Beyond BAPO: Liquid BAPO derivatives for use as photoinitiators in 100% solids and waterbased uv curing

Elena Bellotti, Dr. Gianni Casaluce, Dr. Angelo Casiraghi, Dr. Marika Morone, Dr. Gabriele Norcini, and Dr. Stephen R Postle.

IGM Resins, Gerenzano (VA), Italy and IGM Resins USA Inc.

Abstract

Bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide (BAPO) has been a workhorse photoinitiator for the inks and coatings markets for more than two decades, despite certain shortcomings, like solubility and surface cure. Building upon the recent launch of a polymeric TPO-L photoinitiator, we will present patented chemistry to show what is possible in extending bisacyl phosphine oxide chemistry to offer novel photoinitiators for 100% solids and water-based UV formulations. Collectively called "liquid BAPO", these molecules offer enhanced solubility to aid formulators, options for low migration, and at least comparable reactivity to BAPO itself.

Introduction

Bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide (**Omnirad 819**) is a very efficient and versatile photoinitiator (PI) for UV light-induced radical polymerization of unsaturated resins. The absorption band at 350-420 nm makes it ideally suited for depth curing also with LED lamps operating at 385/395 nm as well as 365 nm. For this reason Omnirad 819 is one of the best choice for thick films, highly pigmented formulations as well as other sectors of the inks and coatings market.

The use of the solid photoinitiators is sometimes associated with undesired crystallization effect which in the final coating can results in optical clarity and reactivity loss.
Liquid photoinitiators, on the other hand, could provide much better dispersion properties and are easier to handle and dissolve in formulations.
With the aim to improve the physical characteristics of Omnirad 819 and to maintain at the same time a comparable reactivity, a series of focused structural changes has been made on the parent compound in order to obtain liquid analogues of bisacylphosphine oxide (BAPO).

Moreover, as part of our program to further expand the use of BAPO in water-borne UV curable systems, a great effort has been made in order to design new water soluble or water compatible efficient Omnirad 819 derivatives.
Waterborne UV curable finishes have found wide acceptance in the wood furniture market and they are becoming popular choices for plastic, soft-feel paper and wood floor coatings[1-2]. WB UV chemistry is gaining market share because it enables the end user to increase production efficiency and to lower solvent emissions.
Total or partial replacement of the reactive diluents by water offers several advantages over "100% solid" systems[3-4]:

- viscosity can be easily controlled to obtain good surface levelling;
- a wide variety of application techniques requiring low viscosity, such as spraying, are possible without the use of monomers or organic solvents;
- reduction of the amount of reactive double bonds and shrinkage after curing;
- better rheological control to reduce excess penetration into porous substrates;
- better and easy cleaning of coating equipment.

Omnirad 819DW, BAPO water-based dispersion, represents a valid solution to combine the excellent curing properties of BAPO with the advantages of using a WB UV curable system. To overcome issues of solid

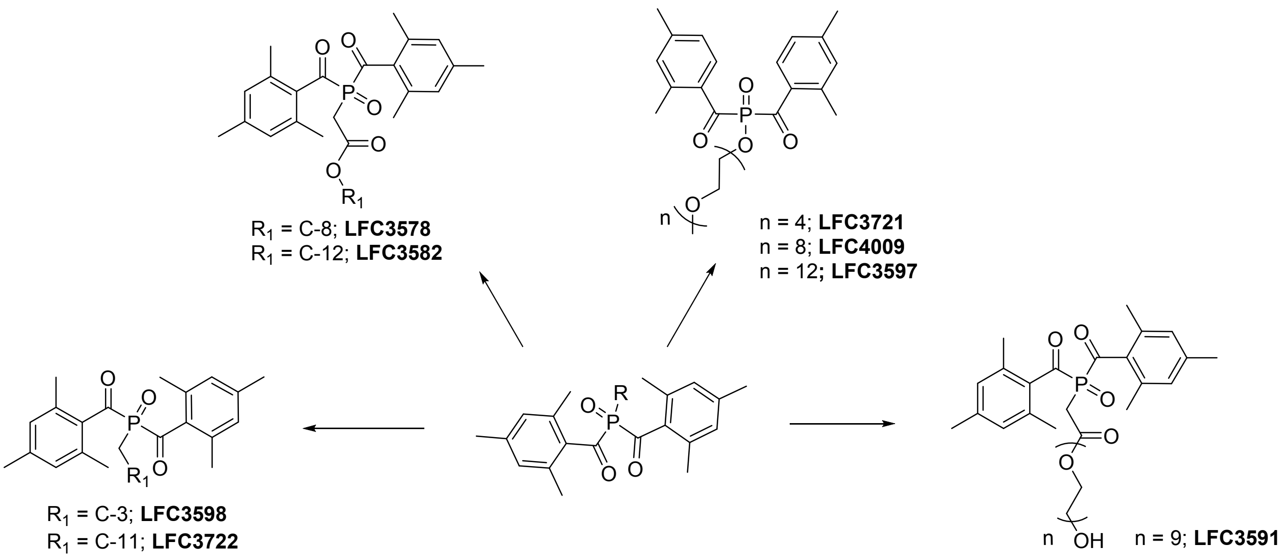
dispersion, new water compatible derivatives were prepared introducing structural modifications to improve water solubility.
The novel BAPO analogues are especially suited in graphic arts (e.g. inkjet, offset, flexo and screen inks, overprint varnishes), 3D printing, medical applications, wood coatings, glass coatings, adhesives and electronics.

Results and discussion

Chemistry

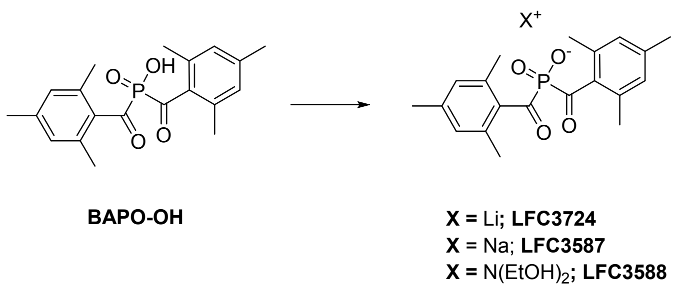
The synthetic strategies to obtain the new bisacylphosphine oxides were already reported in US5399770, WO2006056541 and WO2014095724.

New liquid BAPO with different R substituents were synthesized (*scheme 1*).



Scheme 1. General scheme of liquid BAPOs.

On the basis of structural characteristics and the predicted logP value, **LFC3721** has been selected for further investigation also in WB UV curable systems, together with phosphinic acid salts (*Scheme 2*).



Scheme 2. Phosphinic acid salts derivatives of BAPO.

UV Curing Tests.

***FT-IR*:** To evaluate the reactivity of the selected liquid BAPOs, the double bond conversion was measured by FT-IR (1408 cm^{-1}) in a clear coating using both a Hg or a LED lamp as irradiation source.

The UV clear formulations were prepared by dissolving the photoinitiator at a concentration of 4% each in a mixture 99.5:0.5 wt of bisphenol-A epoxy diacrylate (Photomer 3016-25R) and a slip agent (Omnivad 280). Bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide (**Omnirad 819**) was used as reference.
The best reactivity was observed with the derivatives bearing an aliphatic chain on the phosphorous atom like **LFC3578**, **LFC3582** and **LFC3722** (*Figure 1 and 2*).
When the phosphorous atom is substituted with an ethoxylated chain, a lower reactivity is observed. This behavior is more evident when the Hg lamp is used as irradiation source, in particular for **LFC3591** that shows a significant decrease with both Hg and LED lamps (*Figure 3*).

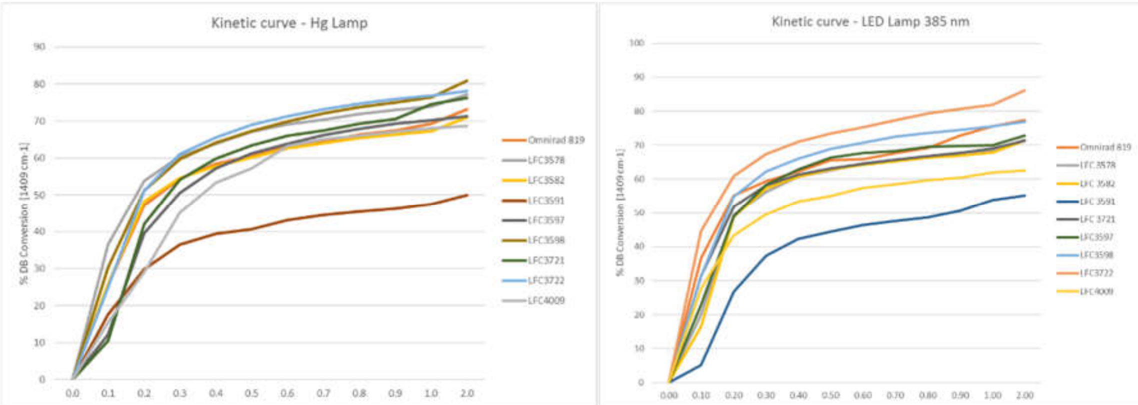


Figure 1 and 2. FT-IR in clear coating. Conditions: PE substrate, 6 mm thickness, under air.

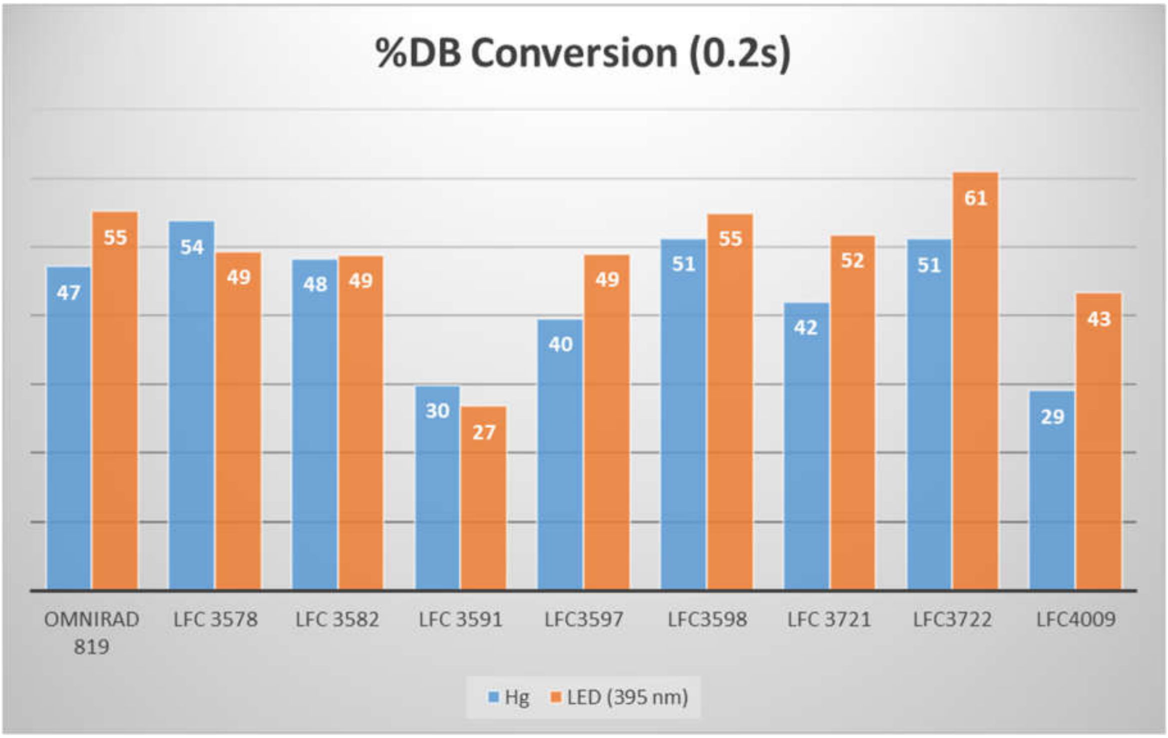


Figure 3. Reduction of the peaks area at 1408 cm-1 (%DB Conversion) after 0.2 sec irradiating with a Hg (blue) and with a LED (orange) lamp.

Tack free experiment: Tack free measurements in a clear system were performed with Hg and LED 395 lamp.
As expected, a relevant worsening in the surface curing is observed in the tack free test for the selected ethoxylated analogue **LFC4009**. On the other hand, the P-alkyl derivative **LFC3598** shows a reactivity close to **Omnirad 819** (*Table 1*).

Compound	UV Hg Lamp-Tack-free in m/min	UV LED 395 nm Lamp-Tack-free in m/min
Omnirad 819	82	89
LFC3578	43	21
LFC3582	31	20
LFC3598	72	71
LFC3722	39	43
LFC4009	18	2

Table 1. Belt speed (m/min) to achieve a tack free curing. Conditions: 4 % PI, under air.

Through-Cure experiments. The photoinitiated inks samples for the test were prepared by dissolving the photoinitiator at a concentration of 4% by weight in a cyan offset ink.

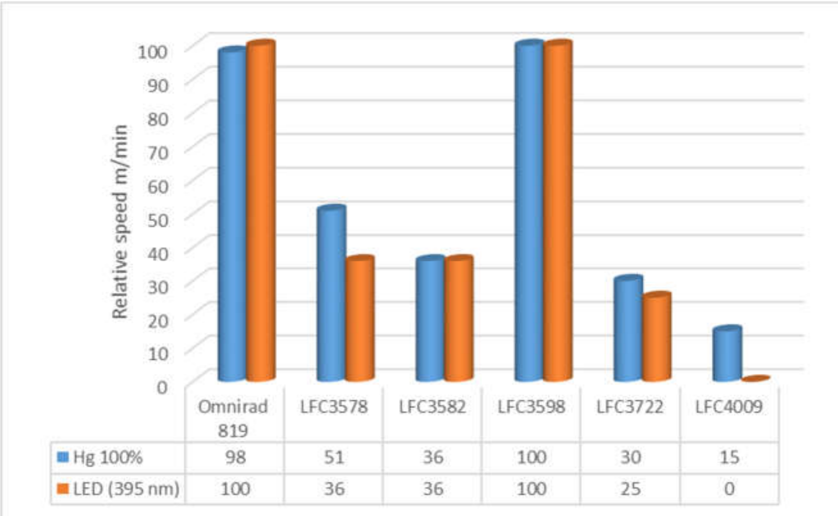


Figure 4. Line rate (m/min) at which a complete photopolymerization occurs (through-cure) under Hg (blue) and LED (orange) irradiation. Conditions: cartonboard, 1.5 µm thickness.

Also in through cure experiment, **LFC3598** shows a reactivity significantly higher than the other selected compounds and comparable with **Omnirad 819**.

***Hardness and solvent resistance*:** The photopolymerizable compositions for the test were prepared by dissolving the photoinitiator at a concentration of 4% by weight in a white pigmented system. Compounds **LFC3598** and **LFC3722** shows an hardness comparable to **Omnirad 819** and a good solvent resistance (*Table 2*).

Compound	Hardness	MEK
Omnirad 819	185	>300
LFC3578	166	>300
LFC3582	166	>300
LFC3598	184	>300
LFC3722	182	>300
LFC4009	169	>300

Table 2. Hardness and solvent resistance evaluated on a white pigmented system. Conditions: glass support, 100 µm thickness, Ga lamp (line speed 10m/min) and with a Hg lamp (10 m/min x 2 pass).

According to the results showed with different formulations, **LFC3598** showed a reactivity profile superior to other liquid BAPO derivatives and similar to the reference compound.

Water-borne UV curable systems. As a consequence of the growing interest that water-based UV curing technology has gained in the last decade, we developed a new series of water compatible BAPO derivatives.
A series of BAPO-OH salts with improved solubility in water have been synthesized. Ethanolamine salt derivative **LFC3588,** as already reported[5-6], showed a better water solubility in comparison with other salts (*table 3*) and has been selected as candidate to evaluate its reactivity in a WB-UV curable system.

Product		Water solubility
BAPO-OH	free acid	< 0.1% (w/w)
LFC3724	lithium salt	4.0% (w/w)
LFC3587	sodium salt	5.0% (w/w)
LFC3588	ethanolamine salt	>10.0% (w/w)
LFC3721	ethoxylated analogue	0.5 (w/w)

Table 3. Solubility table[5] of the BAPO derivatives in water (w/w).

Moreover, on the basis of its structural features, low logP values (*<2*) and its reactivity (*Fig. 3*), the ethoxylated BAPO analogue **LFC3721** has been evaluated in comparison with **Omnirad819 WD**.
The photopolymerizable compositions for the test were prepared by dissolving the photoinitiators (40°C) at a concentration of 1% by weight in a mixture of a liquid urethane acrylate dispersion (83.6%), a polyurethane polymer 5% in water as thickener (4.2%), a defoamer (0.2%), a wetting agent (0.1%), water (11.9%) and Omnirad 500 (1%). Solvent resistance (*double rubs using methylethylketone, MEK*) was measured and results are reported in Figure 5.

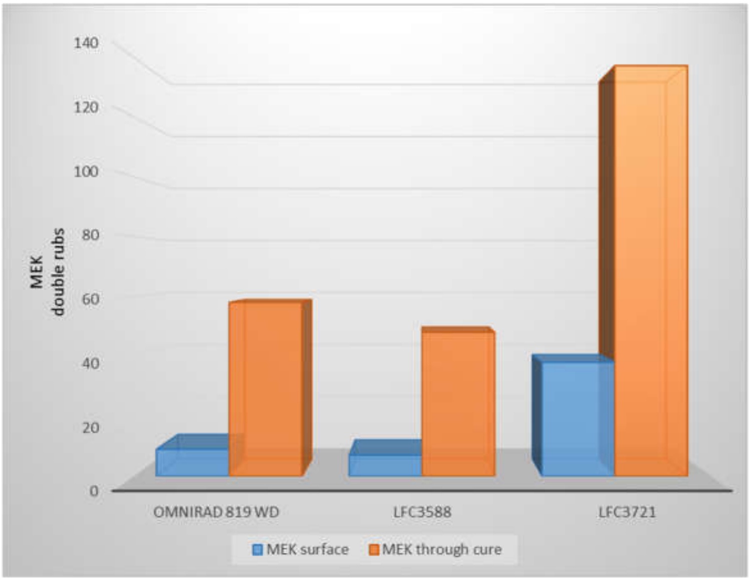


Figure 5. Solvent resistance evaluated on a water based system as a measurement of surface and deep curing. Conditions: glass plate, 100 µm thickness. Hg lamp (120 W/cm) under air (30 m/min).

***Yellowing**:* The color stability of **LFC3588** and **LFC3721** (b* value) was measured by a color guide (45/0 BYK) directly after curing, after 1h and after 72h.

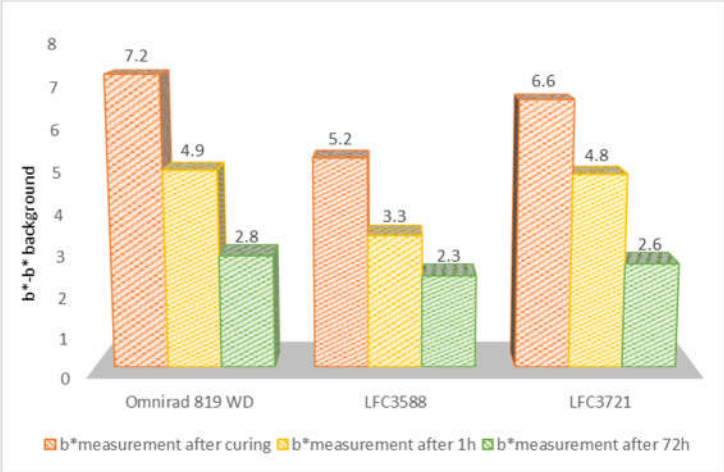


Figure 6. Color stability over time evaluated on a urethan-acrylate varnish (b value). Conditions: Hg (200 W/cm) lamp 5m/min under air; 100 µm thickness; concentration PI: 3% w/w.*

Under the conditions used for the test, the ethoxylated analogue **LFC3721** showed the best reactivity profile with a surface and through cure superior to **Omnirad 819 WD**. Ethanolamine salt **LFC3588** showed a reactivity comparable to the reference.

Initial yellowing (b*) was found to be lower than the reference with **LFC3588,** whereas comparable values were found for **LFC3721**. All the three compounds showed similar color stability over time.

Conclusions.

A set of liquid derivatives of **Omnirad 819** has been tested in order to identify a new PI with improved physical characteristics and reactivity comparable with BAPO. **LFC3598** showed the best results in application tests both using Hg and LED lamps and was selected for development.

About water-borne UV curable systems, the ethoxylated compound **LFC3721** and the ethanolamine salt **LFC3588** were chosen on the basis of their excellent curing performance.

The good solubility of **LFC3588** in water allows the possibility to increase the photoinitiator concentration in a WB formulation and further expands the possible applications.

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[6] Kurt Dietliker presentation in RadTech China 2017.