Low Extractable/Low Odor Acrylates for Food Packaging Applications

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Abstract

Energy-curing technologies have recently emerged as commonly used technologies in food packaging inks and overprint varnishes. This communication will present new low odor/low extractable acrylates. These new raw materials are able to meet when formulated, the stringest migration and impurity requirements proposed in new legislation. The development of an analytical testing protocol streamlined for the study of the migration of acrylates at the part-per-billion level is also discussed.

Introduction

Due to the numerous advantages (high gloss, excellent resistance properties, high printing speed and immediate further processing, no VOC, low system cost) they provide over other technologies, the UV and EB technologies have already made significant inroads into non food applications. Today penetration of these technologies into food applications is however still limited to offset inks and overprint varnishes (OPVs). Very limited has been achieved yet for example in the fast growing flexographic packaging ink segment. Today constraints usually mentioned to prevent unlocking the full potential provided by food applications are:

- Potential for odor and taste transfer.
- Potential for migration of existing raw materials.
- Lack of a cost-effective migration testing protocol.
- Acceptable adhesion on uncoated polyolefins more difficult to achieve than with other technologies.
- Limited availability of UV equipment for wide web printing.

Raw materials suppliers and ink makers have up to now mainly focused on solving odor issues. The upcoming tightening of the food contact regulations, especially in Europe, will oblige them to consider more thoroughly impurity profiles and migration levels.

A Global Look at Regulations for Food Contact Inks and OPVs

US

Any packaging ink component reasonably expected to become a component of the food that is not generally recognized as safe (GRAS) or covered by a prior Food Additive Petition, needs FDA

clearance. The fastest and most cost effective way for a component to be approved by the FDA is to submit a Food Contact Notification (FCN).[1] If the FDA does not object to the material's use within 3 months, the component is approved as specified in the FCN. Besides a full physico-chemical description of the component and an environmental assessment of the impact of its production, use and disposal, the FCN dossier must contain data showing the quantity expected to become part of the food as well as anticipated cumulative estimated daily intake (CEDI). The CEDI is the component's total exposure from all sources, not just from the specific FCN application use. Whenever CEDI is estimated to be higher than 0.5 part-per-billion (ppb), the following toxicological data should also be provided:

- 2 favorable mutagenicity results if CEDI < 50 ppb
- 3 favorable mutagenicity results and 2 subchronic oral studies if CEDI < 1000 ppb

Regardless of FDA-compliance, low enough odor and taste transfer should of course always be guaranteed to not adulterate organoleptic properties of the food.

The FDA Food Contact Notification procedure and its exposure-based approach make the penetration of energy-curing materials relatively easy in the US. Getting clearance in Europe is unfortunately a much less straightforward process.

Europe

To this date, there are 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):

- These inks and OPVs must be manufactured in accordance with good manufacturing practices,
- They 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, *i.e.,* they must not adulterate food.

For food contact materials that are not yet the subject of specific EU law, work toward the elaboration of common rules in Europe is generally being made in the forum of the Council of Europe (CoE), a pan-European political organization independent from the EU.[2] The CoE's Committee of Experts on Materials Coming into Contact with Food is deemed to have the necessary expertise to develop guidelines, in the form of "Resolutions". Although Resolutions adopted by the CoE Council of Ministers are not legally binding, CoE members may decide to implement them in their national laws. 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 (aka "Ink Resolution") has been voted by the CoE Council of Ministers,[3] after nearly 15 years of difficult negotiations between the different stakeholders.

The main provisions included in this Ink Resolution may be summarized as follows

- Inks should not content 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).[4]

- 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 3 favorable mutagenicity results.

Although still vehemently criticized by the ink manufacturers and the raw materials suppliers as not being based on real-life scenarios of consumers' exposure to substances, the Ink Resolution will act as a precursor for a EU binding law. As such, it poses unprecedented challenges to the ink industry with regards to impurity profiles and migration levels. As packaging manufacturers often require a global solution, these challenges will have to be met by any ink manufacturer with customers active on the European market.

From DEO to LEO

Solutions used up to now by ink makers for food packaging applications included the "DEO" (for *DEO*dorized) resins. These resins show application properties as good as regular grades, a lower residual odor, reduced residual acrylic acid (typically <200 ppm) and residual solvent (typically <10 ppm) contents. Acknowleding that the DEO attributes might no longer meet in a near future its customers' needs in food packaging applications and so enable further adoption of UV and EB curing technologies for food packaging printing, Cytec has proactively developed *L*ow *E*xtractable/low *O*dor ("LEO") resins to the most commonly used products in energy-cured packaging inks and OPVs.[5] Besides good printability properties, the LEO resins show attributes in line with the Ink Resolution's requirements:

- Low residual odor after curing.
- Low taste transfer.
- No 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 order of magnitude lower reported specific migration limits.
- Low migration of the acrylate in inks and OPVs.

In order to meet this challenging product profile, new raw materials and catalysts have been developed with upstream manufacturers and inhibitors with food contact clearance in the US and in the EU have been selected. Manufacturing processes and production sequences have been carefully designed so as to avoid batch-to-batch cross contamination by unwanted impurities. The absence of carryovers is checked on every industrial batch.

Last but not least, appropriate sensory and migration assessment tools to show compliance with the product profile have been developed.

Sensory analyses

Discriminatory off-odour and taste transfer tests are run on aluminum printed foils, observing well-established international norms (ISO3972, ISO ISO5496, ISO6658, ISO8586-1, ISO8586-2 and ISO8587). While preliminary tests are usually run internally recruited assessors, final assessments are

based on tests done by an external ISO/IEC 17025 accredited lab. Large enough panels (up to 24 assessors having been selected and trained) are used to ensure statistically meaningful discrimination. Assessors are asked to place on an unstructured scale the perceived odor or taste intensity of the samples (see figure 1). Intensities are then analyzed through well-established statistical methods.[6] Whether the mean intensities of each sample are significantely different is determined through an analysis of the variance (ANOVA). If significant difference is evidenced, a Fisher's Least Significant Difference (LSD) test is run to determine the smallest statistically significant observable difference for a single repeat examination that would represent a true change, *i.e.*, change over and above the inherent variability of the measurement. From the LSD, the samples can be ranked in classes showing statistically different odor or taste intensities.

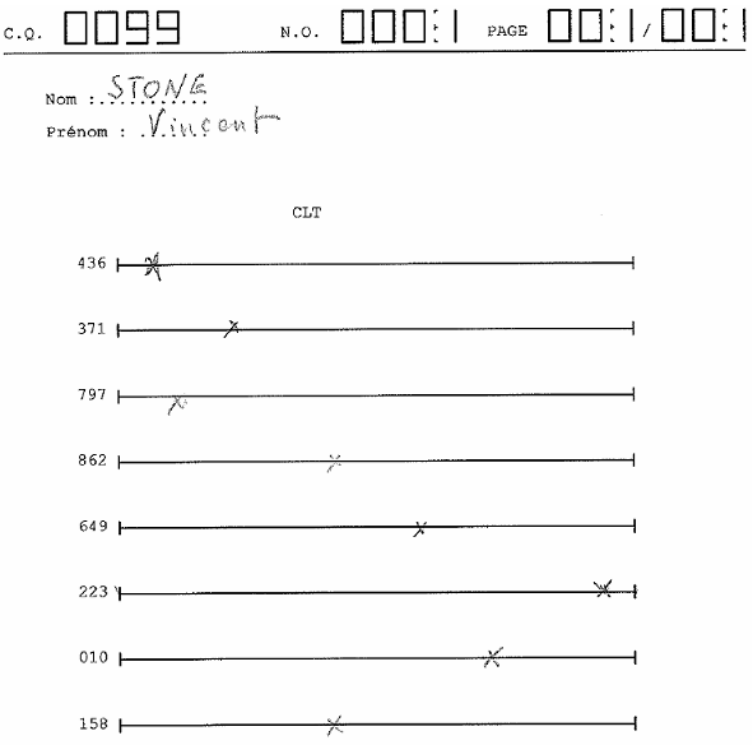


Figure 1: Sample questionnaire for the sensory discriminatory tests (one unstructured scale per sample).

Migration

Migration properties of the LEO resins are assessed in two steps. For the components of the acrylate which have been evaluated by the EFSA, a worst case calculation is performed with the following assumptions:

- the formulation is only made up of the acrylate into consideration
- 6 dm^2 packaging is in contact with 1 l food
- the packaging is printed with a y g/m^2 ink layer
- the component is fully migrating from the print layer to the food (100% migration)

Worst case migration from a print containing this component can then be computed as

Migration (ppb) = 0.06 x y x Component content in acrylate (ppm)

Maximum content is set such as this number is order of magnitude lower than the Specific Migration Limits found in the EU Synoptic Document.[4]

The migration of the unlisted components is experimentally studied using single-side extraction cells filled with an appropriate food simulant similar as described elsewhere.[7] Water (EU simulant A) and ethanol 95% as simulant for fatty foods are used. Analysis of the acrylates extracted by the simulant is performed using GC-MS *and* LC-MS. The shortcomings of GC-MS compared to LC-MS have been pinpointed by A. Lin *et al.* [8] LC-MS can detect volatile as well as non volatile compound, and thanks to the larger sample amounts injected, can be usually performed without a concentration step. On the other hand, GC-MS does not require setting time-consuming separation conditions as LC-MS, and, when operated in the Electron Ionization mode, allow an easy identification of the extracts, a crucial information when structure should be optimized for low migration. Anytime LC-MS and GC-MS spectra showed a similar pattern of peaks, GC-MS remained 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.

Developing lean quantification methods able to demonstrate compliance at ppb migration levels is another challenge to meet.

A Streamlined Migration Quantification Method

Acrylates are complex multicomponent products for which no standard are available. The quantification of the migration of each acrylate of the formulation goes generally through the following steps:

- For each major component i of the acrylate ($1<i<n$), plot a calibration curve peak area ratio A_i / A_{IS} vs. the total acrylate concentration normalized with the internal standard concentration C_A/C_{IS}.
- Identify in the forest of peaks displayed by the chromatograms of the extracts, the n peak originating from the acrylate under consideration.
- Calculate the acrylate concentration $C_{A,S}$ in the simulant by summing the n contributions

$$C_{A,S}\ (ppb) = \Sigma_i\ (\%A_i \times C_A/C_{IS}\ (A_i / A_{IS}) \times C_{IS}) \text{ with } \%A_i = A_i / (A_1+A_2+...+A_n)$$

This procedure makes two major hypotheses that are usually not observed:

- Whatever the migration level, the composition of the extracts will be the same. At the ppb level, this will often no longer be true. Some hardly detectable components in the resin may preferentially be extracted and so become predominant in the chromatograms of the extracts, making a calibration on the main components of the resin questionable.
- By summing the n contributions through area percentages, one further assumes that all the components response the same towards the MS detector (same response factors): $\%A_i = \%w_i$. In order to check this hypothesis, GC-MS response factors $R_{X,\ GC\text{-}MS}$ on pure (>90%) fractions (obtained through preparative HPLC) of ethoxylated TMP triacrylates ($TMP(EO)_XTA$) with

increasing ethoxylation degree X have been determined (Figure 2). $TMP(EO)_5TA$ responds nearly 5 times less than TMPTA. $TMP(EO)_6TA$ cannot be detected ($R_{X,\,GC\text{-}MS}$ is infinite).

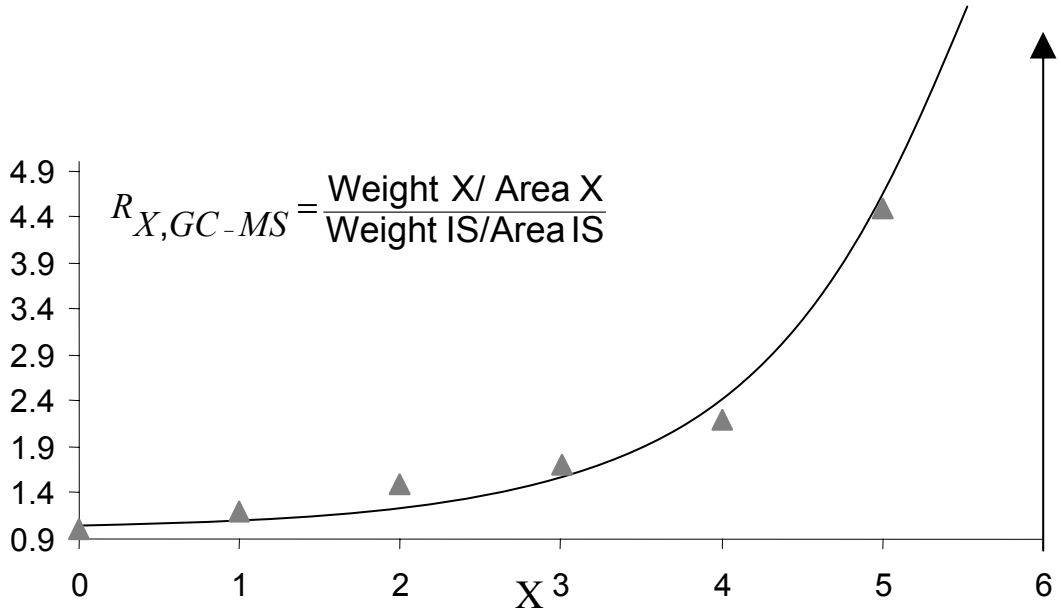


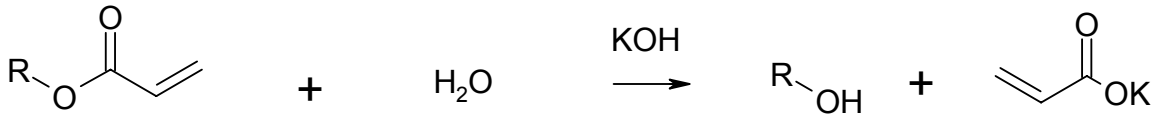
Figure 2: GC-MS Response Factors $R_{X,\,GC\text{-}MS}$ vs. ethoxylation degree X for $TMP(EO)_xTA$.

As the above method is tedious and based on shaky assumptions, there is a clear need for a streamlined method for the quantification of acrylates at the ppb level, at least for screening purposes. This quantification method should be

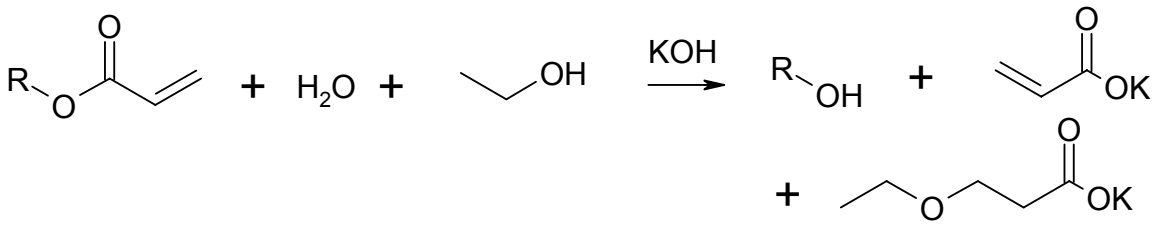
- Faster and at least as accurate as current methods.
- Using mainstream GC equipment only.
- Sensitive enough to quantify ppb's acrylates.
- Giving at least a worst case absolute figure on acrylate migration.
- More cost effective.

In our new method, the complex mixture of acrylated extracts is converted to acrylic acid, being itself easily quantified by gas chromatography. The concentration in migrating acrylate can be found back from acrylic acid through the average acrylate equivalent weight. This method has been validated for water as simulant and has been estimated to be able to save 40% of man hours to quantify the migration. Tests with ethanol aqueous solutions simulant are in progress. It involves the following steps:

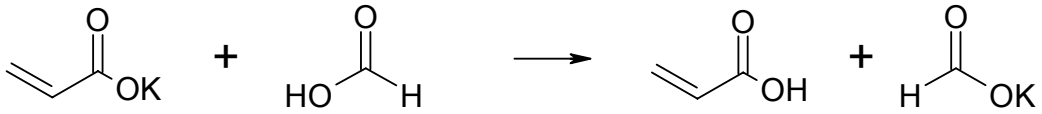
- Hydrolyze the acrylated extracts in the simulant with KOH in a tight-closed bottle, in presence of 4-methyl valeric acid (internal standard) and methyl hydroquinone (polymerization inhibitor). While with water as simulant, only the potassium salt of acrylic acid is generated,

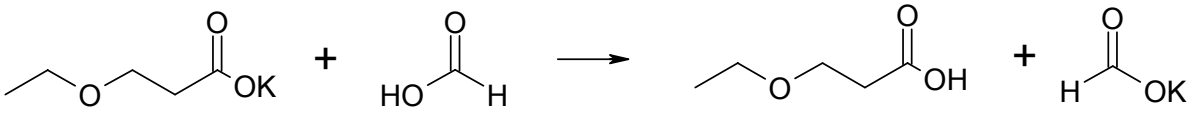


with aqueous solutions of ethanol, the potassium potassium salt of 3-ethoxyethanoic acid is also generated



- Concentrate by evaporation. Losses can be easily avoided.since the potassium salts are not volatile.
- Add formic acid to free up acrylic acid and, when aqueous solutions of ethanol are used, 3-ethoxyethanoic acid





- Determine the acrylic acid (C_{AA}) and 3-ethoxyethanoic acid (C_{EEA}) concentrations in ppb in the simulant. Pure standards are commercially available for both acids. Due to specific adsorption by active site within the liner and columns, traces of underivatized organic acids are notoriously difficult to quantify by gas chromatography. The presence of formic acid is however known to lead to good peak shapes and reliable quantification,[9] due to the formic acid taking up preferentially the active sites of the chromatographic system.
- For a single acrylate formulation, the acrylate concentration $C_{A,S}$ in the simulant can then be computed from the resin's average acrylate equivalent weight $\overline{N}_w$ (g/eq):

$$C_{A,S}\,(\text{ppb}) = (C_{AA}/72.1 + C_{EEA}\ /132.16)\ \text{x}\ \overline{N}_w$$

For a formulation containing different acrylates, a worst case concentration can be computed, taking the highest average acrylate equivalent weight (g/eq) of all the resins in formulations.

Case Study

Ebecryl™81 (AA) is a low viscosity amine-modified polyether acrylate commonly used in OPV for primary food packaging, showing very good reactivity, very good solvent and water resistance and good substrate wetting. Its impurity profile and typical migration levels are however not compliant with the Ink Resolution. A LEO alternative (LEO AA) has been developed to help our customers to meet the new requirements.

Printability

It has first been checked that LEO AA shows printability properties at least as good as AA in the below OPV formulations

AA	96.5	
LEO AA		96.5
para-phenyl benzophenone	3.5	3.5
Silicone Levelling Agent	0.3	0.3
Cure speed (m/min)	**30**	**40**
Viscosity C/P (mPa.s)	95	105

Varnishes made from AA and its LEO alternative show similar cure speeds and viscosities. Solvent and water resistance as well as substrate wetting has also been checked to be at least as good with the LEO resin.

Off-odor

The intensity of the off-odor emitted from the above UV-cured varnishes was then blindly evaluated by a panel of 24 selected assessors. The theoretically odorless bare aluminum substrate was added as reference. Figure 3 gathers the mean odor intensities for the three samples. An ANOVA test showed that these means were statistically significant with a confidence level of 99.9%. A Fisher's LSD test allowed to compute the smallest statistically significant observable difference to be 1.14 at confidence level of 95%. As their mean intensities differ by less than the LSD, the LEO AA-based varnish (mean intensity=1.81) and the reference (mean intensity=0.75) cannot be distinguished and has thus been gathered in a same "low odor" class ("class#1"). Mean intensity for the AA-based varnish (3.19) is high enough to be stated as different than the other two samples and be put in a separate "high odor" class ("class#2").

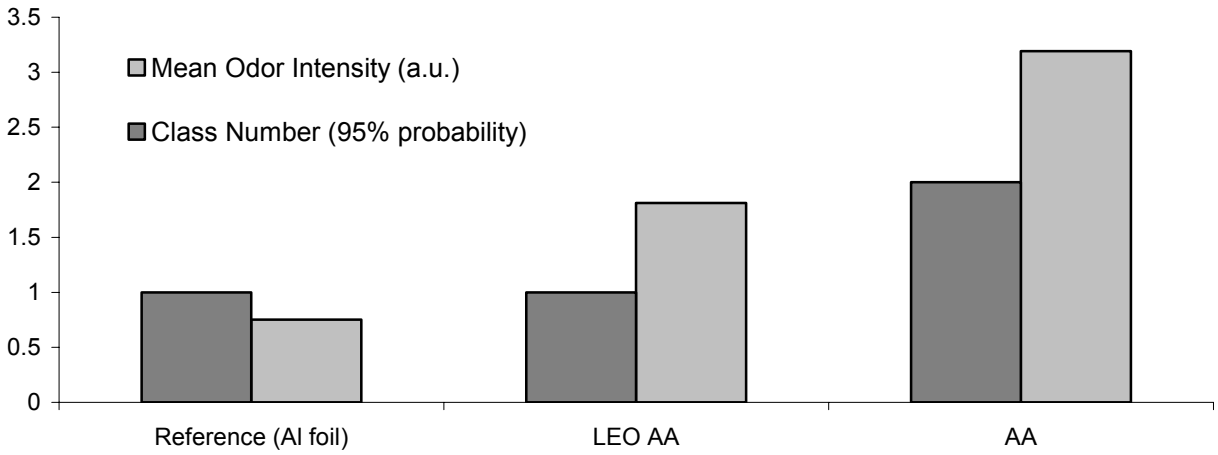


Figure 3: Mean odor intensity and odor class number as derived from an off-odor test performed by 24 trained assessors.

Migration

Migrating potentials in water of LEO AA and AA have been compared in the above-described varnishes cured at the cure speed of the slowest system (AA, 30 m/s). 2 dm^2 of the cured varnishes were put in *direct* contact with 200 ml of water for 3 days at ambient temperature. These exposure conditions are worst case conditions for water food simulants. Even in such conditions, a SPE pre-concentration step was found needed to detect something.

After having checked that no additional compound was detected by LC-MS and that no losses occurred during preconcentration, GC-MS spectra were analyzed so as to identify the different peaks. The left-hand part of Figure 4 show the GC-MS chromatograms of the extracts from the LEO AA and AA varnishes.

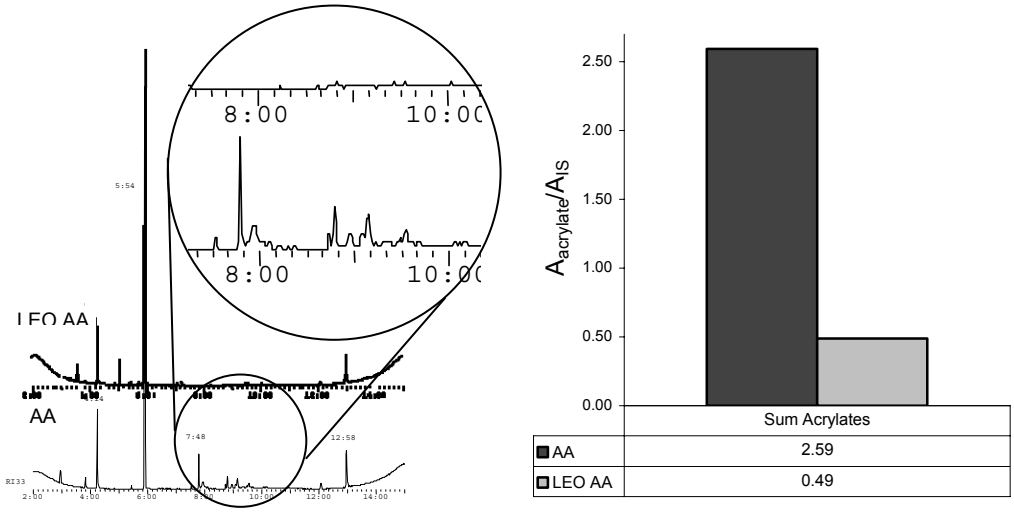


Figure 4: GC-MS chromatograms of the extracts (left). Total normalized areas of the peaks arising from acrylated species (right).

As an indicator of the migration potential, the total area ($A_{acrylate}$) of all peaks containing fragments characteristic to acrylates have then been computed from both chromatograms and normalized by the area of the internal standard peak (A_{IS}). The righ-hand part of figure 4 shows that this ratio can be reduced by a factor higher than 5 using the LEO alternative. A variance of less than 20% has been found doing the test on 4 printed samples for each resins.

Snapshot of a fast expanding range

Following the approach detailed above, seven LEO resins have been developed so far:

- A trifunctional acrylate diluent compatible with many acrylated resins having performance characteristics similar to TMPEOTA but with significantly improved odor-release and migration properties.
- A low viscosity amine-modified polyether acrylate.[5]
- A medium viscosity amine-modified polyether tetraacrylate.[5]
- An undiluted bisphenol A epoxy diacrylate specifically developed for use in conjunction with the LEO resins.
- A low viscosity epoxy acrylate.

Other resins allowing ink makers to fully formulate litho and flexo inks and varnishes with LEO products are in preparation.

Conclusions

Cytec is developing a whole new range of LEO resins specifically designed for indirect food contact applications. The new LEO range combines depth by the numerous attributes each product shares and breadth by the number of different chemistries available. The first seven LEO resins are available, others are about to be commercialized or under development. A full LEO range is targeted for 2006. These products will help ink makers to formulate inks and varnishes meeting the most stringent legal requirements ahead. In order to show compliance with the new rules in a cost-effective way, Cytec has developed a streamlined method to quantify the migration of acrylates at the ppb level .

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