Photoinitiator selection to advance the UV curing industry in an uncertain world

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Abstract

The UV curing industry stands at the brink of a number of compliance and performance challenges. Photoinitiators including acyl phosphine oxides and alpha amino ketones are under activist regulatory threat. In this paper, we will present alternates to workhorse photoinitiators like TPO, novel photoinitiator blends offering dual cure options, acrylated photoinitiators for ultra-low migration, and patented acyl phophine photoinitiators offering superior performance for sensitive packaging, ink jet, wood coatings and other sectors.

Rogue One(s)

A number of photoinitiators and associated amine synergists (co-initiators) have recently come under close regulatory scrutiny, principally in Europe, under the oversight of ECHA and the member states of the EU. Here are the principal actors involved. They are not "rogues" in the conventional sense, but have been shown to have toxicological properties in non-human life forms that cause one or more regulatory authorities to classify and, often, restrict their use. This list will almost certainly only continue to grow.

TPO (CAS # 75980-60-8)

TPO has been self-reclassified by the Lead Registrant under REACh, following extensive additional toxicological testing. Harmonized reclassification to 1B Reprotoxin will be a decision for the Swedish Authority when they undertake the dossier evaluation in 2021 (this was going to be during 2020, but was put back a year). It is likely to eventually become an SVHC (n.b. this is speculation, not fact!), but the classification is not the only consideration. The uses and effectiveness of RMM (rapid microbiological methods) are taken into consideration and, if shown to be controlled and effective, could avoid regulatory action for some time as other, more hazardous, substances are targeted.

Omnirad 369 (2-dimethylamino-2-benzyl-1-(4-morpholin-4-yl-phenyl)-butan-1- one CAS # 119313-12-1) and Omnirad 907 (2-Methyl-1-[4-(methylthio) phenyl]-2-morpholinopropan-1-one CAS # 71868-10-5)

These have recently (January 16th, 2020) been added to the Candidates List for SVHCs (substances f Very High Concern) by ECHA on account of their reprotoxicity. Restriction and/or Authorization, with the Austrian authority leading, are likely to follow. The SVHC classification applies only in Europe, although it is expected, as with all reclassified or restricted substances, that other regulatory authorities will follow suit. With regard to specific market sectors where one or other of these photoinitiators are used, currently the case would be that outside the EU it would strongly depend on customer or end use policies.

- Nestle still had a minimise use for Omnirad 369 in Table 3 on the Nestle guidance note on Packaging Inks (Oct 2018) but on page 2 they exclude any SVHC substances where suitable alternatives do exist. Therefore, it is expected that printed packaging for Nestle outside the EU will also be affected and that a decline is to be expected.

Any suppliers of IKEA need to comply to IKEA Specifications and the most common Specification is:

- Surface coatings and coverings – general requirements IOS-MAT-0066 (15-11-2017) restricts the use of CMR substances category 1A or 1B and Substances of Very High Concern (SVHC).

In the Automotive Industry there are similar restrictions in place.

4PBZ (4-Phenyl benzophenone CAS # 2128-93-0)

This was reclassified by ECHA as a 1B Reprotoxin in the summer of 2018. A further issue with 4PBZ is its very low solubility in several common monomer and oligomer systems.

EDB (Ethyl-4-(dimethylamino) benzoate CAS #10287-53-3) and EHA (2-Ethyl Hexyl-4-. (dimethylamino) benzoate CAS #21245-02-3)

These have been reclassified by ECHA during 2018 as Reprotoxin 1B, rendering them very difficult to use for many applications e.g. sensitive packaging, for example. These two have been the workhorses for those requiring amine synergists for general applications.

The Empire Strikes Back

While many regulatory bodies around the world have programs to scrutinize all chemical substances, it is fair to say that ECHA takes the most activist role in chemical substance evaluation and reclassification.

ECHA's declared future plans

Grouping of substances

ECHA has indicated, both in 2018 and in 2019, that they will increase their use of grouping of ostensibly similar substances (https://echa.europa.eu/support/registration/how-to-avoid-unnecessary-testing-on-animals/grouping-of-substances-and-read-across and https://newsletter.echa.europa.eu/home/-/newsletter/entry/want-to-know-about-grouping-substances-to-manage-risks-of-chemicals-). Their view is that read-across obviates some of the need for extensive toxicological testing. However, the chemical world is littered with examples where very slight structural changes make huge differences in toxicological or pharmacological efficiency upon the human body. Codeine and morphine are an interesting pair, as are ethanol and methanol. Also, Omnirad 369 and Omnirad 3709 differ only by a single methyl group, yet the former is Reprotoxin 1B and the latter Reprotoxin 2 (H361). One great fear for the uv curing industry is that, with TPO on point of a harmonized classification of Reprotoxin 1B, BAPO (Omnirad 819: CAS #162881-26-7) and TPO-L (CAS #75980-60-8) will be grouped with it for dossier review.

Re-evaluation of all dossiers

ECHA announced in July 2019 (https://echa.europa.eu/-/echa-to-scrutinise-all-reach-registrations-by-2027) that all REACh dossiers would be liable for inspection, at all tonnage bands, and that approximately 20% of registered chemicals in each band, or 30% of all registered chemicals overall, would be inspected. Our experience is that inspection almost invariably leads to a request for further toxicological data. This will put further cost and resource strain onto the whole of the chemicals industry in Europe. Further, ECHA's strategic plan through 2023 (https://echa.europa.eu/documents/10162/26075800/echa_strategic_plan_2019-2023_en.pdf/3457ccff-7240-2c1f-3a15-fa6e5e65ac56) indicates that the dossiers of all registered chemicals in tonnage bands Annex VII and above will be inspected by end-2023.

BfR

Photolytes

The BfR has published draft guidelines on photoinitiators for food contact applications, working with, *inter alia*, EuPIA and the Swiss authorities: (https://www.bfr.bund.de/en/bfr_recommendations_on_food_contact_materials-1711.html). They are concerned not only with substance toxicity, but also with the fate of uv curable components after irradiation, i.e. photoinitiator photolytes.

NGOs

It's hard to quantify the current and future influence of NGOs on national and regional regulatory bodies, but they are known to have influence with various governments who, in turn pass along recommendations to their regulatory authorities. It is a widely held view by many within the chemical industry (opinion, not fact!) that some NGOs do not discriminate between the various uses of chemicals.

Jedi Master Tricks

Given the current reclassifications and expected trajectory of regulatory investigation into other chemicals, including photoinitiators, it is prudent not only to consider alternates to those realizing a 1B or SVHC classification, but also to consider how innovating in photoinitiators can allow the industry to stay ethically at least one step ahead of the regulatory authorities and their influencers. Consider Figure 1. This notionally reduces innovation in photoinitiators to a conventional Boston Matrix.

Photoinitiator functionality

different	**Microparticulate PIs**	**e.g. High solubility low migration PIs; novel LED-uv and visible light PIs; quantum dots**
same	**Existing products**	**Alternates to TPO, AAKs etc.**
	same	***different***

Photoinitiator selection

Figure 1 – options for photoinitiator development

The remainder of this section will look at the various options for the reclassified photoinitiators through the lens of this matrix, as well as consider new presentations of existing photoinitators (same PI selection/different PI functionality box) with different properties thereby.

Alternates to TPO

The industry has been quick to evaluate alternates to TPO. Principal substitutes are Omnirad 819 (BAPO) – which can be used at approximately 50% the concentration of TPO – and TPO-L – which can be used at approximately 140% of the concentration of TPO, both on a w/w basis. ***Omnipol TP (CAS # 1834525-17-5)*** offers a further alternative, with the advantages of very high solubility and low migration potential. It can be used at approximately the same w/w concentration as TPO. APO blended with difunctional alpha hydroxy ketones like Esacure ONE, Omnirad 127 or Esacure KIP 160 also offer possibilities, especially for LED cure, as does APOs blended with Esacure 1001M.

Alternates to Omnirad 369 and 907

Alternates to Omnirad 369, like difunctional alpha hydroxy ketones (e.g. Esacure KIP 160, Omnirad 127, Esacure ONE) and acyl phosphine oxides, as well as blends comprising one or both of these groupings, were discussed at RadTech 2016[1] None is a "drop in" based either on absorption wavelength or cost.

Omnirad 379 (2-dimethylamino-2-(4-methyl-benzyl)-1-(4-morpholin-4-yl-phenyl)-butan-1-one CAS # 119344-86-4) is, of course, the closest match to Omnirad 369, but its future (see "ECHA Grouping" above!) is thought uncertain by some. It is a workhorse for ink jet, where one photoinitiator to cover all end uses from signage through t food packaging is desirable.

Omnirad 389 (2-Benzyl-2-dimethylamino-1-(4-piperidinylphenyl)-1-butanone CAS # 119312-76-4), another alpha amino ketone, is available as an alternate to Omnirad 907, especially for the Asian electronics industry.

For sensitive packaging applications, polymeric alpha amino ketones, such as ***Omnipol 910 (Polyethylene glycol di(beta-4-[4-(2-dimethylamino-2benzyl)butanoylphenyl]piperazine)propionate CAS # 886463-10-1)*** are available. Polymeric PIs display very low migration tendencies, but are not usable in all formulatory applications, on account of their impact on formulation rheology.

Silylated Alpha Hydroxy Ketones

This is a new class of photoinitiators, still at the laboratory level, based on silylated alpha hydroxy ketones. Certain materials in this class show properties very close to alpha amino ketones, unlike their parent alpha hydroxy ketones[2]. Figure 2 is an example of the relative reactivity of certain members of this class versus Omnirad 907 at medium pressure Hg wavelength irradiation.

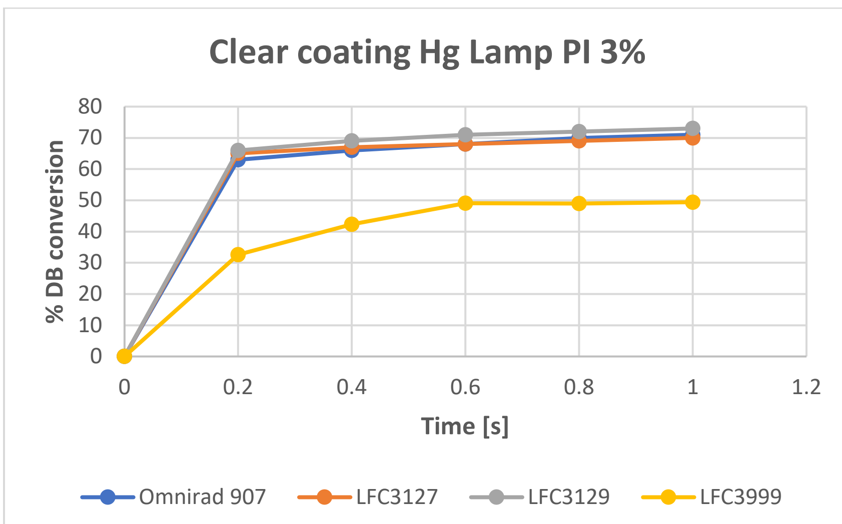

Figure 2: the relative reactivities of experimental silylated alpha hydroxy ketones (all with "LFC" code numbers) versus Omnirad 907

Alternates To EDB and EHA

These two amine synergists have been widely used in conjunction with Type II photoinitiators. Hitherto, the only alternates are higher performance/higher cost amine synergists, designed specifically for indirect food contact packaging. ***Omnipol 894 (a TMPTA/NMA adduct. CAS # 2407644-16-8)*** will be launched in 2020 to offer a new, and patented, alternative to these existing amine synergists[3].

Alternates to 4PBZ

In addition to its current classification, 4PBZ suffers from very low solubility in many monomeric and oligomeric acrylate blends, and this adds cost to its use. Various methylated benzophenones, which might be used in its place, also suffer from some solubility and toxicological restrictions. ***Omnirad 991*** (2-(1,1'-Biphenyl-4-ylcarbonyl) benzoic acid 2-ethylhexyl ester CAS # 75005-95-7) is a patented[4] highly soluble analog of 4PBZ that will be launched during 2020. Polymeric materials have also been claimed, in this context[5].

The Rebel Alliance

Given the regulatory issues surrounding photoinitiators, it behooves the industry to speak with a single voice to the various regulatory authorities, and on other issues impacting photoinitiators. So, in late 2018, the **Photoinitiator Project** ("PIP") **(**https://www.photoinitiators-platform.org/) was formed. Founding members were IGM Resins, BCH, Rahn, and DSM, and the consortium now includes many photoinitiator manufacturers, distributors and downstream users based in North America, China and Europe. The consortium is currently engaged in several programs, including:

- a dialog with ECHA on the grouping of photoinitiators
- a dialog with the BfR on photoinitators for food contact
- a joint program with EuPIA on the correlation of photolytes from Type I photoinitators "*in vitro*" (i.e. in a test tube) and "*in vivo*" (i.e. in actual printed/coated assemblies)
- tariffs on imports from China to the USA, working with RadTech and NAPIM
- working groups on alpha amino ketones and on acyl phosphine oxides aimed at defending appropriately against the grouping of all members of these photoinitator classes

Padawans – our Future Jedi Knights

Two evident trends within the printing and coating market sectors are the conversion from medium-pressure mercury lamps to uv-LEDs (principally 385/395 nm, but also 365nm) and the continued growth of specialty and sensitive packaging systems. So, it is appropriate to look at the new photoinitiator classes being developed, patented and commercialized to see how they will assist in safeguarding and growing the uv curing industry. Many of these innovations have been the subject of detailed presentations elsewhere, so I will mention them only briefly in this paper.

3-Ketocoumarins

Ketocoumarins have been known since the early 1980s as Type II photoinitiators, but were never commercially viable, principally for three reasons:

- relatively low insolubility in many common acrylate systems

- no discernable cost-based advantages over other photoinitiators at Hg lamp wavelengths
- Inability to function at uv-LED wavelengths

These issues were overcome with the introduction in 2018 of the patented[6] material ***Esacure 3644 (CAS # 2243703-91-3).*** There have been several presentations surrounding this new product[7, 8]. It is highly suitable for uv-LED cure and is less yellowing than existing Type II photoinitiators such as the thioxanthones. Further, it is up to 20% soluble in many monomers (Figure 3) and shows very low migration tendencies. It currently finds favor in graphic arts and in wood coatings.

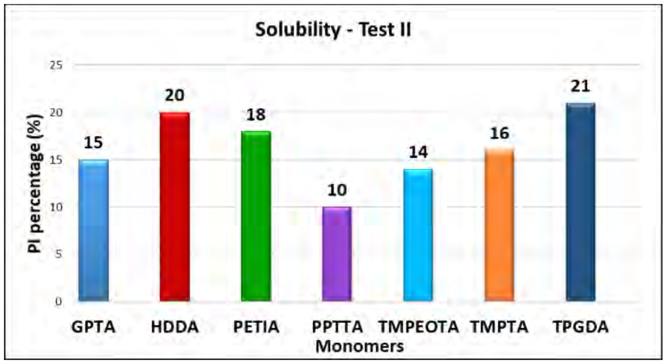

Figure 3: solubility percentage of the 3-Ketocoumarin Esacure 3644 in common monomers

Polymeric APOs

Omnipol TP (CAS # 1834525-17-5) has been mentioned above as an alternate to TPO. It functions as a very low migration and highly soluble alternate to TPO-L and is trifunctional. It is patented[9] and was introduced in 2018. It has been presented on at a number of conferences[8]

Liquid BAPOs

BAPO has been a workhorse photoinitator for many years. Given the possibility that it might be included in a lengthy and expensive toxicological study under ECHA's oversight (see above), it is prudent to consider what alternates there might be. BAPO is also not the most soluble photoinitiator available. So, a next generation offering would include intrinsic improvements in formulability and in sensitive packaging systems as well. The first introduction in this area will be the patented[10] ***Omnirad 820 (CAS # applied for).*** Details of this and other liquid BAPO developments have been presented previously[11]

Water-compatible Photoinitiators

With the growth in waterborne uv, for a number of well-documented reasons (rheological control and the elimination of monomers in ink jet, and film thickness control in wood coatings, as two examples), it is appropriate to consider truly water-compatible photoinitiators. Such exist already for Hg lamp cure. For LED cure, ***Omnirad 820*** (discussed above) had the virtue of being entirely compatible with aqueous formulations as well as 100% solids systems[11]. Another promising development, falling under the "new presentations of existing photoinitators" aegis, lies in micro-dispersed versions of existing photoinitiators[12], developed by Professor Shlomo Magdassi and team at the Hebrew University of Jerusalem Such dispersions, which are freely water-compatible, comprise particles of size 200nm and above, so are unlikely to fall prey to any nanoparticle legislations or restrictions. Initial work was conducted on TPO dispersions for 3D hydrogel formation. Recent, unpublished work on BAPO dispersions shows very interesting reactivity at low concentrations.

Dual Cure – The Phantom Menace?

A recent, but repeated, request from the graphic arts community is for photoinitator systems that will function equally well under both uv-LED and Hg lamp irradiation. Although never published in any detail, it is known that Alpha Hydroxy Ketone/APO Blends will function well at a range of wavelengths, with sensitization of the alpha hydroxy ketones a likely mechanism of action. Additionally, several photoinitiators, including alpha amino ketones, acyl phosphine oxides and 3-ketocoumarins, will initiate polymerization over a wide range of uv wavelengths**.**

A related approach is to blend photoinitators not only having good cure response over a wavelength range, but offering complementary properties. A recent development in this area lies in blends comprising 3-Ketocoumarins with liquid BAPOs and other APOs. The benefit here lies through and surface cure, accompanied, in certain cases, by much higher reactivity than is obtained with either of the component photoinitators[13].

UVA LED – Death Star or Light Saber?

Many photoinitiators are excellent at through cure, often in quite thick assemblies, but less efficacious in ensuring good surface cure. Acyl phosphine oxides are well-known in this regard. Thus, the industry has seen a number of lamp manufacturers develop an LED-UVA lamp to “crisp up” the surface of a coating or ink. There are evident benefits to this process, countered by the lifetime of the semiconductors used to generate UVA and the dangers to human life of UVA itself. The approach is a complementary one to photoinitiator blends, as discussed above.

The Force Is Strong…. But In Which One?

Much innovation in photoinitators has been in support of the development of low migration molecules. These options can perhaps be divided into two camps, which I will call The Tortoise Versus The Hare. The “tortoise” option lays emphasis on the photoinitator becoming a part of the final polymeric structure of the cured film. It is exemplified by Allnex’s acrylated 4PBZ substances[14] and a number of other acrylated photoinitiators including acrylated 4-thiobenzophenones[15], ketocoumarins[16] and Agfa’s thioxanthones[17]. The desire for zero migration is tempered by lower reactivity as the photoinitiator becomes a part of the growing polymer chain and is thus unable to diffuse to new sites for polymer initiator, or to reach the co-initiator. The “hare” option can rely on higher molecular weight photoinitiators, which rely on entanglement in the polymer matrix for low migration potential. They generally have higher reactivities, and recent developments, such as the 3-ketocoumarins are more suited to LED cure. They may show advantages for regulatory compliance, as bigger molecules, less soluble in perhaps less toxic to aqueous-based life forms? Rheology of formulations and water balance in offset inks are other factors to consider.

So, who wins – the "tortoise" or the "hare"? In figure 4, one study comparing the unacrylated ketocoumarin Esacure 3644 versus the acrylated Omnipol 3TX from Agfa shows that the ketocoumarin (represented in the figure as "LFC 3644") has higher reactivity with a 385 nm LED light source than does the acrylated thioxanthone – or indeed any other thioxanthone. Esacure A198 was employed as the co-initiator. As mentioned above, ketocoumarins are also superior in regard to post-cure yellowing than thioxanthones.

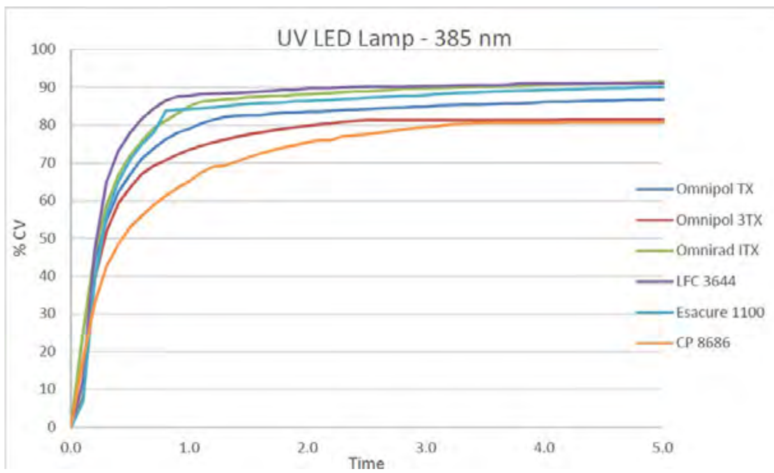

Figure 4: comparative reactivities of ketocoumarin LFC 3644 (now Esacure 3644) against acrylated and conventional thioxanthones with a 385 nm irradiation source

Conclusions: A New Hope

I have listed a few of the challenges facing photoinitiators, both from a compliance standpoint and a performance one as both the regulatory authorities expand their oversight of our industry, how we may compensate for photoinitiators receiving Reprotoxin 1B and/or SVHC classifications, and how increased performance is required – and will be met through ongoing innovation at the molecular and formulation levels - for the further growth of the technology. In summary, in 2025 (or 2030?), we might expect to see the resolution of some of the existing challenges, the resolution of some and the incursion of new ones, as we continue to develop and optimize photoinitiator performance in an uncertain world. Predictions (guaranteed inaccurate or your money back!) include:

- The grouping and reclassification of all APOs by ECHA is fended off
- A similar prolonged assault on alpha hydroxy ketones is resisted
- Alpha amino ketones are (slowly) going, going, gone…

- The spiraling cost of new chemistry innovation (with/without a global recession).
- Blends with measurable synergies will offer technical advantages and less regulatory and synthetic strain
- Sustainability, as regards photoinitiators, will largely comprise the optimization of energy costs, and recycling of solvents and other by-products
- The continued growth of UV-LED brings new molecules to the formulators' palette
- There will be some use of visible light-sensitive photoinitiators in fields outside of the current niches of additive manufacturing/rapid prototyping and medical/dental applications.
- There will continue to be short-term supply chain issues, but these will lessen as other countries than China establish manufacturing bases for core and specialty photoinitiators, and the existing European manufacturing base increases in importance.

So, which is the future of UV curing technology best characterized as: "frozen in carbonite" or "the taming of Jabba the Regulator"? Definitely, the industry has many pathways open, both for innovation, and for providing a more rational basis for regulatory compliance, especially when working together as a single body. There is well-founded hope for the future.

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