UV Curable Inkjet Inks: Is There Anything They CAN'T Do?

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Abstract

ncreasingly, the answer to this question is "not much!" The printing market continually presents new challenges and formulators of UV-curable inkjet inks have risen to the occasion by providing multipurpose inks. It's now possible to digitally print on most substrates. Clear inks provide abrasion resistance with variable-gloss finishes. Formable inks may be printed on flat stock and post-formed. Low-dose curing inks can be printed in rapid, single-pass mode, and LED inks are just around the corner.

Introduction

Inkjet printing is enjoying a huge surge in popularity due to many factors such as ease of use (graphic manipulations are all done digitally), personalization (each print can be altered via PC), non-contact application so that many different types of media may be used with little fear of processing problems, and vast improvements in both the hardware and fluids to allow companies participating in printing endeavors to supplement and at times even replace their analogue presses with digital inkjet printers. One of the types of hardware experiencing a tremendous amount of advancement is piezoelectric drop-on-demand (DOD) printheads, which have experienced a great deal of improvement in terms of reliability, resolution, and speed, as compared to other inkjet printhead technologies such as continuous inkjet (CIJ, which has very fast print speeds but poor resolution) and thermal inkjet (TIJ, which has fast print speeds and high resolution, but is limited in the type of inks that may be jetted). Among the available ink technologies (solvent, aqueous, hot-melt or phase change, oil based, and UV curable), one fluid type stands out as the leader in growth, and that is UV curable inkjet ink. There are many reasons for the heightened preference of UV curable formulations over other ink choices. Increased restrictions on volatile organic chemicals (VOCs) and hazardous air pollutants (HAPs) have made the 100% reactive UV curable inks increasingly attractive. Instantaneous cure upon exposure to UV radiation is another benefit to these fluids, as the printed product can be immediately packaged for shipping without waiting for the ink to dry and the diminutive UV lamps have a much smaller footprint and consume less power to operate. Also, typical UV curable formulas have a harder, more abrasion resistant surface due to the highly crosslinked polymer network that is formed upon exposure to UV radiation. The focus of this article will be on piezoelectric drop-on-demand printheads and UV curable inkjet ink formulations for the industrial print market.

UV curable inkjet printers have been an important part of the graphic arts market for years. More recently, they have begun receiving attention from the industrial printing arena as well. This market encompasses a broad spectrum of printed items that may be part of other products or consist of final products themselves. It is much wider in scope than traditional printing on flat stock for advertising and promotional purposes. It is forecasted that by 2016 the digital industrial print market will be €300.9 billion (see Table 1)[1]

	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

Table 1. Summary of digital industrial printing revenue, 2006-16 (€ billion).[1]

The wide array of printing applications listed in Table 1 demonstrates the versatility of this technology. One standard inkset will not achieve the desired results for all of these markets – even a UV curable one. Therefore, formulators are faced with the challenge of making custom fluids that will not only meet very specific needs for individual applications, but will also maintain enough broad based properties to make the product viable for a multitude of markets.

Adhesion to Non-Traditional Substrates

Improvements in the hardware and software have made digital printing even more attractive to the industrial market place. However, the inks that dominate the graphic arts market were designed primarily for a relatively small range of substrates and were not faced with the rigorous requirements that the industrial market calls for. Table 2 displays the breadth of media types found in the industrial arena.[1]

Acrylic/plexiglass	2.81
Aluminium	0.56
Backlit film	0.67
Canvas	1.98
Caps/hats	0.45
Card stock/paperboard	4.46
Catheters	0.01
Ceiling tiles	0.23
Ceramics	0.45
Cork	0.00
Corrugated	4.89
Cotton	2.89
Foamcore	0.92
Foil	0.78
Gator board	0.04
Glass	0.40
Heat transfer paper	5.99
Jackets	2.01
Keyboard pads	0.02
Laminates	4.67
Leather	0.03
Metal	0.02
Microfibre	0.03
Moulded plastic	0.87
Neoprene	0.03
Nylon	2.15
Paper	10.66
PET shrink tubing	0.34
Placket/polo shirts	1.34
Plastic cups	1.14
Polycarbonate	0.01
Polycarbonate/Lexan	0.03
Polyester/Mylar	2.44
Polyethylene terephthalate (PET)	0.56
High density polyethylene (HDPE)	2.11
Polyetheretherketon (PEEK)	1.85
Polymide	0.00
Polypropylene (PP)	1.65
Polyethylene(PE)	0.06
PVC (flexible)	3.11
PVC (rigid)	1.76
Rubber	0.03
Satin	0.02
Silk	0.01
Stainless steel	0.02
Styrene/ABS	2.18
Teflon	0.80
Tissue	2.22
Triacetate	1.11
T-shirts/tank tops	6.18
Tyvec	0.60
Urethane wood	0.03
Vinyl	9.45
Vinyl (pressure sensitive)	9.87
Vinyl (static cling)	1.11
Wood	0.02
Wool	0.06
Other	1.87

Source: Pira International Ltd

Table 2. Industrial printing substrates, based on square meters printed, 2006 (%).[1]

As can be seen in Table 2, there are few limits on the type of media that may be printed digitally.

There are several limitations on the physical properties of inkjet inks for piezoelectric DOD printheads. The viscosity needs to be fairly low, (usually at 8-12 cps at the jetting temperature; most printheads have on-board heaters, capable of reaching up to 70^{o}C in many instances). The surface tension of the inks is also important, and depends on the printhead technology being utilized. Some printheads are equipped with a non-wetting faceplate, while others work best with fairly high surface tension fluids (mid to upper 30's, dynes/cm). Also, pigment particle size and stability is highly critical as the inkjet nozzles are fairly small. Submicron sized pigments with a narrow particle size distribution are required to maintain jet stability.

The requirements listed above make formulating UV curable inkjet inks more challenging than for applications where low viscosity is not mandatory. However, there are many excellent monomers (and even some low viscosity oligomers) that may be used to achieve the desired properties, especially adhesion to plastics. Adhesion to more exotic substrates, including ceramics, glass, and metals, requires more formulating finagling. One approach is to use cationic curing components rather than the traditional free-radical type reagents. This improves adhesion in part by lowering the amount of shrinkage experienced by the film. Typical acrylate films undergo shrinkage upon cross-linking, thus lessening the amount of contact the film has with the substrate. Additionally, polymers cured with cationic photoinitiators do not suffer from oxygen inhibition, resulting in a more thorough and complete cure. However, cationic systems are sensitive to moisture and are also more expensive than standard photoinitiators. A hybrid ink system based on both cationic and free radical curing mechanisms has been designed and applied to an inkjet ink platform that will adhere to substrates such as glass, stainless steel, aluminum, ceramics, brass, bronze, and many plastics, including polycarbonate, polyester, polyvinyl chloride, polyvinylidene fluoride, and polyphenylene sulfone. This ink is fairly impervious to moisture, but does perform better after a thermal postbake of 5-10 minutes at 220-260^{o}C. After baking the film is very hard and impenetrable, even after soaking in boiling water for 30 minutes. It can also withstand extended exposure to steam as well as water soaks for 72 hours. Figure 1 shows the results of a crosshatch performed on a print on glass immediately after removing it from a 72 hour water soak.

Figure 1. Glass printed with hybrid cure ink, cured with UV, thermally post cured for 10 minutes at 220^{o}C, then soaked in ambient temperature water for 72 hours, tested for crosshatch adhesion immediately afterwards.

Figure 1 shows that even after soaking in water for 72 hours, the film maintains its integrity and adhesion to the glass.

Clearcoats for Aesthetics and Functionality

Often, inks used for industrial decorating will be subjected to extremely harsh conditions, such as in applications including automotive interiors, decals for automotive exteriors, name plates for appliances, and casings for cell phones, to name a few. In these cases, the prints need to withstand atmospheric attacks from UV light, extreme temperatures, excessive humidity, exposure to cleaning solutions and other solvents, and abrasion. One way to offer added protection is to apply a layer of clear ink over the image. While it seems that this may be a simple formula change from the ink (merely remove the pigmentation from the formulation and add more monomer), it is actually much more complicated. The clear will need to have superior hardness than the colored inks, requiring an increase in crosslink density. It will also need to provide excellent protection from ambient UV, which may be achieved by adding hindered amine light stabilizers and/or UV absorbers. Finally, it must have excellent intercoat adhesion with the colored inks and offer the same degree of flexibility, so that the clear does not crack off upon bending and flexing. All of these requirements add up to a big formulating challenge.

However, occasionally the need for a clear coat is purely cosmetic. A clear coat can add gloss to an otherwise matte print or it can offer variable finishes for a more interesting look. These types of effects can be achieved by correctly matching the surface tension of the ink to the surface energy of the substrate to ensure that the proper amount of flow/wet-out will occur to create either a glossy smooth or finely textured print. Alternatively, the printer hardware may be subtly controlled to only lay down a small amount of ink for areas that require low gloss, while laying down a thicker “flood coat-esque” layer for highly glossy images.

Either way, formulating a clear coat for inkjetting through piezoelectric printheads is not an easy task, but one that is required more and more often, as demands in the market increase.

Inks for Formable Applications

Another area where UV curable inkjet inks are drawing a lot of attention is in formable applications, whereby inks printed on flat stock are cured with UV radiation, and then vacuum formed to create a three-dimensional part. Markets that are currently investigating this technology include automotive interiors (cluster gauges, gear shifters, consoles, door panels, etc), molded electronics (cell phones and cameras), and fleet graphics (vehicle wraps).

It is a significant challenge to design a UV curable inkjet ink capable of this type of elongation, as UV curable inks are inherently highly cross-linked and brittle. In fact, by their very nature UV curable inks are thermosets, meaning that their modulus is typically higher than the thermoplastic material even above the Tg, while a thermoplastic formula has a modulus that is high below the Tg and low above the Tg. One way to address this issue is to select monomers and low viscosity oligomers that are more thermoplastic in nature. Another approach is to lower the crosslink density significantly, allowing the film to have more flexibility. The tradeoff is that lowering the crosslink density also reduces the hardness of the film and prevents it from withstanding abrasion and scuff resistance, which is crucial for the automotive industry in both the interior and exterior of their product. Applying a protective thermoformable laminate is an inexpensive way to improve the durability of the print. Additionally, a clear ink or jettable laminate could be printed onto the image for protection.

Figure 2. Figure 2 shows an image that was printed flat, cured with UV radiation, laminated, and then post formed with no cracking or loss of opacity.

Figure 2 shows a print of a formable ink, which was designed just for these markets and shows excellent elongation when compared to screen inks.

Rapid Curing for Single Pass Printing

Many industrial printing applications require fast line speeds that preclude the use of a scanning printer. In this case the object being printed will pass under a fixed array of printheads and then experience a single exposure to the UV lamp. This is a much lower dosage than inks receive on scanning printers, where the carriage containing the printheads and the lamp(s) shuttle back and forth over the same area multiple times. In order to achieve full cure at these fast line speeds and low energy densities, careful selection of photoinitiators is required as well as highly functional monomers to promote fast-film building. Additionally, it is highly critical that the ink have excellent jet stability in whatever printhead is chosen, as single pass systems show each missing nozzle with painful precision. Some industrial inks that can cure rapidly under low energy densities (~65 mJ/cm^2) with exceptional nozzle stability have been developed. This is due in part to the Newtonian nature of the fluid as well as the submicron (<300 nm D50) pigment particles present. Figure 3 shows an example of a single pass print using a rapid cure ink – no missing nozzles are evident, demonstrating the robustness of the ink.

Figure 3. Single pass print of a rapid cure ink on PVC cards.

Inks that can achieve a full cure using a solid state-curing unit such as an LED are still under development, as these inks must be tuned to cure not only with a low energy density, but also at a single wavelength (typically 395 nm or higher). However, if the market decides that the benefits of LED lamps, such as low energy consumption and low heat emission, are desirable enough to make the switch to LED lamps, ink makers will be forced to produce inks with similar costs and cured film properties that will cure under those conditions.

Conclusions

As the lure of personalization grows and the realization of the process and time savings that are possible with digital printing dawns on more and more companies, UV curable inkjet sales will continue to enjoy double digit growth. However, this growth is dependent upon the ingenuity of formulators to create inks that can fulfill all of the demanding requirements of industrial printing. Additionally, equipment manufacturers and integrators much continue to expand the frontiers of print quality and speed to make inkjet not just a supplement to traditional print processes, but an actual replacement.

References

1. Romano, F. J., "The Future of Digital Industrial Printing: Strategic Ten-Year Forecasts," *Pira International,* **2007.**