Dual Cure Digital Inks for Industrial Printing

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Abstract

UV curable digital inks are required to adhere to myriad substrates such as plastics, metals, glass, and ceramics. In addition, they are also expected to exhibit good flexibility, abrasion and chemical resistance. Multiple substrate adhesion coupled with rapid turnaround times for digitally printed UV curable inks opens up promising avenues for industrial inkjet printing. This paper highlights the careful balance required in ink formulation and properties to meet the varying requirements.

Introduction

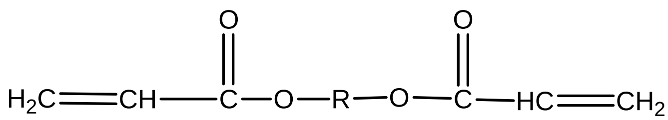
UV curing technology offers several well known advantages such as low VOC's, rapid curing, low energy consumption resulting in its use in wide variety of coatings and inks.[1] The technology has played a significant role in traditional inks such as UV offset, litho, flexo as well as screen inks. It has also entered into the realm of digital printing and has witnessed considerable growth in the traditional graphic arts type market where customization and personalization are the main focus. However, the transition to UV digital for industrial printing is demanding[2] as formulating inks to meet customer specific demands has been a challenge. This is primarily due to the stringent requirements being placed on the fluid component both in terms of viscosity and also the properties these inks needs to exhibit both during delivery as well as upon cure.[3,4]

Although there are significant challenges, UV digital inks are well poised to enter the industrial arena. They exhibit advantages such as fast cure speeds permitting in-line processing on industrial presses. Compared to solvent and aqueous inks they typically exhibit better durability and abrasion resistance as well as environmentally friendly features. In terms of market size the total value of global printing was approximated to be at $ 690 billion in 2005 and is projected to increase to $ 817 billion by 2010.[5] Although inkjet printing was a relatively small segment of about 3.2% in 2005, its overall growth is expected to be around 4.4% by the year 2010. In terms of the print market, the UV inkjet segment is still minuscule and will account for less than 1% of the print and packaging market globally. The projected revenue is about $ 7.4 billion by 2010 from about $ 547 million in 2005, a corresponding growth of over 1000%. The traditional solvent inkjet market is expected to convert to UV inkjet due to environmental concerns related to use of volatile solvents and the cost associated with removal of the solvents after printing over the substrates.

The digital industrial printing market segment has far more demanding requirements than the traditional point of sale, point of purchase, signage based graphic arts market segment. Customized ink sets are generally required to meet properties which are substrate specific and process specific. For instance, a graphic arts ink needs to have good adhesion and abrasion resistance when printed on plastics. However, this ink may not be suitable for industrial application over glass, ceramic and metals that may require good chemical resistance in addition to adhesion. Digital prints on ceramic and glass require the printed ink to maintain excellent chemical resistance against cleaning agents containing caustic, ammonia and good adhesion under high humidity. Currently, UV screen inks are used in these applications. However a digital solution that exhibits similar properties such as chemical resistance and adhesion remains elusive. This paper focuses on a UV curable digital ink which addresses such a need for the industrial printing market.

UV Cure: Polymerization Types

Free radical polymerization is the most common type used in the UV cure industry. The formulations generally contain a mixture of monomers, oligomers, photoinitiators and additives. Acrylates are commonly used as a monomer and **Figure 1** shows an example of a generic acrylate monomer used for this polymerization. Some of the advantages of free radical polymerization include rapid cure, versatile photoinitiator packages, ease of availability and low cost of raw materials. However, they also have some disadvantages such as oxygen inhibition, high shrinkage leading to poor adhesion on multiple substrates, difficulty in curing 3D parts.



Acrylate

Figure 1. Chemical structure of an acrylate. R denotes an alkyl, aryl chain.

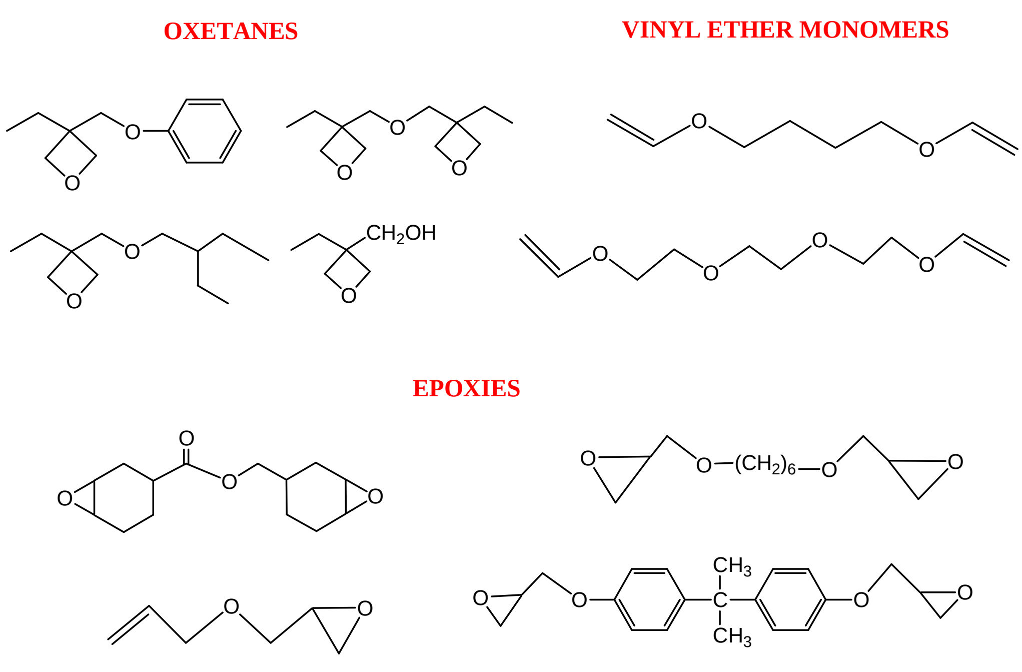


Figure 2. Chemical structure of cationically polymerizable monomers.

Cationic polymerization is another major type of polymerization used in the printing industry. The formulations generally contain a mixture of monomers such as epoxies, oxetanes, vinyl ethers (**Figure 2**). The polymerization can be initiated by either thermal or UV radiation. For the UV cure, the photoinitiators most commonly used include commercially available hexafluoro phosphate or hexafluoro antimony salts of aryl iodonium and triaryl sulfonium. These photoinitiators generate superacids upon UV irradiation which initiate the cationic polymerization. Some advantages include absence of oxygen inhibition, low shrinkage resulting in multiple substrate adhesion, good flexibility, and dark cure i.e. after initiation with UV radiation the cure proceeds in the absence of UV light making it very useful in curing 3D parts. Disadvantages include polymerization inhibition by moisture leading to slow cure, less versatility in photoinitiator packages and expensive raw materials. Coatings based on cycloaliphatic epoxies have a fast cure but the coating can be brittle. Polyols are generally used as chain transfer crosslinkers and flexibilizers to overcome it.[6,7]

Dual Cure

A dual cure combining free radical and cationic polymerization offers the advantages of both polymerization types. While the cationic part of the formulation has low shrinkage which affords multiple substrate adhesion, the free radical portion provides fast cure response. The dual cure also presents the versatility to fine tune the ink to a specific industrial application. For instance, if ink needs to be applied on 3D part, then it needs to exhibit the ability to dark cure. The dark cure was investigated for a 9 micron thick film of a dual cure ink irradiated with 250 mJ/cm^2 energy density using a Hanovia H lamp. The conversion of acrylate -C=C- and epoxy groups was measured using an FTIr and the values are shown in **Table 1**. The acrylate group peaks were measured at 1410 cm^{-1} and the epoxy group peaks measured at 915 cm^{-1}. The acrylate groups have no dark cure whereas the epoxy group undergoes complete conversion after 24 hours. The acrylate polymer network provides film integrity to the coating whereas the dark cure of the epoxy leads to low film shrinkage and good adhesion.

Properties	**Conversion**
Acrylate initial	94.05
Acrylate 24 hours	94.4
Epoxy initial	83.29
Epoxy 24 hours	99.64

Table 1. Conversion of acrylate and epoxy functional groups in a dual cure ink showing dark cure of the epoxy groups after initial UV exposure.

Ink Adhesion

Substrate adhesion can result from either van der Waals or non-covalent interactions such as hydrogen bonding or via more stable covalent bonds. Free radical polymerization results in rapid cure and high shrinkage leading to high stress in the coating. Hence, it is difficult to obtain adhesion over multiple substrates. Cationic polymerization exhibits low shrinkage and it involves charged species propagating the chain growth. Monomers such as epoxies and oxetanes have lone pair of electrons on the oxygen which can help in a non-covalent interaction with the substrate leading to good substrate adhesion. However, the polymerization is slow since ambient moisture can affect cure speed. Dual cure inks can be utilized to overcome and in addition provide multiple substrate adhesion (**Table 2)**.

Substrate	Adhesion
Glass	5B
Aluminum	5B
Ceramic	5B
Steel	5B
Polyethylene terephthalate (PET)	5B
Polycarbonate/Acrylontrile butadienestyrene (PC/ABS)	5B
Polyphenylene sulfone	5B
Delrin/Acetal polymer	5B
Polyvinylchloride (PVC)	5B
Acrylic	5B
High impact polystyrene (HIPS)	5B
Carbon fiber	5B

Table 2. Adhesion of Dual cure ink on different substrates.

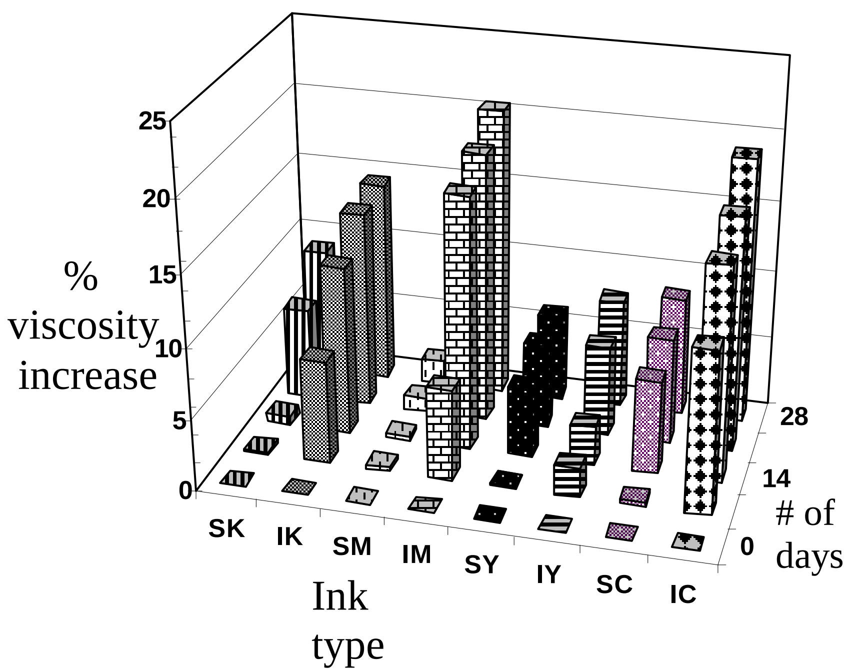


Figure 3. Room temperature stability of iodonium and sulfonium photoinitiator based dual cure inks. (Legend for the X-axis, the prefix S denotes sulfonium photoinitiator and I denotes iodonium photoinitiator; suffix CYMK denote cyan, yellow, magenta and black colors).

Ink Stability

Digital inks need to exhibit viscosity between 8-14 cps at the jetting temperature of 40-70℃. Hence, low viscosity monomers rather than oligomers are preferred. The cationic monomers can be cured by using reactive iodonium and sulfonium photoinitiators which release superacids upon UV irradiation. But, these monomers can interact with the photoinitiators at room temperature during storage or at jetting temperatures of up to 50-70℃. The iodonium photoinitiator, in particular, has low thermal stability which can lower ink shelf life. The effect of a cationic photoinitiator on stability of dual cure inks was investigated (**Figure 3**) by aging the inks at room temperature and periodically measuring viscosity at 25℃ using a Haake cone and plate rheometer. It is evident that the inks with sulfonium photoinitiators have better stability. Inks with iodonium photoinitiator are not stable even at room temperatures. When tested at a typical jetting temperature of 50°C, the inks with iodonium photoinitiator gelled.

In general acidic and basic additives as well as transition metals ions can react with the cationic monomers. Ink components such as pigments and dispersants can also interact with these monomers causing shelf life issues or gellation during jetting. **Figure 4** shows the viscosity stability of a cyan pigment with either an epoxy or an acrylate monomer at room temperature. There is a significant increase in viscosity for the epoxy monomer blend compared to the acrylate blend indicating that the pigment is interacting with the epoxy monomer. Stabilizers are frequently employed in UV curable inks to increase storage stability of the inks. **Figure 4** shows the viscosity stability of a sulfonium initiator based dual cure cyan ink in the presence of stabilizers. The ink was aged at 50℃ and viscosity measured at 25℃. It is evident that the cyan ink with the stabilizers has a better stability at elevated temperature compared to the epoxy blend at room temperature.

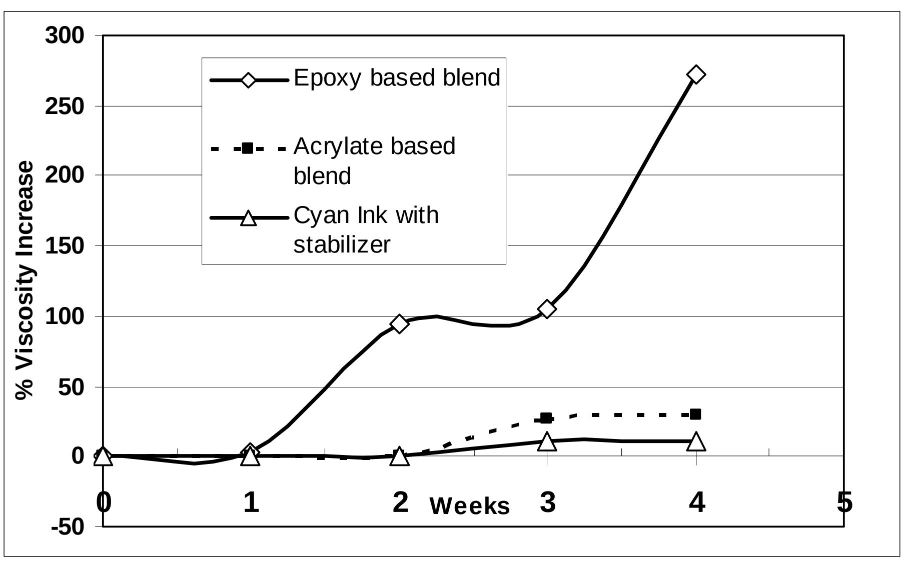


Figure 4. Viscosity stability of blends of cyan pigment with epoxy and acrylate monomers and a cyan ink with stabilizer. The two blends were aged at room temperature whereas the ink was aged at 50℃.

Chemical Resistance

Currently, UV curable screen inks are extensively used in coating glass and ceramics. These coatings have good resistance toward acids, sodium hydroxide, and ammonia. A digital ink should also provide good hardness and adhesion after exposure to these chemicals in order to be used in this application. The chemical resistance of a free radical and dual cure ink was tested. The dual cure ink provides good hydrolytic stability (**Table 5**) compared to the free radical cured ink. However long term hydrolytic stability, and resistance against sodium hydroxide and ammonia is an issue with both types of inks. The chemical resistance is inadequate possibly due to lack of covalent bonding of the ink with the substrate. Another factor causing poor chemical resistance could be the low crosslink density. Hence, components such as an adhesion promoter which can form a covalent bond with the substrate can be useful in increasing the chemical resistance and adhesion. It was observed that a dual cure ink with an adhesion promoter has the best hydrolytic stability and resistance against ammonia, sodium hydroxide, isopropanol, and ethanol.

Properties	**Method**	**Free radical Ink**	**Dual cure Ink**	**Dual cure Ink with adhesion promoter**
Hot Water resistance	80℃, 30 mins	0B	5B	5B
Hot steam resistance	steam, 15 mins	0B	5B	5B
Water resistance	20℃, 72 hours	0B	0B	5B
NaOH resistance	2.3%, 80℃, 30 mins	0B	0B	5B
Isopropanol rub		> 500	140	> 500
Ethanol rub		> 500	65	> 500
Ammonia rub		75	150	> 500

Table 5. Chemical resistance of Dual cure inks on glass. Adhesion results based on ASTM D 3359-B (0B means poor adhesion, 5B means good adhesion).

Jettability

Although dual cure ink with the adhesion promoter has good chemical resistance, they are known to interact with certain components of the printhead/printer. These may include tubing, filters, and printhead components. This can lead to instability rendering the ink unusable. Hence it was decided to investigate the jet stability of the ink. The jet operating window for a cyan ink with the adhesion promoter was tested in a Spectra SE 128 printhead. The ink was left in the printhead system for two weeks at room temperature and the jet operating window was tested in one week time intervals. The ink has a wide initial jet operating window from 35-60℃ as shown in **Figure 5**. Upon aging the ink at room temperature in the printhead for two weeks, the jet operating window remains similar to the initial values. This confirms that the ink is stable with the printhead components. The ink was printed on glass, UV cured and tested for hydrolytic stability. It was found to have good crosshatch adhesion on the glass substrate even after the water soak. This further confirmed the efficacy of the adhesion promoter.

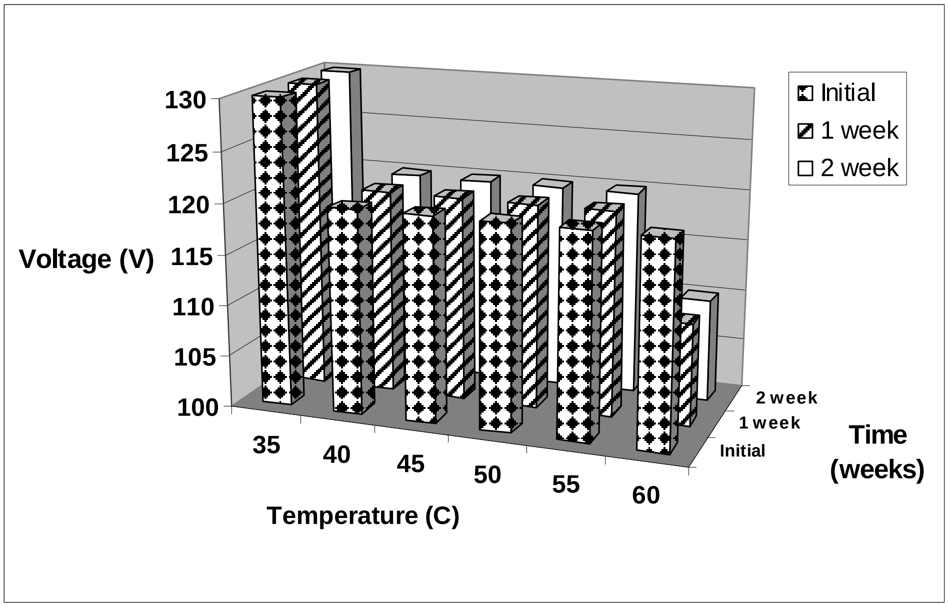


Figure 5. Jet operating window in a spectra SE 128 printhead (16 kHz) for a cyan ink with adhesion promoter. Ink was aged in printhead for two weeks at room temperature.

Conclusion

Dual cure inks offer advantages of both free radical and cationic cure. They provide adhesion to a multitude of substrates. However, ink stability is a major concern at room and jetting temperature and it was addressed using appropriate stabilizers. A wide jet operating window for the ink even upon aging in the printhead, confirmed its stability. The inks provide outstanding resistance to chemicals such as alcohols, sodium hydroxide, ammonia, required for industrial applications such as coatings on glass and ceramics.

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