"*Transcending regulatory issues: alternates to Omnirad 369*"

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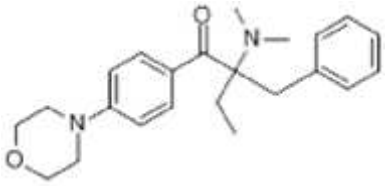
The Focus of our attention

Omnirad™ 369 (formerly Irgacure™ 369) 2-Benzyl-2-(dimethylamino)-1-[4-(morpholinyl) phenyl)]-1-butanone (CAS number 119313-12-1)



Uv absorption spectrum: λ max 322 nm.

What's the Issue?

A harmonized classification for the widely-used and versatile photoinitiator Omnirad® 369 (former Irgacure® 369, CAS number 119313-12-1) of Reprotox Cat 1B has been decided after consultation by the European Chemicals Agency (ECHA) Risk Assessment Committee (RAC). This classification has been reviewed by an independent expert repro toxicologist on behalf of IGM Resins, the European Printing Inks Association (EuPIA) and the European Council of the Paint, Printing Ink and Artists' Colours Industry (CEPE) and found to be correct. The proposal was passed to the EU Commission for inclusion in Part 3 of Annex VI of Classification, Labeling and Packaging (CLP) Regulation. The timing of the inclusion of the classification by the Commission in the CLP annex was uncertain for some time, however. The principal reason for this was that ECHA records show uncertainty as to who the Lead Registrant for substance EC 404-360-3 is and received a divided opinion when it inquired of the SIOEF as to whom they considered the Lead Registrant to be.

So the curious situation exists where toxicological data exists that shows the substance Omnirad 369 (and the other names under which the chemical whose CAS number is 119313-12-1) should be reclassified as a Class 1B Reprotoxin, but ECHA cannot accept the necessary data into the dossier as it was neither developed nor has been offered by the entity whom they currently regard as Lead Registrant. In fact, on February 20th, 2018, ECHA issued a notice, entitled "COMMUNICATION IN RELATION TO THE JOINT REGISTRATION OF SUBSTANCE EC 404-360-3" in which is saw no reason to move away from its position as to whom the lead registrant is. Eventually this will be resolved.

Nevertheless, ECHA has also stated that it has selected 236 substances for further scrutiny by the Member State competent authorities in its annual screening exercise. A manual examination of dossiers will be undertaken to help decide whether regulatory action is needed. And substance EC 404-360-3 (*reference 1*). And substance EC 404-360-3 is expected to be on that list.

Other regulatory authorities are proceeding with more alacrity. In Germany, on February 22nd, 2018, the Verband der deutschen Lack- und Druckfarbenindustrie e. V. amended Article VI of the 13th ATP will add the H360 classification to the CLP regulation, the harmonised classification will then be H360, H400, H410, this will be the minimum legal classification of the substance in the EU. Until the 13th ATP is adopted there is no legal requirement in EU law for companies to add the H360 classification to Safety Data Sheets. Following this, CEPE announced the EU Commission was announcing its intention to adopt – in 2018 - new Union legislation on printed food contact materials. This will be done in the form of a specific measure according to Art. 5 of the Framework Regulation (EU) No 1935/2004.

If a company has information which indicates that the substance should be classified above the harmonised classification (the minimum legal classification level), then the company is free to do so, and indeed is advised to do so in accordance with the CLP regulation (1272/2008). Updating the SDS is not reliant on updating the REACH registration referenced in the SDS, as many of the suppliers will be distributors who do not hold REACH registrations but are legally responsible for the content of their SDS. (reference 2)

The Classification, Labelling, and Packaging (CLP) regulation (1272/2008) sets out the minimum legal requirement for the classification and labelling of substances listed therein. The various adaptations to technical and scientific progress (ATP) place additional substances onto the minimum legal requirements list, or vary the minimum legal requirement for substances already listed. In practical terms this means that until a substance is listed on the CLP regulation, or until the required listed classification and labelling has been changed, all companies within have only to classify and label the substance using the minimum requirements, unless they are in possession of additional information which requires a higher classification.

As it stands, Omnirad 369 (EC 404-360-3) retains the minimum legal CLP listed classification below:

H400	Aquatic Acute 1
H410	Aquatic Chronic 1

After the 13 ATP will have been enacted, this entry should most likely be altered to read thus:

H400	Aquatic Acute 1
H410	Aquatic Chronic 1
H360	Repr. Cat. 1B

Unfortunately, the timing for enactment of this is not known, but IGM will be amending its Safety Data Sheets to reflect what we believe to be the true classification status of the photoinitiator CAS number 119313-12-1, as this appears to be the responsible thing to do, even as the updating of the REACH dossier remains stalled in Helsinki.

Solutions

In this presentation, we present the alternatives, both as single photoinitiators and blends, that mimic the performance of Omnirad 369 for both conventional and LED cure, and offer the benefits of much safer handling and migration species. The first place to look, obviously, for a replacement of Omnirad

369 is within the same chemical family, the alpha amino ketones (also known as the amino acetophenones).

a) Other alpha amino ketones. The family of comprises Omnirad® 907, Omnirad® 369, Omnirad® 379, Omnirad® 264 and Omnipol® 910. Some considerations for this versatile family of active Type I photoinitiators:

- Omnirad® 907 (also known as Omnirad 4817) was reclassified in 2010/2011 as Reprotoxic 1B.
- Omnirad® 379 was reviewed by the European authorities prior to the Omnirad® 369 harmonization process. The review was completed for high volumes and with extensive toxicity data and resulted in a Reprotoxic 2 H361 classification.
- Omnirad® 264/(also known as Omnirad 389 in Asia) has not been reviewed yet by the European authorities on toxicity data. If REACH-registered at high volumes, undoubtedly READ Across could come into play.
- Omnipol® 910 is classifiable as a polymer under REACH. Its starting raw materials are currently not CMR classified. As a viscous liquid, it poses different formulation challenges, but nevertheless won't normally impart a higher viscosity to formulations in which it is employed.

b) Dimeric alpha hydroxy ketones. The photoinitiators presented here are all dimeric in chemical structure (two active photo-fissionable centers per molecule) and have the benefits over basic alpha hydroxy ketones of cure speed, low yellowing and low migration. Their uv absorption (λ max ~ 260nm) is nevertheless quite similar to those of alpha amino ketones (λ max ~ 320nm), but hypocritically shifted by a few nanometers.

    a. Esacure KIP 160
    b. Omnirad 127
    c. Esacure ONE
    d. Esacure KIP 150

c) Acyl phosphine oxides. This highly reactive group of photoinitiators is generally excellent for through-cure and for very low yellowing. Their uv absorption stretches toward the visible, making them suitable for some LED cure applications as well as for conventional mercury lamp cure.

    a. TPO
    b. TPO-L
    c. BAPO (Omnirad 819 and Omnirad 819DW for waterbased formulations)

d) Other photoinitiator types
    a. Esacure 1001M (a beta hydroxy sulfone)
    b. Omnirad EMK (an amino benzophenone)
    c. Blended solutions. Here, the overall typical properties of Omnirad 369 are reproduced by two or more photoinitiators combined. There may be formulatory advantages, too, in enhanced solubility of the blend over the constituents and/or a synergic effect upon reactivity.

e) Future possibilities. These are two new photoinitiators currently being launched that are worthy of consideration as alternates to Omnirad 369

a. Omnipol TP (experimental code PIX16-168: a polymeric TPO-L)
b. Esacure 3644 (experimental code LFC3644: a 3-ketocoumarin: a Type II photoinitiator)

There is no current universal solution to the problem of Omnirad 369. For example, for US users, there is the issue that two of the highest-performing alpha hydroxy ketone photoinitiators, Esacure KIP 160 and Omnirad 127, are both subject to a SNUR, as is Omnirad 379 (40 CFR 721.10041). Nestle are reviewing the listing of Omnirad 369 and we are seeing some regional differences within the same company's usage.

Following is some comparative data for sensitive graphic arts applications for some of the most-widely evaluated alternates to Omnirad 369 (Table 1) and for non-sensitive applications (Table 2). Obviously, those photoinitiators listed in Table 1 can also be employed in non-sensitive ink and coatings applications and may be preferred in those applications not normally regarded as being sensitive (e.g. furniture coatings, 3D printing) but which for which contact with children is possible.

Many of the photoinitiators listed in the Tables are covered by one or more composition-of-matter, process or applications patents, so, for the sourcing of these materials, legal as well as purity and compliance issues must be considered.

PI	Health Risk	EU-REACH status	Inventories where listed	Recommendations
Omnirad® 379	Reprotoxin 2 - H361	Full Reach Registration	EU, US, Aus, Can, China, Korea, NZ, Taiwan	A very close alternative, by chemical structure. High risk in the longer term with regards to Read Across of Classifications. CMR 2 Classed material may give restrictions within company policies or end users specifications. SNUR listed.
Esacure® KIP 160	Not classified	Full Reach Registration	EU, US, Taiwan	A close performance match with better cure performance in dense colors. SNUR listed.
Omnirad® 127	STOT RE 2 - H373	Full Reach Registration	EU, US, Aus, Can, Korea, NZ, Taiwan	A close performance match. Also suitable for pastel shades. SNUR listed.
Esacure® 1001M	Eye Dam. 1 - H318	Full Reach Registration	EU, US, Can, Japan, Korea, Taiwan	A close performance match which can be used in certain applications as 1:1 replacements. A Type II photoinitiator.
Esacure® ONE	Reprotoxin 2 - H361f	Full Reach Registration	EU, US, NZ, Can, China, Korea, Taiwan, Thailand	A good performance match. Also suitable for lighter colors, but limitations in dark dense colors. CMR 2 Classed material may give restrictions within company policies or end users specifications
Omnirad® 819	Skin Sens. 1 - H317	Full Reach Registration	EU, US, Aus, NZ, China, Can, Japan, Korea, Mex, PH, Taiwan, Thailand	An interesting possibility as it provides good in-depth cure performance, thus more suitable for thicker films. It may have it limits in certain colors.
Omnipol® 910	Not Classified	Polymer Exempt, Monomers in Preparation	EU, US (LVE), China, Taiwan	A good performance match, based on similar chemistry to Omnirad® 369 (it is an alpha amino ketone), so there may be some future risk for Read Across. It is a polymer (as classified under REACH) and is a viscous liquid..
Omnirad® TPO-L	Skin Sens 1B - H317	Full Reach Registration	EU, US, Can, China, Korea, NZ, Taiwan, Thailand	A good technical possibility, and suitable for lighter shades. Some limitations in dark dense colors. Reactivity is lower than Omnirad® 369.

Table 1: Comparative Data on Alternate Photoinitiators to Omnirad 369 for Sensitive Applications

PI	Health Risk	EU-REACH status	Inventories where listed	Recommendation
Omnirad® TPO	Skin Sens. 1B - H317 Repr. 2 - H361f	Full Reach Registration	EU, US, Aus, NZ, China, Can, Japan, Korea, Mex, PH, Taiwan, Thailand, Vietnam	Technically an interesting possibility. Low yellowing means it is suitable for pastel colors. CMR 2 Classed material may give restrictions within company policies or end users specifications
Omnirad® 264	Skin Irrit. 2 - H315 Eye Irrit. 2 - H319 STOT SE 3 - H335	In preparation for LVE only	EU (LVE)	A very close performance and chemical match to Omnirad 369. However, there is a considerable risk in the longer term with regards to Read Across of Classifications.
Esacure® KIP 150	Repr. 2 - H361f	Full Reach Registration	EU, US, NZ, Can, China, Korea, PH, Taiwan, Thailand	A good performance match. Also suitable for lighter shades, but with certain limitations in dark dense colors. CMR 2 Classed material may give restrictions within company policies or end users specifications
Omnirad® EMK	Skin Irrit. 2 - H315 Eye Irrit. 2 - H319 STOT SE 3 - H335	In preparation for LVE only	EU, US, Aus, NZ, China, Can, Japan, Korea, PH, Taiwan, Thailand	This is an interesting choice for blended solutions to boost cure and reduce cost. Strongly yellowing, however.

Table 2: Comparative Data on Alternate Photoinitiators to Omnirad 369 for Non-Sensitive Applications

Current Trends: how are market leaders within graphic arts reacting?

At the time of writing (March 2018):

- Company A remains committed to Omnirad 369 (for non-sensitive applications), but is investing also in Esacure KIP 160, and has indicated that there is no migration issue for the latter photoinitiator in sensitive packaging assemblies
- Company B is making a final decision between Omnipol 910 and Omnirad 127 (there are differences in emulsification performance in their offset ink systems)
- Company C is adopting Esacure KIP 160
- Company D adopted Esacure KIP 160 in 2017, following three years of trials for sensitive packaging
- Company E is deciding between Omnipol 910 and Esacure KIP 160
- Company F will use Omnirad 379 in the shorter term

- In general, offset ink manufacturers are looking favorably upon Esacure ONE for low migration inks

Conclusions…….and will there be more Compliance Issues with Photoinitiators?

Is this the end of the workhorse Omnirad 369? Most definitely not: rather it is an acknowledgement that all fine chemicals must be treated with respect and appropriate handling, both in the workplace and in the end-use of the coatings, adhesives, inks and other structures they are designed for, and also that manufacturers and suppliers of photoinitiators must offer their customers as much advice and information as possible about the toxicological and safety-related components of their offerings, not just the cost and performance. Omnirad 369 continues to be used widely, for example in graphic arts and in electronics i.e. in applications where appropriate measures are taken to eliminate the possibility of exposure to process workers and where there is no danger of migration of the photoinitiator or its photolytes in the finished article.

Will there be further compliance Issues with Photoinitiators? Yes, undoubtedly. ECHA is "requesting" additional toxicological testing on the closely-related Omnirad 379 (where ECHA seems to be using Read Across from the toxicological data on Omnirad 369 it cannot formally yet accept!), as well as for BAPO, TPO, TPO-L, Omnirad 184 and Omnirad 1173. Also, new legislation under preparation in Europe for the Printing and Packaging Industry (Packaging Ink Joint Industry Task Force on the planned EU Measure on Printed Food Contact Materials ("pFCM measure") and the resolution of an unclear definition on CMR will impact our industry further.

We can expect therefore for many more substances – photoinitiators and acrylate monomers and oligomers, as well as substances employed in the overall inks, coatings and adhesives marketplaces - to come under scrutiny, particularly from ECHA, in the future. One path forwards lies in embracing the compliance challenges that regulatory authorities raise and quantifying the toxicological and safety-related statuses of the chemicals the UV curing industry uses. Another lies in innovating new materials with enhanced performance, as well as benign toxicological behavior, for the advancement and growth of the UV curing industry. Developments in global compliance issues are far from the only technology driver in our industry –line speeds (cost), enhanced formulability, depth cure in thick films, and the rapid ingress of LED curing are also driving a whole new generation of photoinitiators, for example. Regulatory considerations are increasingly shaping new material developments, and those who do not innovate and behave responsibly, be they regulatory agencies, raw material suppliers, or ink and coating manufacturers, will not enhance their futures or the future of our industry.

References

(1) RadTech Europe RadFlash Newsletter February 2018
(2) Private communication from WSP Regulatory Consultants March 2018