Oxygen Inhibition Effects in UV-Curing Inkjet Inks

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Abstract

UV-Curing inks have been widely used in "traditional" printing processes such as flexography, gravure and screen for many years. More recently, they have been the subject of considerable attention in the world of inkjet. The attraction of UV-curing inks being the possible environmental benefits of having solvent free formulations, fast "drying" (ie curing) by UV exposure of the ink and excellent final properties of the print.

With the ever-increasing speeds of inkjet digital imaging processes the cure speed of UV-curing inks has become a critical aspect of their performance. Due to the inherent need for low viscosity, fast curing inkjet inks are a significant challenge to the inkjet formulator. Various factors affect cure speed some of these being:- ink vehicle chemistry/molecular weight, photoinitiator choice, UV-lamp source, print thickness and lay-down/curing strategy. In addition to these the presence of oxygen can have a detrimental effect on cure speed. This paper examines the effect of oxygen inhibition on the cure speed of drop-on-demand piezo inkjet ink formulations and the potential benefit of nitrogen blanketing during the curing process.

Introduction

Inkjet printing offers the possibility of efficient short run printing for a variety of end uses. In particular DOD piezo head technology in either single pass or scanning mode is attractive for the production of packaging, labels, bank cards, vinyl curtain walling, posters etc. The wide variety of end uses and substrates has predictably spawned a variety of different ink types, including water based, solvent based and UV-curing. Much attention has been paid to UV-curing jet inks because they can offer acceptable properties across a wide variety of substrates and because they can be formulated "solvent free", that is there are essentially no volatile organic emissions and "drying" is "instant" after exposure to the correct UV radiation.

UV-curing inkjet inks suitable for DOD piezo printheads can be formulated in various ways :- using free radical curing meth/acrylate based chemistry, either as 100% active (solids) inks or as water based emulsions, or using cationic curing systems. Each chemistry type offers it's own advantages and disadvantages. This paper is only concerned with 100% solids, acrylate based systems.

Acrylate based, pigmented inks have been developed for piezo DOD print heads, for a variety of applications. These inks, in common with all free-radical curing systems are inhibited by oxygen, that is the adverse effect of the presence of oxygen on the rate and extent of the cross-linking reaction. This inhibition is the effect of two different mechanisms. In the first, molecular oxygen in it's triplet ground state quenches photoinitiator molecules that are in their excited states, producing excited singlet oxygen which quickly reverts to the triplet ground state. This effect is of more importance with Type II photoinitiators (ie those resulting in labile hydrogen abstraction) since the excited states are longer lived and hence more susceptible to oxygen quenching. With the Type I initiators (ie those that fragment upon irradiation) the excited states are shorter lived and so less susceptible to this quenching.[1] The second mechanism is via radical scavenging whereby ground state triplet oxygen forms a peroxyl radical by reaction with a photoinitiator, monomer or propagating-chain radical. Although it is still a radical that is formed, the peroxyl radical is of very low reactivity and so reaction rates cannot be maintained.[2]

This paper will examine how acrylate based inkjet inks are especially affected by oxygen inhibition, and how nitrogen inerting is a powerful tool in the improvement of cure speed.

Viscosity Effects in Oxygen Inhibition

UV-curing jet inks are in many respects similar to UV-curing inks used in traditional printing technologies such as flexo, offset, screen etc, which have been widely used for many years. The single largest difference and the overriding one in terms of cure performance, is the low viscosity requirement of jet ink.

The dramatic effect of viscosity on oxygen inhibition has been investigated by photo-DSC on model acrylate systems. A schematic of the experimental equipment is shown in Figure 1.

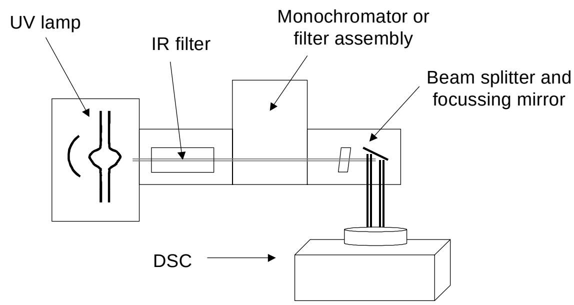

Figure 1. Schematic of photo-DSC

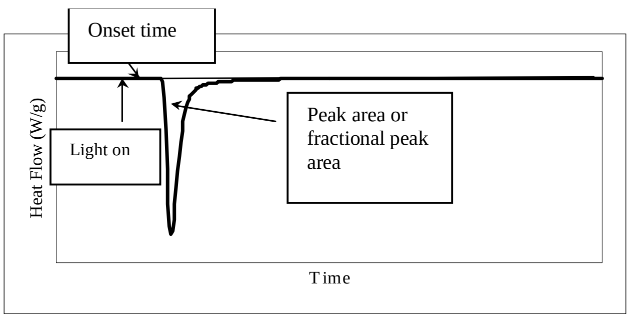

Figure 2. Main features of photo-DSC run

The instrument used in these experiments was a Perkin Elmer DSC7/DPA 7, using a medium pressure mercury UV source. The UV-cross linking reaction in the test sample is monitored by the energy release as it progresses, after exposure by the UV lamp. The atmosphere in the reaction chamber can be varied by flowing gas over the sample. In these trials either air or pure nitrogen were used as the test atmospheres.

The main features extracted from a photo-DSC run are shown in Figure 2.

It has been noted in the traditional UV printing fields that thin films generally suffer from oxygen inhibition to a greater extent than thick films, leading to the conclusion that oxygen transport ie diffusion of oxygen through the film is an important factor. This being the case it would be supposed that the low viscosity of inkjet ink would exacerbate the problem, since lower viscosity should lead to higher oxygen transport and hence inhibition. This has been explored in the two model systems below.

In Figure 3 the rate of reaction, as followed by the DSC exotherm peak area (J/g) is shown, as the percentage of di-pentaerythritol penta-acrylate (Di-PETA) added to a trifunctional urethane acrylate oligomer (Genomer T1200 was used) is increased. The two materials are of similar viscosity and so as the level of the highly reactive DiPETA monomer is increased there is little effect on the viscosity and the reactivity increases (shown by greater peak area exotherms) in both nitrogen and oxygen atmospheres, as would be expected.

In Figure 4 a similar experiment has been carried out, but the *low viscosity* reactive monomer tripropylene glycol diacrylate (TPGDA) has been added to the same urethane oligomer as above. Here as the level of TPGDA is increased the viscosity falls. This time the reactivity in nitrogen and air atmospheres diverge very substantially, indicating that as the viscosity decreases the reactivity in air decreases, relative to the reactivity in nitrogen. Thus it can be concluded that viscosity is having a significant effect on oxygen inhibition.

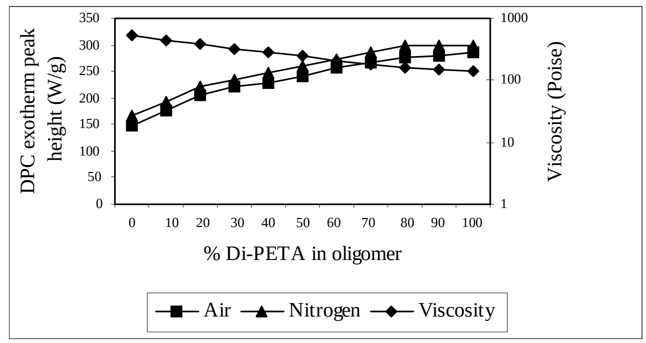

Figure 3.Change in photo-DSC exotherm peak area in air and nitrogen atmospheres and viscosity as a function of Di-PETA content.

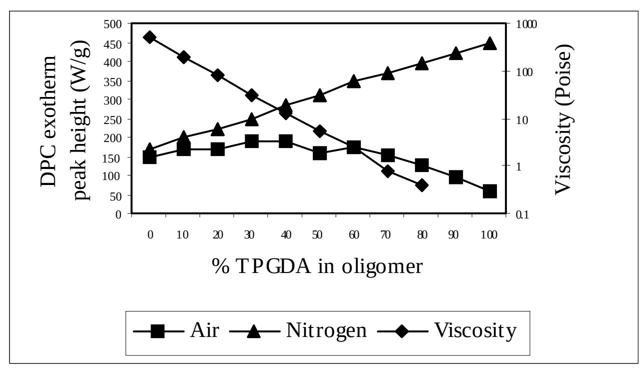

Figure 4.Change in photo-DSC exotherm peak area in air and nitrogen atmospheres and viscosity as a function of TPGDA content

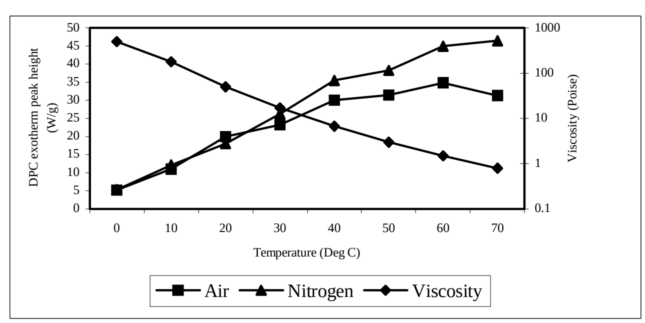

Figure 5. Change in photo-DSC exotherm peak area in air and nitrogen atmospheres as a function of temperature for the high viscosity Di-PETA formulation.

If viscosity is a major factor this should be confirmed by the influence of temperature on viscosity and cure rate. In Figure 5 the cure rate is shown versus temperature for the high viscosity system where di-PETA is being used.

It can be seen from this data that the rate of reaction in air only deviates from that under nitrogen at a temperature around 40 Degrees C. In Figure 6, the low viscosity system, the reaction rate in air diverges considerably from that in nitrogen, but most significantly, the deviation occurs at a much lower temperature - nearer minus-10 Degrees C. With the inherently lower viscosity system, more akin to an inkjet ink, oxygen transport into the bulk of the film becomes a significant inhibiting factor at a much lower temperature.

It can be further inferred from Figure 6 that in fact the rate of reaction of a low viscosity jet ink in air should *increase* at lower temperature. Although the actual rate of each polymerization step will be slower at lower temperature, as would be expected from conventional kinetics, the overall curing process will be faster since at lower temperatures the oxygen transport/inhibition will be diminished - and it is this which is the rate limiting step in the overall process. It is interesting to compare various different technologies of ink from UV-curing jet ink to offset ink. Because the ink vehicles, pigment loading, photoinitiator levels etc will vary greatly between these inks, the comparison is carried out by looking at the reactivity ratio - ie reactivity in air versus reactivity in nitrogen. The data is shown in Figure 7. It can be seen that offset inks have reactivity ratios close to 100% ie are almost completely unaffected by oxygen due to their high viscosity. Flexo and gravure inks are affected to some extent with reactivity ratios in the 50% region, but as would be expected from the proceeding discussion inkjet inks are the most dramatically affected - in air having only 20-30% of their potential reactivity.

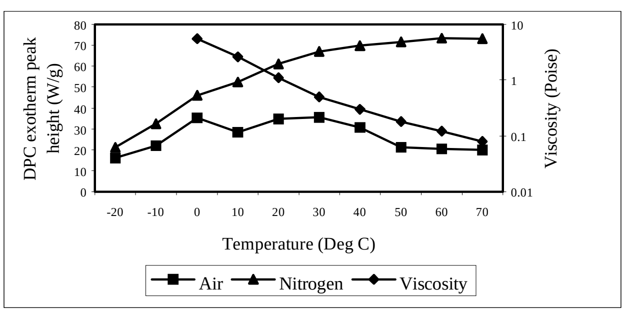

Figure 6. Change in photo-DSC exotherm peak area in air and nitrogen atmospheres as a function of temperature for the low viscosity TPGDA formulation.

Given this large difference between rate of cure in air and nitrogen it can readily be seen that in looking for high line speeds nitrogen blanketing of ink jet prints can be highly advantageous. As well as enhanced speeds, it should also be pointed out that there are other potential benefits to curing under nitrogen, such as the fact that acceptable line speeds may be achieved with reduced photo-initiator levels and this can in turn lead to lower potential "migratables", when for instance printing food packaging. The following section looks at some practical nitrogen atmosphere curing studies.

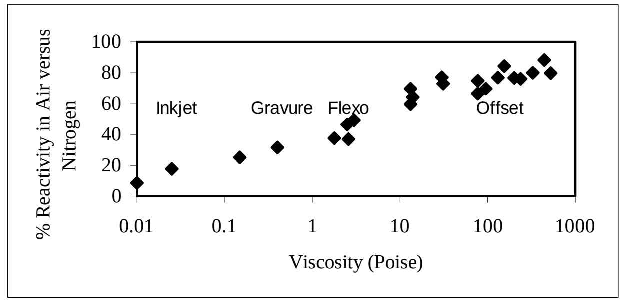

Figure 7. Oxygen inhibition as a function of ink viscosity.

Nitrogen Line Trials

In practical terms oxygen inhibition can affect both surface cure and through cure of the printed article. Poor surface cure manifests itself by a "smeary" or scratchable surface when the print is rubbed. Poor through-cure generally appears as a lack of adhesion onto the substrate or lack of integrity of the interior of the film. In a practical sense these two characteristics are most often assessed by simple "scratch" and "thumb twist" type tests to tell when a film is surface and through-cured respectively. The photo-DSC data discussed above only really provides information pertaining to through cure reactivity and there is no such scientific method available for routinely assessing surface cure, so work often falls back on practical trials.

In the experiments carried out here, a conveyor fitted with a 370 W/inch medium pressure mercury lamp was adapted to allow nitrogen gas to be pumped into the curing region under the lamp by means of a purge and "gas knife". This meant that the atmosphere in the curing region could be continuously varied from pure nitrogen to pure air (21% oxygen). Data presented here only relates to either pure nitrogen or pure air atmospheres although interesting experiments can be carried out to assess what effect "lower" levels of oxygen (but not pure nitrogen) can have on cure.

Inks were printed onto smooth vinyl substrate (signage grade) and subsequently passed under the curing lamp.

In Table 1, Black 1 and the Magenta jet inks are commercial products developed for DOD piezo print heads and optimized for air curing with medium pressure mercury lamps. They contain a conventional mixture of Type I and Type II photoinitiators and synergists. Several points can be drawn from this data. Looking first at the magenta ink, in moving from an air to a nitrogen atmosphere there is a dramatic increase in the maximum attainable speed for adequate surface cure, from below 21m/min to above 51m/min. There is also a lesser increase in the speed for through-cure. With Black 1, however, there is an increase in the surface cure speed but no real effect on the speed obtainable for satisfactory through-cure ie around 21m/min.

This can be explained by the fact that Black 1 and the magenta are inks optimized for air curing. The print has a thickness of approximately 8 microns, (a reasonably typical thickness for an inkjet print using 100% solids ink) and at this thickness the photoinitiators are strongly absorbing the incident UV light, thus, effectively screening the inner ink layer, preventing adequate through-cure at all but the slowest line speeds. The slightly higher through-cure rate obtainable with the magenta formulation is due to the lower screening effect of the magenta pigment compared to the carbon black pigment.

Table 1. Maximum line speed achievable to obtain "through-cure (TC)" and "surface-cure (SC)" - metres/minute

	Black 1		Magenta		Black 2	
	TC	**SC**	**TC**	**SC**	**TC**	**SC**
Air	~21	<21	21	<21	<<21	<<21
Nitrogen	21	51+	31	51+	45	70+

Table 2. Percentage transmission of the principal wavelengths of a medium pressure mercury UV source with Black 1 and Black 2 jet inks. Calculated for 8 micron film thickness and ignoring pigment absorption.

nm	Black 1	Black 2
~313	<10%	10%
~365	50%	80%
~405/8	50%	90%

By re-balancing the photoinitators in the black formulation it is possible to achieve the benefits of the nitrogen inerting blanket. Table 2 shows the percentage transmission of the chief wavelengths of incident UV light from a medium pressure mercury lamp - ignoring any absorption by pigment. It can be seen that for Black 1 the photoinitiator level (optimised for air) is at such a level that there is a very low level of transmission through the film, whereas with Black 2 having a re-balanced photoinitiator package a much higher proportion can penetrate, to facilitate reaction deep in the film and so obtain good through cure.

Referring back to Table 1 now it can be seen that due to the lowering of this screening effect Black 2 can obtain a through cure speed of 45 metres/minute compared to 21 metres/minute with Black 1.

Conclusion

Acrylate based UV-curing inkjet inks suffer heavily from oxygen inhibition due to their low viscosity, however, techniques such as photo-DSC, can be used to better understand this phenomenon and so formulate better curing products.

Nitrogen blanketing is an attractive method for increasing cure speed. Due to the relatively high film thickness' applied by inkjet printing, however, special care must be taken in the formulation of photoinitiator packages for these applications, since inappropriate formulation can lead to screening and poor through cure.

References

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Biography

Nigel Caiger received his degree in Chemistry from Oxford University in 1985. He joined Coates Electrographics in 1989 and is now Development Manager - Ink Jet Products, overseeing activities of a development team working on various inkjet technologies including UV-curing, phase change, water and solvent based inks.

Shaun Herlihy graduated in Applied Chemistry from Trent Polytechnic, Nottingham in 1987. He joined Smith Kline Beecham and worked for 18 months as a process development chemist. In December 1989 he joined Coates Lorilleux R&D Department where he now works exclusively on radiation curing projects. In 1997 he completed a part-time PhD at the University of Kent at Canterbury in "Factors influencing the efficiency of photoinitiation in radiation curable ink formulations".