

Boosting the cure of phosphine oxide photoinitiators.

Sensitisation or Synergy?

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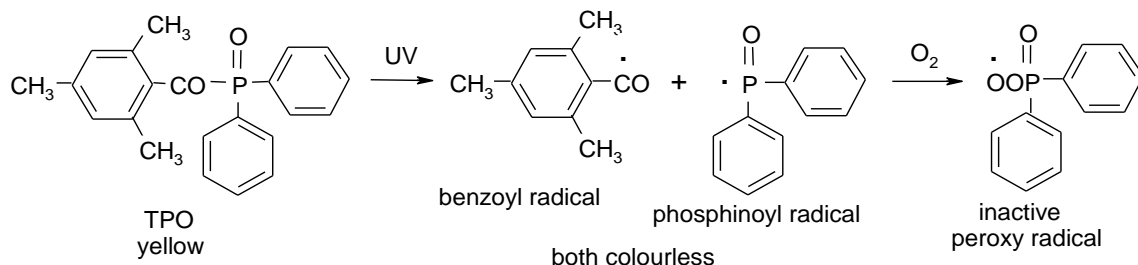
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Introduction.

In this paper, by the use of simple cure tests, a range of sensitizer-phosphine oxide combinations that lead to improved cure has been studied. This leads on to a study of surface cure for phosphine oxides through the synergy of Type II short wave UV photoinitiators and tertiary amines under the mercury lamp.

Phosphine oxide photoinitiators.

Phosphine oxides such as 2,4,6-trimethylbenzoyldiphenylphosphine oxide (TPO) are very efficient photoinitiators that absorb in the long wavelength UV at 380-410nm and are used particularly in thick coatings where photobleaching leads to good depth cure.



Under UV, Type I scission leads to a diphenylphosphinoyl radical that is twice as reactive as the 2,4,6-trimethylbenzoyl radical and is the primary radical for polymerisation. However, the phosphinoyl radical is readily oxidised to a low reactivity peroxy radical and, used alone, the lack of surface cure with phosphine oxides due to oxygen inhibition is a serious problem. This can be overcome by adding a fairly high concentration of short wave UV photoinitiator such as a hydroxyacetophenone (eg. Darocur 1173) to the formulation to give a high radical count at the surface and mixtures of these in a ratio of around 1:3 phosphine oxide to short wave photoinitiator are now marketed to give efficient, full cure. These mixtures rely on the mercury lamp to provide both long wave and short wave UV to generate depth and surface cure.

Using a single wavelength (395nm or 365nm) LED UV lamp, surface cure using phosphine oxides alone cannot easily be attained since there is no available short wave UV to activate other photoinitiators.

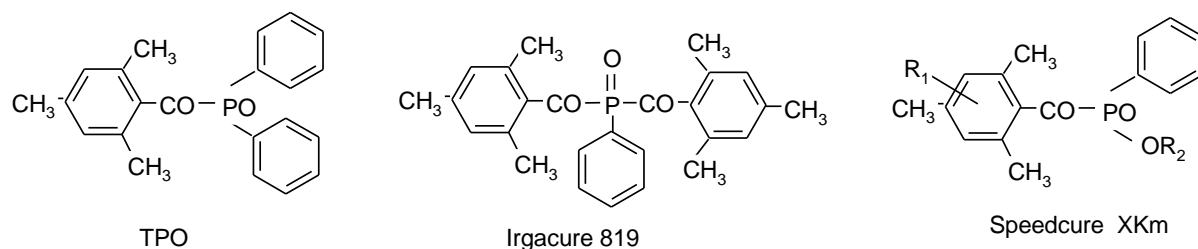
The use of tertiary amines for surface cure.

Tertiary amines can be used to enhance the cure of both Type I and Type II systems. They are used particularly with thin or low viscosity coatings to improve the surface cure via oxygen scavenging and this process can be applied to phosphine oxides under both mercury and LED UV lamps. The process produces active alkylamino radicals from the inactive peroxy radicals that may have been formed, leading to a higher radical count and improved surface cure.

Olamines cannot be used with phosphine oxides since they affect their hydrolytic stability but aminobenzoate esters and oligomeric tertiary alkylamines can be used with care.

Three phosphine oxides were assessed:

1. diphenyl-(2,4,6-trimethylbenzoyl)-phosphine oxide (TPO),
2. phenyl-bis-(2,4,6-trimethylbenzoyl)phosphine oxide (Irgacure 819,) and
3. a recent novel phosphine oxide (Speedcure XKm).



The addition of an acrylated amine such as Sartomer CN 3715 to 1.5% phosphine oxide in a thick, 24 micron clear coating has been shown to give improved cure under both mercury and 395nm LED UV lamps, see Fig. 1 below.

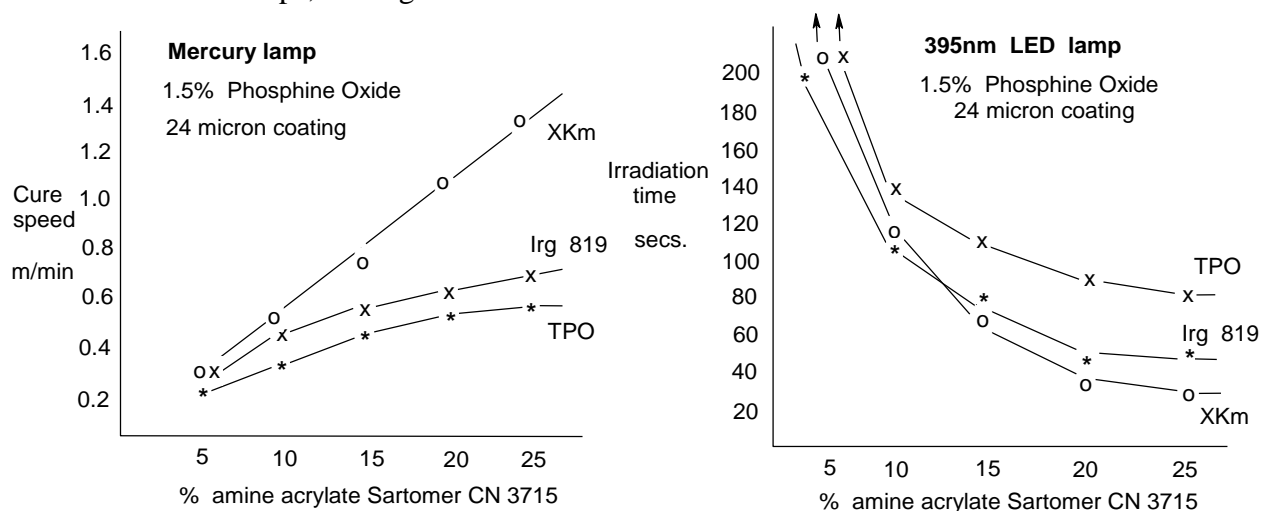


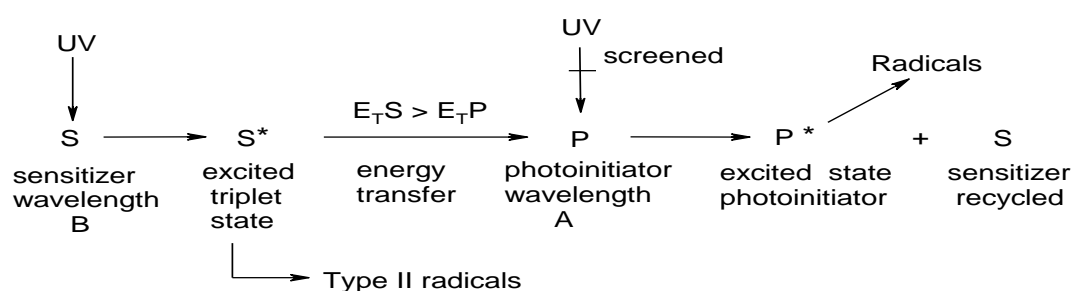
Figure 1. The effect of an amine acrylate on the photocuring of phosphine oxides.

Below 5% amine acrylate, full cure is difficult to achieve with any of the phosphine oxides. At 10% amine and above, full cure can be achieved under both types of lamp. The strong response of Speedcure XKm under the mercury lamp is due to its modified structure which

responds to short wavelength UV. Under a 395nm LED lamp, oligomeric tertiary amines at 10-15% (equivalent to 3-5% aminobenzoate EDB) can provide good surface cure.

The sensitisation process.

The use of long wave sensitizers to activate photoinitiators is well established. For the UV curing industry, this energy transfer effect has already been put to good use in high speed UV inks. Small additions of isopropylthioxanthone (ITX) to aminoalkylacetophenone photoinitiators such as 2-benzyl-2-(dimethylamino)-4'-morpholino-butyrophenone (Irgacure 369) improve the cure speed by a considerable degree. These systems have been studied in some detail to give a good understanding of the sensitisation process^{1,2,3}. Sensitisation of other photoinitiators, such as substituted benzophenones, has also been explored⁴.



The photoinitiator P, absorbing at wavelength A, produces radicals that initiate polymerisation. The use of a sensitizer S, allows absorption at a secondary wavelength (B), giving an excited state sensitizer S*. This energy is rapidly transferred to the photoinitiator P which produces radicals as before without direct UV absorption. The sensitizer returns to its ground state S.

Sensitisation, in effect, extends the UV absorption range of the photoinitiator and leads to higher cure speeds than either that of the initiator or the sensitizer alone. Energy transfer has been shown to be extremely fast and alternative processes that may occur from the excited state sensitizer S*, such as Type II reactions, will be minimal. The sensitizer is essentially catalytic and can be used in small amounts to energise greater concentrations of photoinitiator.

For energy transfer to occur only two parameters are critical:

- The triplet energy E_T of the sensitizer S must be greater than that of the photoinitiator P. $E_T S > E_T P$
- The triplet state of the sensitizer should have a long lifetime (typical of Type II photoinitiators acting as sensitizers).

Sensitisation tests. Experimental.

For cure speed assessment using the Dymax UVC-5 medium pressure mercury lamp, a low reactivity bisphenol-methacrylate resin was diluted with 30% TPGDA. 1.5% of phosphine oxide was added plus 4% 2,2-dimethyl-2-hydroxyacetophenone (Speedcure 73) to provide surface cure.

For the Phoseon RX Firefly 395nm static LED lamp, the resin was changed to a more reactive ethoxylated bisphenol-A-diacrylate plus 25% triacrylate monomer TMPTA. 1.5% phosphine oxide was added plus 10% Sartomer CN3715 acrylated amine to provide surface cure. Thick coatings of 24 microns were made on white card for both lamps.

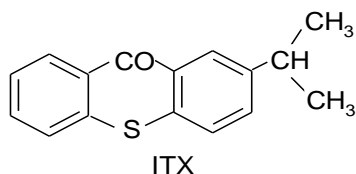
Sensitisation tests with thioxanthenes.

Triplet energy values in kcal/mol. for the phosphine oxides are:

TPO	61.0	Irgacure 819	60.9	Speedcure XKm	ca 60.7
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The sensitisation of phosphine oxides by thioxanthenes has been studied in some detail^{5,6} and is now being used for certain applications. The results below illustrate the improvement in cure speed that can be obtained from the use of 2/4-isopropylthioxanthone (ITX) as a sensitizer.

ITX has a small positive differential in triplet energy (61.4 kcal/mol) over the phosphine oxides.



Triplet energy kcal/mol.

ITX	61.4
PO's	60.7-61.0

The Dymax UVC-5 medium pressure mercury lamp.

A high belt speed was used with the mercury lamp to give an initial cure speed of about 20 passes then small differentials in cure speed could be assessed as additions of sensitizer were made.

The 395nm Phoseon Firefly LED UV lamp.

For the static Firefly 395nm LED lamp placed 5mm above the coating, the time to cure in seconds was measured.

Cure speed measurements from the thumb twist test are somewhat subjective but the results are indicative of trends where improved cure from sensitisation shows up (Fig. 2 below).

Under both the mercury lamp and the 395nm LED lamp quite small additions of ITX lead to an increase in cure due to energy transfer. All three phosphine oxides show a good response.

The performance of the sensitizer will depend to some degree on the triplet energy differential. Sensitizers are energised by the longest wavelength of available UV light that they can absorb, corresponding to the lowest energy UV source, and thioxanthenes are activated primarily by the 404nm output of the mercury lamp⁴.

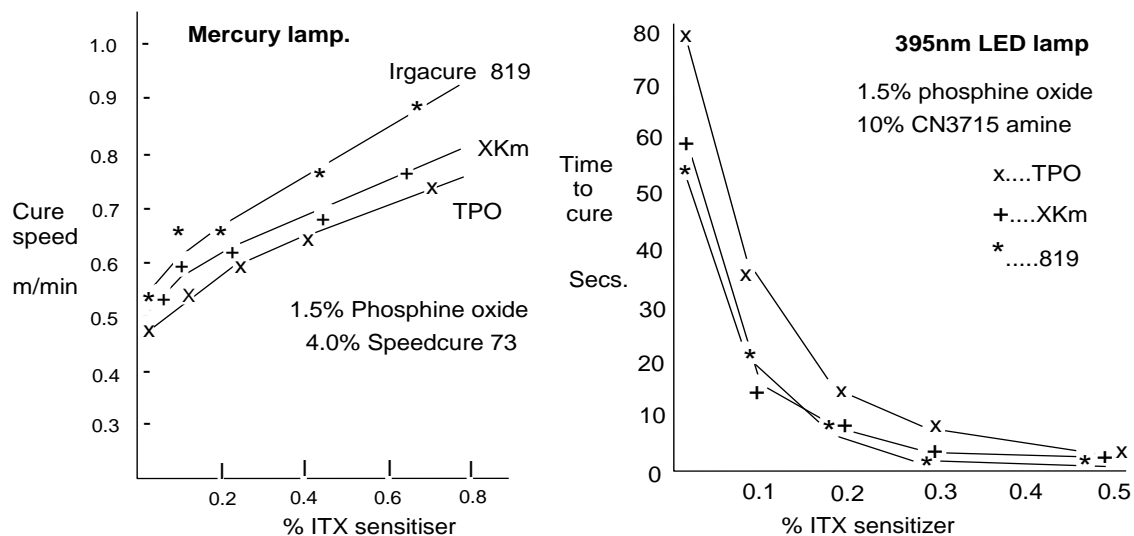


Figure 2. Cure speed vs addition of ITX sensitizer to phosphine oxides.

Several alternative thioxanthenes were examined under the mercury lamp using 1.5% TPO as the photoinitiator in a 12 micron clear coating, Figure 3 below, comparing their performance with 2/4-isopropylthioxanthone, ITX.

These thioxanthenes included 2,4-diethylthioxanthone, DETX, unsubstituted thioxanthone, TX, 2-chlorothioxanthone, CTX, and 1-chloro-4-propoxythioxanthone, CPTX.

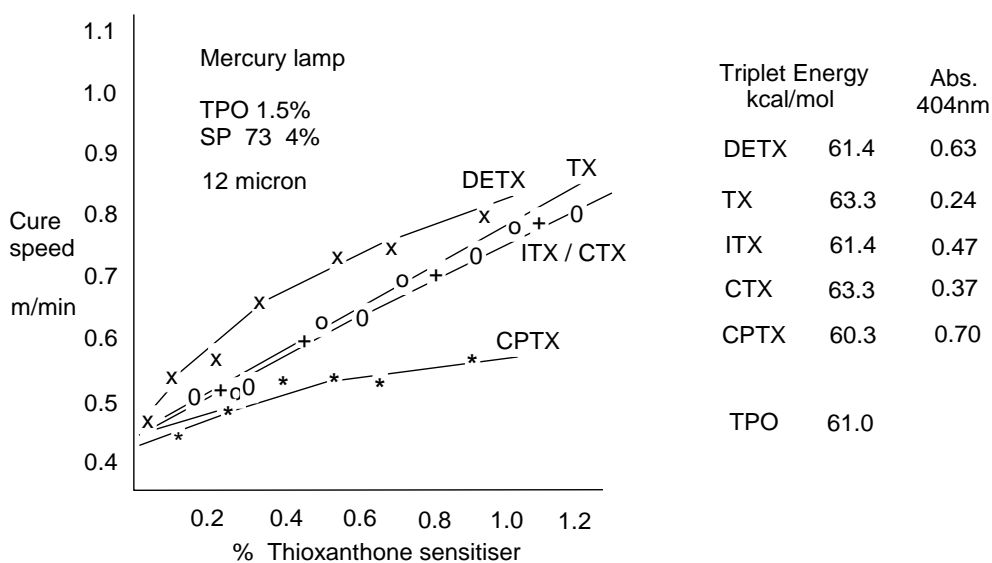


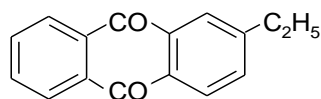
Figure 3. Alternative thioxanthone sensitizers.

DETX is the most efficient thioxanthone for sensitising phosphine oxides, having the same triplet energy differential as ITX but a stronger absorbance at 404nm. Unsubstituted thioxanthone, TX, absorbs at 383nm and is less yellow than ITX. TX and CTX have greater energy differentials over the phosphine oxides but have a lower absorbance, and show little advantage over ITX. CTX and ITX behave identically in these tests.

CPTX has a negative energy balance with TPO and contributes little to the curing process despite having a strong absorbance at 404nm.

All the thioxanthenes will bring some yellowing to the coating.

2-ethylantraquinone (EAQ) as a sensitizer for phosphine oxides.



2-ethylantraquinone

Triplet energy kcal/mol.

EAQ 62.4

PO's 60.7-61.0

2-Ethylantraquinone is a useful sensitizer that has an absorption maximum at 334nm which is readily activated by a mercury lamp. At 395nm from the LED lamp, EAQ has a very low absorbance of 0.0272 (0.05%, 1cm) due to a long, very small 'tailing' effect but this is sufficient to activate energy transfer.

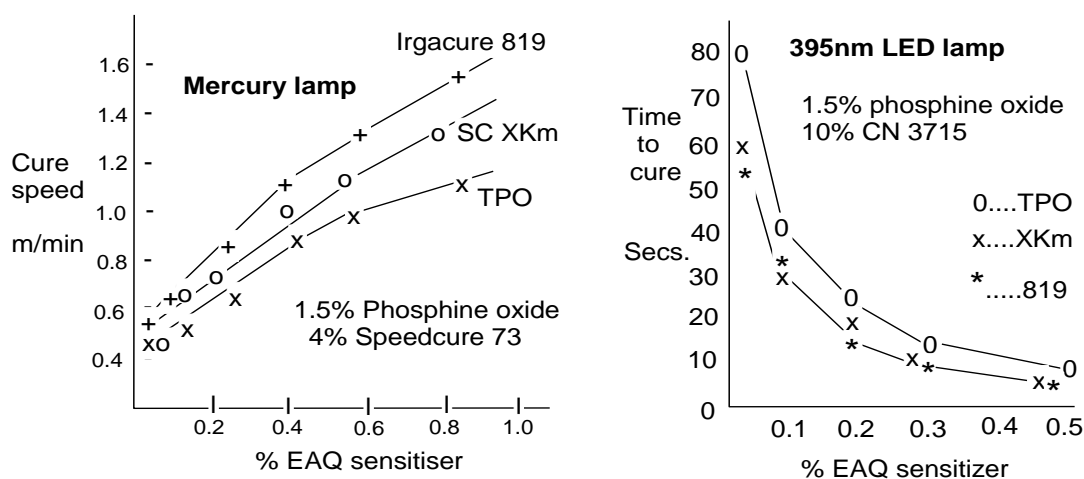


Figure 4. Cure speed vs addition of EAQ sensitizer to phosphine oxides.

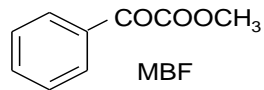
Under the mercury lamp, 1.5% TPO was added with 4% Speedcure 73 for surface cure and with the 395nm LED lamp 10% CN3715 acrylated amine was added as the alternative for surface cure.

24 micron coatings were made and the cure speed measured by thumb twist after small sequential additions of EAQ sensitizer (Figure 4).

2-Ethylantraquinone shows some improvement over isopropylthioxanthone as a sensitizer under the mercury lamp but is less effective under the 395nm LED lamp, most likely due to its very low absorbance at that wavelength.

The one downside is that some brown colouration appears at higher concentrations of EAQ.

Sensitisation tests with methyl benzoylformate, MBF.



	Triplet energy kcal/mol.
MBF	ca 65.7
PO's	60.7-61.0

The ketoesters such as methyl benzoylformate have an absorption maximum at 252nm but there is also a very small n- π^* long wave absorbance at 345nm that tails almost into the visible. Academic studies have shown that this long wave absorption of ketoesters is photo bleached during cure. Methyl benzoylformate, MBF, has a positive triplet energy balance with the PO's.

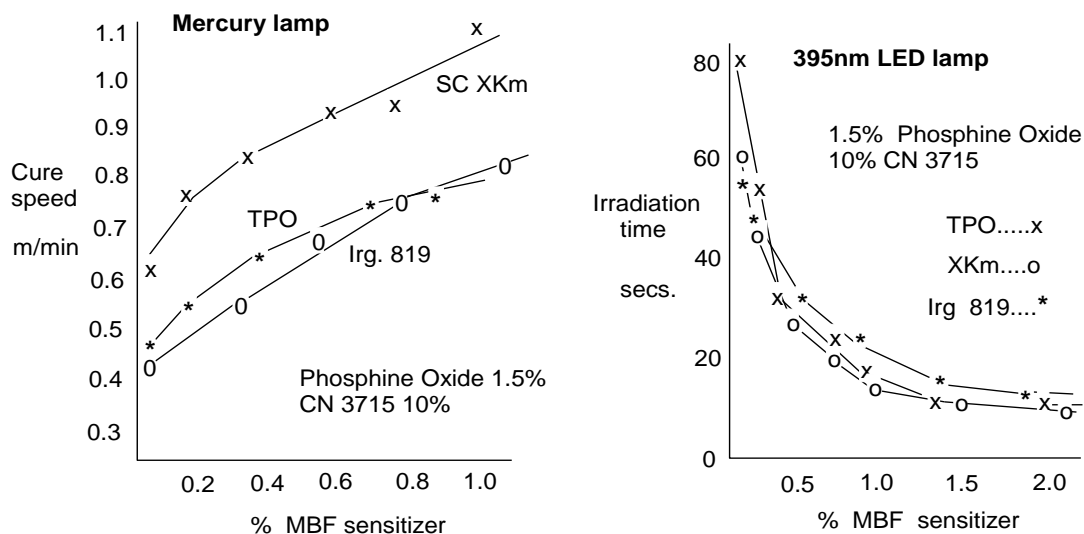


Figure 5. Cure speed vs addition of methyl benzoylformate as a sensitizer/synergist.

Under a mercury lamp using 1.5% phosphine oxide and 10% amine acrylate for surface cure in a 24 micron coating, quite small amounts of MBF show a good response with all the phosphine oxides. The more significant response of XKm is due to its modified structure that responds to tertiary amines.

Under the 395nm LED lamp there is a similar response to MBF from all the phosphine oxides. However, the concentration of MBF needs to be increased considerably to achieve a good cure speed. This may be due to the very small absorbance of MBF at 395nm or perhaps due more to synergism of the MBF with the tertiary amine and a lesser sensitization effect.

MBF has, however, a major advantage in that it is non-yellowing compared to the significant coloration that can occur with the use of both ITX and EAQ and hence the positive response of MBF may be more suitable for clear and white coatings.

Sensitizer or synergist?

In the above tests with methyl benzoylformate, a tertiary amine was used to provide surface cure in the formulations for both lamps.

The tertiary amine was then removed from the formulation for the mercury lamp and the tests repeated with 4% Speedcure 73 to provide surface cure. It was found that the response to the addition of MBF flattened out considerably which suggests that there is little sensitisation occurring and the original positive response is more likely due to synergy of the MBF with the tertiary amine.

Tertiary amines are efficient hydrogen donors for Type II photoinitiators (such as MBF) and oxygen scavengers for surface cure. In this case, the MBF shows very effective synergy with the amine even at quite low concentration. This is effectively a Type II formulation for surface cure that will include oxygen scavenging to some degree.

Type II formulations for surface cure with phosphine oxides.

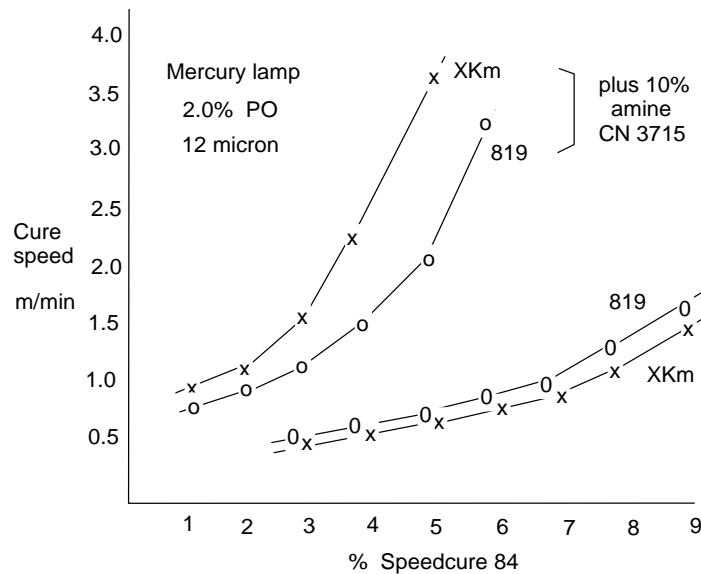


Figure 6. Type I surface cure with additional short wave photoinitiator.

A typical Type I formulation for surface cure with a phosphine oxide is shown in the lower half of Figure 6 where Speedcure 84 is added to 2.0% Irgacure 819 or Speedcure XKm. Cure is difficult to achieve below 3% short wave photoinitiator and it takes 6-8% of Speedcure 84 to give a good cure speed with adequate surface cure.

The addition of an acrylated tertiary amine (10% CN 3715) as an oxygen scavenger to this Type I system, shown in the top half of Figure 6, has a major effect, more than doubling the cure speed, even at low levels of Speedcure 84. Speedcure XKm responds more positively in the presence of the tertiary amine.

A Type II formulation containing 10% acrylated amine CN3715 plus 1.5% Irgacure 819 or Speedcure XKm is illustrated in Figure 7 where additions of a Type II short wave UV photoinitiator such as benzophenone (BP) or methyl benzoylformate (MBF) are made to provide surface cure.

Compared to a Type I system, the use of a tertiary amine with a Type II photoinitiator for surface cure leads to considerably higher cure speeds and lower concentrations of short wave photoinitiator are required.

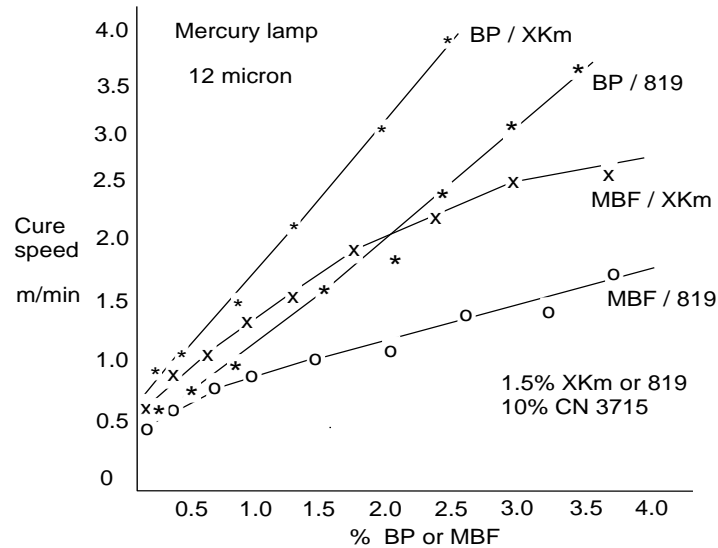


Figure 7. Type II surface cure with additional short wave photoinitiator.

For both Irgacure 819 and Speedcure XKm the addition of benzophenone has the stronger effect but MBF also gives excellent cure and may be preferred due to its non-yellowing properties.

Comparison of the two types of surface curing systems can be seen in Table form below.

Type I Surface cure

Phosphine Oxide	Speedcure 84%	Cure speed m/min	
		2% PO no amine	2% PO 10% amine CN 3715
819	2	no cure	0.82
819	3	0.45	1.1
819	4	0.62	1.5
819	7	0.78	< 5
XKm	2	no cure	1.2
XKm	3	0.41	1.5
XKm	4	0.52	2.5
XKm	7	0.72	< 5

Type II Surface Cure

Phosphine Oxide	BP %	MBF %	Cure speed m/min
			1.5% PO 10% amine CN 3715
819	1		1.1
819	2		1.9
819	3		2.9
XKm	1		1.6
XKm	2		3.1
XKm	3		4.3
819		1	0.8
819		2	1.1
819		3	1.3
XKm		1	1.3
XKm		2	1.8
XKm		3	2.3

The addition of an amine to the Type I system more than doubles the cure speed.

In the Type II system the cure speeds show further increase and very high cure speeds can be obtained with much lower concentrations of short wave photoinitiator.

Discussion: This practical assessment of the use of a sensitizer/synergist simply illustrates trends that may be useful to the formulator.

The formulations used above are not definitive and the response to the sensitizer will depend on the medium in which it is used. In particular, the coating thickness will have considerable influence on the loading of the photoinitiator, requiring higher concentrations at lower weights, and the ratio of sensitizer to photoinitiator may require adjustment.

Other factors will include the use of pigments, which will have a masking effect on the ability of both sensitizer and photoinitiator to absorb UV.

Yellowing has to be considered and thioxanthenes can lead to some degree of yellowing.

The anthraquinones produce a brown colouration.

Solubility is also an important factor. Thioxanthone (TX) and 2-ethylanthraquinone(EAQ) have poor solubility profiles

It is noticeable that it takes very little absorbance by the sensitizer for energy transfer to occur with some efficiency. This fact alone makes the sensitisation process of considerable interest to the formulator. It can be concluded that by careful formulation the benefits of both sensitization and synergy can be exploited with phosphine oxide photoinitiators.

For maximum cure speed it is well worth considering the use of acrylated amines combined with a Type II photoinitiator for surface cure with phosphine oxides.

In particular, Speedcure XKm responds to greatest effect in the presence of a tertiary amine.

For Type II surface cure systems, the low yellowing characteristics of methyl benzoylformate may prove particularly useful in clear and white coatings.

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