Polymeric Photoinitiators: UV Inks and Coatings for Food Packaging

By Roger Küng

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 are usually 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 (PPIs) has been introduced that meets the demands for low migration and odor, and has favorable toxicology.

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

Legislation on Food Packaging

What all legislation 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 versus the U.S. and even within single countries.

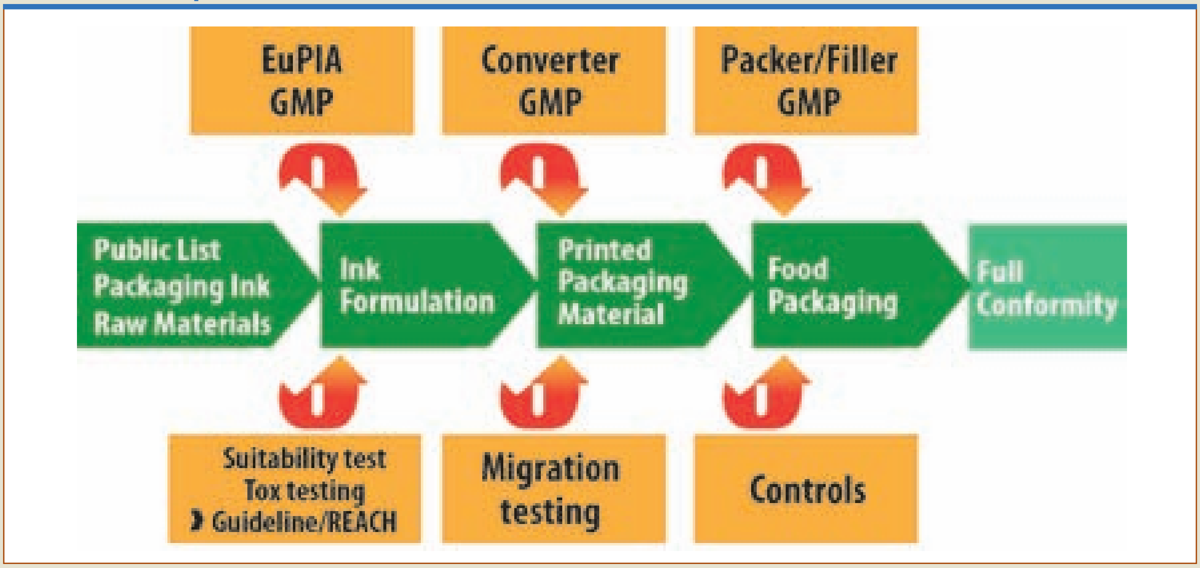
For Europe, the most important reference is Framework Regulation (EC) No. 1935/2004[1] applicable to all food packaging—but, until today, no specific community legislation concerning printing inks for food packaging exists. Article 3 of this regulation requires that materials and articles intended to be brought into contact with foodstuffs must not transfer any components to the packed foodstuff in quantities that could:

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

The main specific directive pursuant to the Framework Regulation is Directive 2002/72/EC[2] 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 is set to 60mg/kg food or 10mg/dm2 of packaging surface area. In addition, for specific substances

Figure 1

Controls and practices flowchart



Source: EuPIA

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 that 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 a food packaging Database Online[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 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 in 2008 approved several UV/EB raw materials for direct food contact as specified in Food Contact Notification 772[5], provided that they are properly cured and that extractable components are below the established acceptable threshold. U.S. and EC regulations 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

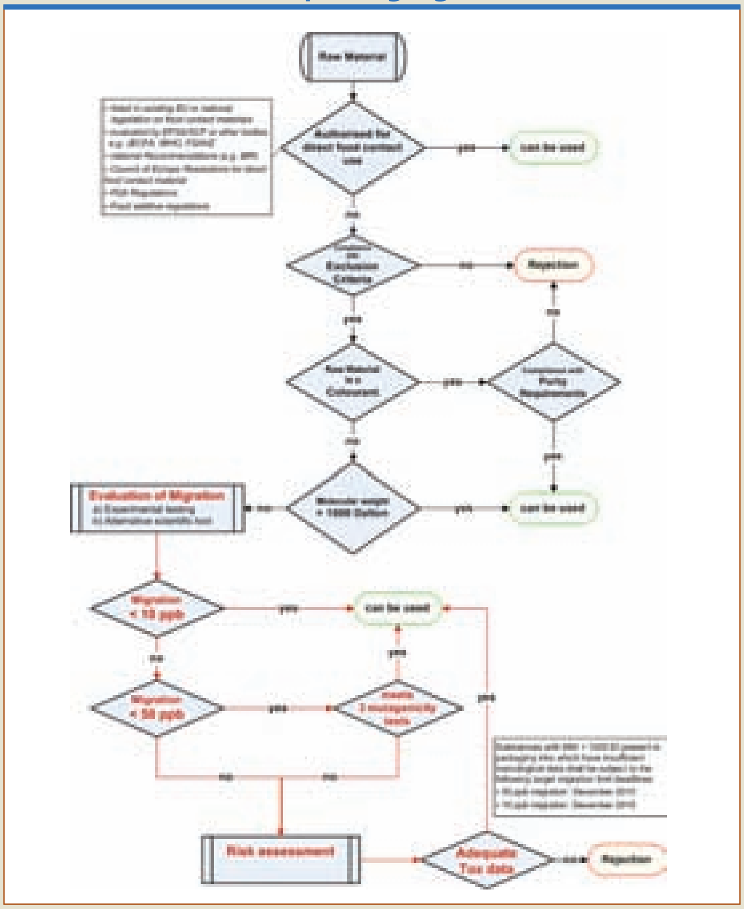
EuPIA Manufacturing Guidelines

Because of the lack of clear legal guidance on how to formulate commercially viable inks and coatings, the EuPIA has issued a "Guideline on Printing Inks" for indirect food contact.[6] 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 and 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 Carcinogenic, Mutagenic, Reprotoxic Category 1 substances and imposing other restrictions.
- The packaging inks shall be formulated and manufactured in accordance with the European Council of Producers and Importers of Paints, Printing Inks and Artists/ EuPIA "Good Manufacturing Practices for the Production of Packaging Inks"[7] formulated for use on the non-food contact surfaces of food packaging.

Figure 2

Selection scheme for packaging ink raw materials



Source: EuPIA

- 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 in Figure 1, full conformity of the final packaging can be achieved.

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 1,000 Daltons is the ultimate objective to be consistent with other food contact materials. For packaging scenarios that do not achieve this limit, it is required to either 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[8] are available.
- greater than 50 ppb, if supported by favorable toxicological data and/or evaluation done in accordance with the EFSA Guidelines.

Figure 2 provides an overview on the selection criteria.

Polymeric Photoinitiators

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

BP-1: Polymeric Benzophenone Derivative

TX-1: Polymeric Thioxanthone Derivative

AB-1: Polymeric Aminobenzoate Derivative

Migration/Odor

During the production process of the PPIs, low-molecular weight substances are removed. Therefore, PPIs are very low in odor. Combined with the ability to link into the UV-cured acrylate matrix, PPIs 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 in Tables 1 and 2 are simplified formulations for two typical applications where PPIs are suitable. Slightly reduced cure speeds are common with polymeric photoinitiators compared to conventional photoinitiator packages.

It has been found that with direct replacement of ITX by TX-1, the

FIGURE 3

The absorption spectra of BP-1, TX-1 (both 0.002% in acetonitrile) and AB-1 (0.001% in acetonitrile)

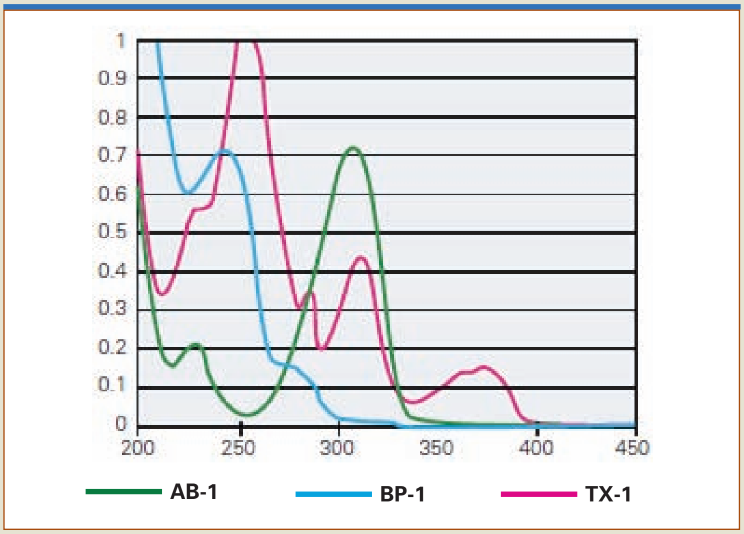
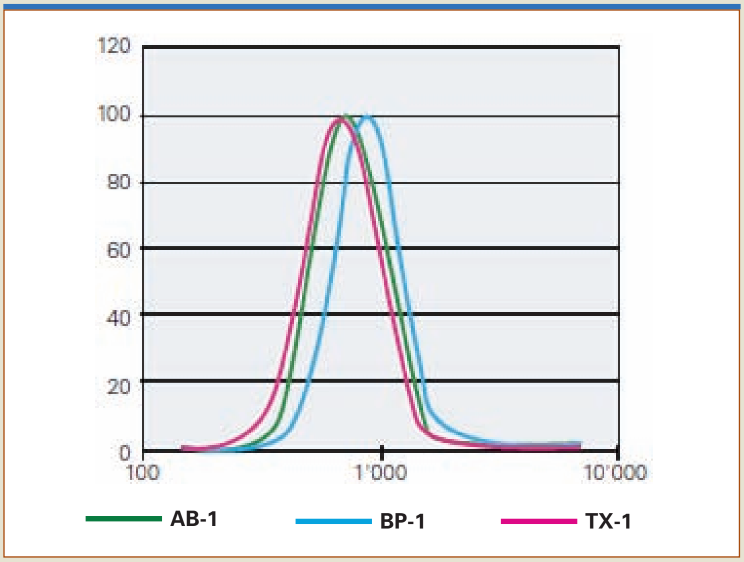


FIGURE 4

The molecular weight distributions of BP-1, TX-1 and AB-1



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 amino benzoate versus the use of straight EPD/EHA allows for the use of similar amounts of TX-1 compared to monomeric ITX while still maintaining cure speed. Also, straight benzophenone has been replaced by BP-1 in this formulation. With this step, the photoinitiators with the lowest molecular weight, highest odor and tendency to migrate have all been fully replaced by polymeric versions.

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

PPIs 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 polymeric photoinitiators 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

PPIs are a reaction product of a low-molecular weight, monomeric photoinitiator and a polymeric[9] 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 PIs is on the residual low-molecular weight photoinitiators which are present in concentrations of typically < 1 %. Other components present in PPIs with a molecular weight below 1,000 Dalton are the polymeric backbone and possibly fractions thereof. The polymer itself is of low toxicity. The toxicity of the relevant components of the polymer is described in detail in the respective IUCLID documents. They are neither mutagenic nor carcinogenic and no adverse effects on reproduction have been observed. The known No Observed Adverse Effect

TABLE 1

Flexographic ink

Product Code	%	Description
Yellow Pigment	14.5	
Modified Epoxy Acrylate	26.0	
TMP(EO)3TA	38.0	
DiTMPTA	9.0	
BP-1	6.0	Polymeric Benzophenone Derivative
TX-1	1.5	Polymeric Thioxanthone Derivative
AB-1	3.0	Polymeric Amniobenzoate Derivative
Norrish Type I Photoinitiator	1.0	
In-Can Stabilizer	1.0	
Total	**100**	
Reactivity	50	m/min @ 240W/cm
Viscosity	1’320	mPas @ 25°C

TABLE 2

Overprint varnish

Product Code	%	Description
Epoxy Acrylate	38.0	
TMP(EO)3TA	48.0	
Oligoamine	8.0	
BP-1	6.0	Polymeric Benzophenone Derivative
Reactivity	40	m/min @ 240W/cm
Viscosity	1’600	mPas @ 25°C

TABLE 3

Polymeric benzophenone derivative BP-1

Studies *	Reference	GLP	Result
Ames (Reverse mutation assay)	OECD 471	yes	Non-mutagenic
Mouse Lymphoma	OECD 476	yes	Non-mutagenic
Micro Nucleus	OECD 474	yes	Non-mutagenic (in-vivo)

* Studies were performed on constituent, low-molecular weight photoinitiator

Level (NOAEL) in repeated dose or sub-chronic toxicity studies are above 200 mg/kg. 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

Records for relevant mutagenicity studies on monomeric, un-reacted photoinitiators in PPIs allow their use for migration levels up to 50ppb. These studies have been performed under current guidelines of EFSA and EuPIA.

A conclusion drawn in an independent expert statement using quantitative structure-activity relationship (QSAR) with benzophenone led to an estimated NOAEL for a 90-day rat study in the range of 5-15mg/kg/d for the constituent monomeric PI in BP 1, indicating that the regulatory 50ppb level is far below the actual toxicological threshold of concern. The SML of 0.6mg/kg (600ppb) into food for benzophenone is another indicator of the potential feasibility of higher migration levels than 50ppb.

EFSA re-evaluated benzophenone and hydroxybenzophenone in 2009 and increased the TDI by a factor of 3. Considering this new TDI of 0.03mg/kg b.w., the SML of benzophenone and hydroxybenzophenone should consequently be set to 1.8mg/kg (1800ppb). However, the commission has not changed the SML yet.

TABLE 4

Polymeric aminobenzoate derivative AB-1

Studies *	Reference	GLP	Result
Ames (Reverse mutation assay)	OECD 471	yes	Non-mutagenic
Mouse Lymphoma	OECD 476	yes	Non-mutagenic
Micro Nucleus	OECD 474	yes	Non-mutagenic (in-vivo)

* Studies were performed on constituent, low-molecular weight photoinitiator

Based on toxicity studies performed with AB-1 and monomeric constituents, an independent expert statement[10] resulted in the following conclusion—AB-1 and its metabolites are of low toxicological concern, as they are neither mutagenic nor carcinogenic. The regulatory 50ppb level is far below the toxicological threshold of concern. The product assures the health and safety of humans according to Article 3 of the European Directive 1935/2004.

Polymeric Thioxanthone Derivative TX-1

The monomeric photoinitiator of TX-1, a thioxanthone derivative, has been toxicologically assessed by QSAR[11] with the conclusion of being non-mutagenic and non-carcinogenic. Therefore, it can be concluded that TX-1 is of low toxicological concern and that the migration level for indirect food contact of constituent low-molecular weight photoinitiator may be up to 50ppb. Considering the usage of TX-1 in printing inks with a concentration of approximately 1-3% and the low level of non-reacted, low-molecular weight photoinitiator, a worst case scenario calculation for migration is below 10ppb.

Conclusion

PPIs are scientifically evaluated products suitable for food packaging (indirect contact) that requires 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 PPIs 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 which explicitly lists PPIs on its positive list of substances that can be used.[12] PPIs assure the health and safety of humans according to Article 3 of the European Directive 1935/2004.

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