Polymeric Photoinitiators: UV Inks and Coatings for Food Packaging

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INTRODUCTION

UV/EB-curing printing inks and coatings are widely used in a variety of packaging applications. When it comes to food packaging for indirect contact, odor and the potential migration of mobile components are a concern for every formulator, independent of the curing mechanism. In UV-curing inks and coatings, the main focus is on photoinitiators that usually are of low molecular weight and which have a tendency to migrate, either through the substrate or via reverse-side migration (set-off). In response to existing and pending legislation on permissible migration levels for inks used in food packaging, a product range of polymeric, high molecular weight photoinitiators (PPI’s) has been introduced, that meet the demands for low migration and odor and have favorable toxicology.

LEGISLATION ON FOOD PACKAGING

What all legislative mandates with regard to printed packaging and food contact have in common is that the packaging ink manufacturers are responsible for preparing compositions in accordance with those requirements. It is the printer/converter/food-packaging manufacturer who is responsible for the regulatory compliance of its packaging.

The legislation on printing inks and coatings for indirect food contact is diverse, somewhat unspecific and quite different in Europe vs. the U.S. and even within single countries.

For Europe the most important reference is a Framework Regulation (EC) No 1935/2004 applicable to all food packaging, but until today no specific Community legislation concerning printing inks for food packaging exists. Article 3 of this regulation requires that materials and articles which are intended to be brought into contact with foodstuffs must not transfer any components to the packed foodstuff in quantities which could:

- endanger human health
- bring about an unacceptable change in the composition
- bring about deterioration in organoleptic properties

The main specific directive pursuant to the Framework Regulation is Directive 2002/72/EC relating to plastic materials and articles intended to come into contact with foodstuffs. To ensure the protection of consumers’ health, two types of migration limits have been fixed in this directive. The overall migration
limit (OML) is set to 60mg/kg food or 10mg/dm² of packaging surface area. In addition, for specific substances the maximum content or the specific migration limit (SML) is established. Since ink components may contribute to the total quantity of substance(s) released by a packaging material, they shall be included in the determination of the overall migration.

The Swiss Authorities have issued the 2007 revision of the “Ordinance on Materials and Articles in Contact with Food” (SR 817.023.21)³ which introduces a new regulation on printing inks for food packaging. One of the main aspects of the new regulation is the positive list of authorized substances. Printing inks for food packaging will be cleared for manufacture only if they are made of substances which are on this positive list. The European Printing Inks Association (EuPIA) submitted a complete list of substances used in the manufacture of printing inks for food packaging (DOL)⁴ to the Federal Office of Public Health in the second quarter of 2009. A list of evaluated and non evaluated substances will be published.

While U.S. laws do not make any specific statements comparable to the ones issued by the EC or Switzerland, product liability issues make it advisable also for U.S.-based formulators to apply great diligence when manufacturing printing inks for food packaging applications. In acknowledging the general ‘fit-for-use’ of UV-curing systems, the American Food and Drug Administration (FDA) in 2008 has approved several UV/EB raw materials for direct food contact as specified in Food Contact Notification 772 (FCN 772)⁵, provided that they are properly cured and that extractable components are below the established acceptable threshold. U.S. and EC regulation are based on different models. The U.S. regulations are clearly less restrictive and consequently not applicable in the EC.

MANUFACTURING GUIDELINES AND RAW MATERIAL SELECTION

Manufacturing Guidelines by EuPIA
Because of the lack of clear legal guidance on how to formulate commercially-viable inks and coatings, EuPIA has issued a “Guideline on Printing Inks” for indirect food contact⁶. While it is important to note that this guideline is not enforceable legislation, it has become an industry standard and has been adopted as an internal guideline by multinational food & beverage manufacturers. The guideline states the following important principles:

- The raw materials shall be selected in accordance with a defined “Selection scheme for packaging ink raw materials”, excluding CMR category 1 substances and imposing other restrictions.
- The packaging inks shall be formulated and manufactured in accordance with the CEPE/EuPIA “Good Manufacturing Practices for the Production of Packaging Inks”⁷ formulated for use on the non-food contact surfaces of food packaging.
- The printed or overprint varnished surfaces of food packaging shall not come into direct contact with food.
- There shall be no or negligible visible set-off or migration from the printed or varnished non-food contact surface to the food contact surface.
- Global and specific migration from the packaging in its finished state shall not exceed the relevant limits.
By following the controls and practices depicted below, full conformity of the final packaging can be achieved:

![Diagram showing the process from EuPIA GMP to Full Conformity]

Source: EuPIA

RAW MATERIAL SELECTION AND SAFETY EVALUATION

According to EuPIA Guidelines, a target migration limit of “no concern” equaling 10 ppb for non-evaluated substances with molecular weight below 1000 Daltons is the ultimate objective to be consistent with other food contact materials. For packaging scenarios which do not achieve this limit, it is required either to modify the packaging designs, develop lower migration products, or obtain additional toxicological data to demonstrate that the use is acceptable.

In particular, a substance is acceptable if its specific migration does not exceed:

- 10 ppb, in the case of insufficient toxicological data
- 50 ppb if three negative mutagenicity tests requested by European Food Safety Authority (EFSA) Guidelines are available
- greater than 50 ppb, if supported by favourable toxicological data and/or evaluation done in accordance with the EFSA Guidelines
The following flow-chart provides an overview on the selection criteria:
POLYMERIC PHOTOINITIATORS (PPI’s)

Photoinitiator selection is key when formulating low odor, low migration UV inks and coatings. The discussed PPI’s are a range of high molecular weight polymeric photoinitiators that meet the demands of low migration and odor and that have been toxicologically evaluated.

GENOPOL* BP-1: Polymeric Benzophenone Derivative
GENOPOL* TX-1: Polymeric Thioxanthone Derivative
GENOPOL* AB-1: Polymeric Aminobenzoate Derivative

Properties

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<tr>
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</thead>
<tbody>
<tr>
<td>GENOPOL* BP-1</td>
<td>960</td>
<td>~160</td>
<td>245, 325</td>
</tr>
<tr>
<td>GENOPOL* TX-1</td>
<td>820</td>
<td>~160</td>
<td>255, 310, 375</td>
</tr>
<tr>
<td>GENOPOL* AB-1</td>
<td>860</td>
<td>~15</td>
<td>310</td>
</tr>
</tbody>
</table>

The absorption spectra of BP-1, TX-1 (both 0.002% in acetonitrile) and AB-1 (0.001% in acetonitrile) is shown in the following graph:

The molecular weight distributions of BP-1, TX-1 and AB-1 are shown in the following graph:
Migration/Odor
During the production process of the PPI’s, low molecular weight substances are removed. Therefore, PPI’s are very low in odor. Combined with the ability to link into the UV cured acrylate matrix, PPI’s will exhibit an extremely low tendency to migrate. Migration data for food packaging should always be generated under realistic and practical conditions, by accepted analytical methods and considering commercial printing inks, substrates, pre-treatment, printing conditions, etc.

Formulations
The starting point recommendations listed below are simplified formulations for two typical applications where PPI’s are suitable. Slightly reduced cure speeds are common with polymeric photoinitiators compared to conventional photoinitiator packages.

**Flexographic Ink**

<table>
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<tr>
<th>Product code</th>
<th>%</th>
<th>Description</th>
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<tbody>
<tr>
<td>Irgalite Yellow LBG</td>
<td>14.5</td>
<td>Pigment CIBA/BASF</td>
</tr>
<tr>
<td>Genomer* 2259</td>
<td>26.0</td>
<td>Modified Epoxy Acrylate</td>
</tr>
<tr>
<td>Miramer M3130</td>
<td>38.0</td>
<td>TMP(EO)3TA</td>
</tr>
<tr>
<td>Miramer M410</td>
<td>9.0</td>
<td>DiTMPTA</td>
</tr>
<tr>
<td>BP-1</td>
<td>6.0</td>
<td>Polymeric Benzophenone Derivative</td>
</tr>
<tr>
<td>TX-1</td>
<td>1.5</td>
<td>Polymeric Thioxanthone Derivative</td>
</tr>
<tr>
<td>AB-1</td>
<td>3.0</td>
<td>Polymeric Amniobenzoate Derivative</td>
</tr>
<tr>
<td>Genocure* BDMM</td>
<td>1.0</td>
<td>Norrish Type I Photoinitiator</td>
</tr>
<tr>
<td>Genorad* 16</td>
<td>1.0</td>
<td>In-Can Stabilizer</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100</strong></td>
<td></td>
</tr>
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</table>

Reactivity 50 m/min @ 240W/cm
Viscosity 1'320 mPas @ 25°C

With direct replacement of ITX by TX-1, the amount has to be significantly increased to maintain cure speed. Therefore, TX-1 should always be used in combination with AB-1. The synergistic effect of this polymeric aminobenzoate allows for the use of similar amounts of TX-1 compared to monomeric ITX while still maintaining cure speed.

**Overprint Varnish**

<table>
<thead>
<tr>
<th>Product code</th>
<th>%</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>Genomer* 2263</td>
<td>38.0</td>
<td>Epoxy Acrylate</td>
</tr>
<tr>
<td>Miramer M3130</td>
<td>48.0</td>
<td>TMP(EO)3TA</td>
</tr>
<tr>
<td>Genomer* 5275</td>
<td>8.0</td>
<td>Oligoamine</td>
</tr>
<tr>
<td>BP-1</td>
<td>6.0</td>
<td>Polymeric Benzophenone Derivative</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100</strong></td>
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</table>

Reactivity 40 m/min @ 240W/cm
Viscosity 1’600 mPas @ 25°C

BP-1 is also used in UV varnishes where combinations with crosslinking amine synergists such as oligoamines or amine modified polyether acrylates are recommended.
Manufacturing process capabilities
PPI’s are polymeric in nature and contain no reactive acrylate bonds. It is therefore possible to temporarily heat these products to temperatures in excess of 100°C without the risk of further reaction. This property allows the PPI’s to be used as a medium to dissolve, disperse or grind other photoinitiators or non polymerizable additives in order to produce an intermediate for downstream production.

SAFETY ASSESSMENT OF POLYMERIC PHOTOINITIATORS
PPI’s are a reaction product of a low molecular weight, monomeric photoinitiator and a polymeric backbone. From a toxicological and application point of view, it is the residual content of un-reacted photoinitiator that has the biggest potential for migration. Thus the focus of the safety evaluation of PPI’s is on the residual low molecular weight photoinitiators that are present in concentrations of typically < 1%. Other components present in PPI’s with a molecular weight below 1000 Dalton are the polymeric backbone and possibly fractions thereof. The polymer itself is of low toxicity. Other impurities are only present in concentrations that result in levels of no concern based on ‘worst case scenario’ calculations.

Studies on low molecular weight Photoinitiators
RAHN is the owner of records for relevant mutagenicity studies on monomeric, un-reacted photoinitiators in PPI’s, allowing their use for migration levels up to 50ppb. These studies have been performed under current guidelines of EFSA and EuPIA.

<table>
<thead>
<tr>
<th>Studies *</th>
<th>Reference</th>
<th>GLP</th>
<th>Result</th>
</tr>
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<tbody>
<tr>
<td>Ames (Reverse mutation assay)</td>
<td>OECD 471</td>
<td>yes</td>
<td>Non-mutagenic</td>
</tr>
<tr>
<td>Mouse Lymphoma</td>
<td>OECD 476</td>
<td>yes</td>
<td>Non-mutagenic</td>
</tr>
<tr>
<td>Micro Nucleus</td>
<td>OECD 474</td>
<td>yes</td>
<td>Non-mutagenic (in-vivo)</td>
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* Studies were performed on constituent, low molecular weight Photoinitiator

CONCLUSION
PPI’s are scientifically-evaluated products suitable for food packaging (indirect contact) that require low odor and low migration. Since the individual manufacturing methods of formulators, the nature of the foods used, and the specific environment converters operate in are quite diverse, it is required that real-life migration studies be performed by ink manufacturers and converters in order to ensure compliance with legislation and guidelines. However, past experience shows that it is possible to formulate and convert inks and coatings with PPI’s that result in migration levels of below 50 ppb of residual photoinitiator, thus – in combination with existing toxicology data – providing full conformity with guidelines and regulations. This has also been verified by downstream users such as Nestlé who explicitly lists PPI’s on its positive list of substances that can be used. PPI’s assure the health and safety of humans according to article 3 of the European Directive 1935/2004.
REFERENCES

4. DOL http://dol.fca.cefic.org/dol/member/login
5. FCN 772 http://www.radtech.org/whats_new/FCN.html

ABBREVIATIONS

CEPE European Council of producers and importers of paints, printing inks and artists’ colors
CMR Carcinogenic, mutagenic, reprotoxic
DOL Database Online
EFSA European Food Safety Authority
EuPIA European Printing Inks Association
FCN Food Contact Notification
FDA American Food and Drug Administration
NOAEL No Observed Adverse Effect Level
OML Overall Migration Limit
QSAR Quantitative structure-activity relationship
SML Specific Migration Limit