Investigating the Practical Issues of Nitrogen Inerting in UV Curable Processes

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Introduction

From early applications in wood coatings and printing, free radical polymerisation has developed into a very successful process for the production of inks, coatings and adhesives. Today UV curable coatings are used in applications as wide ranging as flooring, automotive parts, CDs/DVDs, solar panels, optical fibres, electronics, adhesives on tapes and labels and numerous packaging applications.

The majority of these curing processes take place in air, under normal atmospheric conditions, and do so very effectively. However, there are occasions when the process, or the final properties of the end product, may be enhanced by curing in an atmosphere where the oxygen concentration is significantly reduced, i.e. by curing in an inert atmosphere such as nitrogen.

This paper will look at some of the benefits to a coating performance by curing under nitrogen and also some of the factors that influence the requirement for nitrogen or the efficacy of the process when in place.

There have been many studies into the influence of oxygen on the kinetics of the free radical polymerisation process using analysis and monitoring of model formulations, or single component systems. Such studies have been invaluable in setting the guidelines and providing an understanding of the process. This paper will look at the issues of curing under nitrogen as part of a final manufacturing process; approaching from the point of view of the end user and the process conditions that should be taken into account when considering the use of nitrogen.

Taking fully formulated coatings, designed to be used curing in air, can they be used in other more oxygen-sensitive applications and can the process, or properties of the coating, be enhanced by curing under nitrogen.

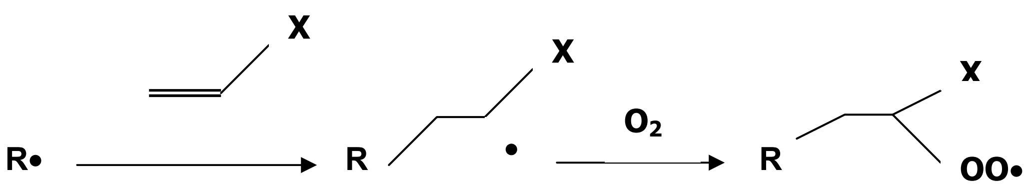
Free Radical Polymerisation and Oxygen Inhibition

The free radical polymerisation process can be inhibited by the presence of oxygen, which, can react with both the initiating and propagating radicals resulting in peroxy radicals. These are relatively un-reactive species and unable to attack the acrylate double bond they cause inhibition, and finally, termination of the polymerisation process.

Oygen inhibition of the initiation reaction resulting in a peroxy radical

$$\mathbf{PI} \xrightarrow{hv} [\mathbf{PI}*] \longrightarrow \mathbf{R\bullet} \longrightarrow \mathbf{ROO\bullet}$$

Oxygen inhibition of the propogation reaction resulting in a peroxy radical



The adverse effects of oxygen inhibition are usually seen at the surface of a coating where the oxygen present in the air/coating boundary layer is able to diffuse into the top layer of the coating. This usually presents as a tacky surface or one with poor scratch or mar resistance. As oxygen inhibition is a surface phenomenon, the problems are usually more evident for thin coatings.

To overcome oxygen inhibition there are two approaches that may be considered; in many cases they are complimentary, not competing techniques.

- Increase the concentration of initiating and propagating radicals
  - Use higher intensity UV light and a higher concentration of photoinitiator to increase the number of initiating radicals
  - Use more reactive oligomers and monomers to promote the propogation reactions.

- Reduce the rate of oxygen diffusivity
  - Reduce the oxygen concentration at the boundary layer of coating during curing
  - Make it more difficult for the oxygen to penetrate into the coating by increasing the viscosity of the coating.

Experimental conditions

A variety of formulated coatings were used to evaluate the issues surrounding oxygen inhibition and the potential benefit of curing under nitrogen.

To begin with a simple model formulation consisting of a di-functional urethane acrylate with the addition of a di-functional acrylate monomer and Type I photoinitiator, 1-hydroxyl cyclohexyl phenyl ketone (HCPK).

Others were either commercially available coatings, or development systems with a mixture of oligomers and monomers and photoinitiator packages. Coatings were applied to polyester film or aluminium test panels using drawdown bars.

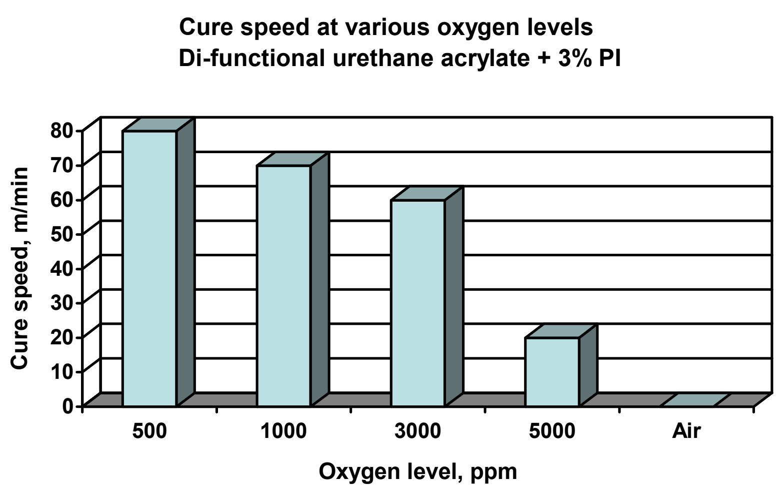
Curing was carried out using a microwave powered lamp system with a nominal power output of 240W/cm, fitted with an H (mercury) bulb. This lamp system utilizes a small diameter bulb (13mm) and an elliptical reflector that focuses the UV light to a high intensity at a specified distance from the face of the lamp. By running the substrate through the UV light at this specified distance, the coating is exposed to the highest light intensity; by adjusting the height of the lamp above the coating, the intensity of the light can be varied, without significantly affecting the total UV energy delivered to the coating.

The majority of the coatings were assessed using simple tests immediately after UV exposure; surface tack using finger touch, mar or scuff using a fingernail and MEK rubs.

Model formulation, Sample A - Effect of oxygen level on cure speed

To investigate the basic principle of reducing oxygen level to overcome inhibition and increase cure speed, a model formulation (Sample A) based on a di-functional urethane acrylate diluted with a di-functional monomer with 3% photoinitiator, was applied onto PET at 6μ and then cured under nitrogen with varying oxygen levels.

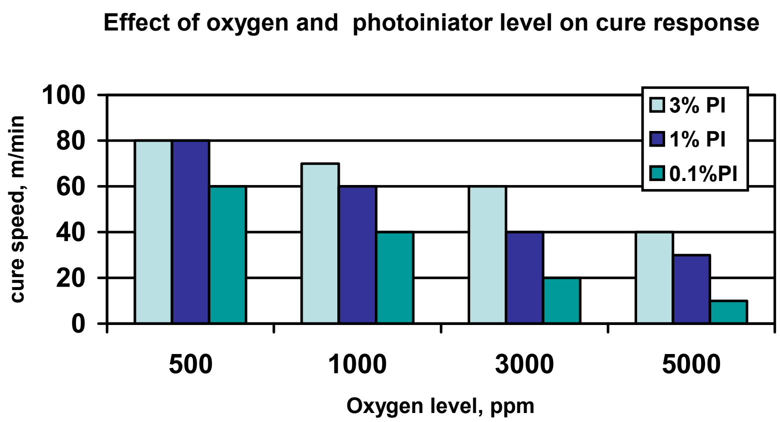
Graph 1, clearly shows the increase in cure speed as the oxygen level is reduced incrementally from air to 5000 to 500ppm.



Graph 1

Effect of photoinitiator level on cure speed when using nitrogen

Furthermore, the increase in cure speed as the oxygen level is reduced, is greatest with the lowest photoinitiator level of 0.1%. In fact, at 500ppm oxygen, reducing the photoinitiator level from 3% to 1% has no adverse effect on the cure speed. Reducing photoinitiator levels can have benefits in reducing odour, reducing migration of unreacted species and can offset the cost of using nitrogen in the process.



Graph XXX

UV light intensity and oxygen inhibition

Photo DSC can be used to monitor the conversion of a UV curable material under known light intensity, and this can be carried out under air and nitrogen. This analysis gives information on the overall conversion of the bulk material as can be seen in Diagram 1 below. As the light intensity increases, the degree of conversion increases and the time to achieve this decreases. When the same process is carried out under nitrogen, both the conversion and speed are further enhanced.

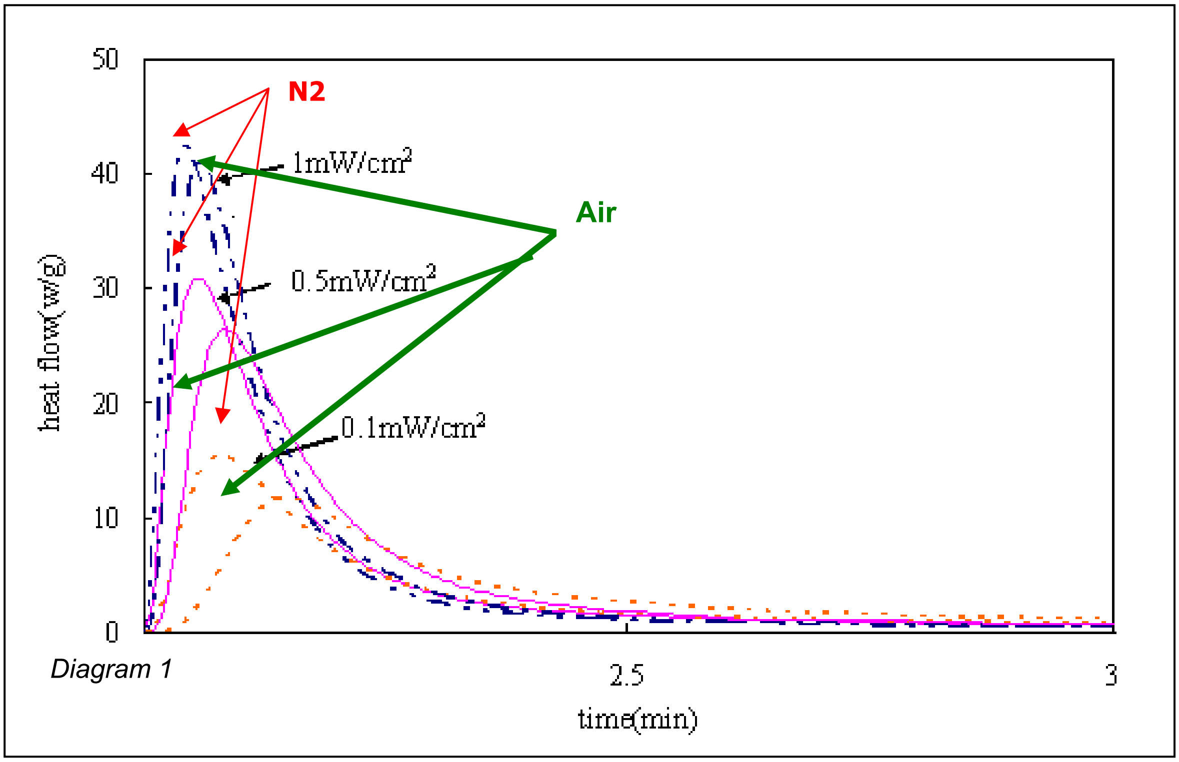
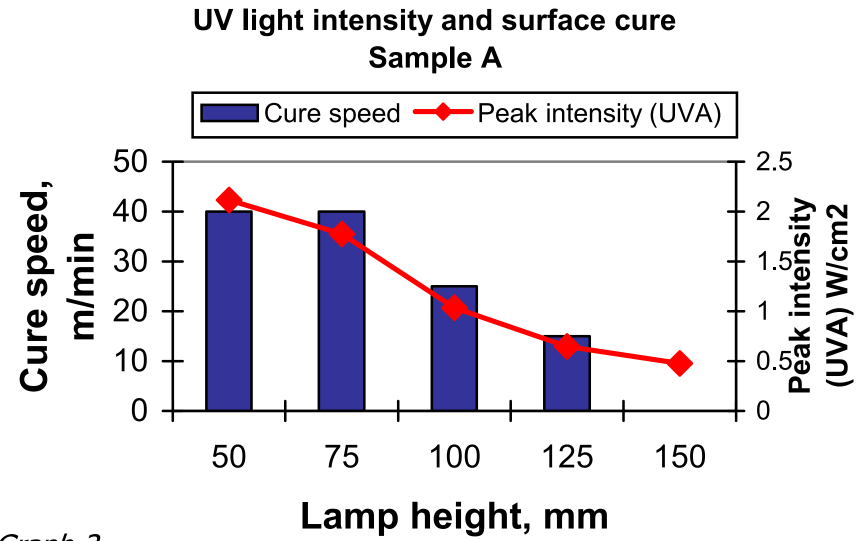


Diagram 1

As was mentioned above, using higher intensity UV light could be one way to help overcome the adverse effect of oxygen inhibition on the surface cure of coatings.
To evaluate the effect of light intensity in production conditions, a coating formulated for use in metal coating applications (Sample B), was applied at 6μ on aluminium test panels. The cure speed – surface tack - was determined with the UV lamp set positioned at various distances from the substrate, thus reducing the intensity of the incident UV light.

As Graph 2 shows, as the intensity of the UV light increases, as the lamp height is reduced, the speed at which the coating surface becomes tacky is also increased, i.e. a faster cure speed is achieved. Thus demonstrating that using higher intensity UV light can help in overcoming oxygen inhibition.



Graph 2

Effect of oxygen level on cure speed – Sample B

Using the same formulation (Sample B) as in the previous experiment, and with the UV lamp set in position to deliver the highest UV intensity, what is the effect of the oxygen level on the cure speed. The coating was applied, at 4μ, to aluminium test panels and assessed using surface tack and MEK rubs. The results are shown in Table 1
A number of variables were investigated:-

- cure speed under air and at 1000ppm O_2
- effect of varying oxygen levels on tack and MEK rubs
- cure speed using 500ppm O_2

Table 1

No.	Speed m/min	Atmosphere	Surface	MEK rubs
1	30	Air	No tack	>100
2	40	Air	Tacky	40
3	40	1000ppm O_2	No tack	>100
4	50	1000ppm O_2	No tack	>100
5	60	1000ppm O_2	No tack	60
6	50	2000ppm O_2	No tack	>100
7	50	30000ppm O_2	No tack	>100
8	50	4000ppm O_2	No tack	85
9	50	5000ppm O_2	Tacky	40
10	50	500ppm O_2	No tack	>100
11	60	500ppm O_2	No tack	>100
12	70	500ppm O_2	Tacky	75

The improvement in coating properties in terms of surface tack and MEK rubs, when curing under nitrogen, was clear at a range of oxygen levels. In air, the maximum cure speed, ie not tacky and with MEK rubs greater than 100, was 30m/min. Switching to 1000ppm oxygen, the cure speed increased to 50m/min. Furthermore, at 50m/min, the oxygen level could be increased to 4000ppm, without adversely affecting the coating properties. In a production process running at a higher oxygen level of 4000ppm would be reduce the nitrogen consumption and therefore the running costs of the process.

A further small increase to 60m/min was achieved when the oxygen level was reduced to 500ppm. However, it would be important to weigh the considerations of a relatively small increase in speed against higher nitrogen consumption.

Effect of film thickness – Sample C

Using a development formulation based on a tetra-functional polyester acrylate (Sample C) a coating was applied to PET film at a range of film thicknesses and cured in air and under nitrogen with an oxygen level of 1000ppm, see Table 2 below. The initial coating contained 3% photoinitiator, HCPK, and the second formulation contained 1% photoinitiator.

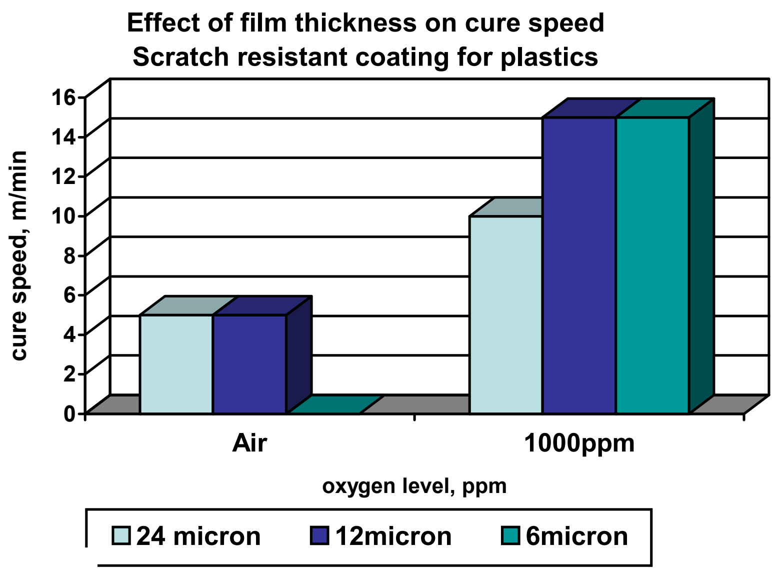
Thickness, µm	Maximum cure speed, m/min		
	Air / 3% PI	**Air / 1% PI**	**1000ppm O_2 / 1%PI**
24	100	30	70
12	100	20	70
6	100	Did not cure	60

Table 2

At 3% photoinitiator level, the coating cured at 100m/min (maximum speed of the conveyor) regardless of the film thickness. At 1% photoinitiator, all coatings showed a significantly slower cure speed in air. However, when the oxygen level was reduced to 1000ppm, the cure speed at all thickness increased.

Effect of film thickness - Sample D

A further experiment (Graph 3) was carried out to investigate the effect of film thickness using a fully formulated coating based on a urethane acrylate resin. Designed for use on plastic substrates, this scratch resistant coating would be cured applied to give a dry film thickness of 12-24µ and would be cured in air.



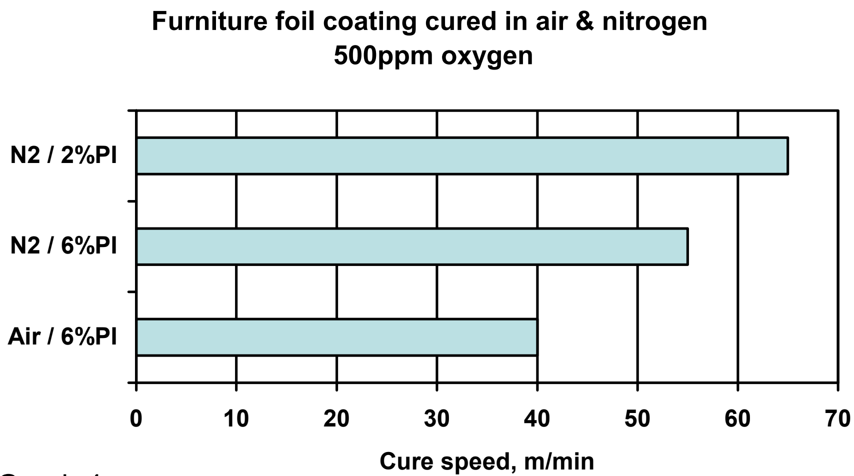
Graph 3

The coating is formulated to produce tough, weatherable, scratch resistant coatings and as such requires a high UV dose to cure the coating and produce these properties; hence the slow cure speed in air, which is as expected. When the film thickness is reduced to 6µ it wasn't possible to cure the coating in air. However, under nitrogen (1000ppm oxygen), the coating cured successfully to at 15m/min. Reducing the oxygen level further to 500ppm did not have any effect on the speed. This could open up new application opportunities for the coating on different substrates and in different manufacturing processes.

Optimising Photoinitiator Level – Sample E

In order to increase the cure speed of a fully formulated coating (Sample E) designed as a scratch resistant coating for furniture foils, the use of nitrogen was investigated. In production, the coating would normally be applied at 8-12µ, therefore a coating thickness of 12µ was used in the tests.

When cured in air a maximum cure speed of 40m/min was reached. At this point, the coating had a tack free surface with good adhesion to the furniture foil substrate. When cured under nitrogen (500ppm oxygen), the surface remained tack-free until a speed of 55m/min was reached. However, the coating failed the adhesion test. It seemed that although the surface cure had been improved, this was at the expense of through cure and the adhesion was adversely affected.



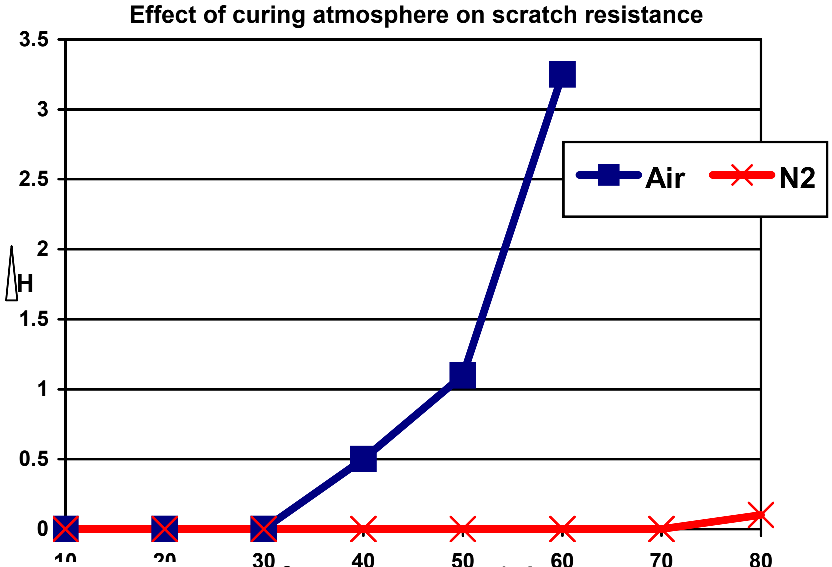
Graph 4

To achieve better through cure, that is, reduce absorption of the incident UV light at the surface to allow a greater percentage to travel to the bottom of the coating, the photoinitiator concentration was reduced from 6% to 2%. The result was that the cure speed increased to 65m/min – at this point the surface started to show signs of mar and scuff when tested with a fingernail, but the coating had good adhesion to the substrate.

Effect of curing under nitrogen on scratch resistance

Using nitrogen to reduce oxygen inhibition has shown benefits in terms of increasing the reactivity of various types of coatings and enabling lower levels of photoinitiator to be used. A clear coating was applied to polyester film and passed under the UV lamp at a range of speeds, in air and under nitrogen. Using a Taber Haze test to measure the degree of mar, expressed as haze, brought about by abrading the surface coating with rubber wheels over a set number of cycles. The results are shown in Graph 5 as the change in Haze value.

By reducing the oxygen content in the curing atmosphere and thereby reducing the effect of oxygen inhibition on the surface of coating, there is a clear improvement in scratch resistance as shown by the reduction in haze.



Graph 5

Conclusion

The work has shown that using high intensity UV light can help to overcome oxygen inhibition and increase the cure speed of a coating. If nitrogen inerting is used, then a further increase can be achieved. It is not always necessary to reach very low oxygen levels to overcome oxygen inhibition; significant improvements were noted at 1000ppm and 4000ppm oxygen with some coatings. Curing under nitrogen also enabled coatings to be successfully cured at lower film thickness, which, could open up new potential applications for such coatings. It was also seen that the photoinitiator level played a significant role and there were opportunities to reduce the photoinitiator levels when curing under nitrogen. Furthermore, coating properties such as, scratch resistance, can be enhanced by curing under nitrogen.