

# Analytical methodology to evaluate potential migration in coatings and inks

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## Introduction

The use of UV and EB curing inks is growing in the European Graphic Arts market. Not only do they give excellent print quality but they are also solvent free, a huge benefit in this environmentally driven world. One particular application where UV and EB curing inks continue to develop is in the prestigious food packaging market. In order to sustain the growth the subject of low migratable species within UV and EB curing inks has had to be addressed. This paper outlines progress within the analytical aspects of low migratable UV and EB curing inks.

For Europe this is based on two driving forces :

- the voluntary agreement within the Printing Inks manufacturers group (EuPIA) who have published a guideline [1] to comply with the Framework Regulation to food packaging,
- the ever increasing consumer demands for 'safer' products

## UV and EB cured Printing Inks

UV/EB printing inks are complex mixture of several components including pigments, additives, photoinitiators, and resins. Each component has to be considered individually since each could be a source of migration.

There have been many studies on the potential migrants which have concluded that in UV systems, the photoinitiator has the most potential to migrate [2]. Some benefits have been seen with development of polymeric photoinitiators which can be shown to reduce the level of migratables [3].

However, there is still work to be done on the acrylate resin components - the monomers and oligomers which compose the main part of the ink formulation (60 – 70%).

This paper concentrates only on the acrylate constituents as potential migrants. It describes the specific analytical methodology we implemented to understand the migration behaviour of acrylated species and the manner the acrylate resins can be improved to fulfil the food packaging industry requirements. This approach is based on :

- a detailed analysis of the monomers since the low molecular weight components present in the monomers are suspected to have a high migration potential,
- the qualitative and quantitative characterisation of the "total extractables" from model varnishes in a strong solvent or in food simulants.

## Regulations and directives

There are some European legislative instruments which relate to the use of materials and articles in contact with food. However none are specific to Printing Inks and indirect food contact. Therefore guidelines on this topic have to be drawn from a combination of legislative documents [4].

The EC 1935/2004 regulation, article 3 indicate that printed materials and articles intended to come into contact with foodstuffs, should not, in their finished state and under normal and foreseeable conditions of use, transfer their constituents to foodstuffs in quantities which could :

- endanger human health
- bring about an unacceptable change in the composition of the food,
- bring about a deterioration in the organoleptic characteristics thereof.

The EC 2023/2006 regulation establishes Good Manufacturing Practice GMP for materials and articles meant to come into contact with food stuff. In particular Point 7 "for printing inks applied to the non-food contact side of a material or article GMP should in particular ensure that substances are not transferred into food by set off or transfer through the substrate", however if there's a transfer, it must be in concentration by which art.3 CE 1935/2004 is still satisfied.

The main specific directive, 2002/72/EC relates to plastic materials and articles intended to come into contact with food. It lays down an overall migration limit of 60mg/kg of food or 10 mg/dm<sup>2</sup> of surface area. Specific migration limits are set for some individual substances too.

Although the directive contains a list of monomers, substances and additives allowed for use in the manufacture of plastic materials for direct food contact, substances used only in the manufacture of packaging inks applied to the non-food contact surface of food packaging are not listed and thus packaging inks are not under the scope of this directive. And yet, ink components may contribute to migration and must be included in the determination of the overall migration set in the Plastic Directive 2002/72/EC.

For these reasons the EuPIA (European Printing Ink Association) developed a Guideline which gives detailed recommendations to formulate printing inks used to the non-food contact surface of food packaging in order to enable the printed packaging in its finished state to achieve legal requirements. These recommendations are in line with the Resolution ResAP(2005)2 adopted by the CoE Council of Ministers on packaging inks applied to the non-food contact surface of food packaging. According to this guideline, ink raw materials which meet one of the following exclusion criteria are excluded :

- carcinogenic, mutagenic and reprotoxic (CMR) substances categories 1 and 2 of the Dangerous Substances Directive 67/548/EEC. Some category 3 substances will only be used under specified conditions depending on the evaluation done by the European Food Safety Authority (EFSA) or if the migration study confirm a migration level below 10ppb
- substances classified as toxic and very toxic
- colorants based on Sb, As, Cd, Cr (VI), Pb, Hg, Se
- all substances listed in Directive 67/769/EC (relating to the restrictions on the marketing and use of certain dangerous substances and preparations) and its amendments.

Existing materials used for printing inks are listed. This list is used by all ink makers. The EuPIA guideline define their "acceptable use" depending on their specific migration. Any component evaluated by the EFSA should have a specific migration level below a specific migration limit set from its toxicological data. For non-evaluated substances, the level of migration will not exceed :

- 10 ppb if no toxicological data is available,
- 50 ppb if negative mutagenicity tests are obtained according to EFSA guideline [5].

EuPIA guideline mention new materials too. They will need to be evaluated for toxicology and migration potential in the same manner before use.

In addition of these regulations and guidelines, Food Packaging industry set a high level of quality standards for low migratable packaging. It has very tight approval procedures and are reviewing continually the list of substances which should not be present in their ink systems (or at a specified very low level).

### **Migration tests**

Transfer of printing ink components from a packaging material into food can take place either directly as migration through the substrate or as set-off migration via contact to the reverse side in the reel or stack or by gas phase transfer.

In principle, testing for compliance with the EU regulations relating to plastic materials involves to carrying out specific and overall migration using different food simulants and test conditions (time, temperature...) specified in EU Directive 82/711/EEC and its amendments and Directive 85/572/EEC and its amendments. The experimental determination of migration [6, 7] is often a complex analytical task which requires a lot of work, time, expertise and costs. Furthermore, there are no specific international standards for packaging inks dealing with determination of migration of ink components. However, it is possible to use extraction tests in place of migration tests if the results obtained using these tests are at least equal to those obtained by migration testing using the conventional EU tests. So a method based on a total extraction test using a strong solvent is usually carried out. The results obtained from this extraction test are used to calculate a maximum possible migration. In this so called "worst case calculation", it is assumed that migration of a substance into the food is 100%. The amount of the actual substance in the print or in the package or article must be either known or

determined by exhaustive extraction. The maximum possible migration M is then calculated by the formula :

$$M \text{ (ppb)} = A \times W \times C \quad \text{equation (1)}$$

A in m<sup>2</sup> is the area of package in contact with 1kg food. This is normally 0.06 m<sup>2</sup> but could be adapted to specific configuration.

W is the ink weight (g/m<sup>2</sup>) on the surface of the printed packaging assuming the packaging is fully covered by an ink layer.

C is the concentration of the substance in the print in ppm.

### **Evaluation of the migration of acrylated constituents**

When migration involves diffusion of small molecules (< 1000 Dalton molecular mass), the resins which make up for the main part of the UV/EB printing inks and more specifically acrylate components such as acrylated monomers and oligomers may contain possible migrants.

As resin manufacturer, CRAY VALLEY - SARTOMER have a constant objective to prevent and anticipate migration coming from our products.

Although resin manufacturers can not fully control the ink formulation, printing and curing conditions, it can leverage the potential migrants in the final printed ink coming from the acrylated components by controlling the raw material (and specifically its by-products), the level of subacrylated products and by-products in the acrylate, the process to avoid any cross-contaminant during the acrylate manufacturing.

These controls involve the development of different analytical techniques to be able to characterize acrylates from the raw material to the final resin and its behaviour during curing. Because the main monomers used for inks are normally acrylated ethoxylated or propoxylated polyols, they are more subjected to migration as they contain small molecular weight components.

It is the reason we focus our analytical approach to the analysis of this monomer part.

The use and the developments of different techniques are necessary to follow its "life" from the selection of the starting alcohol to the printed ink, going through the acrylation process and the formulation.

#### Alcohol analysis

The quality of monomers such as ethoxylated trimethylol propane triacrylate (TMP(EO)<sub>n</sub>TA) depend on the quality of the starting polyol. It is well known that such product may contain by-products with low molecular weight and/or with a low functionality : trimethylolpropane, ethylene glycol, di-, tri-ethylene glycol (respectively TMPOH, EG, DEG, TEG). These components after acrylation have a high potential of migration (TMPTA, EGDA, DEGDA, TEGDA). It is important to select the alcohol with the lower level of these by-products.

The preferred analytical technique to quantify these by-products in the raw material is the gas chromatography / Flam Ionisation Detection (GC/FID) which gives a good resolution of the low molecular weight alcohols when they are derivatized by silylation and a good sensitivity.

As shown in the table 1, it is possible to find alcohol with a better quality for the low migratable products than the standard grade by an optimisation of the synthesis process.

	EG (ppm)	DEG (ppm)	TEG (ppm)	TMPOH (ppm)
Standard grades	100	600	1500	4500
improved grades	10	50	100	1200

Table 1 : typical values of by-products in different grades of TMP(EO)<sub>n</sub>

#### Acrylated monomer

Although maximum care is undertaken for a proper selection of the alcohol grade (high purity, low level of by-products), it is not enough to ensure the quality of the acrylate. Actually a commercially available acrylate is a complex mixture of the "ideal" molecule plus subacrylated alcohol and acrylated

by-products. Added to this are residual starting substances (acrylic acid, solvent,...). These components are possible migrants in the formulation and consequently must be fully under control.

With an accurate control of the manufacturing process, it is possible to get products with levels of acrylic acid and solvent far below acceptable levels and without any risk of cross-contamination.

The optimisation of the process is supported by controlling the product synthesis with different kind of analytical tools and more specifically with gas chromatography – mass spectrometry coupling (GC/MS). GC/MS technique is very suitable to verify that no unexpected low molecular weight components are present.

Intrinsic components of acrylated ethoxylated or propoxylated polyols are preferentially analysed by reverse phase liquid chromatography (RP-HPLC) equipped with a diode array detector. Indeed, it is possible to separate the constituents of these products by both their degree of acrylation and their degree of ethoxylation or propoxylation .

Consequently, using both GC/MS and RP-HPLC, a full fingerprint of the acrylate monomer is available.

Finally, in the case of TMP(EO)nTA, it is very important to determine the level of EGDA, DEGDA, TEGDA and TMPTA because these components (low functionality, low molecular weight) are potentially the species most prone to migration. GC/FID is the classical technique to quantify these components.

Once again, depending on both quality of the raw material and process, it is possible to control the level of potential migratable components as shown in table 2 and select the best products for low migratable monomers grade.

	EGDA (ppm)	DEGDA (ppm)	TEGDA (ppm)	TMPTA (ppm)
Standard grades	150	350	1000	4500
improved grade	50	90	180	1500

Table 2 : typical values of low molecular weight by-products in different grades of TMP(EO)nTA

These results can be capitalized to calculate the maximum possible migration with the “worst case calculation”. If we assume than 100% of the formulation is made of the acrylate monomer, 6dm<sup>2</sup> packaging is in contact with 1kg food, fully covered with 3g/m<sup>2</sup> ink and the low molecular weight components are not cured at all and migrate fully, the following results (tables 3, 4) are obtained using equation (1) from the levels of by-products indicated in table 2.

Standard grade monomer	EGDA	DEGDA	TEGDA	TMPTA
Conc. of by-products in liquid monomer	150 ppm	350 ppm	1000 ppm	4500 ppm
<b>Worst case calculation</b>	<b>27 ppb</b>	<b>63 ppb</b>	<b>180 ppb</b>	<b>810 ppb</b>

Table 3 : worst case calculation on a standard TMP(EO)TA grade

Improved grade monomer	EGDA	DEGDA	TEGDA	TMPTA
Conc. of by-products in liquid monomer	50 ppm	90 ppm	180 ppm	1500 ppm
<b>Worst case calculation</b>	<b>9 ppb</b>	<b>16 ppb</b>	<b>32 ppb</b>	<b>270 ppb</b>

Table 4 : worst case calculation on a improved TMP(EO)TA grade

Although the result of worst case calculation is greatly improved for a high quality grade of TMP(EO)nTA, the value obtained for the TMPTA is still high. It highlight the assumptions used to calculate the maximum possible migration are very rigorous because a large amount of the by-products are cured in the ink, especially the TMPTA. With its functionality of 3, the probability that it is linked to the network and will not migrate is statistically very high.

For that reason, we implemented other tests of extraction and analyses with “model cured varnishes” in order to have a better knowledge of the level of maximum possible migration of a print.

### Model varnishes

To evaluate the “worst case calculation” by performing extractions on cured formulations require to get the effective and efficient analytical technique with the following criteria :

- high selectivity to avoid matrix interferences with components of interest,
- high sensitivity to detect levels of targeted components as low as possible (below 0.1 ppm),
- good accuracy in the concentration range aimed,
- which do not need any previous sample preparation step whatever the simulant solvent used (acetonitrile, water, ethanol, acidic water...)
- which is as exhaustive as possible according to the variety of chemical characteristics of the components involved.

To meet these tightly requests, Liquid Chromatography – Mass Spectrometry coupling (LC/MS) is obviously the most appropriate technique. Depending on the requirements, many operating modes may be selected.

In the scenario of quantification of potential migrants in TMP(EO)nTA, Single Ion Recording (SIR) allows the determination of the concentration of the targeted low molecular weight components : TMPTA, EGDA, DEGDA, TEGDA. In this mode, these components are ionised by Electro Spray Ionisation to get the ion of interest for each of the selected acrylates. The detection is focused on these ions which are used for quantitative analysis.

This ionisation is enough sensitive to detect “multi-traces” with a good reproducibility and stability in the range of required concentration. For each components, linearity, quantification and detection limits have been determined using standard solutions. These standard solutions were made in the three solvents tested (acetonitrile, 10% ethanol, 95% ethanol) with concentration ranges form 1 to 1000 ppb. The results confirm SIR is the most relevant mode to quantify all the acrylate components of interest in extracts from the cured samples. For each extract, only one trial is required to quantify the targeted acrylate without any preliminary concentration step.

Different “simplified” UV curable formulations were done with Sartomer raw materials including standard or improved TMP(EO)nTA grades (table 5).

	TMP(EO)nTA Standard grade (SR454)	TMP(EO)nTA Improved grade	TPGDA (SR306)	BADGEDA (CN104)	Amine-modified acrylate monomer (CN3715)	Esacure One (*)
varnish 1	40		35	20		5
varnish 2		40	35	20		5
varnish 3	35		35	20	5	5
Varnish 4		35	35	20	5	5
varnish 5	35		35	20	5	5
varnish 6	97.5					2.5
varnish 7		97.5				2.5

Table 5 : “simplified” UV curable formulations. (\*) : Esacure One is provided by Lamberti

For each formulation, extractions were carried out with two different simulants – 10% and 95% ethanol – and acetonitrile as strong extraction solvent.

The UV curable formulations shown in table 5 were applied with a 12µm K-bar on glass panels. Immediately after the coating have been applied, the panels are cured at 5m/mn. under a commercial UV curing system which is equipped of a 160W/m<sup>2</sup> medium pressure mercury arc lamp.

The cured films were scraped off and about 300mg of each sample was immersed into 10ml acetonitrile (strong solvent) or food simulant (10 or 95% ethanol) in a clean glass vial. The vials were sealed and placed in a forced air oven at 40°C for 24h. After the storage, each vial was cooled at room temperature. The simulating liquid was transferred by filtration into a 22ml sealed vial and stored in dark condition before analysis by LC/MS.

Except for the varnish 6, the concentration of EGDA, DEGDA, TEGDA and TMPTA in the extracts are below the detection limits (respectively, 0.5ppm for EGDA and 0.2ppm for DEGDA, TEGDA TMPTA in our analysis conditions) whatever the solvent of extraction. This correspond to less than 1ppb of maximum possible migration in the “worst case calculation” framework assuming a 3g/m<sup>2</sup> varnish coating, 6dm<sup>2</sup> coated /kg food.

In the case of varnish 6, made of standard grade TMP(EO)nTA and photoinitiator only, traces of TMPTA are detected unlike varnish 7 made of improved grade TMP(EO)nTA.

	EGDA	DEGDA	TEGDA	TMPTA
Varnish 6	< 0.5ppm	<0.2ppm	<0.2ppm	20ppm
<b>Worst case calculation Varnish 6</b>	<b>&lt;0.1ppb</b>	<b>&lt;0.05ppb</b>	<b>&lt;0.05ppb</b>	<b>19ppb</b>
Varnish 7	< 0.5ppm	<0.2ppm	<0.2ppm	0.2ppm
<b>Worst case calculation Varnish 7</b>	<b>&lt;0.5ppb</b>	<b>&lt;0.5ppb</b>	<b>&lt;0.5ppb</b>	<b>&lt;0.5ppb</b>

Table 6 : acetonitrile extraction and worst case calculation on a standard TMP(EO)TA grade compared with improved grade

The results of total extraction performed on the cured films clearly show that potential migrants (by-products, low molecular weight species) are converted and cross-linked in the formed network. Nevertheless, in the “worst conditions”, the analysis have shown some residual uncured material in the film based on standard grade of TMP(EO)nTA (ie TMPTA in varnish 6).

Obviously, the improved grade of TMP(EO)nTA which was developed for use in formulation for low migration UV/EB printing inks is relevant. In this case, the level of maximum possible migration is far below the acceptable limit of 10ppb.

To sum up, extraction work on “simplified” UV-curable formulation combined with an effective and quantitative analytical method highlights the possibility to get low migration potential of acrylate monomers such as TMP(EO)nTA provided that a meticulous choice of the raw material is carried out.

## Conclusion

As the legislation on Food Contact and Food Packaging develops it is likely that the demands on the ink makers and resin manufacturers to supply compliant products will intensify. To meet these demands there has to be a greater understanding of the chemistries involved and the potential to migrate. This paper demonstrates that, by continually developing and upgrading analytical techniques, increased understanding and measurement of the potential of UV curable materials to migrate is possible. These analytical techniques thus form the cornerstone of any future product development for this exacting application.

## References

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