FOOD PACKAGING COMPLIANT INKS AND SET-OFF MIGRATION

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Abstract

The challenges associated with migration when working with low viscosity inkjet systems for food packaging applications are well understood in the industry. We will discuss the terms 'low migration' and 'food packaging compliant' and will then review a migration study completed with a food packaging compliant ink set with specific focus on set-off migration.

Introduction

The requirement to prevent contamination of food via migration of printing inks through the packaging is well understood. Food packaging materials are covered by the Commission Regulation (EC) No 1935/2004 which provides a harmonised legal EU framework and it sets out the general principles of safety and inertness for all Food Contact Materials (FCMs)[1].

Significant focus has been put on understanding this issue since the photo initiator ITX (Isopropyl Thioxanthone) was found to have migrated from the UV cured offset ink printed on the outside of the packaging into baby milk in September 2005[2]. In this case, the transfer of the ITX was most likely as a result of set-off migration. Later in December 2005, ITX was also found to have migrated through the packaging into olive oil and fruit juice[3]. Following these incidents, significant effort has been put into formulating inks to minimise or prevent migration.

The term ‘low migration’ was introduced to the printing industry more than fifteen years ago to refer to inks that were suitable for indirect food packaging applications in that they had been formulated to meet the required migration limits. The term ‘low migration’ could only be used as a relative term, as there is no absolute value associated with it. When the term is used, it usually refers to the fact that the inks are compliant with the Swiss Ordinance and in some cases the Nestlé Guidance Notes on Packaging Inks[4].

In 2018, the European Printing Ink Association (EuPIA) announced that they would no longer be using this term[5] in light of advances that had been made in this field and were reflected in the 2016 revision of the EuPIA Good Manufacturing Practice (GMP) for printing inks used on food contact materials[6]. This change has now also been reflected in the printing industry and many ink suppliers are now referring to ‘food packaging compliant’ inks.

Development of a food packaging compliant ink for inkjet is considerably more difficult compared to analogue inks such as flexo due to the viscosity requirements of the commercially available print heads. Inkjet print head technology necessitates use of low viscosity inks to achieve reliable jetting and as a consequence, low molecular weight photo initiators and monomers are required to control the viscosity. The mobility of such molecules is therefore far greater making migration a larger challenge.

Types of Migration

Migration is the transfer of substances from the printing ink into the food. Figure 1 illustrates the different routes that migration can occur.

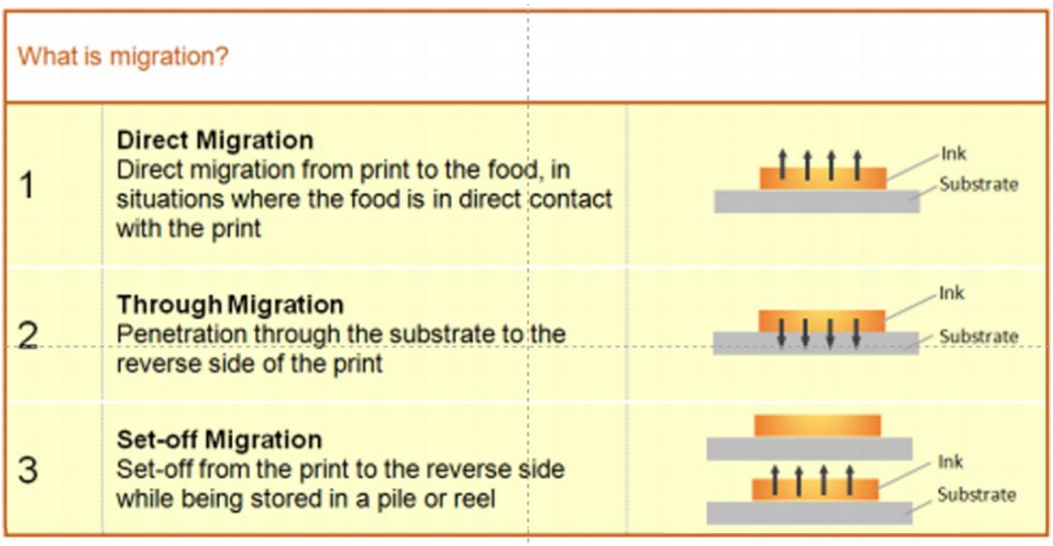

Figure 1. Three main routes that migration can occur from a printing ink into food

Direct migration can occur when the printed ink is in direct contact with the food material. Due to the chemical nature of the photo initiators and monomers / polymers used in inkjet inks, they are not suitable for direct food contact and as result direct migration is not discussed in this paper.

Through migration occurs when components of the printing ink pass from the printed image on the outside through the label and packaging and into the food inside. This can be reduced through careful selection of the label or packaging material which can act as a barrier. This form of migration is of significant concern for digitally printed labels using ink jet ink.

Set-off migration can occur when prints are stored in a stack or tightly wound roll and when under pressure, components from the printed surface can migrate to the non-printed, reverse side of wound labels or stacked sheets, and it is then this surface that comes into contact with the food. This form of migration is of less concern when self-adhesive label stock is used as these usually have a liner that is removed when the label is applied to the packaging. However, for foils, flexible packaging and liner less substrates, this form of migration must be considered.

Migration Analysis Methodology

A simulant which mirrors the properties of the food stuffs is used in place of the food sample and is chosen to reflect the product intended to be inside the packaging[7,8]. Figure 2 provides an explanation of the simulants typically used.

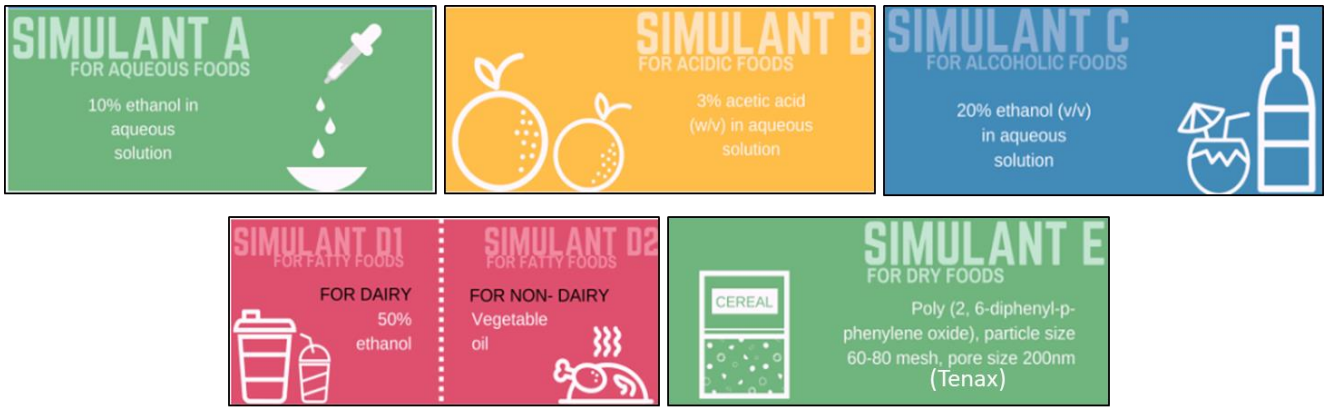

Figure 2. Food simulants used for migration testing

Once the appropriate simulant has been chosen, the testing conditions (temperature and exposure period) are selected, again to represent the environment and time that the product will be stored under[9]. Figure 3 gives an overview of the standard test conditions that can be employed.

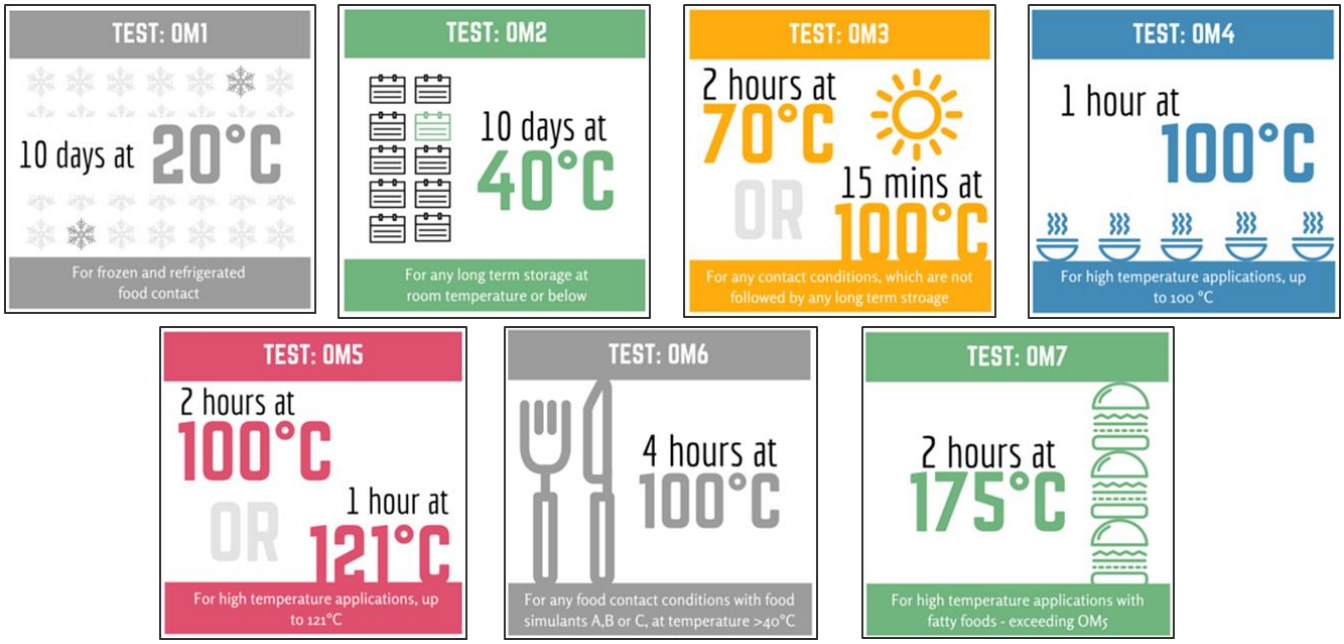

Figure 3. Migration testing conditions available to represent storage conditions of food packaging

Similar methodology can be used to analyse for though and set-off migration[10] and for both, standard stainless-steel migration cells (cell type B of EN 1196-1) are used.

For through migration, the sample is positioned so that the printed surface is in direct contact with the steel plate of the migration cell so that the ink is not in direct contact with the simulant. The migration cell is then closed and filled with the simulant of choice. The cell is then placed in the incubator using one of the standard conditions shown in Figure 3.

For set-off migration, a similar process is used, but instead of placing the printed sample in the cell, a piece of unprinted film that has been in contact with the printed image with a weight on top of both films for 10 days is used. The unprinted sample is then positioned in the cell so that the surface that was previously in contact with the printed image is in direct contact with the food simulant. The cell is then filled with the simulant of choice and placed in the incubator.

After the incubation period, the migration cells are cooled to room temperature and the simulant transferred to suitable vials for analysis *via* liquid chromatography-mass spectrometry (LC-MS).

Migration Study

Liquid chromatography-mass spectrometry (LC-MS)

The analysis was carried out using ultra high-performance liquid chromatography (uHPLC)-mass spectrometry (MS). The studies were performed on a Thermo Q Exactive Focus mass spectrometer equipped with a Dionex RS 3000 uHPLC system. The chromatographic separation was performed on an ACE Excel C18 column, 50 x 2.1 mm I.D., 1.7 µm particles. The mobile phase consisted of (A) water/0.1% formic acid and (B) acetonitrile/0.1% formic acid. An increasing linear gradient (v/v) of solvent B was used (t(min), %B): (0, 10), (10, 90), (11-15, 90), (16-20, 10) with a flow rate of 0.25 mL/min and a column temperature of 25^{o}C. The mass spectrometer was operated in electrospray positive ion mode. The capillary voltage was kept at 3.5 kV (positive mode) and the capillary temperature at 320^{o}C. Nitrogen was used for sheath gas (flow rate: 46), aux gas (flow rate: 11) and sweep gas (flow rate: 2).

Formulation and Specific Migration Limits

A simplified set of inks that had been formulated to be food packaging compliant were used for this migration study. Table 1 shows the acrylate and photo initiators that were used in the formulations together with their specific migration limits.

Component	Specific Migration Limit (SML)
Hexane-1,6-diol diacrylate (HDDA)	10 µg/Kg
Esacure KIP 160	50 µg/Kg
Omnirad TPO-L	10 µg/Kg

Table 1. Acrylate and photo initiators used in simplified inks for migration study

Sample Preparation

Through Migration

Circles consisting of 2 layers of white ink (200% coverage) plus 1 layer of cyan ink (100% coverage) plus 1 layer of yellow ink (100% coverage) to represent worst case conditions were printed onto PE (82µm, AH941 PE TOP WHITE 1S-85, Fasson™) and PET (45µm, Shrink PET CL 1S-45 UHS, Fasson™) films using the N610i digital printing press at 50m/min , the pinning lamp set to 40% for the white layers and a further pinning lamp set to 80% for the colour layers (both Phoseon FP200 395nm rated at 8W/cm^2) and a GEW iron doped mercury NUVA2 lamp (rated at 240W/cm^2) set to 50%.

Migration was then investigated for all food types using 10% ethanol (aqueous foods), 4% acetic acid (acidic foods) and 95% ethanol (worse case simulant for fatty foods). Incubation parameters were used to cover usage on food packaging items for long term storage at room temperature – 50^{o}C for 10 days. In all cases, the ratio was equivalent to 6dm^2 per kilogram of food ("EU cube, 10x10x10 cm, 1 kg food ").

Set-Off Migration

The printed image shown in Figure 4 was used for this part of the study. In this case the image was printed onto a 50µm PET substrate using the N610i digital printing press at 50m/min, with the pinning lamp (Phoseon FP200 395nm rated at 8W/cm^2) set to 100% and a GEW iron doped mercury NUVA2 lamp (rated at 240W/cm^2) set to 100%.

Figure 4. Printed label used for set-off migration study

Four different samples were prepared to simulate conditions that the prints may experience when printed on a hybrid digital/analogue press where several flexo stations may be present after the digital unit:

1. No extra treatment
2. One extra pass through the iron doped mercury NUVA2 lamp (50m/min at 95% power)
3. Two extra passes through the iron doped mercury NUVA2 lamp (50m/min at 95% power)

4. Three extra passes through the iron doped mercury NUVA2 lamp (50m/min at 95% power)

The printed image was then put into contact with a 50µm PET unprinted film with a 1Kg weight on top of both films for 6 days. The film that had previously been in contact with the printed image was then used for the set-off migration test. The chosen simulant was 50% ethanol (dairy foods) and the incubation parameters were 40°C for 10 days.

Results

Through Migration

The data in Table 2 shows that on PE, when the LC-MS peak areas found from the migration test samples were compared to the peak areas for the standard solution, the HDDA was found to migrate to a level significantly above the specific migration limit for all food simulants tested. No further analysis was therefore carried out for the photo initiators.

	82 µm PE			45 µm PET		
Simulant	HDDA	KIP 160	TPO-L	HDDA	KIP 160	TPO-L
10% Ethanol	**> SML**	**Not completed due to HDDA results**		**< SML**	-	-
4% Acetic Acid	**> SML**			**< SML**	-	-
95% Ethanol	**> SML**			**< SML**	**< SML**	**< SML**

Table 2. Through migration results on PE and PET substrates

When the substrate was PET, traces of HDDA was found in all simulants, however the two photo initiators were only found to migrate in the fatty food simulate (95% Ethanol). In each case, when the LC-MS peak areas found from the migration test samples were compared to the peak areas for the standard solutions, the concentration of each was below the specific migration limits.

These results indicate that even though the simplified inks were formulated to be compliant with the Swiss Ordinance and the Nestlé Guidance Notes, to be food packaging compliant, a functional barrier (in this case 45 µm PET) was still required to prevent through migration above the specific migration limits, when worst case print coverage (400%) was used.

Set-Off Migration

The set-off migration samples printed with the simplified inks were analysed for HDDA, Esacure KIP160 and Omnirad TPO-L. No evidence of set-off migration of Esacure KIP 160 was found in any of the samples.

The data in Figures 5 and 6 show that where no additional passes were made through the iron doped mercury lamp, the concentrations of both the acrylate HDDA and the photo initiator TPO-L were above the specific migration limits. However, only one additional pass through the lamp was required to

reduce the set-off migration in each case to below the specific migration limits with further reductions in set-off migration being measured with additional passes.

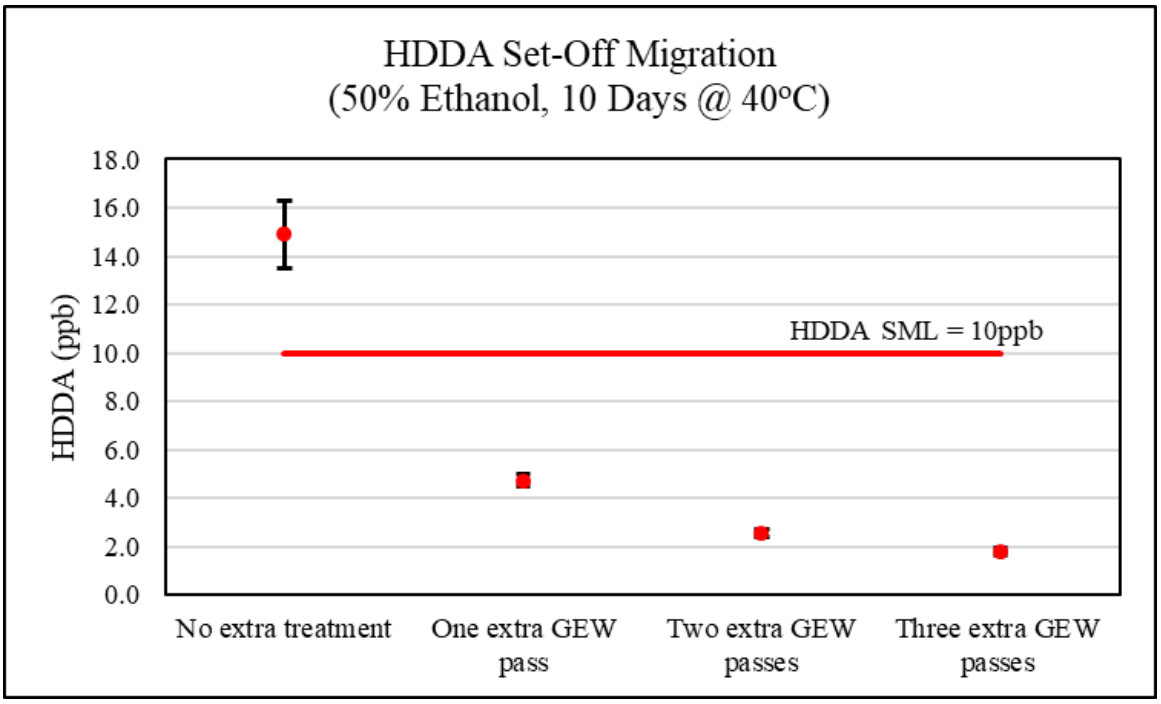

Figure 5. Set-off migration data for acrylate HDDA

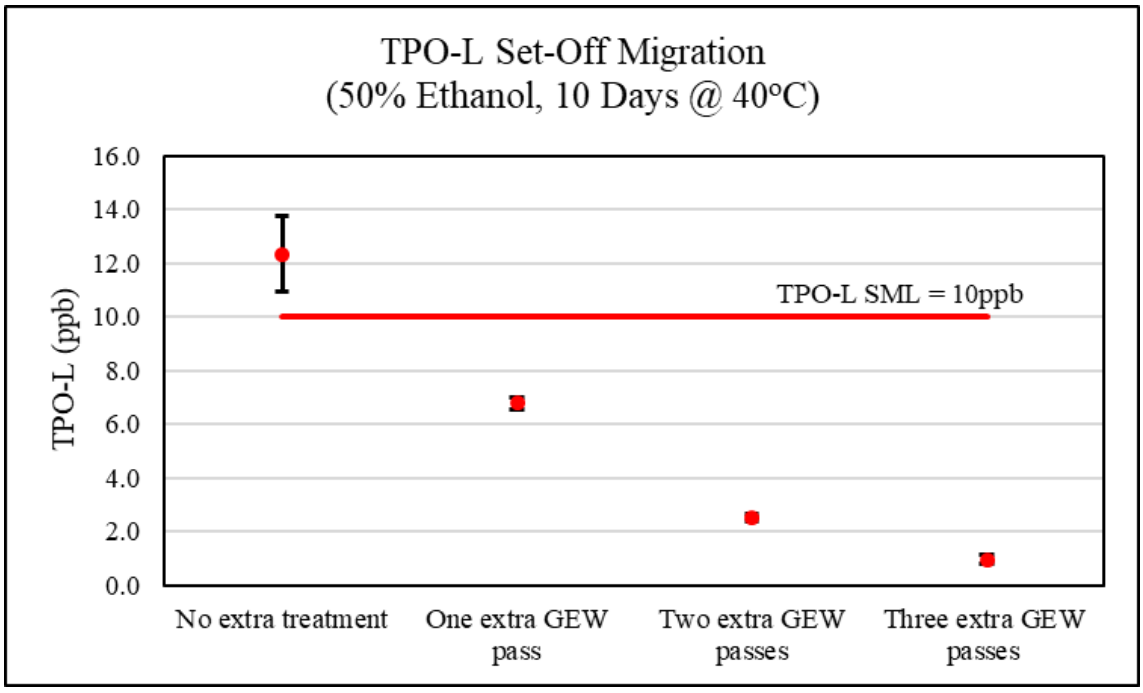

Figure 6. Set-off migration data for photo initiator TPO-L

Conclusions

Although the use of the term ‘low migration’ is still prevalent in the printing industry, it is becoming widely understood that as there are no absolute values associated with it, it can only be used as a relative term. Because of this, the industry is moving towards using terms such as ‘food packaging compliant’.

The data presented show that even when an inkjet ink set has been formulated to be food packaging compliant, through migration can still occur when high levels of ink are deposited, unless a functional barrier such as 45µm PET is present.

Set-off migration should also be taken into account when a liner-less substrate is used and again should not be considered safe just because the ink set has been formulated to be food packaging compliant. The data shows that for some components (in this case the acrylate HDDA and photo initiator TPO-L), set-off migration above the specific migration limit was measured unless additional passes through a mercury arc lamp were included.

Many printers are now investing in hybrid presses which merge the capabilities of analogue and digital printing techniques by integrating a digital press into a flexo line. This typically results in one or more flexo stations being positioned after the digital print engine allowing the digitally printed image to receive a larger dose of UV to achieve better cure and so removing the concern for set-off migration.

Acknowledgements

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