UV Inkjet Inks with Improved Stray Light Resistance

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Abstract

Energy curable inkjet inks are susceptible to build up of cured material at the nozzle where ink is ejected, which leads to jet deviation and ultimately lost jets. This causes a reduction in image quality and the need to replace the printhead. Traditional stabilizers do not reduce the susceptibility of energy curable inkjet inks to stray light or if they do, cure is compromised. It has been discovered that nitroxyl stabilizers will significantly reduce the build up of cured ink caused by exposure to low levels of UV light from stray light sources without compromising cure speed. In this paper a new test method for assessing the stray light resistance of energy curable inkjet inks is detailed. The major types of stabilizers are described and their effect on stray light resistance and cure for UV curable inkjet inks is determined.

Introduction

The ability of inkjet technology to deposit materials with different chemical and physical properties has made it an important technology. Inkjet finds applications in many graphics applications including point of purchase, vehicle wraps, wide format printing plus it has also been used in electronics including the manufacture of solar panels and PCBs.

A typical drop-on-demand(DoD) inkjet printhead consists of several ink channels in parallel. Each channel has a piezo-actuator, which on application of a standard actuation voltage pulse generates pressure oscillations inside the ink channel. These pressure oscillations then push the ink drop out of the nozzle.

The print quality delivered by an inkjet printhead depends on the properties of the jetted drop. The following drop properties are required to be precisely controlled to give acceptable image quality, reliability and printhead performance:

Drop Velocity
Drop Mass/Volume
Drop Shape (ligaments and satellites)
Jet Straightness

A potential problem with UV inkjet inks is susceptibility to 'stray light' causing the build up of cured or partially cured ink around the nozzle. In the first instance this may result in a degradation of jet straightness, resulting in deviated jets and a degradation in image quality (see Figures 1, 2 and 3). Ultimately nozzles may become blocked by cured ink and the print head may require replacing. The term 'stray light' includes visible or ultraviolet radiation which could interact with thin (UV curable) ink films and cause curing reactions to take place.

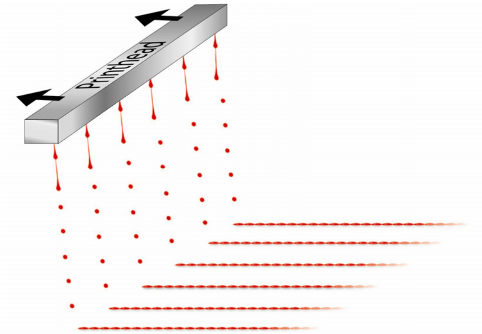

***Figure 1**: Normal operation of a printhead with no nozzle deviation.*

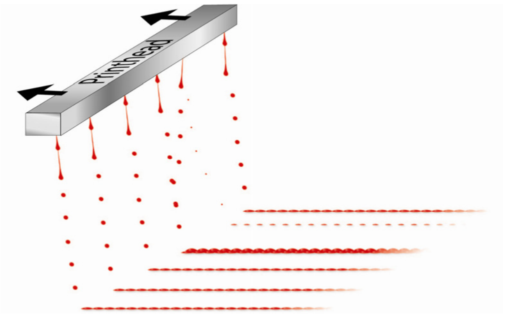

***Figure 2**: Operation of a printhead with nozzle deviation. Note the main drop has merged with the adjacent drop with a small satellite drop thrown to one side.*

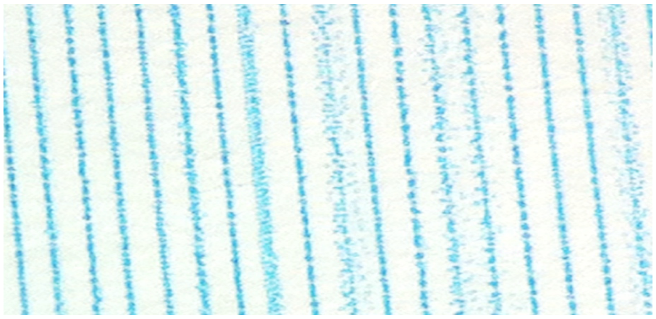

***Figure 3:** Scanned image of a real printhead nozzle test pattern from a flat bed wide format graphics printer suffering from this effect of stray light.*

The most obvious source of stray light in a scanning head UV inkjet printer would be the UV source itself, hence care must be taken to remove/ baffle any reflective surfaces that the lamp may travel over during a print stroke. The height and spacing of the curing system from the printhead cluster is also an important factor in controlling reflected light. Even with the optimization of the design of the cure unit the inks will still be subjected to some stray light. Another source of 'stray light' can be natural daylight which contains light in the Ultraviolet A region 315-400nm, Ultraviolet B region 280-315nm and Ultraviolet C region 100-280nm. Artificial fluorescent light can over time be another source of ‘stray light’ as the emission spectrum contains light in the Ultraviolet B and C regions.

Stabilizers

Free radical initiated polymerization is a three step process: 1) initiation; 2) propagation; and 3) termination. In inks and coatings based on acrylates, polymerization should ensue rapidly and completely only when it is required, i.e. when the printed substrate is exposed to UV light or EB radiation. The ink or coating should however remain liquid and free flowing before and while it is being applied to the substrate, and also remain unchanged from when it was first manufactured during shipping and long periods of storage. In reality the potential for polymerization exists at every step of the process, because some free radicals are formed from purification of acrylated monomers and oligomers by distillation, heating of oligomers to make them free flowing, shear and heat built up during milling to grind and distribute pigments, during storage prior to use, and while the ink remains on the inkjet printer. The ideal polymerization inhibitor can disable the initiation and propagation of unwanted free radicals without interfering with the rate or extent of cure when it is needed. It needs to be effective at low concentration in the absence or presence of oxygen to avoid issues in sealed bottles during storage and with degassing units on printheads, and is effective over the entire temperature range to which the ink and its ingredients will be exposed during manufacture, storage, and application.

There are seven major types of stabilizers used in energy curable inkjet inks, these are described as follows:

1. Phenolic Based

Phenolic inhibitors are not effective in the absence of oxygen and can discolour the final coating. These inhibitors are chain breaking donors as they donate the proton on the phenolic hydroxyl group to stabilize energy curable inks. Common examples are hydroquinone(HQ), methyletherhydroquinone(MEHQ) and butylhydroxytoluene(BHT).

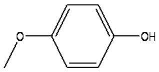

Figure 4: MEHQ

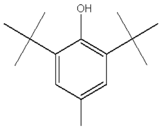

Figure 5: BHT

2. Phenothiazine

These inhibitors do not require oxygen as they work via an anaerobic mechanism. The mechanism for phenothiazine includes hydrogen atom donation with subsequent radical scavenging and hydroperoxide decomposition. Reaction products of phenothiazine (dimers, trimers, quinone-imines) also inhibit polymerization.

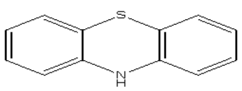

Figure 6: *Phenothiazine*

3. Nitrosophenylhydroxylamine (NPHA) based stabilizers

NPHA, amine salts, and metal salts (Al salt, N-PAL) are available commercially as neat solids and as dilute solutions in acrylate ester monomers (Albemarle, IDLCHEM, Rahn). N-PAL solutions typically contain 4 to 8% inhibitor in acrylate monomers of oligomers.

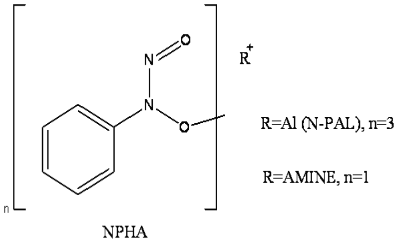

Figure 7: *NPHA based stabilizers*

NPHA based inhibitors are effective in the absence of oxygen as they work by an anaerobic mechanism. Multiple radicals can be scavenged with the formation of alkoxyamine (NOR) compounds.

4. Aromatic amine stabilizers

Typical aromatic amine stabilizers are diphenylamine(DPA) and phenylenediamine(PPD) The stabilization mechanisms of the aromatic amines involves both scavenging of free radicals and reaction with oxygen, followed by reactions of the oxygenated amines with free radicals.

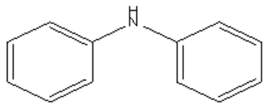

Figure 8: Diphenylamine

5. Metal Deactivators

Preventive inhibitors, or secondary antioxidants, are classified as peroxide decomposers and metal deactivators or metal chelators. Metal ions can catalyze the decomposition of peroxides which can lead to the formation of free radicals causing instability in the ink. Metal deactivators include ureas, oxamides, carbazides, and benzotriazole.

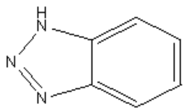

Figure 9: Benzotriazole

6. Alkoxylamine (NOR) HALS stabilizers

Hindered Amine Light Stabilizers (HALS) are derivatives of 2,2,6,6-tetramethyl piperidine . NOR derivatives tend to be more effective than NH or NR types as they enter the stabilization cycle quicker.

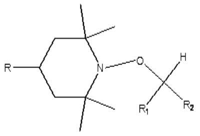

Figure 10: Alkoxy derivative of 2,2,6,6-tetramethyl piperidine

7. Nitroxyl Stabilizers

Nitroxyl stabilizers can be effective stabilizers for UV inkjet inks at low concentrations but the level they are used at needs to be carefully optimized or cure can be retarded. In some cases the cure can be retarded to such an extent that wrinkle is seen. Wrinkle is the phenomenon when sufficient initiating free radicals do not reach the base of the coating which leads to monomer migration through the cured film with eventual softening of the surface. This gives a soft cured surface with no water/solvent resistance with a matt wave type appearance. The inventors have discovered that by using the nitroxyl stabilizers in energy curable inkjet formulations excellent resistance to stray light can be obtained with no retarding of the cure profile.

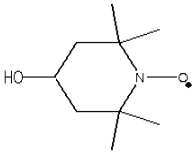

Figure 11: OHTEMPO

Experimental

One material from each stabilizer family was tested in model ink formulations and tested for stray light resistance, along with water and solvent resistance as a measure of the degree of cure.

Stray Light Resistance Index (SLRI)

1. An EXFO Omnicure Series 2000, aperture size 5%, flash length 0.2 seconds is set to deliver 2mj/cm^2 dose of UV.
2. Draw down a 12µm layer of the ink onto a ISO 8037/1 glass microscope slide using a RK K bar.
3. Place a 22mm x 22mm Menzel glass slide gently on top of the ink layer so the cover is completely wetted.
4. Immediately place the side perpendicular to the beam with the beam going through the centre of the Menzel glass slide.
5. Give one flash of UV light and continue to flash with UV light until it is not possible to move the Menzel glass slide.
6. The number of flash required so it is not possible to move the Menzel glass slide is equal to the Light Resistance Index.

***Figure 12:** EXFO 2000*

Solvent/Water Resistance

1. Draw down a 12µm layer of ink onto Leneta 2A card.
2. Cure using 150mj/cm^2 dose of UV from either a Fusion UV curing or Nordson LED unit.
3. Saturate a cotton tipped applicator in either isopropyl alcohol or water.
4. Wipe the ink coating with the applicator from left to right and back to the starting position which counts as one rub. Maintain even pressure throughout.
5. Repeat until the card is visible through the coating. Record the number of rubs taken to reach this stage.

Examples:

Table 1: Inkjet formulations

Ink Composition	A	B	C	D	E	F	G
PONPGDA	52.5	52.5	52.5	51.4	51.3	52.0	51.5
DiTMPTA	7.0	7.0	7.0	7.0	7.0	7.0	7.0
TMPEOTA	13.5	13.5	13.5	13.5	13.5	13.5	13.5
Rapicure DVE3	12.0	12.0	12.0	12.0	12.0	12.0	12.0
Esacure KIP100	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Omnirad BP	5.0	5.0	5.0	5.0	5.0	5.0	5.0
CN3715	7.0	7.0	7.0	7.0	7.0	7.0	7.0
Tego A115	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Stabilizer Level	0	0.01	0.05	0.1	0.2	0.5	1.0

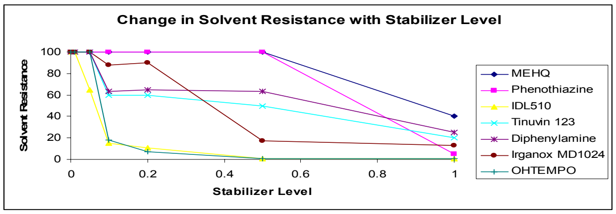

***Figure 13:** Change in solvent resistance with stabilizer level*

The phenolic based stabilizer, MEHQ, can be seen to have the least effect on cure as the level is increased. Phenothiazine does not effect the cure up to 0.5% but after that a marked reduction in cure is observed. IDL510 an NPHA based stabilizer gives the worst performance with a reduction in cure seen at addition levels of above 0.01%. A reduction in cure is seen with the alkyoxyamine HALS stabilizer (NOR) Tinuvin 123, diphenylamine, the dual acting metal deactivator/phenolic based antioxidant Irganox MD1024 and OHTEMPO at levels of 0.1% and above.

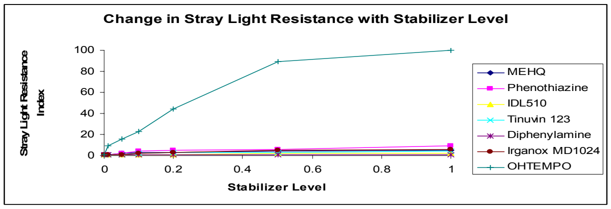

Figure 14: *Change in SLRI with stabilizer level*

The only stabilizer to show good stray light resistance was OHTEMPO.

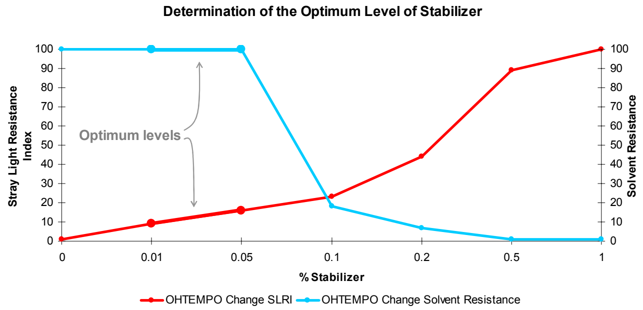

Figure 15: *Determination of the optimum level of stabilizer*

The optimum stabilizer level, giving good stray light resistance, can be seen to be between 0.01 and 0.05 for the ink formulation shown in table 1.

Conclusion

Jet deviation and lost jets can be a significant problem with the formulation of energy curable inkjet inks. A new test method has been validated that can detect differences in stray light resistance for UV curable inkjet inks. This test method has been successfully used to determine the optimum type and level of stabilizer required to maintain cure and minimize issues relating to stray light.

References

[1] Plastics Additives Handbook, 5th Edition, 2001
[2] Encyclopedia of Science and Technology, Chapter 5, Mark, Overberger & Bikales

Author Biography

Hugh Allen graduated from Cambridge University in 1985 and initially worked on the development of flexographic and gravure inks in various locations in Europe. In 1998 he moved to SunChemical's inkjet laboratory near Bath, UK. Currently Development Manager with SunJet, he is responsible for product development in UV, solvent, hot melt and aqueous inkjet inks.

Steve Hall graduated from Bath University in 1983 and joined Cray Valley where he progressed to Technical Manager, Electronic Resins. In 2003 he moved to SunChemical where he holds the position of Senior Research Associate leading the SunJet UV Development Group.

Kirsty McVean graduated from Bath University in 2009 and works as a Technician in the SunJet UV Development Group.