Photoinitiators for Water Based UV Curing.

Sink or Swim?

W. A. Green.
Ex Great Lakes Fine Chemicals.
ag@arthurgreen.cc
**Why water based UV?**

Two main parameters that provide advantage:

<table>
<thead>
<tr>
<th>Very low viscosity</th>
<th>Very thin, low weight coatings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spray, roller or curtain coatings.</td>
<td>From aqueous dispersions of high molecular weight acrylate oligomers.</td>
</tr>
<tr>
<td>Digital inkjet</td>
<td></td>
</tr>
</tbody>
</table>

Specific UV resins that can be thinned with up to 25% water. Polyurethane dispersions, or PUDs, solids content of 25-40%.

There is no need for viscosity reduction via high concentrations of monomers which will affect the polymer properties.
Advantages and Applications.

Low shrinkage, low odour, good adhesion, high gloss.
Hard, scratch resistant coatings with some flexibility.
Remove water by warm air jet at 50-60 deg. C prior to UV cure.
Photoinitiators must be non-steam volatile.

<table>
<thead>
<tr>
<th>Clear coatings.</th>
<th>Inks.</th>
<th>Others.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood.</td>
<td>Digital WB inkjet</td>
<td>Fabrics, textile printing.</td>
</tr>
<tr>
<td>Plastics.</td>
<td>for packaging.</td>
<td>Biomedical devices.</td>
</tr>
<tr>
<td>Metals.</td>
<td>Labels.</td>
<td>3D printing.</td>
</tr>
<tr>
<td>Soft touch.</td>
<td></td>
<td>Etc.</td>
</tr>
<tr>
<td>Aerospace low build.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mostly from PUD’s.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Water soluble photoinitiators – Historical.

1970-80’s Initial drive to make water based UV products.
Some early photoinitiators were ionic salts, very water soluble.

1980

Increased long wave absorbance.

Later, 1996.

These quaternary salts are more photoactive than the precursors.
Quantacure BTC and QTX commercialised, but sales did not last.

Why? Ionic nature interfered with dispersing agent?
Increased hydrophilic nature of polymer?
Too costly?
Why the increased photoactivity of quaternary salts?

The quaternary salt affects the Type II electron transfer process. This is reversible, with some degree of back electron transfer reducing the efficiency of the process.

The cationic nature of the quaternary group repels the amine radical cation and inhibits back electron transfer. The overall process becomes more efficient in generating radicals. This ‘ionic atmosphere’ effect is typical of micelles and dispersions.

30 years on, is there just cause to re-visit these quaternary salts in the light of modern day dispersion technology?
Present day water soluble photoinitiators.

Irgacure 2959.

\[
\begin{align*}
CH_3 & \quad CO \quad C-CH_3 \\
\text{HOOCH}_2\text{CH}_2\text{O} & \quad \text{Absorption 273nm} \\
\text{H}_2\text{O} & \quad \text{Water solubility 0.5\%}
\end{align*}
\]

From the 1980’s.

Low water solubility limits more efficient formulation.

5% solubility would allow increased concentration of PI.

MBS.

A sulphonated version of Irgacure 369, sodium salt.

For water based solder resists.

pH sensitive. At low pH the sulphonic acid is insoluble.
The use of dispersions and emulsions of oil soluble photoinitiators for water based formulations.

For inkjet the particle size of the dispersion has to be small enough to pass the digital sub-micron filters.

Esacure KIP 150 EM (oligo-hydroxyacetophenone) emulsion for **short wave** UV surface cure. Used in coatings.

Esacure DP250 (mix TPO, 1173 and trimethyl BP) dispersion for **long wave** UV depth cure in thicker coatings.

Irgacure 819DW 45% solids dispersion for **long wave** UV. Can lead to low gloss and stability problems. Unsuitable for inkjet.

Polyurethane dispersions (PUDs) are quite sensitive materials and care is needed with additives to avoid the formation of ‘creams’ and ‘aggregates’.
Direct use of oil soluble photoinitiators for water based UV.

Low MW oil soluble photoinitiators can be incorporated using high speed stirring. Liquids respond much better than solids.

**Short wave UV  250nm.**

**Irgacure 500** (liquid mix 184/BP) is widely used for coatings. **Darocur 1173** is steam volatile and easily lost but **Omnirad 1000** (mix of 1173 and 184) is a popular choice. **Irgacure 127** is a much less volatile version of 1173 with enhanced cure and, being liquid, can be used in WB UV. **Benzophenone** has some solubility in WB formulations. **Speedcure BEM** (liquid mix BP/MBP) is more easily used. **MBF** is easily incorporated but is slower curing than the above. Widely used in the wood coating industry. **Irgacure 754**, a faster version of MBF has been used in WB UV via PUDs for thin base coatings on plastics and metals.
Oil soluble photoinitiators for water based UV.
Long wave UV 370-410nm.

TPO-L is the least yellowing of the phosphine oxides. Some compatibility with WB formulations. Preferred choice for depth cure.

TPO-L can occasionally crystallise out of these formulations.

Irgacure 2100 (liquid mix BAPO/MAPO) is becoming the choice for higher photoactivity in water based systems.

Irgacure/Omnirad 4265 (TPO/1173) is also another useful liquid mixture.

TPO and Irgacure 819 These are difficult to get into solution unless used in very low concentration.

Solubility of PIs in WB formulations can be improved by the addition of small amounts of solvent such as butyl glycol.
Oil soluble photoinitiators for water based UV.

Tertiary amines for Type II formulations.

Liquid acrylated amines or specific oligomeric amines can be used as normal by high speed mixing. Not easy to disperse.

For Type II WB inks, aminobenzoates such as the liquid Speedcure EHA will provide higher cure speeds.

N-phenylglycine

Has been shown to be an excellent hydrogen donor for water based systems but it liberates carbon dioxide and may lead to stability problems.
Conclusions

In short, most liquid oil soluble photoinitiators can be ‘whizzed’ into water based formulations.

But photoinitiators with some water solubility would be preferred.

There is a notable absence of mid-UV, high speed photoinitiators that are compatible with WB formulations.

Photoinitiators such as Irgacure 369 and 379, Speedcure PBZ and BMS are very difficult to get into WB solutions.

There are no suitable thioxanthones or alternatives to phosphine oxides for depth cure in WB UV.
LED formulations for water based UV.

A recent study examined several photoinitiators in low solids water based coatings under a mercury lamp and a 395nm LED UV lamp.

Conversion %

<table>
<thead>
<tr>
<th>Mercury lamp.</th>
<th>395nm LED lamp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2% Dar. 1173</td>
<td>92%</td>
</tr>
<tr>
<td>1% Irg. 819</td>
<td>87%</td>
</tr>
<tr>
<td>2% Irg. 819</td>
<td>73%</td>
</tr>
<tr>
<td>2% Es. DP 250</td>
<td>93%</td>
</tr>
<tr>
<td>1% Es. DP 250</td>
<td>66%</td>
</tr>
<tr>
<td>2% Irg. 2100</td>
<td>92%</td>
</tr>
<tr>
<td>1% Irg. 2100</td>
<td>84%</td>
</tr>
<tr>
<td>2% Dar. 1173</td>
<td>43%</td>
</tr>
</tbody>
</table>

Tack free.

Hardness 201 s.

Reducing the oxygen levels to 6% gave good hardness with LED.
New developments in water soluble photoinitiators.

1. Photoinitiators with carbohydrate residues. 2002
   Hydrophilic ‘tails’ of glucose, fructose etc.
   Similar to Irgacure 2959. Good water solubility.
   Applied to benzophenones, thioxanthones and hydroxyalkylacetophenones.

2. Thioxanthone-2-oxy and 2-thio-acetic acid sodium salts. 2010

   ![Chemical Structure](image)

   Good water solubility.
   pH sensitive. The acid can precipitate at low pH.
New developments in water soluble photoinitiators.

3. Alkali salts of bis-acylphosphonic acids. 2015

For low migration PUDs. Water solubility 5-10%. pH sensitive? The TEOA salt is twice as active as the other salts under a mercury lamp. With LED lamp, the lithium salt is the most active.

4. FUJIFILM USA. Photoinitiator FFI-1. 2015

Hydrophilic, short wave UV. Good water solubility. Few details available.

It remains to be seen if any of these four developments become commercial.
Sink or Swim?

Floating along perhaps. There is a desire for photoinitiators with a water solubility more of the order of 5-10%.
For innovation, a hydrophilic nature is probably the best choice but quaternary salts offer improved photoactivity.
Salts of acidic photoinitiators are limited by pH sensitivity.

New, high speed, medium wavelength photoinitiators are essential to take water based UV a step further.

Innovators must consider the physical properties of a photoinitiator. For water based UV these are just as important as the photoactivity and absorption. Either water solubility or a liquid nature is desirable.
Modified molecules. ‘Magic methyl groups’.

Can we modify present day photoinitiators?

Adding a single methyl group to Irgacure 369 has reduced the melting point and improved the solubility of Irgacure 379.

The solubility in HDDA is improved six-fold but the material still remains a solid, difficult to incorporate into WB UV systems.
Modified molecules. ‘Magic methyl groups’.

Non-linear substitution has a great effect on physical properties. This can be seen in modified BMS molecules.

Such modifications on a part of the molecule that has little effect on the photoactivity can deliver liquid versions relatively easily in some cases.

Even small modifications come at a cost.

Is the water based market sufficiently large to sustain new products?
Innovation for industry.

New products have to show an advantage to succeed. Innovation is plentiful. Commercialisation is difficult. The high cost of a complex regulatory system brings a less than pragmatic approach to novelty.

To quote:

‘The overarching legislative architecture can be extremely complex and navigating the constantly changing international regulations can be a significant challenge in itself. We have a dedicated team of experts working closely with authorities.......’

Chief Marketing Officer. An International UV Company.

How are innovative small companies supposed to deal with this? We are stifling innovation.

Do we need a more cooperative approach between innovators, formulators and end-users?