

# Multiple Photoinitiators for Improved Performance

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## Abstract

Higher levels of photoinitiator can increase extractables, reduce weatherability, limit film thickness, and increase cost. To achieve fast cure speed and limit these disadvantages, low levels of multiple photoinitiators can be used. This approach takes advantage of the different UV absorption spectra of three or four photoinitiators to more broadly utilize the full UV output of the lamp. Real-time FTIR data shows that multiple photoinitiators at a lower total level can achieve faster cure speed than a higher level of just one photoinitiator.

## Introduction

One of the primary advantages of UV curable coatings is their rapid cure speed relative to other coating chemistries. Even though these coatings already cure much faster than their non-UV counterparts, the trend has been towards ever faster cure speeds. In order to address this trend, or perhaps to further this trend, much faster photoinitiators have been developed. The initial compounds such as benzophenone, benzoin ethers, benzil, and diethoxy acetophenone once provided sufficient cure speed, but in many applications today are inadequate. The newer photoinitiators, in particular the acyl phosphine oxides and bis acyl phosphine oxides, are able to provide much faster cure speed than their predecessors.<sup>1,2</sup> This is due to three main factors: 1) their absorption into the UVA/visible region, 2) their molar absorptivity, and 3) their quantum yield.<sup>3-5</sup> Though photoinitiators have made great improvements in these areas, no single PI is yet able to make full use of the lamp energy available.

One approach to improve cure speed is to raise the level of PI. This can raise cure speed by generating more free radicals, but at higher levels can inhibit through-cure by absorbing the light at the surface and limiting the amount of light reaching the coating/substrate interface. Even when the optimum level of PI is determined for surface-cure and through-cure, it may be at a sufficiently high level to cause other problems such as blooming, extraction, yellowing,<sup>6,7</sup> or excessive raw material cost.

To more fully utilize the UV lamp's output, multiple photoinitiators have been used. This has most often been the case in pigmented systems, where the PI absorbs in the same region as one or more UV-absorbing materials (pigments) that do not produce free radicals and contribute to curing. Though used less often in clear systems, multiple PI's can provide much faster cure speed in these compositions as well.<sup>6,7</sup>

## Experimental

### Real-time FTIR Cure Speed

A Nicolet Nexus 860 FTIR was used for measuring the disappearance of acrylate double bonds during UV exposure. The lamp was an Oriol 100-Watt mercury lamp and a Teflon spacer was used to control the coating thickness to 50 microns. The acrylate unsaturation band at  $810\text{ cm}^{-1}$  was monitored vs. a reference band in the  $750\text{-}780\text{ cm}^{-1}$

range that does not change during exposure to UV light. The % reacted acrylate unsaturation (RAU) is calculated from:

$$\%RAU = \frac{R_L - R_C}{R_L} \times 100$$

Where  $R_L$  is the ratio of the acrylate peak to the reference peak in the liquid coating and  $R_C$  is the ratio of the acrylate peak to the reference peak in the UV-exposed (or “cured”) coating.

## Results and Discussion

The spectral output of a medium pressure mercury arc lamp is shown in Figure 1. In this study, four photoinitiators were evaluated (see Table 1). The absorption spectra are shown in Figures 2-5<sup>8</sup>. These photoinitiators represent two classes widely used in clear coatings. The HCPK and HMPP belong to the  $\alpha$ -hydroxyketone class while the TPO and BAPO belong to the acyl phosphine oxide class.

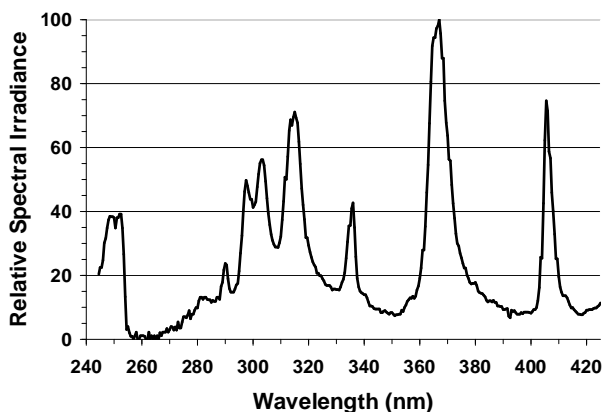


Figure 1. Spectral output of the Oriol 100-Watt mercury arc lamp.

Table 1. Photoinitiators Studied

Abbreviation	Trade Name	Chemical Name
HCPK	Irgacure 184	1-hydroxy-cyclohexylphenyl ketone
HMPP	Darocur 1173	2-hydroxy-2-methyl-1-phenyl-1-propanone
TPO	Darocur TPO	diphenyl (2,4,6-trimethylbenzoyl)-phosphine oxide
BAPO	Irgacure 819	phosphine oxide, phenyl bis(2,4,6-trimethylbenzoyl)

To compare the effect on cure speed of multiple photoinitiators, HCPK was chosen as the single-photoinitiator control. This photoinitiator is widely used in clear UV coatings due to its fast cure speed, low yellowing, and relatively low cost. It was compared to blends of three and four photoinitiators in two different formulations (see Tables 2 and 3 and Figures 6 and 7). It can be seen that the multiple PI's provide significantly faster cure speed than the single HCPK at a constant total PI level. Both types of PI systems reach essentially the same maximum level of reaction, but the multiple PI package reaches this level at a lower UV dose.

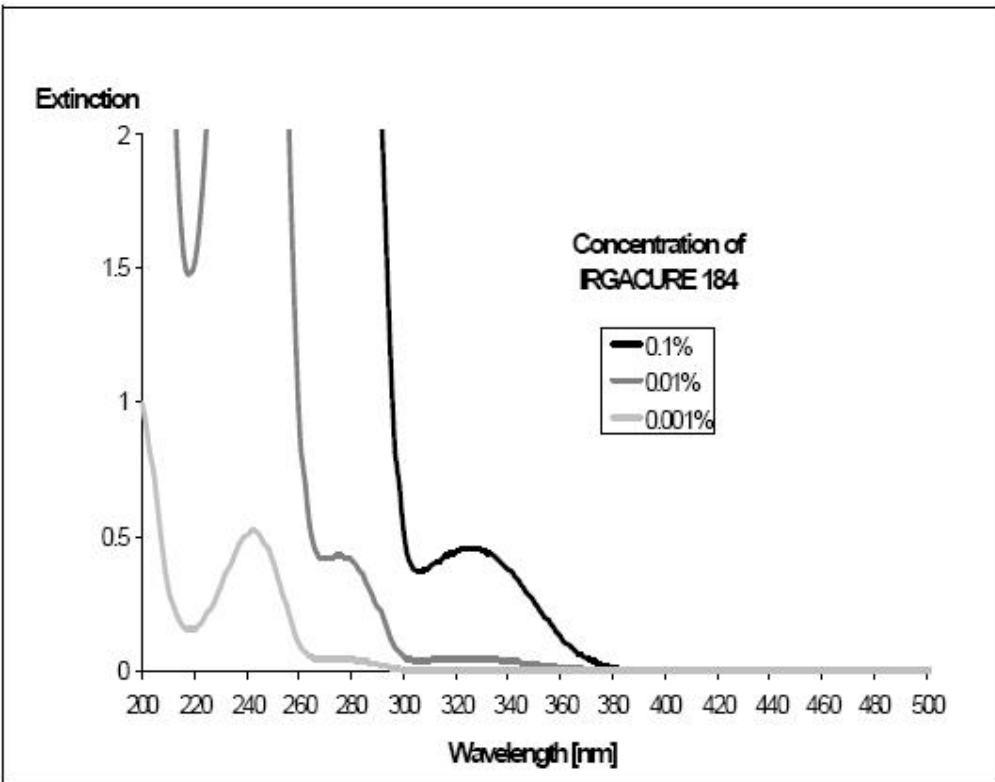


Figure 2. Absorption of HCPK

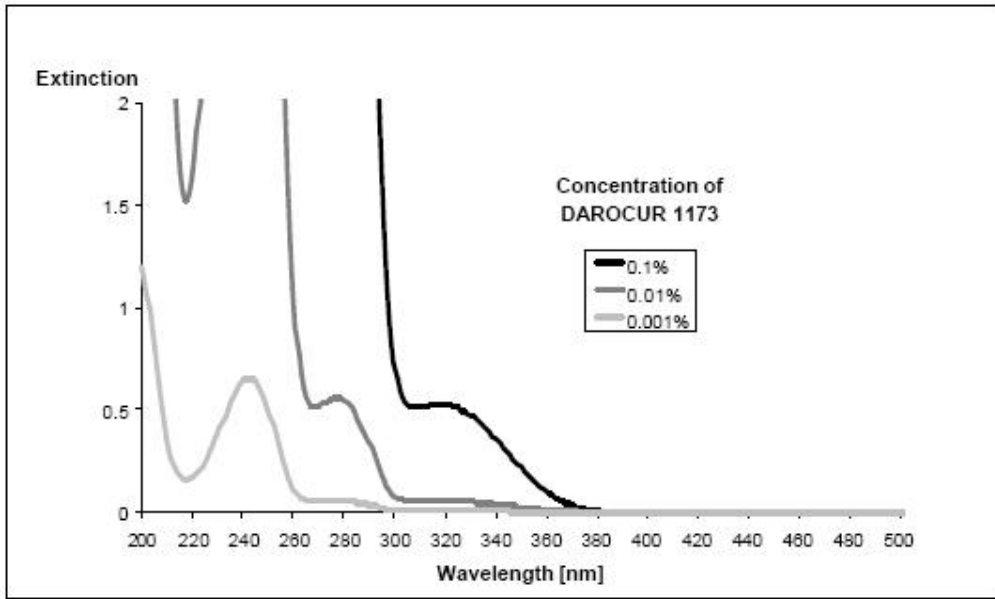


Figure 3. Absorption of HMPP

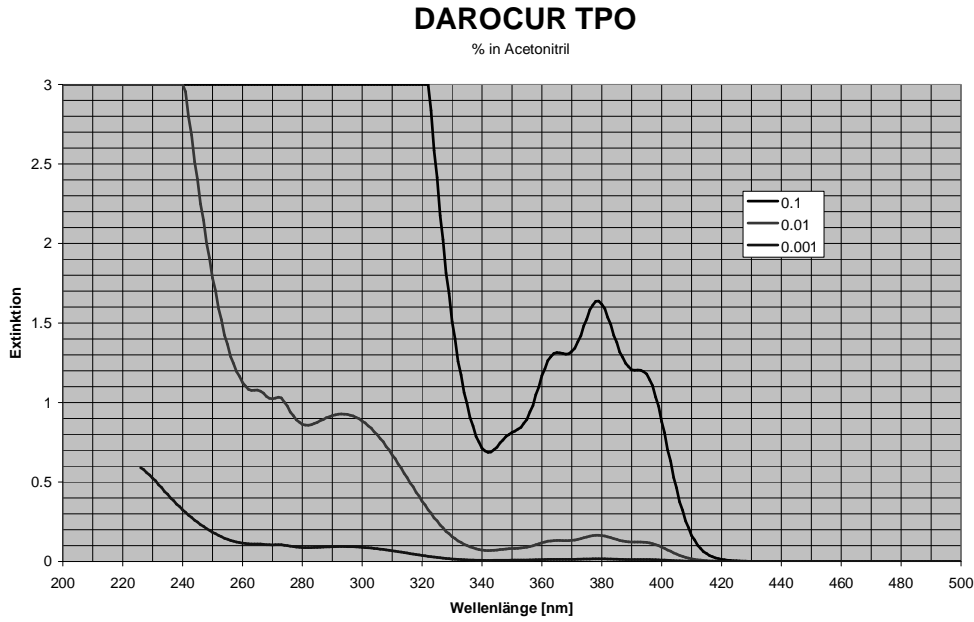


Figure 4. Absorption of TPO

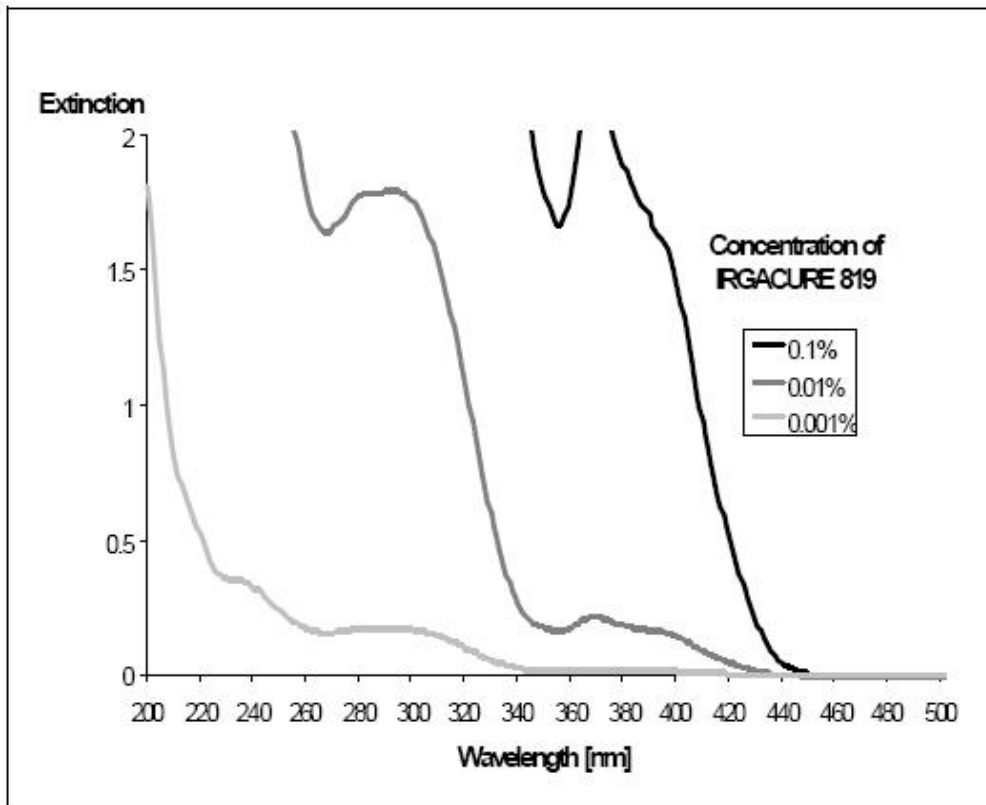


Figure 5. Absorption of BAPO

The HCPK's primary absorbance is in the 240-250 nm range with a smaller absorption peak in the 320-335 nm range. While the other  $\alpha$ -hydroxyketone photoinitiator HMPP has a similar absorbance in the 320-335 nm range, it also has a peak in the 265-280

nm range. The combination of these two PI's alone already begins to take better advantage of the UV lamp's output (Figure 1). The TPO and BAPO have significantly different spectra with the TPO having a strong absorption in the 360-395 nm range and the BAPO having an even stronger absorption in the 360-410 nm range. The addition of these PI's now takes advantage of two additional major emissions of the mercury lamp at 370 and 408 nm (Figure 1).

Table 2. Comparison of multiple PI's vs. 4% HCPK.

Components	4% HCPK	4% Multiple PI's
Urethane acrylate 1	35.0	35.0
Urethane acrylate 2	35.0	35.0
HDDA	25.0	25.0
HCPK	4.0	1.0
HMPP	-	1.0
TPO	-	1.0
BAPO	-	1.0
Stabilizer	1.0	1.0
% RAU at 4.5 mJ/cm <sup>2</sup>	24.8	79.6

Table 3. Comparison of multiple PI's vs. 6% HCPK

Components	6% HCPK	6% Multiple PI's
Urethane acrylate 3	56.0	56.0
Propoxylated nonyl phenol acrylate	36.5	36.5
HCPK	6.0	3.0
HMPP	-	2.0
TPO	-	1.0
Stabilizer	1.0	1.0
Silane	0.5	0.5
% RAU at 4.5 mJ/cm <sup>2</sup>	18.9	67.2

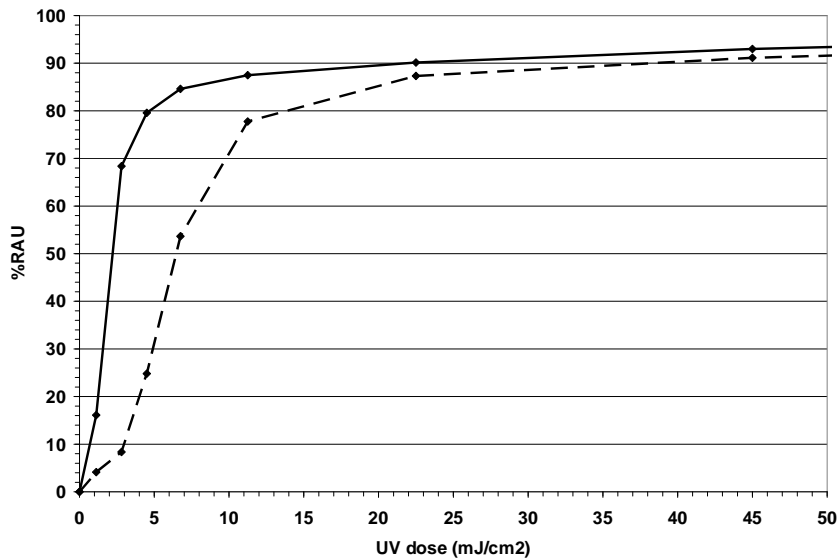


Figure 6. % RAU of multiple PI's (solid) vs. 4% HCPK (dashed)

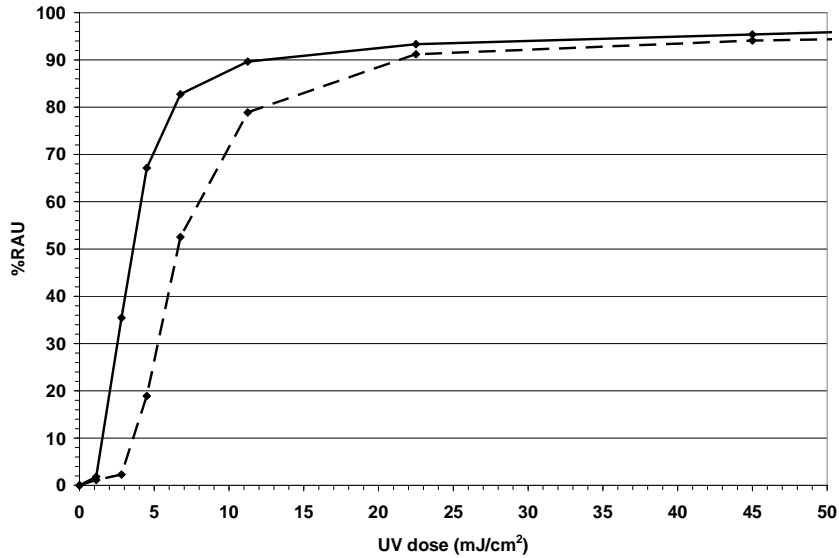


Figure 7. % RAU of multiple PI's (solid) vs. 6% HCPK (dashed)

To determine if the multiple PI approach could provide equal or faster cure speed when used at lower levels than a single PI, new formulations were prepared based on the above but with reduced multiple PI levels (see Tables 4 and 5 and Figures 8 and 9).

Table 4. Comparison of 3% multiple PI's vs. 4% HCPK.

Components	4% HCPK	3% Multiple PI's
Urethane acrylate 4	35.0	35.0
Urethane acrylate 5	35.0	35.0
HDDA	25.0	26.0
HCPK	4.0	1.0
HMPP	-	1.0
TPO	-	0.7
BAPO	-	0.3
Stabilizer	1.0	1.0
% RAU at 4.5 mJ/cm <sup>2</sup>	50.9	66.8

Table 5. Comparison of 4.5% multiple PI's vs. 6% HCPK

Components	6% HCPK	4.5% Multiple PI's
Urethane acrylate 6	56.0	56.0
Propoxylated nonyl phenol acrylate	36.5	38.0
HCPK	6.0	2.0
HMPP	-	2.0
TPO	-	0.5
Stabilizer	1.0	1.0
Silane	0.5	0.5
% RAU at 4.5 mJ/cm <sup>2</sup>	58.3	67.9

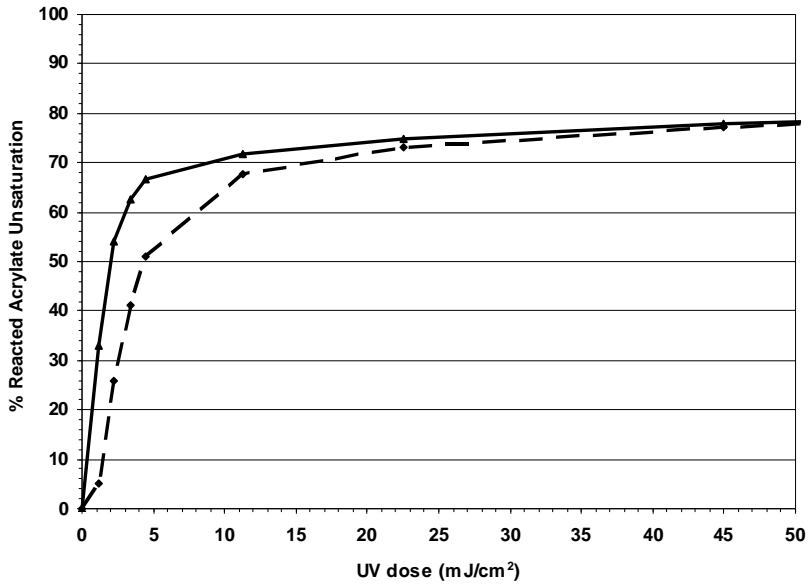


Figure 8. % RAU of 3% multiple PI's (solid) vs. 4% HCPK (dashed)

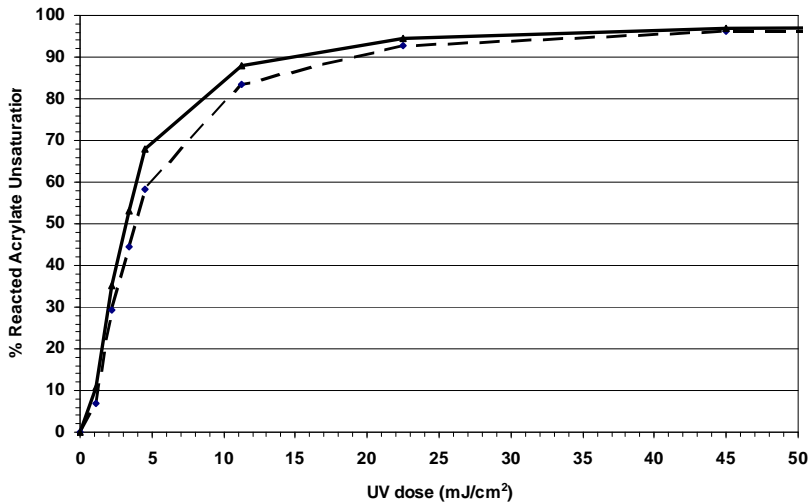


Figure 9. % RAU of 4.5% multiple PI's (solid) vs. 6% HCPK (dashed)

The increased efficiency of these blends is seen in that, even at 25% lower PI levels, the blends still have faster cure speeds than the single HCPK photoinitiator. The % RAU values of the single-photoinitiator controls are different from the first samples since different urethane acrylate oligomers were used. As before, the same maximum degree of reaction is reached in both PI systems, but the multiple PI approach reaches this level sooner.

## Conclusion

The approach of using low levels of multiple photoinitiators offers the UV coating formulator several benefits. These include primarily faster cure speed, but also include potentially lower cost, better through-cure, lower blooming, lower extractables, and lower yellowing due to the lower levels of photoinitiator.

## Acknowledgements

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