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

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A long time ago
in an industry
far, far away…

Rogue One(s) – *"I have a bad feeling about this…"*

- **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

- **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.

Rogue One(s) – *"This is how liberty dies…"*

- **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.

Rogue Ones(s) – *"There will be no bargain, young Jedi..."*

- ***Omnirad 379 (2-dimethylamino-2-(4-methyl-benzyl)-1-(4-morpholin-4-yl-phenyl)-butan-1-one CAS # 119344-86-4)***
  - The closest chemical and performance match to Omnirad 369.
  - The Austrian Authority announced in February 2020 that it would seek reclassification to Reprotoxin 1B status

The Empire Strikes Back – *Initiatives By ECHA*

- 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.
  - One 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.
- 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.
- 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.
- ECHA is considering ending the polymer exemption

The Empire Strikes Back – *Initiatives By Other Bodies*

- **BfR**
  - 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.

Jedi Mind Tricks – *"These aren't the photoinitiators you're looking for"*

Photoinitiator performance	Photoinitiator chemistry	
different	• Nanoparticulate PIs • Synergistic blends	• High solubility/low migration PIs • Novel LED-uv and visible light PIs • Quantum dots
same	Existing products	• Existing alternates to TPO, AAKs, 4PBZ, EDB, EHA • Blends
	same	*different*

Jedi Mind Tricks – *Alternates To TPO*

- **Existing APOs:**
  - **BAPO (CAS#**:162881-26-7) Omnirad 819– which can be used at approximately 50%(w/w) the concentration of TPO
  - TPO-L **CAS#** 84434-11-7 – which can be used at approximately 140% (w/w)of the concentration of TPO,
  - An existing 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.

- ***Omnipol TP (CAS # 1834525-17-5)***
  - This new photoinitator offers a further alternative, with the advantages of very high solubility and low migration potential.

Jedi Mind Tricks – *alternates to AAKs*

- ***Omnirad 379 (2-dimethylamino-2-(4-methyl-benzyl)-1-(4-morpholin-4-yl-phenyl)-butan-1-one CAS # 119344-86-4)***
  - Oops!

- ***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.

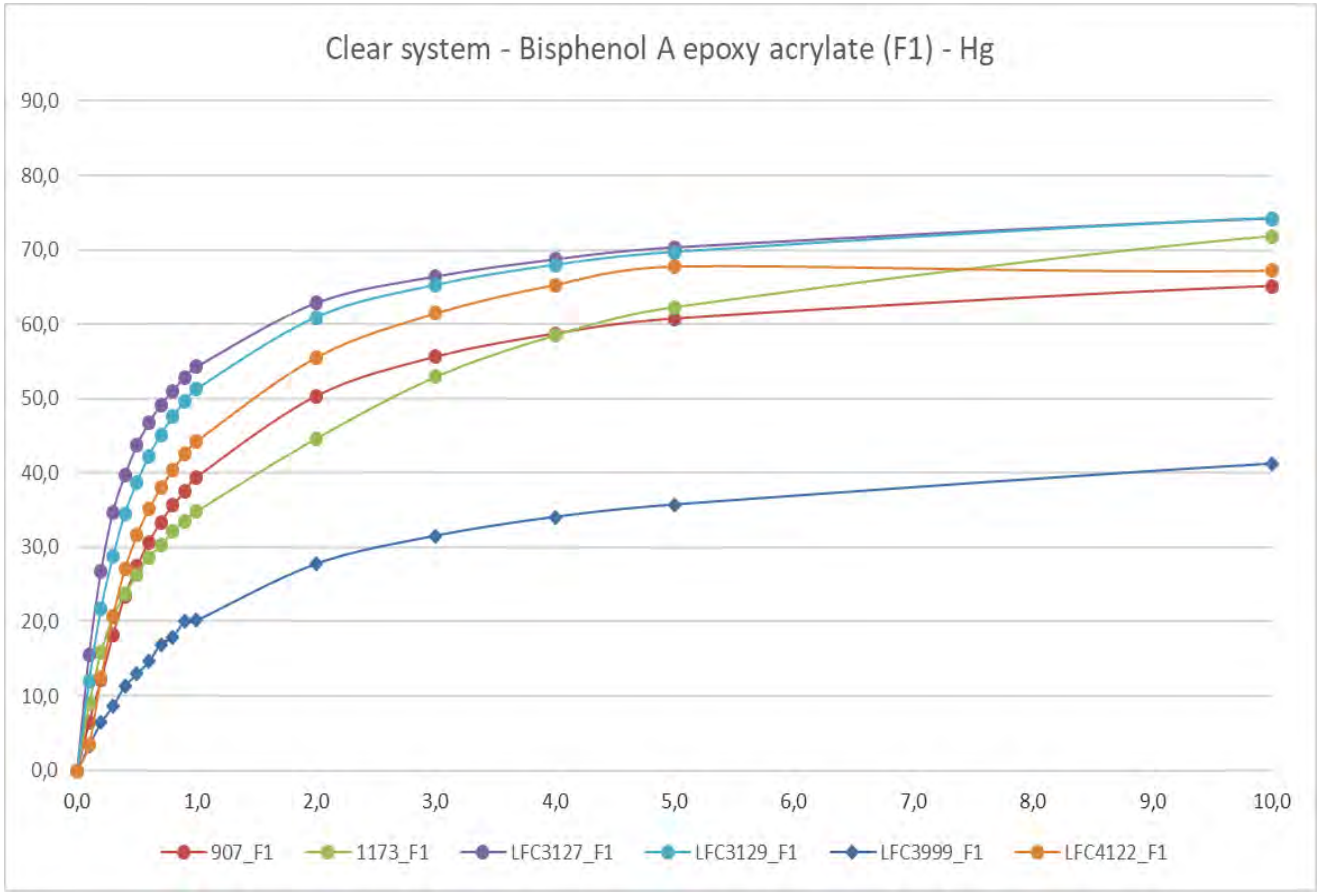
- For sensitive packaging applications, polymeric alpha amino ketones, such as ***Omnipol 910 (Polyethylene glycol di(beta-4-[4-(2-dimethylamino-2benzyl) butanoyl phenyl]piperazine)propionate CAS # 886463-10-1)*** are available.
  - Polymeric PIs display very low migration tendencies, but are not usable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

- An existing APO blended with difunctional alpha hydroxy ketones
  - For example, Esacure ONE, Omnirad 127 or Esacure KIP 160 also offer possibilities, especially for LED cure, as does APOs blended with Esacure 1001M.

Jedi Mind Tricks – *Silylated Photoinitiators as alternates to AAKs*

- A new class of photoinitiators – still at the developmental phase – offers a longer-term alternate to AAKs.

% double bond conversion at 1409 cm^{-1}

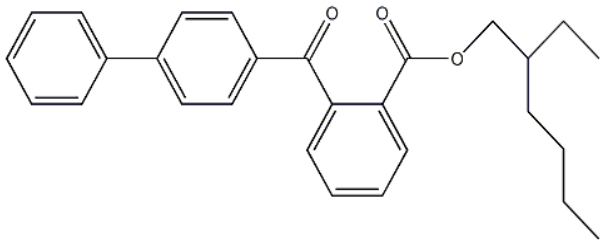


6mm thick clear coating

Jedi Mind Tricks – *A Successor to 4PBZ*

- Various substituted benzophenones have been considered, but none is a performance match and none is likely to escape at least a Class2 classification, in time e.g. 4MBZ

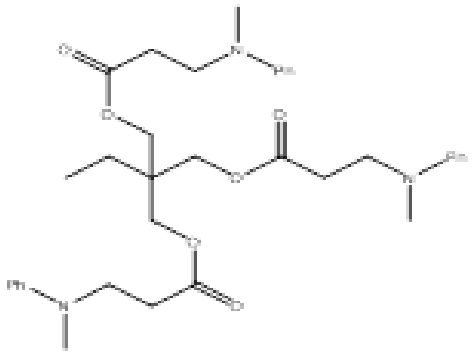
- ***Omnirad 991***
  - 2-(1,1'-Biphenyl-4-ylcarbonyl) benzoic acid 2-ethylhexyl ester
  - CAS # 75005-95-7
  - Patented
  - First registered 35 years ago (but not as a photoinitiator)
  - Highly and rapidly liquid soluble analog of 4PBZ
  - Low migration possibilities
  - To be launched during 2020



- Additionally, polymeric materials have also been claimed in the patent literature as partial alternates to 4PBZ

Jedi Mind Tricks – *alternates to EDB and EHA*

- ***Omnipol 894***
  - A TMPTA/N-methyl aniline (NMA) adduct
  - CAS # 2407644-16-8
  - Patented
  - This trifunctional amine synergist will be launched in 2020 to offer a fresh alternative to existing amine synergists.
  - Proven suitable in offset inks.



The Rebel Alliance – *PIP: The Photoinitiator Project*

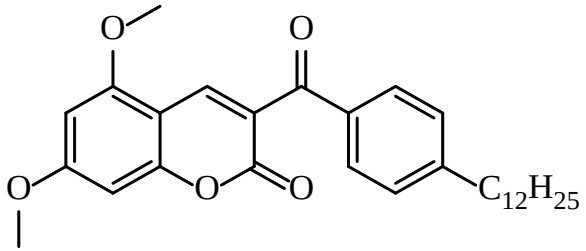
- In late 2018, the **Photoinitiator Project** ("PIP") **(**https://www.photoinitiators-platform.org/) was formed
- A single, global voice for the photoinitiator industry
- Founding members were IGM Resins, BCH, Rahn, and Miwon,
- The consortium now includes many photoinitiator manufacturers, distributors and downstream users based in North America, China and Europe.
- PIP is 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 – *"Do, or do not. There is no try"*

- Innovation in photoinitators has not slowed!
- Recent and future introductions include:
  - 3-ketocoumarins
  - Polymeric acyl phosphine oxides
  - Liquid BAPOs
  - Dimeric BAPOs
  - Novel oxime esters
  - Synergists for oxime esters
  - Nanoparticulate photoinitators
  - Silylated PIs
  - LED-curable cationics
  - Quantum dots

Padawans - *Ketocoumarins*

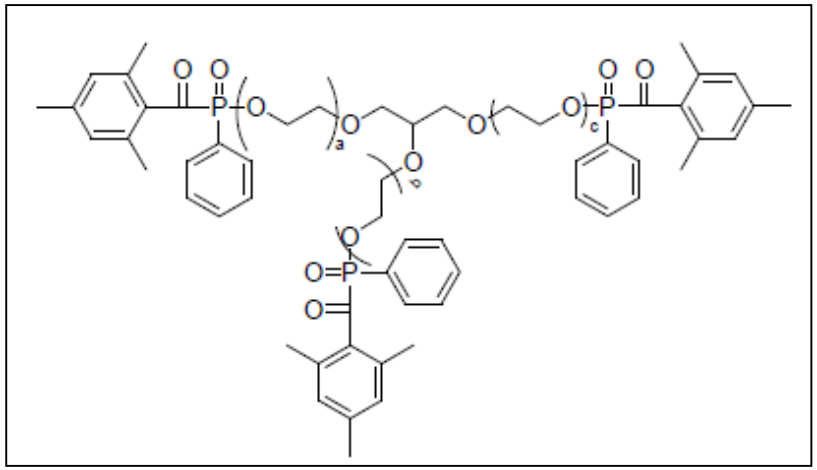
- Ketocoumarins have been known since the early 1980s as Type II photoinitiators, but were never commercially viable, principally for three reasons:
  - relatively low insolubility in many common acrylate systems
  - no discernable cost-based advantages over other photoinitiators at Hg lamp wavelengths
  - Inability to function at uv-LED wavelengths



- These issues were overcome with the introduction in 2018 of the patented photoinitiator ***Esacure 3644 (CAS # 2243703-91-3)*** in 2018
- Suitable for uv-LED cure
- Excellent surface cure
- Less yellowing than thioxanthones.
  - Suitable for whites and clears
- Up to 20% soluble in many monomers
- Low migration capability
- Being exploited in graphic arts and in wood coatings.

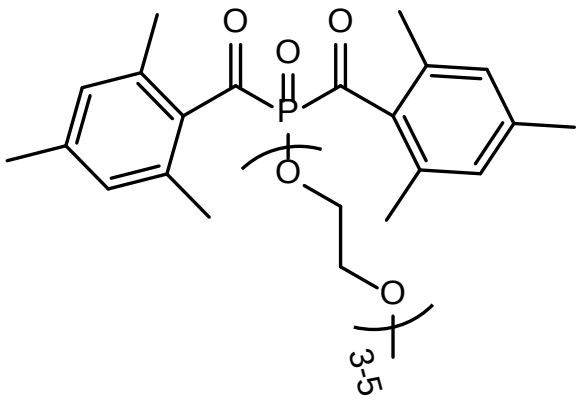
Padawans – *Polymeric Acyl Phosphine Oxides*

- **Omnipol TP *(CAS # 1834525-17-5)***
- Introduced in 2018
- Liquid APO
- Highly soluble
- Reactivity = or > than TPO-L
  - Unlike most polymeric PIs versus their monomeric counterparts
- Low migration potential
- Patented

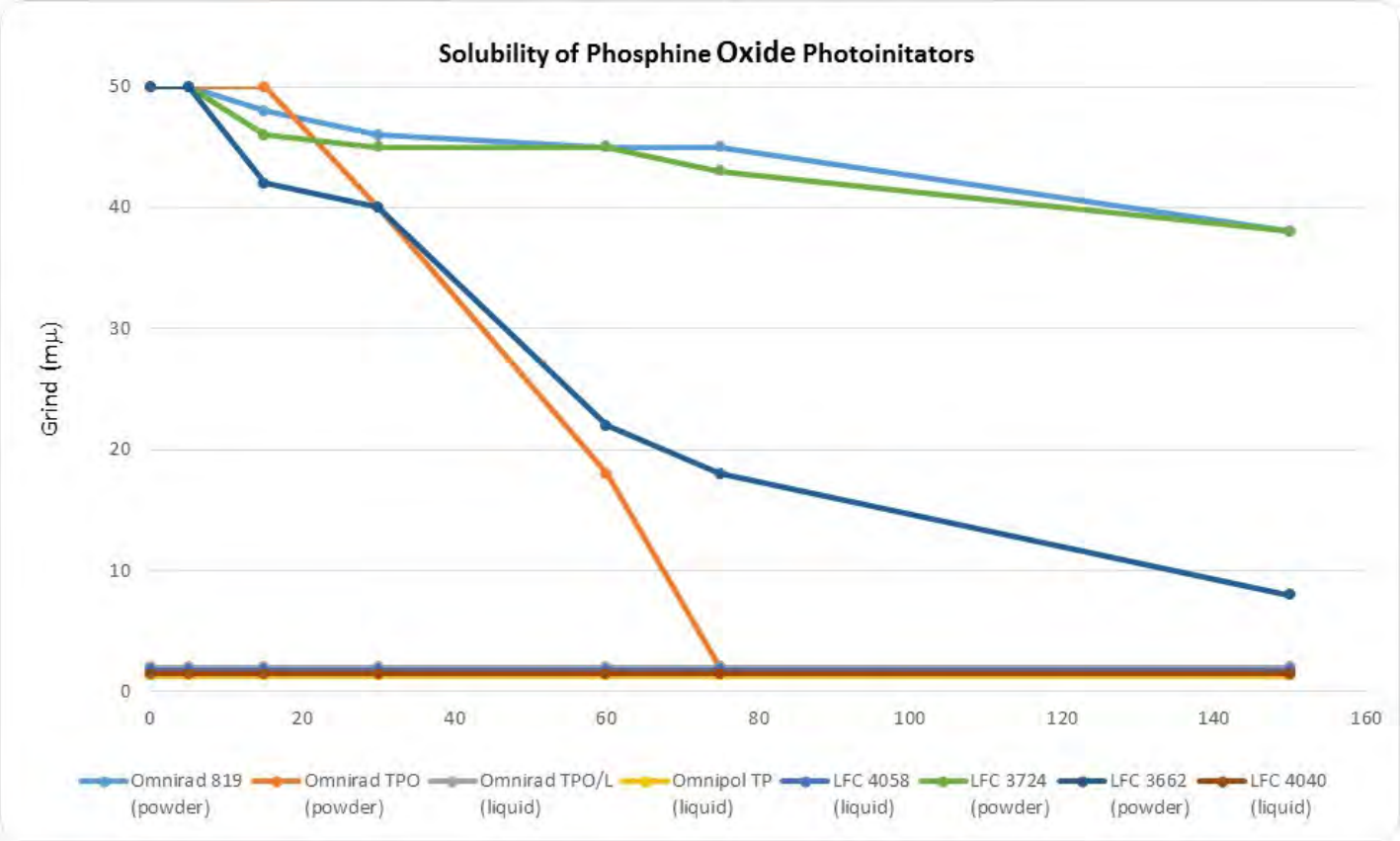


Padawans – *Liquid BAPOs*

- 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 ***Omnirad 820 (CAS # applied for)*** (formerly known as LFC 4058) during 2020.
- Details of this and other liquid BAPO developments have been presented previously



Padawans – *Liquid APO rate of solution*



- *Phosphine oxide photoinitiators were added at 4% to a clear epoxy-acrylate formulation and mixed with a rod stirrer at 1500 RPM.*
- *The grind was measured at 0,15,30,60,75 and 150 minutes stirring time, to assess the dispersibility of each photoinitiator. The results are expressed in mm on a grind gauge*

Padawans – *water-compatible PIs*

- Waterborne uv formulations are growing. Drivers include:
- rheological control and the elimination of monomers in ink jet, and film thickness control in wood coatings, it is appropriate to consider truly water-compatible photoinitiators.
- Water-compatible photoinitiators exist already for Hg lamp cure
  - E.g. hydroxyalkyl benzophenones; Omnirad 819 DW
- For LED cure, the liquid BAPO ***Omnirad 820*** is entirely compatible with aqueous formulations as well as 100% solids systems
- Salts of BAPO-OH are also of interest in waterborne formulations
- Another promising development, falling under the “new presentations of existing photoinitators” aegis, lies in micro-dispersed versions of existing photoinitiators, 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
  - Initial work was conducted on TPO dispersions for 3D hydrogel formation.
  - Recent work has focused on BAPO dispersions

The Phantom Menace? – *Dual Cure Photoinitiators*

- 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.
- It is known that Alpha Hydroxy Ketone/APO Blends will function well at a range of wavelengths
  - sensitization of the alpha hydroxy ketones is a likely mechanism of action.
- 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 in simultaneous good through and surface cure, accompanied, in certain cases, by much higher reactivity than is obtained with either of the component photoinitators.

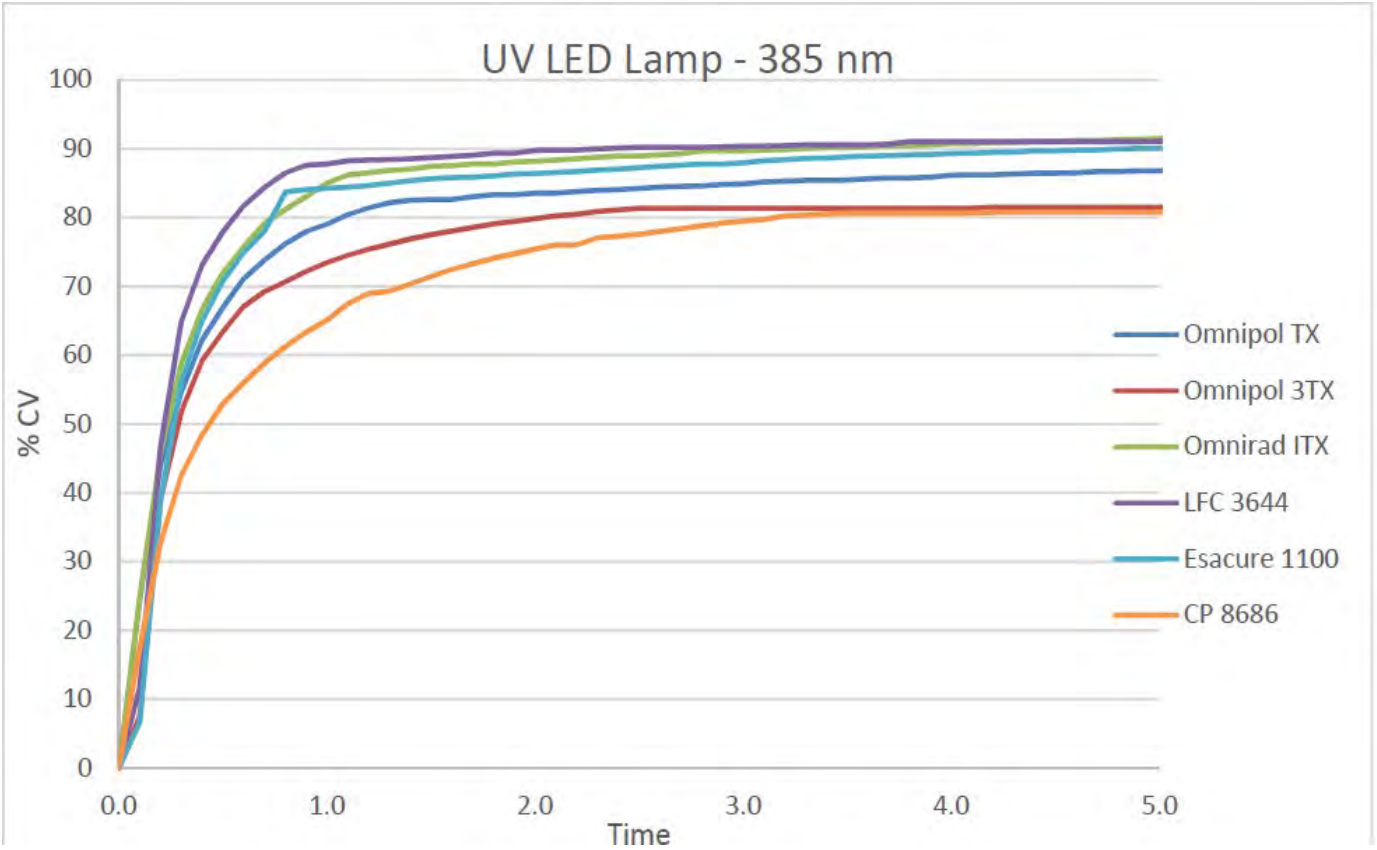
Death Star or Light Saber? – *UVC LEDs*

- 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
- The industry has seen a number of lamp manufacturers develop an LED-UVC lamp to “crisp up” the surface of a coating or ink
  - A spin-off from the water disinfectant market
- There are evident benefits to this process
- Caveat emptor:
  - The lifetime of the semiconductors used to generate UVA
  - The dangers to human life of UVA itself
- The approach is a complementary one to photoinitiator blends

The Force - *"The Emperor will show you the true nature of the Force…"*

- Approaches to zero migration photoinitiators for sensitive packaging
  - Type I versus Type II PIs
- Polymer-bound photoinitiators
  - Benzophenone and 4-dialkylamino benzophenone analogs
  - 4-phenyl benzophenones
  - Ketone resins
- Acrylated photoinitiators
  - The patent literature includes, at least, acrylated versions of:
    - Hydroxy benzophenones
    - Thio benzophenones
    - Thioxanthones
    - Acyl phosphine oxides
    - Ketocoumarins
  - Reactivity versus functionality versus rheology
  - Addition levels
- High molecular weight photoinitiators
  - Reactivity versus migration versus post-cure performance
- Predicting toxicological performance

The Force - *"The Force is strong in this one…"*



Comparative reactivities of ketocoumarin LFC 3644 (now called Esacure 3644) versus acrylated and conventional thioxanthones with a 385 nm irradiation source

A New Hope - *"I find your lack of faith disturbing…"*

- The grouping and reclassification of all APOs by ECHA is fended off
- A similar prolonged assault on alpha hydroxy ketones by the regulatory authorities is resisted
- Alpha amino ketones are (slowly) going, going, gone…
- The design and implementation cost of new chemical innovation (with/without a global recession) will spiral, in part due to compliance costs
- Blends with measurable synergies will offer technical advantages and less regulatory and synthetic strain . Ditto, nanoparticulate PIs
- The continued growth of UV-LED brings new molecules to the formulators' palette…..and stay on jump ahead of regulators
- 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.
- Sustainability, as regards photoinitiators, will largely comprise the optimization of energy costs, and recycling of solvents and other by-products
- 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.

Predictions guaranteed inaccurate, or your money back!

“Help me, Obi-Wan Kenobi, you're my only hope!” – *Predicting the Future of the UV-Curing Industry*

In 5 – 10 years, will it be

or

?

My Clone Army - *Acknowledgements*

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