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# Low Odor/Low Extractable Energy Curable Acrylates for Food Packaging Applications

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**Introduction**

UV and EB technologies have already made significant inroads into non food applications due to the numerous advantages which they provide over other technologies (e.g. high gloss, excellent resistance properties, high printing speed, fast drying or cure times, no VOC, low system cost).
Penetration of these technologies into food packaging applications, however, is still limited to offset inks and overprint varnishes (OPVs). Only limited penetration has been achieved into the fast growing flexographic packaging ink segment. Constraints which are usually quoted as preventing the realization of the full potential available in food packaging applications are odor and taste transfer, migration of existing resins + additives, lack of a cost-effective migration testing protocol, acceptable adhesion to uncoated polyolefins which is more difficult to achieve than with solvent based technologies, and limited availability of UV equipment for wide web printing. To date resin suppliers and ink makers have mainly focused on solving odor issues. The future tightening of the food contact regulations in Europe will force them to consider impurity profiles, migration levels and manufacturing practices more thoroughly.

**EU regulations for food contact inks and OPVs**

There is no specific EU directive or regulation relating to food contact inks and OPVs. The regulatory requirements applicable to such products are limited to compliance with the article 3 of the Framework Regulation (EC1935/2004). The inks and OPVs must be manufactured in accordance with good manufacturing practices and must not transfer their constituents to foodstuffs in quantities that could "endanger human health" or bring about an unacceptable change in the composition of the food or its organoleptic characteristics.

In September 2005, a resolution on packaging inks applied to the non-food contact surface of food packaging materials and articles intended to come into contact with foodstuffs (“Ink Resolution”) has been voted by the Council of Europe (CoE) Council of Ministers.[1] According to this resolution, inks should not contain any product known as carcinogenic, mutagenic or reprotoxic (CMR) EU category 1 or 2, or any CMR EU category 3 if the latter is not evaluated by the European Food Safety Authority (EFSA),[2] and may only contain constituents that are contained in an inventory list. Any component being evaluated by the EFSA should lead to migration levels below a specific migration limit set from its toxicological profile. All other components should migrate into the food at levels lower than 10 ppb if no toxicological data is available, lower than 50 ppb with favorable mutagenicity results.

Although still vehemently criticized by the industry as not being based on real-life scenarios of consumers’ exposure to substances, the Ink Resolution will act as a precursor for EU binding laws. A EU Regulation (EC 2023/2006, also known as the “GMP Regulation”) ruling good manufacturing practices for materials and articles to come into contact with food has already been voted and will apply as from August 1, 2008.[3] It provides general principles for all food contact materials and detailed rules for printing inks.

**Meeting the new regulatory constraints**

Solutions used so far by ink makers for food packaging applications included the deodorized resins. These resins have application properties as good as standard grades, lower residual odor, reduced residual acrylic acid (typically <200 ppm) and residual solvent (typically <10 ppm) contents. Acknowledging that the deodorized resins attributes may no longer meet its customers' needs in food packaging applications in the near future and so enable further adoption of UV and EB curing technologies for food packaging print, Cytec has proactively developed *L*ow *E*xtractable/Low *O*dor versions of the most commonly used resins in energy-cured packaging inks and OPVs. Besides having print properties at least as good as the standard resin grades, those resins show attributes in line with the Ink Resolution's requirements:

- Low residual odor after curing.
- Low taste transfer.
- No known resin component being CMR EU category 1 or 2, or CMR EU category 3 not evaluated by the EFSA.
- Worst case migration of EFSA listed resin components being an order of magnitude lower than reported specific migration limits.
- Migration levels that commensurate with thresholds of no toxicological concern.

In order to meet this challenging product profile, new raw materials and catalysts have been developed with raw material suppliers, inhibitors with food contact clearance have also been selected. The Low Extractable/low Odor resins design process includes a master strategy for minimizing the transfer of acrylates from the packaging matrix. This is based on increasing the size and cross-link density of the resin components. This strategy permits the migration of acrylate resins into food, under normal conditions at levels below 10 parts per billion (ppb), a generally accepted threshold for toxicologies. In cases such as when the UV or electron beam source accidentally malfunctions, printing conditions may lead to slightly higher migration levels. In order to address this risk, the non-toxic nature of each Low Extractable/low Odor resin has been demonstrated through appropriate mutagenicity tests, which allows a migration up to 50 ppb. Any unfavorable test results trigger an internal in-depth root cause analysis in our development process and a modification of the composition of the resin to remove the source of mutagenicity.

**Migration**

The migration properties of the Low Extractable/low Odor resins are assessed in two steps. For the minor components of the resin listed by the EFSA (unreacted raw materials, additives, processing solvents or by-products), a worst case calculation is performed. It is assumed that the formulation is only made up of the acrylate, 6 $dm^2$ packaging is in contact with 1 liter food, the packaging is fully covered with a Y $g/m^2$ ink layer and the acrylate migrates fully from the print layer to the food (100% migration). A worst case migration in ppb can then be calculated as:
0.06 x Y x content of acrylate (ppm).
The Low Extractable/Low Odor resins are designed so that this number is an order of magnitude lower than the Specific Migration Limits found in the EU Synoptic Document.[2]

For the minor components (e.g. catalyst) and major components (multifunctional acrylates) of the resins *not* listed by the EFSA, the migration properties are experimentally determined using a single-side extraction cells filled with water as an aqueous food stimulant or ethanol 95% as a fatty food simulant. Analysis of the acrylates extracted by the simulant is performed using gas chromatography-mass spectrometry (GC-MS) and liquid chromatography-mass spectrometry (LC-MS) analytical techniques. If LC-MS and GC-MS spectra showed a similar pattern of peaks, GC-MS was our method of choice as it is easier and faster to operate. In this case, pre-concentration of the simulant through solid phase extraction (SPE, for water) or vacuum evaporation (for ethanol 95%) is needed.

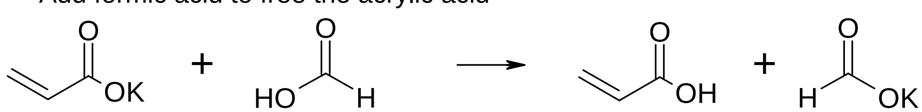
Acrylates are multicomponent products for which no standards are available. The migration of each acrylate component is generally quantified by plotting a calibration curve for each major component of the acrylate. The peak for each component is then identified in the chromatogram. The amount of each component is proportional to the area under the peak. This procedure makes three major assumptions:

1. The proportions of each component are independent of migration level. At the ppb level, this is often no longer the case.
2. Some components which are hardly detectable in the resin may be preferentially extracted and so become more visible in the chromatograms.
3. By summing the contributions through area percentages, one further assumes that the response of the MS detector is the same for all components. Response factors determined for ethoxylated TMP triacrylates (TMP(EO)$_X$TA) have shown that response for TMP(EO)$_5$TA is almost one fifth of that for TMPTA.

As the above method is time consuming and based on shaky assumptions, a simplified method for the quantification of acrylates at the ppb level has been developed. This quantification method is more cost effective and at least as accurate as current methods. It uses only mainstream gas chromatography (GC) equipment and is sensitive enough to quantify the acrylate at the ppb level. In this new method the complex mixture of acrylated extracts is converted to acrylic acid, this can be easily quantified by GC. The concentration of the migrating acrylate can be calculated from acrylic acid levels through the average acrylate equivalent weight. This has been validated for water and ethanol 95% as simulant, this method involves the following steps:

- Hydrolyze the acrylated extracts in the simulant with KOH to generate the potassium salt of acrylic acid,


- Concentrate by evaporation. Losses can easily be avoided since the potassium salts are not volatile.
- Add formic acid to free the acrylic acid




- Determine the acrylic acid concentration ($C_{AA}$) in the stimulant in ppb.
- For a single acrylate formulation, the acrylate concentration $C_{A,S}$ in the simulant can then be

calculated from the resin's average acrylate equivalent weight $\overline{N}_w$ (g/eq): $C_{A,S}$ (ppb) = $C_{AA}/72.1 \times \overline{N}_w$. For a formulation containing different acrylates, a worst case concentration can be calculated, taking the highest average acrylate equivalent weight (g/eq) of all the resins in the formulations.

**Good Manufacturing Practices**

Except for the so-called "starting substances", the GMP Regulation calls for taking the following measures at all stages of the manufacture of the food contact materials:

- Secure traceability of materials
- Select raw materials complying with pre-established specifications
- Document all the operations, specifications and product compositions using pre-established instructions and procedures

Being considered as reaction products obtained from "starting substances", the Low Extractable/Low Odor resins will fall under the scope of the Regulation and should thus be subject to a stricter quality control process than the standard grades:

- Raw materials qualities suitable for food contact are selected. Food contact specifications (e.g. special purity criteria) are set up and documented. Traceability is requested at the supplier site.
- Specific rules are followed for the manufacturing of the Low Extractable/low Odor resins A specific layout is adopted for the production log sheets. Any deviation from the instructions, recipe or process change is reported to the Product Stewardship and Regulatory Affairs department, which then re-assesses compliance. Batch to batch cross contamination is avoided by optimizing the production sequence and/or by producing in campaigns and/or cleaning reactor and piping before production. Internal specifications are set and documented on potential contaminants.
- Contamination of finished products during storage and transport is avoided by delivering the Low Extractable/low Odor resins in new drums.

**Snapshot of the current Low Extractable/Low Odor resins range**

Following the approach detailed above, eight Low Extractable/Low Odor resins resins have been developed so far:

- A trifunctional acrylate diluent compatible with many acrylated resins having performance characteristics similar to TMPEOTA
- A low viscosity tetrafunctional polyether acrylate
- A low viscosity amine-modified polyether triacrylate
- A medium viscosity amine-modified polyether tetraacrylate
- A low viscosity amine-modified polyether tetraacrylate
- An undiluted bisphenol A epoxy diacrylate specifically developed for use in conjunction with the above mentioned resins
- A low viscosity epoxy acrylate
- An ethoxylated bisphenol A derivative diacrylate

A polyester acrylate providing outstanding lithographic behavior and pigment wetting is in preparation. This will allow ink makers to fully formulate their inks and varnishes using Low Extractable/Low Odor products.

**Conclusions/Perspectives**

Cytec is developing a new range of Low Extractable/Low Odor resins specifically designed and manufactured for indirect food contact applications. The different chemistries used in the new Low Extractable/Low Odor resins range give a broad performance profile.
The first eight Low Extractable/Low Odor resins are commercially available, others are being developed. These products will help ink makers to formulate inks and varnishes meeting the most stringent future legal requirements. In order to show compliance with the new rules in a cost-effective way, Cytec has developed a simplified method to quantify the migration of acrylates at the ppb level.

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**References**

[1] The CoE Resolution ResAP(2005) is available online: http://www.coe.int/T/E/Social_Cohesion/soc-sp/Public_Health/Food_contact/Resolution%20AP-2005-2%20ON%20PACKAGING%20INKS.asp.

[2] All the products evaluated by the EFSA and their SML can be found in the Synoptic Document available on http://cpf.jrc.it/webpack.
[3] Available on http://eur-lex.europa.eu/LexUriServ/site/en/oj/2006/l_384/l_38420061229en00750078.pdf.