

Novel Phosphine Oxide Photoinitiators

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Abstract

This paper presents the work completed on the synthesis of a range of novel phosphine oxides which show enhanced surface curing of acrylate systems when exposed to both high pressure mercury lamps and LED's operating at 365/395 nm, without the addition of other photoinitiators. The new phosphine oxides are less prone to oxygen inhibition, this is demonstrated by extensive curing tests and RT-FTIR analysis of the double bond conversion of the exposed samples. Furthermore, TR-EPR and CIDNP experiments were performed to test the initiation mechanism. The novel phosphine oxides show other beneficial properties such as high solubility, increased response to photosensitization and very low yellowing.

Introduction

Acylphosphine oxides are well known photoinitiators for the photopolymerisation of ethylenically unsaturated compounds, namely acrylates. Monoacylphosphine oxides such as Speedcure TPO, Speedcure TPO-L and bisacylphosphine oxides such as Irgacure 819 (BAPO) have been commercially available for a number of years.

In a recent presentation¹, acylphosphine oxides were presented as intermediate between low cost commodity photoinitiators and high cost low volume specialties. Broad UV absorption spectra and effective production of reactive radicals upon irradiation combined with good solubility in resin systems and photobleaching properties make them the photoinitiators of choice for many industrial applications.² In order to meet future market demands, two current limitations of acylphosphine oxides need to be overcome – migration and oxygen inhibition.

Whilst acylphosphine oxides are excellent at facilitating depth cure in coatings, they all are susceptible to inhibition of surface cure by oxygen³. When mercury lamps are used as the source of radiation, additives such as α -hydroxyacetophenones can be used to bring about surface cure. When Light Emitting Diodes (LED's) are used, however, then the use of α -hydroxyacetophenones does not facilitate surface cure because the UV absorption of these materials lies at shorter wavelength i.e. higher energy than the light emitted by the LEDs (these are readily available at acceptable cost in wavelengths of 405, 395 and 365nm). There has been a lot of recent activity, both in academia⁴ and industry⁵, aimed at improving or enhancing the properties of acylphosphine oxides.

Work objective

The aforementioned problem in the context of LEDs is slowing down the use of LEDs in curing of coatings based on acrylates. It is an object of the present work to address this problem. The research work focused on the development and testing of novel acylphosphine oxide compounds shown in Figure 1. The acylphosphine oxide compounds prepared are all derived from well-known commercial

photoinitiators, namely TPO, TPO-L and BAPO. All exhibit beneficial effects on cure in the presence of oxygen, which may be especially advantageous when LEDs are used.

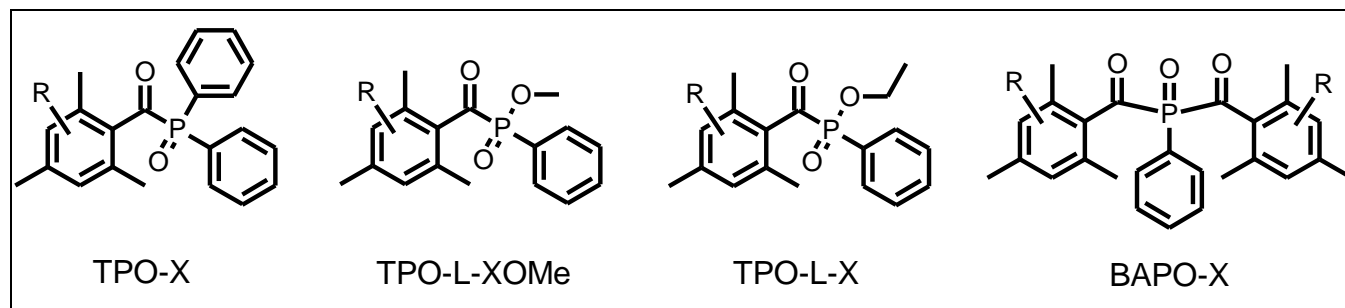


Figure 1

Comparison of physical form and UV absorption properties of compounds TPO-L-X and BAPO-X with TPO and BAPO is shown in Table 1. Compounds TPO-X and TPO-L-XOMe were found to be viscous liquids.

Product name	TPO-L-X	BAPO-X	TPO-L	BAPO
Physical form	Off-white solid	Yellow solid	Yellow liquid	Yellow solid
Assay (HPLC area %)	> 98 %	> 98 %	> 95 %	> 98 %
UV maxima above 300 nm	364 nm (MeCN) ($E_{1\%}^{1cm} = 5.61$)	369 nm (MeCN) ($E_{1\%}^{1cm} = 14.5$)	369 nm (MeOH) ($E_{1\%}^{1cm} = 8.50$)	377 nm (MeOH) ($E_{1\%}^{1cm} = 22.0$)

Table 1

Solubility data (20 °C, in g/100 mL solvent) are shown in Table 2. TPO-L-X shows good solubility in organic solvents and common aliphatic diacrylate resins, comparable to TPO.

Product name	TPO-L-X	TPO	BAPO
Acetone	>50	50	14
toluene	>50	n/a	20
HDDA	22	22	10
TPGDA	16	16	5
TMPTA	13	14	5

HDDA = 1,6-Hexanediol diacrylate, TPGDA = Tri(propylene glycol) diacrylate, TMPTA = Trimethylolpropane triacrylate.

Table 2

UV curing tests

Curing was carried out using a Dymax UVC-5 Curing System. This incorporates a conveyor belt, which was set at 16.5 m/min. Two UV sources were used:

- 900W metal halide mercury lamp supplied as part of the Dymax UVC-5 Curing system.
- An LED light source, replacing the Hg lamp. The LED source used was a Phoseon Firefly, emitting a peak power output of 2 W/cm² at 395nm.

The resin mixture consisted of:

60 wt% Sartomer SR348L (Ethoxylated-2EO-Bisphenol A Dimethacrylate)

25 wt% Sartomer SR306 (Tripropylene glycol dimethacrylate)

15 wt% Sartomer CN3715 (Acrylated amine synergist)

The resin mixture was mixed at 40-50 °C with one or more photoinitiators. The levels of photoinitiator are quoted as parts per 100 parts of resin mix by weight.

The test substrate (i.e. resin mixture and photoinitiator(s)) was applied to a waxed paper substrate at various thicknesses using K-bars to give a smooth film for testing. The test pieces were then placed on the conveyor and passed under the UV source. The hardening and eventual full curing of the films were measured by applying a thumb twist procedure - the fully cured films do not leave any observable mark from placing a thumb on the film and twisting. The results quoted are number of passes under each UV source to give a fully cured film. By inference, the lower the number of passes, the more active the photoinitiator in the sample under test.

Comparisons were made with other commercial Speedcure® photoinitiators, available from Lambson Ltd, and Irgacure 819 (BAPO) available from BASF.

Tables 3 and 4 detail curing results obtained using the mercury lamp.

Entry	Acylphosphine oxide (wt %)	Additive	Curing results			
			Film thickness	Passes to full cure	Film thickness	Passes to full cure
1	2.9 % TPO	none	24	22	100	24
2	2.6 % TPO-L	none	24	16	100	15
3	2.6 % TPO-L-X	none	24	7	100	5-6
4	3.5 % BAPO	none	24	9	100	7
5	3.5 % TPO-L-X	none	24	5	100	4
6	3.4 % TPO-L-XOMe	none	24	4	100	5
7	2.9 % TPO	1 % BP	4	9	12	6
8	2.6 % TPO-L	1 % BP	4	11	12	4
9	2.6 % TPO-L-X	1 % BP	4	9-10	12	4
10	3.5 % BAPO	1 % BP	4	7	12	3
11	3.5 % TPO-L-X	1 % BP	4	6	12	2
12	3.4 % TPO-L-XOMe	1 % BP	4	6	12	3
13	5.1 % BAPO-X	1 % BP	4	4	12	3

BP = benzophenone

Table 3

It can be seen that the curing speed of TPO-L-X compares favourably with that of TPO-L and BAPO at the same weigh loading (entries 2 vs 3 and 4 vs 5). When used in combination with benzophenone (1 wt %), higher speed of cure is seen for all formulations, and at 3.5 wt % loading, the cure speed of TPO-L-X is marginally higher than for BAPO (entry 10 vs 11).

Entry	Acylphosphine oxide (wt %)	Additive	Curing results			
			Film thickness	Passes to full cure	Film thickness	Passes to full cure
1	2.6 % TPO-L	2.4 % Speedcure 7005	24	6	100	5
2	3.5 % BAPO		24	4	100	3
3	3.5 % TPO-L-X		24	3	100	3
4	3.4 % TPO-L-XOMe		24	3	100	3
5	2.6 % TPO-L-X		24	5	100	3-4
6	2.6 % TPO-L		4	12	12	8
7	3.5 % BAPO		4	9	12	4
8	3.5 % TPO-L-X		4	6	12	3
9	3.4 % TPO-L-XOMe		4	7	12	4
10	2.6 % TPO-L-X		4	10-11	12	5-6
11	2.6 % TPO-L	1.0 % Speedcure 7010	4	11	12	7
12	3.5 % BAPO		4	8	12	5
13	3.5 % TPO-L-X		4	7	12	3
14	3.4 % TPO-L-XOMe		4	6	12	3
15	2.6 % TPO-L-X		4	9-10	12	6
16	2.6 % TPO-L	1.0 % Speedcure 7006	4	12	12	5
17	3.5 % BAPO		4	8	12	4
18	3.5 % TPO-L-X		4	6	12	3
19	3.4 % TPO-L-XOMe		4	6	12	3
20	2.6 % TPO-L-X		4	10-11	12	4

Speedcure 7005, 7010 and 7006 are polymeric photoinitiators provided by Lambson Ltd.

Table 4

Further comparisons of curing performance in combination with polymeric type II photoinitiators (Speedcure 7000 series) are shown in Table 4. For Speedcure 7005, the TPO-L-X shows comparable or higher cure speed than BAPO (at 3.5 wt % loading, entries 2 vs 3 and 7 vs 8) and TPO-L (at 2.6 wt % loading, entries 1 vs 5 and 6 vs 10), the positive effect being more pronounced in thinner coatings. Similar effect is seen for Speedcure 7010 and 7006.

Table 5 details curing results obtained using the LED lamp. The curing mixture comprised of 8.5g standard acrylate mix (as described above) and 1.5g CN3715 acrylated amine.

Entry	Acylphosphine oxide (wt %)	Additive	Curing results			
			Film thickness	Passes to full cure	Film thickness	Passes to full cure
1	2.9 % TPO	0.4 % ITX	24	>40	-	-
2	3.75 % TPO-X	0.4 % ITX	24	30	-	-
3	2.9 % TPO	0.8 % ITX	24	25	100	20
4	2.6 % TPO-L	0.8 % ITX	24	17	100	16
5	3.5 % TPO-L-X	0.8 % ITX	24	14	100	14

6	2.9 % TPO	1.2 % ITX	24	14	100	11
7	2.6 % TPO-L	1.2 % ITX	24	9	100	8
8	3.5 % BAPO	1.2 % ITX	24	7	100	7
9	3.75% TPO-X	1.2 % ITX	24	8	100	7
10	3.5 % TPO-L-X	1.2 % ITX	24	8	100	7
11	3.4 % TPO-L-XOMe	1.2 % ITX	24	8	100	7

ITX = 2- and 4-isopropyl thioxanthone

Table 5

At 0.4 % ITX, surface cure is difficult to achieve. At 0.8 % ITX, full surface cure is achieved for all three photoinitiators tested. When comparing equimolar quantities (entries 3, 4 and 5), TPO-L-X shows improved surface cure compared to TPO and TPO-L. The difference is more pronounced at 1.2 % ITX, with TPO-X, TPO-L-X and TPO-L-XOMe approaching the cure speed of BAPO (entries 8 vs 9, 10 and 11).

Table 6 shows further results with clear varnish and acrylated amine (same resin composition as for data in Table 5), focusing on curing performance in thin films with ITX sensitization. All results were obtained using the 395 nm LED lamp.

Entry	Acylphosphine oxide (wt %)	Additive	Curing results			
			Film thickness	Passes to full cure	Film thickness	Passes to full cure
1	2.6 % TPO-L	1.2 % ITX	4	20	6	14
2	5.2 % TPO-L		4	14	6	9
3	2.6 % TPO-L-X		4	9	6	8
4	5.2 % TPO-L-X		4	7	6	7
5	3.5 % BAPO		4	13	6	9
6	2.6 % TPO-L		12	9	24	8
7	5.2 % TPO-L		12	7	24	7
8	2.6 % TPO-L-X		12	7	24	8
9	5.2 % TPO-L-X		12	6	24	6
10	3.5 % BAPO		12	7	24	8

Table 6

As expected, in all examples in Table 6, the cure speed drops off as the film thickness is reduced. This is due to a relatively larger proportion of the resin being directly exposed to atmospheric oxygen in case of thinner films. Crucially, the tested photoinitiators differ widely in their sensitivity to oxygen inhibition. In case of TPO-L and BAPO, the cure speed drops off by approximately 50 % when going from 24 μm to 4 μm (cf. Entries 1 vs 6 and 5 vs 10). For TPO-L, the oxygen inhibition effect appears to be independent of the photoinitiator loading (cf. Entries 1 and 2 vs 6 and 7). This dramatic reduction in curing performance demonstrates the sensitivity of these phosphine oxides to oxygen inhibition. The novel TPO-L-X photoinitiator significantly outperforms both photoinitiators, mainly in 4 μm and 6 μm films, where it gives about double the cure rate of TPO-L at the same weight loading (cf. Entries 1 vs 3). Remarkably, the novel TPO-L-X photoinitiator appears to be almost unaffected by oxygen inhibition under the test conditions (cf. Entries 3 and 4 vs 8 and 9).

Response to photosensitization

Sensitization of the TPO-L-X phosphine oxide photoinitiator was examined in greater detail under the 900 W metal halide lamp, checking for cure speed and yellowing. Comparisons were made to TPO, TPO-L and BAPO.

The following resin mixture was used:

80 wt% Sartomer SR348L (Ethoxylated-2EO-Bisphenol A Dimethacrylate)

20 wt% Sartomer SR306 (Tripropylene glycol dimethacrylate)

24 μm coatings (No 3 K-bar, green) were drawn on white card to give a thick coating that would consider depth cure as well as surface cure. The Dymax UV-5 curing unit was set at 7 rpm giving a belt speed of 10.78 m/min. Full cure was established by thumb twist to the number of passes leaving no marks.

1.5 wt % of the phosphine oxide under test was added to the curing resin together with 4 wt % Speedcure 73 (this combination being widely used in industry) to provide good surface cure.

In effect, this allows examination of depth cure. Results are shown in Table 7 and 8.

Photoinitiator	Sensitizer	Passes to full cure
TPO	none	22
	0.13 % ITX	19
	0.28 % ITX	18
	0.41 % ITX	17
	0.68 % ITX	15
	1.04 % ITX	14
TPO-L	none	25
	0.13 % ITX	19
	0.33 % ITX	18
	0.45 % ITX	17
	0.69 % ITX	15
	1.13 % ITX	14

Table 7

Photoinitiator	Sensitizer	Passes to full cure
BAPO	none	20
	0.13 % ITX	16
	0.25 % ITX	16
	0.43 % ITX	14
	0.67 % ITX	12
	1.00 % ITX	11
TPO-L-X	none	20
	0.13 % ITX	18
	0.25 % ITX	17
	0.43 % ITX	16
	0.67 % ITX	14
	1.00 % ITX	12

Table 8

In the absence of ITX sensitizer, the phosphine oxides cured as expected with TPO-L being a little slower than TPO. The new phosphine oxide TPO-L-X was faster curing and performed as well as BAPO. The addition of ITX as sensitizer led to improved cure in all cases with TPO-L-X performing better than TPO but not as well as BAPO. TPO-L sensitization matched that of TPO despite the initial lower cure speed. At 0.4% ITX, the increase in cure speed was 31% for TPO, 46% for TPO-L, 44% for BAPO and 26% for TPO-L-X.

In the absence of ITX there was no difference between any of the phosphine oxides in a visual examination of the cured film, with no apparent yellowing. The addition of just 0.1% ITX produced a trace of yellowing that was similar in all the phosphine oxides. At 0.25% ITX the yellowing would inhibit its use in a clear coating for whites or pastels.

The TPO-L-X sensitization testing was then extended to include Speedcure 7010 (SC 7010) and unsubstituted thioxanthone (TX). The test conditions were the same as for the ITX sensitization test in Tables 7 and 8 (24 μm coating, on white card, cured at 10.78m/min with a metal halide lamp, 1.5 wt % of TPO or TPO-L-X with 4% Speedcure 73). Unsubstituted thioxanthone, TX, was also chosen as a sensitizer as it has a blue shifted absorption of 378nm compared to that of ITX at 383nm. This means that it is less yellow than ITX and may be more suitable for clear varnishes.

Photoinitiator	Sensitizer	Passes to full cure
TPO	none	21
	0.11 % SC 7010	19
	0.33 % SC 7010	19
	0.48 % SC 7010	16
	0.62 % SC 7010	16
	0.79 % SC 7010	15
	1.17 % SC 7010	15
TPO-L-X	none	20
	0.23 % SC 7010	20
	0.43 % SC 7010	21
	0.73 % SC 7010	21
	1.07 % SC 7010	22

Table 9

Photoinitiator	Sensitizer	Passes to full cure
TPO	none	21
	0.12 % TX	19
	0.34 % TX	16
	0.57 % TX	14
	0.76 % TX	12
	0.97 % TX	11
	1.48 % TX	11
TPO-L-X	none	20
	0.14 % TX	18
	0.29 % TX	17
	0.47 % TX	15
	0.81 % TX	12
	1.11 % TX	11

Table 10

As shown in Table 9, TPO responds only moderately to the polymeric Speedcure 7010 and TPO-L-X shows no response to 7010. This is probably due to the lack of triplet energy differential between TPO and 7010 compared with TPO and ITX. The relevant triplet energies are (in kcal/mol): ITX 61.4, 7010 ~60.3, TX 63.3, TPO ~60 (reported values from 60 to 62.6).

TPO-L-X must therefore have a triplet energy somewhat higher than that of 7010 at 60.3 kcal/mol and lower than ITX at 61.4 kcal/mol (since TPO-L-X shows good sensitization with ITX as shown in Table 8). An estimated triplet energy for TPO-L-X is therefore around 60.5-61 kcal/mol.

Thioxanthone has a higher triplet energy (63.3 kcal/mol) than ITX and therefore a higher positive energy differential. This may be the reason why TX as a sensitizer is around 15% more efficient than ITX for both TPO and TPO-L-X which both respond in similar fashions (Table 10).

Regarding discoloration during cure, temporary yellowing is seen immediately on initial cure with ITX and TX but this reduces on full cure. Formation of transient photoproducts from phosphine oxides has been reported, and this may be due to traces of 2,4,6-trimethylbenzaldehyde from hydrogen abstraction by the benzoyl radical. 7010 shows less yellowing than either ITX or TX.

Response to amine synergist

A similar formulation was used to test the effect of an aromatic amine synergist as oxygen scavenger on surface cure. To an acrylic resin with 1.5 wt % phosphine oxide, but without the Speedcure 73 for surface cure, increasing amounts of ethyl *p*-dimethylaminobenzoate (Speedcure EDB) were added up to 10 wt % to assess the effect on both surface and full cure (film thickness 24 μm).

Photoinitiator	Aromatic amine	Passes to full cure
TPO	2 % EDB	27
	3 % EDB	23
	4 % EDB	20
	5 % EDB	18
	7 % EDB	17
	10 % EDB	16

Table 11

Photoinitiator	Aromatic amine	Passes to full cure
TPO-L-X	2 % EDB	25
	3 % EDB	20
	4 % EDB	19
	5 % EDB	16
	7 % EDB	14
	10 % EDB	12

Table 12

Below 2 wt % tertiary amine, full cure is difficult to achieve. The addition of EDB in both cases improves cure but with TPO the cure rate levels off above 6 wt % EDB (Table 11). TPO-L-X continues to show improved cure with up to 10 % EDB and beyond (Table 12).

As opposed to TPO, the new phosphine oxide TPO-L-X appears to react with the excess amine (above that required for oxygen scavenging) to provide additional radicals that promote surface cure and ultimately full cure. This demonstrates enhanced reactivity of TPO-L-X under short wavelength UV light.

Real time FTIR measurements

Real time FTIR measurements were performed to assess the double bond conversion during cure. Formulation films of approximately 5 μm thickness on polyethylene foils were cured with a 400 nm LED light in air. Comparative results for TPO and TPO-X are plotted in Figure 2.

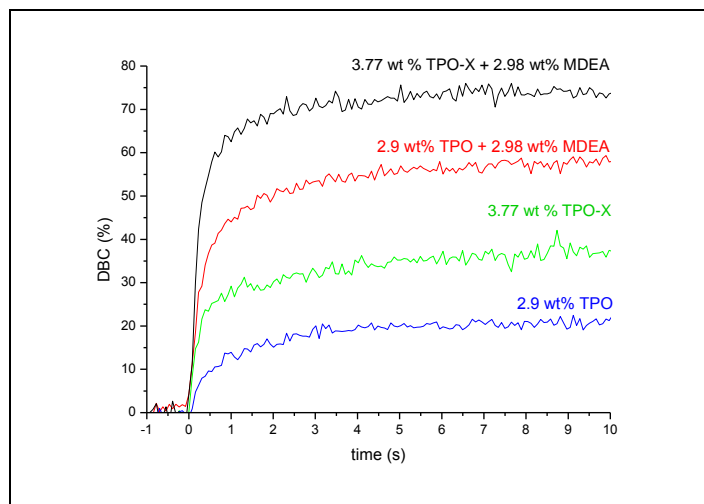


Figure 2

- LED curing at 400 nm
- Light intensity at the surface = 85 mW/cm²
- Formulation: Bomar BR-344/DPGDA 50:50
- MDEA = N-methyldiethanolamine (2.98 wt%, 3 molar eq. to initiator)
- TPO-X and TPO used in equimolar quantities
- Samples measured 5 times and averaged

It can be seen from Figure 2 that under the test conditions (NB: The Bomar BR-344/DPGDA represents a simplified wood coating formulation) the TPO-X achieves a higher initial rate of cure and final double bond conversion than an equimolar amount of TPO. This is observed both in the presence and also absence of MDEA amine synergist.

Quantum yield

The quantum yield of decomposition was measured at 365 nm using o-Nitrobenzaldehyde as actinometer. The quantum yield for TPO-X was measured at 0.60 ± 0.05 (vs 0.55 measured for TPO).

Magnetic Resonance experiments

Time-resolved electron paramagnetic (TR-EPR) resonance measurements of the initiators were performed to determine if there is any difference in the initiation mechanism compared to known TPO. Different experiments performed also in presence of monomers / hydrogen donors do not reveal any radical activity of the benzophenone moiety (at 355 nm Nd:YAG irradiation). A difference can only be detected in signal intensities caused by the polarization mechanisms (see Figure 3).

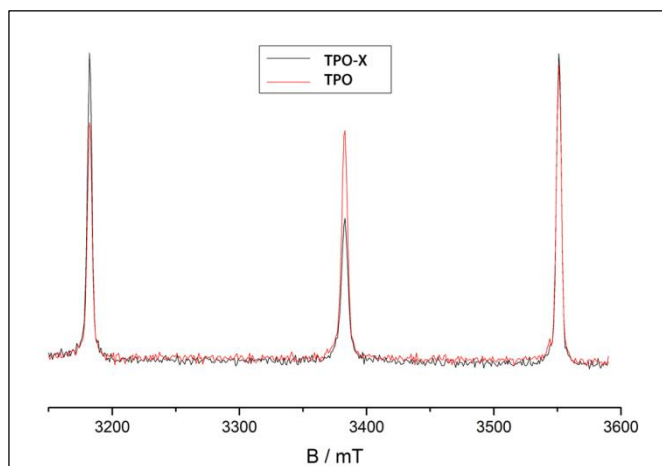


Figure 3 TR-EPR spectra of TPO/TPO-X recorded 1 μ s after the laser pulse

Furthermore, chemically induced dynamic nuclear polarization (CIDNP) measurements were done to complement the TR-EPR data. Also here no significant difference to TPO/TPO-L could be found. The new initiators showed the expected behaviour in ^{31}P and ^1H CIDNP.

From these results it is indicated that there is no significant difference in initiation mechanism (esp. at higher wavelength) and the improvements are most likely a result of secondary reactions and improved sensitization potential.

CIE Whiteness measurements

In order to assess the impact of residual photoproducts on the colour of a white flexographic ink, CIE whiteness was measured according to BS ISO 11475:2007. For each test, five pieces of paper substrate were coated with 50 μm of an industry standard UV flexographic ink containing the tested photoinitiator. All samples were fully cured with a 900 W metal halide lamp and preconditioned at 23 ± 2 $^\circ\text{C}$, 50 ± 5 % rel. humidity for 16 hours. The CIE whiteness was then measured for each sample at D65/10 $^\circ$ (outdoor daylight) using a Technidyne Colourtouch PC instrument. Results are shown in Table 13.

Photoinitiators	CIE Whiteness (%)
4 wt% TPO-L-X + 2 wt% Speedcure 73	78.6 ± 0.49
6.6 wt% TPO-L-X + 0.4 wt% Speedcure ITX + 5 wt% LED01	79.3 ± 0.82
2 wt% BAPO + 2 wt% Speedcure 73	74.8 ± 0.55

Table 13

Even at increased loadings, TPO-L-X can provide a marginally higher whiteness index than BAPO.

Conclusions

In conclusion, advantageous properties of a range of novel acylphosphine oxide photoinitiators have been demonstrated. By comparison with existing commercial phosphine oxides, the new materials provide improved UV cure for acrylate coatings, mainly in the presence of an amine synergist and/or a thioxanthone sensitizer. Superior surface cure is achieved with a conventional mercury lamp as well as a 395 nm LED source. Other beneficial properties include high solubility in resin systems and very low yellowing.

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