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UV-Curing under Oxygen-Deficient Conditions

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Summary: Four different coating formulations have been formulated with different amounts of photoinitiator and cured under different atmospheres (21, 5, 1 and 0% of oxygen). Surface cure and through cure were assessed for each combination. It was observed that the cure process for all formulations was strongly affected by the atmospheric conditions, and that the formulations required substantially less photoinitiator if cured under 5% of oxygen if compared to curing under air. Calculations show that the lower price of the formulation due to the decreased photoinitiator level may outweigh the additional equipment and running costs in specific cases. Therefore, UV-inertisation is not only attractive from a product quality point-of-view, but can also offer economic advantages.

Keywords: UV-curing; inertisation; oxygen level; photoinitiator concentration

Introduction

UV-curing represents a clean and fast technology for the curing of coatings for a vast amount of applications. The technology can be considered as a standard technology in the printing industry, in the wood coating industry and in the electronics industry.

A specific drawback of most UV-coatings is their sensitivity to oxygen during the cure step. The problems concerning this oxygen sensitivity can generally be solved by modification of the formulation, but this goes at the expense of the final coating properties. For a number of applications these decreased properties pose no real problem, but for other potential applications this intervention in the formulation makes UV coatings less attractive or even unsuitable. Therefore, when a technically and economically attractive method could be found that counteracts oxygen inhibition without damaging the final coating properties, this would certainly be of interest for a large number of paint and coating appliers.

In recent years, UV curing under inert gas has attracted already considerable attention as one of the possibilities to counteract oxygen inhibition. A lot of information is already available on the

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positive effects of curing under completely oxygen-free conditions, but only very limited data are available on UV-curing under partially inert conditions.

In the current investigation we have studied the effect of atmospheres with different oxygen concentrations on the cure behaviour of four different coating formulations and briefly evaluated its economical impact.

Brief theoretical background

An oxygen molecule is a biradical species, which, when dissolved in a formulation during a free-radical curing process, will interfere with the normal cure reaction in different ways. It is generally accepted that, under normal conditions, the main source for the inhibiting effect is the scavenging by oxygen of the growing free-radical chain end. Scavenging can be represented as:

Normal propagation (1): $R\cdot + M \rightarrow R\text{-}M\cdot$ (R = reactive chain end, M = monomer)

Oxygen scavenging (2): $R\cdot + O_2 \rightarrow R\text{-}O\text{-}O\cdot$ (R = reactive chain end, O_2 = oxygen)

The „normal“ product R-M· has a reactivity very similar to the starting radical R·, whereas the radical formed by reaction with oxygen, the peroxy radical R-O-O·, is orders of magnitudes less reactive than R·. Formation of peroxy radicals therefore effectively retards the polymerisation process.

The reactivity ratio of the two processes is given by the expression:

$$\text{Rate}(1) / \text{Rate}(2) = k(1)/k(2) \times [M]/[O_2] \qquad (1)$$

In this expression the rate constants k(1) and k(2) are roughly known; they depend only slightly on the exact structure of R· and M (in case of acrylates). The ratio k(1)/k(2) is approximately 10^{-4}, which means that the the speed of the reaction with oxygen is approximately 10,000 times faster than the desired chain growth reaction. This means that, in order to have an appreciable polymerisation rate, the concentration ratio $[M]/[O_2]$ has to be large. The consequence is that, if carried out in air, the polymerisation will not effectively start before a large part (in radiation curable coatings typically >98%) of the dissolved oxygen in the coating has been removed. In practice, this leads to induction periods, a drop of the polymerisation rate and to incomplete conversion of double bonds in the surface layers of the coating, where diffusion of fresh oxygen is also a factor.

A lot of measures can be taken to overcome oxygen inhibition problems, including an increase of photoinitiator concentration, an increase of UV light intensity, addition of compounds that lower the solubility of oxygen in the coating, use of additives that act as oxygen diffusion barriers and the use of additives that react faster with oxygen than the growing chain ends and lead to relatively harmless side products (oxygen scavengers).

The most effective way to get rid of oxygen inhibition is the removal of oxygen from the system, i.e., the execution of the cure step in an oxygen-free atmosphere. However, such a procedure will increase both installation and running costs of the coating line. The main aim of this investigation is to find out if, and for which applications, the investments required for inerting the line can be compensated for by profits in the area of (decrease of) photoinitiator need.

Materials and methods

Base materials

In order to have complete control over the constituents of the formulations, we have used only very simple formulations based on a number of chemically different commercially available UV-resins. The following resin types were used:

A. A flexible aliphatic acrylated polyurethane (containing some HDDA)
B. A non-acrylic oligomer based on an aliphatic polyurethane and containing both maleate and vinyl ether functional groups, diluted with 33% of a special diluent of the same material type
C. A flexible aromatic acrylated polyester
D. A highly flexible acrylated epoxy (containing some TPGDA)

All materials were used as obtained. Resins A, C and D were further diluted with 33% of HDDA. All formulations had a viscosity in the range 2-10 Pa.s.

To these formulations the required amount of photoinitiator (PI) 2-hydroxy-2-methyl-1-phenylpropan-1-one (Darocur® 1173) was added in 0.05-5% concentrations (w/w) (see below).

Coatings were deposited on Bonder-type galvanised steel substrates with a coating knife with a slit of 40 μm, affording coatings in the thickness range 20-40 μm.

Methods

Coated substrates were placed in an aluminium frame covered with a 2-mm thick drawn HSQ synthetic quartz plate with a transparency of approx. 90% in the wavelength area 270-400 nm and of approx. 75% in the 230-270 nm area. The frame was supplied with a gas inlet and outlet. In order to carry out irradiations under a specific atmosphere, a specified gas mixture was administered to the frame, while an oxygen meter (Systech EC-90 MD MK II, useful for both % and ppm measurements) was attached to the outlet. Gas administration was continued until the measured oxygen level had stabilised and then continued for another 3 minutes. Both inlet and outlet were then closed and the frame was passed under the UV lamp. The frame was then opened and the samples investigated. Under the conditions used, temperature effects during irradiations can be considered to be of minor importance.

The gas mixtures (supplied by AGA Gas BV, Amsterdam) that were used in this investigation:

21% O_2: synthetic air
5% O_2: N_2/O_2 mixture (analysis: 5.12 ± 0.16%)
1% O_2: N_2/O_2 mixture (analysis: 0.993 ± 0.003%)
0% O_2: minimum nitrogen content 99.999% (AGA PLUS 5.0)

The samples were irradiated with a standard 100 W/cm Philips HOK UV lamp using two different intensities (110 and 190 mW/cm^2) and a conveyor speed of 4 m/min. The measured (International Light IL 390B Light Bug) UV-A doses were 360 and 700 mJ/cm^2, respectively.

After irradiation, through cure and surface cure of the samples were assessed. For through cure assessment, the standard MEK rub test was used: when 200 single rubs did not lead to any visible damage to the coating, the coating was considered well cured. Surface cure was assessed by pressing a finger on the irradiated surface and determining whether a print remained after removal or not (yes/no determination).

Experiments and results

UV cure experiments were performed inside the aluminium frame under different atmospheres and irradiation conditions and using different concentration of photoinitiator. After irradiation the two properties were assessed leading to results that are typified for one particular example (the formulation based on the acrylated polyester named C in the Materials and Methods section) in the following table.

Table 1. Example of assessment of properties of formulation based on an acrylated polyester of curing

Exp. #	% of O_2	UV-A dose mJ/cm^2	% of PI	Thickness (μm)	Tacky (yes/no)	# of MEK-rubs
B-1	21	360	5.0	43±8	no	>200
B-2	21	360	4.0	38±4	yes[a]	>200
B-3	21	360	3.5	39±5	yes[b]	>200
B-4	21	360	3.0	48±8	yes	>200
B-5	21	360	2.5	not meas.	yes[b]	>200
B-6	21	360	2.0	31±4	yes	>200
B-7	21	700	2.0	39±17	no?	>200
B-8	5	360	2.0	37±4	no	>200
B-9	5	360	1.5	not meas.	yes[a]	>200
B-10	5	700	1.5	40±12	no	>200
B-11	5	360	1.0	34±6	yes[a]	>200
B-12	5	700	1.0	29±7	no	120
B-13	1	360	1.0	44±5	no	>200
B-14	1	360	0.5	31±9	no	140
B-15	1	700	0.5	24±7	no	80
B-16	1	360	0.1	not meas.	yes	60
B-17	0	700	0.5	30±8	no	>200
B-18	0	360	0.1	61±2	no	75
B-19	0	700	0.1	47±15	no	100

[a] tackiness disappeared after 1 day

[b] only slightly

This specific example teaches us, that at high oxygen concentrations (21%) the surface cure forms the limiting factor. At the photoinitiator concentrations investigated, the through cure is good, as witnessed by the MEK-rub results, whereas at PI concentrations of 4% and lower the surface is always tacky. At low oxygen concentrations (0%), the through cure forms the limiting factor. At PI concentration down to 0.1% the surface is dry, whereas the MEK rub tests show increasing solvent sensitivity (no efficient through cure).

Similar tables have been composed for all different formulations. The following observations were made:

A. Formulation based on a flexible aliphatic acrylated polyurethane (containing some HDDA)

At 21% of oxygen concentration, no tack-free surface could be generated, not even at a PI level of 5%. By increasing the UV intensity from 360 to 700 mJ/cm2, the amount of PI required for a good surface cure is lowered from >5% to 3.5%.

At oxygen concentrations of 5%, the formulation can be cured to a dry coating at a level of approx. 2% of PI. Increasing the UV-dose leads to further decrease of required PI concentration (<1%).

At an oxygen concentration of 1%, the addition of <0.5% of PI is sufficient to realise a good surface cure and under pure nitrogen this amount decreases even to <0.1%. However, under these conditions through cure becomes the limiting factor: the coatings always seem to require ≥1% of PI in order to be fully cured.

B. Formulation based on a non-acrylic oligomer

These coatings are all relative thick due to rheology factors and this will have some consequences for the final values.

It appears that this formulation is also quite sensitive to the concentration of oxygen, present in the cure atmosphere. In air, only the formulation containing 5% of PI gives a completely dry coating. Decreasing the oxygen concentration to 5% leads to a significant improvement: 2% of PI suffices for a tack-free surface. Increase of the irradiation dose leads to further improvement. In an atmosphere with 1% of oxygen the amount of PI required for a tack-free surface drops further to approx. 0.5%, and in pure nitrogen an amount as low as 0.1% gives good surface cure.

Again, the MEK-rub tests show that the amount of photoinitiator required for a well-cured coating is ≥1%.

C. Formulation based on a flexible aromatic acrylated polyester

In air, 3.5% of PI already gives a dry surface, whereas 3% gives a tacky surface. Increase of UV-intensity enables the use of <2% of PI. Again, a decrease of the oxygen content to 5% leads to improvements concerning the photoinitiator requirements. At 360 mJ/cm2, 1% of PI is sufficient, at 700 mJ/cm^2, 0.5% even suffices. A 1% oxygen concentration leads to a further decrease: 0.5% and 0.1% of PI give dry surfaces at low and high intensities, respectively.

For these formulations, the MEK rub tests did not discriminate. Even at concentrations of 0.1% of PI, the maximum amount of MEK-rubs (200) did not lead to coating damage.

D. Formulation based on a highly flexible acrylated epoxy (containing some TPGDA)

This formulation shows the same over-all picture as the previous ones. Its sensitivity to oxygen in air can be best compared with formulation B. At the low UV dose, 5% of PI gives a good surface cure. The coating sharply reacts to a decrease of the oxygen content of the atmosphere to a 5% level: 1% of photoinitiator is already sufficient to cure its surface. Further decrease to 1% and 0% oxygen leads to limiting PI concentrations of 0.5 and 0.1%, respectively.

Formulations containing ≥1% of photoinitiator show good resistance against MEK.

Summary of relevant findings

The most relevant data are summarised in the following table. For each oxygen depletion step (starting point: air) it gives the attainable decrease in photoinitiator concentration for realising coatings with a dry surface and the concentration difference with the situation in air.

Table 2. Summary of relevant findings

form.	UV-A (mJ/cm^2)	O_2-level 21% → 5%	PI-diff.	O_2-level 21% → 1%	PI-diff.	O_2-level 21% → 0%	PI-diff.
A	360	PI >5 → 1.5%	>3.5%	PI >5 → 0.5%	>4.5%	PI >5 → <0.1%	>4.9%
B	360	PI 5 → 2%	3%	PI 5 → 0.5%	4.5%	PI 5 → <0.1%	>4.9%
C	360	PI 3.5 → 1%	2.5%	PI 3.5 → 0.5%	3%	PI 3.5 → <0.1%	>3.4%
D	360	PI 5 → 1%	4%	PI 5 → 0.5%	4.5%	PI 5 → <0.1%	>4.9%
A	700	PI 3.5 → <1%	>2.5%	PI 3.5 → <1%	>2.5%	PI 3.5 → <0.1%	>3.4%
B	700	PI 2 → <1%	>1%	PI 2 → <0.5%	>1.5%	PI 2 → <0.1%	>1.9%
C	700	PI 2 → <0.5%	>1.5%	PI 2 → <0.1%	>1.9%	PI 2 → <0.1%	>1.9%
D	700	PI 3 → <0.5%	>2.5%	no data	--	PI 3 → <0.1%	>2.9%

At UV-A irradiation doses of approx. 360 mJ/cm^2, the influence of inertisation is dramatic. Lowering the oxygen content of the atmosphere from 21% to 5% enables a reduction between 60 and 80% of the photoinitiator concentration. The absolute difference between the two concentrations ($[PI]_{21}$ – $[PI]_5$) lies between 2.5 and 4%. Further reduction of the oxygen content leads to a further possible decrease: $[PI]_{21}$ – $[PI]_1$ and $[PI]_{21}$ – $[PI]_0$ lie between 2.5 and 5%. However, these very low oxygen concentrations tend to add only a limited amount to the possible photoinitiator reduction. Moreover, the photoinitiator levels that are possible for obtaining a tack-free surface at low oxygen concentrations are less meaningful, because it is clear that at these levels the through-cure of the coating will be endangered. We have found that for all investigated formulations (and using coating layers of 20-40 μm thick) the useful lower limit of photoinitiator concentration is close to 1%.

At higher doses, the relative effect of a decrease of oxygen concentration is similar to the one at lower doses. However, as the amount of photoinitiator for the 21%-case is significantly lower than for the low-intensity examples, the absolute decrease in photoinitiator concentration is significantly lower. In this case $[PI]_{21}$ – $[PI]_5$ is generally close to 2%.

Discussion

Calculation of effect of photoinitiator reduction

The effect of the reduction of the oxygen level for the coating formulator can be easily calculated. If such a reduction leads to a possible lowering of the photoinitiator concentration of Δ_{PI}, then the price difference G between 1 kg of the two formulations concerned is given by:

$$G = [\, \Delta_{PI} (\$_{PI} - \$_{BF}) \,] / 100 \qquad (2)$$

in which $\$_{PI}$ represents the price of 1 kg of photoinitiator, $\$_{BF}$ the price of 1 kg of base formulation without photoinitiator and in which Δ_{PI} is given in absolute percentage.

For a situation in which a base formulation costs 10 €/kg and a photoinitiator costs 30 €/kg and the PI concentration can be reduced from 4% in air to 1.5% in an atmosphere with 5% of oxygen, this affords a price reduction of G = 2.5 (30 – 10) / 100 = 0.50 €/kg formulation. This price reduction of the formulation can, in principle, be passed along by the paint producers to their customers, as this does not affect the profit margin.

A price reduction of this order of magnitude can be significant. If we assume, that a UV topcoat parquet lacquer station applies coatings of 1 m width at a thickness of 20 g/cm^2 at a speed of 40 m/min (productive period 1400 h/year), and that (partial) inertisation of the station would lead to a possible photoinitiator reduction from 4% (in air) to 1.5%, the following calculation can be made:

- Production: 40 x 60 x 1400 = 3,360,000 m^2/year
- Lacquer use: 3,360,000 x 0.02 = 67,200 kg/year
- Photoinitiator savings: 67,200 x 0.50 = 33,600 €/year.

This possible profit has to be compared with the additional costs that are connected with the use of an inerted production line, which are:

- Nitrogen (or other inert gas such as CO_2) consumption
- Rental or purchase of a inert gas installation (e.g., a liquid nitrogen tank + accessories)
- UV-line adaptations

Of these, the inert gas consumption generally is by far the largest cost factor. It is difficult to give a reliable estimation of these additional costs, as a lot depends on the situation on the spot. The price of liquid nitrogen is variable in time and differs from country to country. Also other factors such as the cheap availability of other inert gases (CO_2) will strongly affect the total picture.

However, the possible savings in photoinitiator use form a significant factor that contributes to the economic attractiveness of inertisation of UV-processes. Some application areas in which inertisation will be economically most attractive will include the following:

1. Of course, high throughput applications are interesting. The main reason for this is that the contribution of the investment costs becomes relatively small in the total cost calculation;
2. High-speed processes, where the residence time of the coating under the lamps is short. In these applications a good cure is generally realised by using relatively high amounts of photoinitiator and/or oxygen scavengers (other expensive solutions in the area of equipment are also possible). Inerting will significantly decrease the price of the formulation used, as the value of ΔPI in the G-formula given above will become relatively large;
3. In applications, where it is impossible or undesirable to use an oxygen scavenger. This can be the case in systems where the scavenger (mostly a tertiary amine) interferes with the cure chemistry or where high demands are exacted to certain properties of the product (e.g., related to smell, yellowing, and chemical resistance);
4. In applications, where an expensive photoinitiator is used. It is obvious that in that particular

case the G-value in the formula will be relatively large. Expensive photoinitiators are initiators that are specifically used in pigmented coatings (acylphosphine oxides and similar systems).

Conclusions

This investigation has shown that UV-curing under an oxygen-deficient atmosphere has many advantages. The most important outcomes are:

1. For „normal“ UV-curable coatings, the effect of inertisation is not only noticed at oxygen levels in the 1-1000 ppm range, but even oxygen levels of 5% show already significant effects in comparison with air;
2. Curing under inerted conditions enables the formulator to use significantly less photoinitiator in his formulations. In general, this concentration can be decreased from 2-5% under air to 0.5-1.0% under inerted conditions, while maintaining the same cure speed;
3. The cost reduction due to a lower photoinitiator concentration may outweigh the extra costs necessary for running the UV-process under inert conditions (investments + running costs). Of course, the position of this „equilibrium“ for a coating end user (coating applier), strongly depends on the willingness of his coating supplier to fully pass the cost reduction on to his customers and on the exact production conditions (location, production size, etc.);
4. Lower photoinitiator concentrations obviously lead to lower levels of odour and migration of initiator residues. In addition, the weatherability properties of the coatings will, in general, also be improved. This adds to the economic attractiveness of this process.

The inertisation conditions used in the current investigation (closed cell with excellent control over the atmosphere) are not fully comparable with the situation in an actual inerted UV-curing process, in which, e.g., dissolved oxygen will have much less time to leave the coating and oxygen can be dragged along with the fast-moving coating into the inerted chamber. However, it is reassuring that it was found that an oxygen content of 5% already has a markedly positive effect, which means that the levels of dissolved oxygen and mechanically introduced oxygen have to be quite high before they will actually seriously affect the observed results.