with a 4.5-micron bar using an automatic drawdown instrument on PET substrate and then cured with a 300-Watt/inch^2 standard mercury vapor bulb at a dosage of 65 mJ/cm^2. Immediately following the cure step, the ink film was placed face up on the bed of a Little Joe Offset Color Swatching Press and a Leneta opacity chart was placed face down on top of the ink film (after the CIE L*a*b* values were collected for the clean chart). The Little Joe press was run across the sample one time. The opacity chart was peeled off of the ink film and cured with a dose of 700 mJ/cm^2, then the color values were reread and the Delta E was calculated based on the transferred ink (Table 2). In this test a Delta E of <0.85 typically indicates a degree of visual ink transfer that is visually acceptable. The "C" inks were all visually acceptable and cured much faster than the comparative inks, having tack-free surfaces after an exposure of 65 mJ/cm^2 (this was the lowest setting available on the curing unit, the inks may actually cure at even lower exposures).

TABLE 2

Delta E values for standard inks and Ink "C"

Comparative Inks			
░	▓	□	■
38.3	26.6	21.6	26.77
Ink C			
░	▓	□	■
0.64	0.6	0.64	0.67

Table 3 shows the percent cure based on the amount of unreacted acrylate (%RAU) left as measured by FT-IR (monitoring the 810 cm^{-1} peak). These samples were prepared in the same fashion as described above, using PVC rather than PET. The inks all had complete adhesion to this substrate and excellent hardness, as measured by pencil hardness.

Yet another ink development that is useful in both the graphic arts and industrial market is the emergence of a white UV-curable inkjet ink. This has many uses, especially for second surface printing for the CMYK colors on transparent substrates. The biggest challenge to formulators is overcoming the sedimentation that occurs when a dense particle such as TiO_2 is dispersed in a low-viscosity fluid. Equipment manufacturers found a mechanical solution by incorporating on-board agitators to continuously mix the white ink and keep the TiO_2 suspended. However, this adds extra cost to the press. This presents an even greater challenge to formulators to develop a solution that allows the TiO_2 to remain evenly dispersed throughout the ink.

Figures 4 and 5 show the sedimentation profiles for two different UV-curable white inkjet ink formulations Ink "D" and comparative white. These profiles were collected with a Turbiscan LabXpert Sedimentometer. For this experiment, a vial of each ink was prepared and the amount of backscattering was measured (the purple line in each profile, shown on the Y-axis in time) along the length of the vial (shown on the X-axis in mm). The vials were stored in an oven set to 60°C and rescanned weekly for four weeks (30 days). The ink in Figure 4 had much better resistance to settling than the ink in Figure 5, which was not formulated with the patent-pending chemical method of suspension. This ink does not require any onboard agitation and can sit unused in the printhead for up to two weeks.

TABLE 3

Cured properties of Ink "C"

	% Cure	Adhesion to PVC	Pencil Hardness
▒	91	100	6H
▓	87	100	9H
□	93	100	9H
■	92	100	4H

FIGURE 4

Sedimentation profile of white Ink "D"

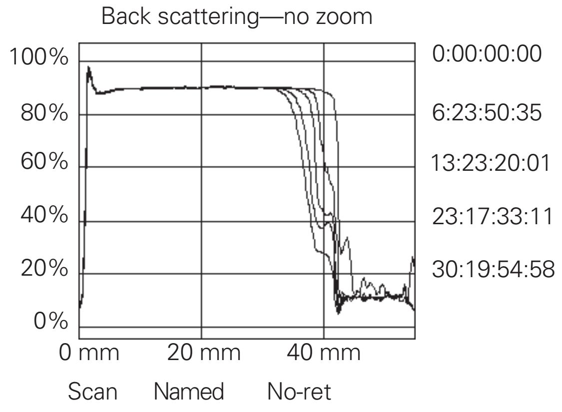
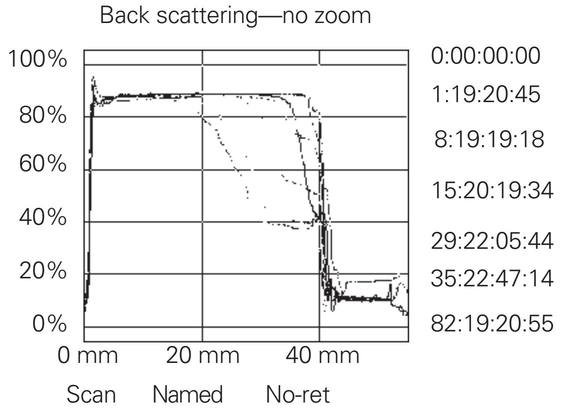


FIGURE 5

Sedimentation profile of comparative white ink



Conclusions

The industrial inkjet market is a new and exciting area ripe with growth opportunities. As digital printing expands into more traditional print areas, formulators will be faced with increasing challenges to make robust inks that can meet the demands of each application. There is often a trade-off as one attribute is enhanced; others may suffer (for example, increasing elongation but decreasing solvent resistance). UV-curable inkjet inks are especially well suited for the industrial market and will continue to provide innovative solutions for each new opportunity. ◗

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—S.E. Edison, Ph.D., is a senior technical development specialist, Hexion Specialty Chemicals, Cincinnati, Ohio.