Low Migration UV-Curable Inkjet for Food Packaging

Derek Illsey*, Steve Hall, Sam Moncur, Damian Ward, Tom Budden; Sunjet; Bath, UK

Abstract

UV-curable inks for single pass (web) inkjet printing with low migration potential and suitable for the printing of food packaging have been developed and optimised by mixtures design-of-experiment (DOE) methodologies. The inks have acceptable cure response in air (<250 mJ/cm2) and can deliver levels of contact migratables below 10ppb (0.01mg/Kg(foodstuff)) for each migratable monomer and photoinitiator species measured in this study. The inks can be prepared at viscosities suitable for all common printheads and their performance on commercial presses has been confirmed.

Introduction

Inkjet is becoming increasingly important in the printing of labels, and of flexible and rigid plastic films intended for packaging. The current global markets for these applications have been estimated at £900Mn, £26Mn and £20Mn, with anticipated growth through to 2016 of 31, 53 and 31% respectively [1]. A significant proportion of these markets are targeted at food packaging and it is anticipated that inkjet will be used in printing the majority of food packaging segments [1,2].

In Europe, legislation requires that food packaging should not transfer materials to the packaged food in quantities that could bring about a change in the nature, substance or quality of the food and must not be injurious to health [3]. The European Printing Ink Association (EUPIA) provides a guideline on the raw materials that may be used in printing inks intended for the non-contact side of food packaging [4]. This guideline reflects the position in Switzerland (Swiss Ordinance (SR 817.023.21)) which is at the forefront of legislation [5].

The inks reported here have been formulated using only those materials which are included in the EUPIA guideline. In the case of photoinitiators, it is highly preferable that they have associated specific migration limits (SML) and are contained on List 1A of the EUPIA guideline, i.e. those with recognized low migration potential and supported by sufficient toxicological data. Photoinitiator types suitable for the preparation of low migration inks include polymeric, polymerisable and multifunctional types [6,7,8]. The use of polymeric photoinitiators in the formulation of UV-inkjet needs to be carefully controlled so that their incorporation does not lead to viscosities exceeding the requirements of the targeted printhead. This is an aspect that the work in this paper addresses.

For most monomers and oligomers used in the formulation of UV-curable inks the allowable maximum level of contamination of any foodstuff is 10ppb (0.01mg/Kg(foodstuff)), or 10µg/6dm2, as defined by the standard EU package model, where 1 Kg of food requires a package area of 6dm2 to enclose it. These low migration limits for monomers place greater emphasis on the careful formulation of low migration potential UV-inkjet to ensure that the low molecular weight and low functionality monomers used do not exceed these limits when cured at acceptable press speeds.

There are a number of modes by which unbound material in a UV-cured ink film can contaminate the packaged food stuff, which are described in figure 1. For UV-cured inks applied to either labels or the primary packaging of a foodstuff, the most likely route to contamination is through contact migration, or ‘set-off’ migration. Different plastic films have varying degrees of solvency towards the unbound components of a UV-cured ink; low density polyethene (LDPE) is a particularly susceptible film towards contact migration. For this reason, LDPE is commonly used in the assessment of the migratable components from cured UV-ink films by the contact mode.

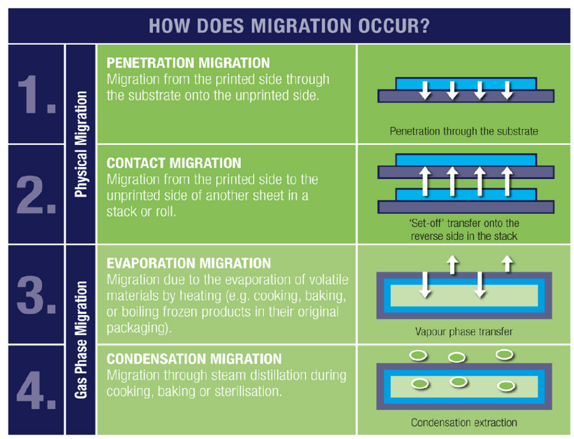

Figure 1: *The different modes of migration*

The preparation of low migration potential UV-curable inkjet has been reported but often the use of some form of inerting has been employed to exclude the majority of the atmospheric oxygen from the ink film. This allows sufficient conversion of the monomer to achieve acceptably low migration levels [9]. This paper demonstrates how to formulate UV-curable inkjet products having acceptably low levels of migratables when cured under atmospheric conditions at acceptable press speeds.

Experimental

Ink Formulation

Mixture designs-of-experiment (DOE) were used in establishing inks having the optimum concentrations of monomers and photoinitiators, for both viscosity and the required low levels of migratable components from cured ink films. The following monomers were used in this study; dipropylene glycol diacrylate (DPGDA), ethoxylated (3 moles equivalent) trimiethylolpropane (TMP(EO)TA), and Mon-1, a proprietary difunctional acrylate monomer. The photoinitiators (PI) used were; Genopol TX (a polymeric thioxanthone, ex. Rahn), Genopol AB1 (a polymeric aminobenzoate, ex. Rahn) and Irgacure 819 (a difunctional phosphine oxide type photoinitiator). Also included in the inks was 2% (w/w) of a proprietary blend of photoinitiators and synergists ('PI1'). The composition of the inks was as follows;

DPGDA:	19.6-79.6%
TMP(EO)TA:	0-30%
Mon-1:	0-30%
(Total monomer concentration = 79.6%)	
Genopol TX:	0-6%
Irgacure 819:	0-3%
Genopol AB1:	0-4%
'PI1':	2.0%
(Total photoinitiator concentration = 10.0%)	
Stabiliser:	1.0%
Wetting Aid:	0.4%
Black Pigment Dispersion (based on DPGDA):	9.0%

Assessment of the Contact Migratables

To determine the contact migratables, 8µm ink films were applied to a 36µm PET film (Melinex S) and the inks were then cured in air at 225 mJ/cm^2, using a medium pressure mercury (H-bulb) lamp. The surfaces of the cured ink films were blocked to a 30µm LDPE film at room temperature for 3 days at 10 tonnes pressure, to mimic the situation of contact migratables to the reverse side of a food package film (laminate) comprising LDPE. 90cm^2 samples of the blocked LDPE film were then extracted into 2 ml of methanol, containing 0.025% (w/w) of MEHQ (stabilizer) for 3 hours before the methanol solutions were analyzed. A Hewlett Packard 6890 GC, equipped with a 5973 mass selective detector was used to analyse the extracted solutions for migratable monomer and PI decomposition by-products. For the photoinitiator analysis an Agilent 1200 series HPLC equipped with a DAD and Finnigan LPQ duo MS detector was used. In both cases the instruments were calibrated with solutions of the specific analytes at concentrations covering the target range for migratables (equivalent to 1ppb to 100ppb for monomer and 6ppb to 100ppb for the photoinitiator).

It should be noted that blocking the cured ink films for longer periods did not result in significantly different levels of migratables, and nor did extracting the blocked LDPE films for extended periods at either room temperature or at 40^{o}C. The level of migratables determined from the cured ink films are reported as the level of contamination that would occur for 100% ink coverage of a package according to the standard EU model (that is; 600cm^2 package area for 1Kg of foodstuff). In these experiments methanol has been found to be a more effective extracting solvent than the blended ethanol/water food simulants recommended by EuPIA for this purpose.

Further Optimised inks

Using the results from the DOE above (as well as other DOEs not reported here), CMYK and white ink sets having improved performance, particularly in delivering low migratables at lower UV-doses, have been developed and their performance confirmed under both laboratory and commercial printing conditions. By altering the monomer composition, whilst maintaining DPGDA and Mon-1 as principal monomer components, it has been possible to prepare low migration potential inks suitable for low viscosity printheads (e.g. Kyocera). As well as assessing the contact migratables for these inks the total extractables from cured ink films have also been determined. The total extractables from cured ink films were determined by immersing 30cm^2 of the cured ink print in stabilized methanol, and then following the method outlined previously for the analysis of migratables.

Migratables from Commercially printed material

An ink set as described in the previous section, and having viscosities of around 9.0mPa.s at 45^{o}C, has been printed commercially at speeds up to 50 m/min on a variety of plastic film stock. The inks were found to cure satisfactorily under all conditions, even at reduced lamp power and the migratables from prints were determined and are reported later. Prints from this commercial run have also been assessed by a second (approved) laboratory and the results of that analysis corroborate our own findings.

Results and Discussion

Viscosity Control

Figure 2 shows how the viscosity of the inks prepared according to the principles outlined in the experimental section can be readily adjusted to that required. The coefficient of determination (R-Sq.) of 99.3% indicates that the fit of the model to the data is excellent. For the assessment of the migratable species from cured ink films, in relation to changes in photoinitiator composition, inks based on the centre point monomer formulation of figure 2 were used (50.4% DPGDA, 15.0% Mon-1, 15.0% TMP(EO)3TA). These inks had viscosities in the range of 9.0-11.0mPa.s at 50^{o}C.

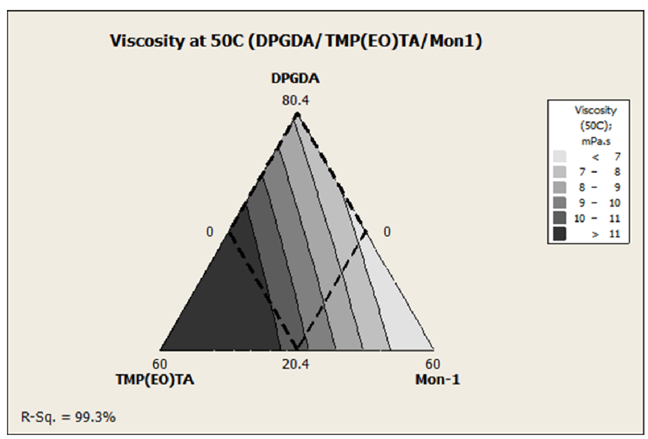

***Figure 2**: Contour Plot for Viscosity (mPa.s) at 50^{o}C; showing the dependence on Monomer Composition (based on an ink containing 4.0% Genopol TX, 2.0% Irgacure 819 and 2.0% Genopol AB1)*

Contact Migratables from cured ink films

Figure 3 shows the amount of mesitaldehyde, a decomposition by-product from Irgacure 819, that migrates from cured ink films by set-off to the LDPE film. The model fit is good, with an R-Sq. value of 95.6%. Clearly, as the concentration of Irgacure 819 increases the amount of migratable mesitaldehyde from cured ink films consequently increases. However, the amount of migratable mesitaldehyde for all the cured ink films remains below the desired 10ppb level. It is worth noting here that the nature of the materials used in the formulation of LM potential UV-inks can have a dramatic effect on the amount of mesitaldehyde generated from Irgacure 819. Those materials which are prone to H-abstraction can produce significantly higher concentrations of mesitaldehyde. For example, it has been found that the use of propoxylated monomers can result in higher concentrations of mesitaldehyde in the migratable component from cured ink films.

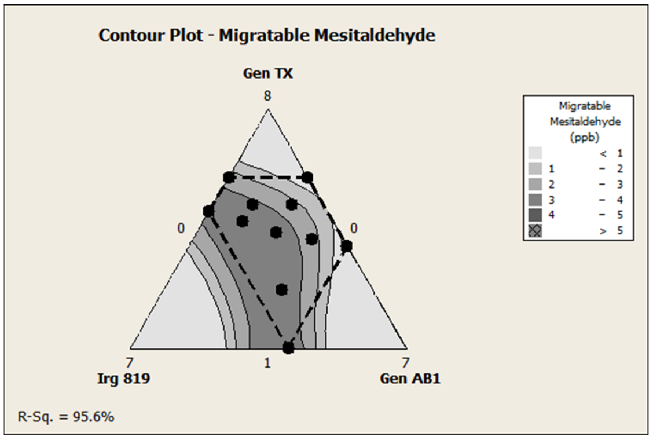

Figure 3: Contour Plot for migratable mesitaldehyde, a decomposition by-product of Irgacure 819, emanating from 8µm ink films cured on PET film, in air, at 225mJ/cm^2.

Figures 4 and 5 are the contour response plots for the amounts of migratable DPGDA and Mon-1 that migrate from cured ink films by set-off to LDPE. The plot for migratable TMP(EO)TA is not shown here, since for a number of the inks the migratable level fell below the detection limit, thereby leading to poor model fits. This finding supports the widely held notion that monomers of lower functionality are less likely to react into the cured network and can thus lead to potentially unacceptably high migratable levels. For this reason it has been a strategy to exclude the use of monofunctional monomers in developing these low migration UV-inkjet products. Indeed, we have found that when using concentrations of any monofunctional monomer of much greater than 5.0% (w/w) that the contact migratables for these species, at even high UV-doses of 250 mJ/cm^2, can lead to contact migratable levels exceeding the required 10ppb level.

The quality of fit for the 2 models represented in figures 4 and 5 is very good, with R-Sq. values of around 98%. Considering the models and the actual migratable analysis data it is clear that there is a limited space within the photoinitiator design that results in cured ink films having migratable monomer levels below the desired 10ppb level, as denoted by the lighter grey areas in figures 4 and 5. By further analysis of the models, an optimum photoinitiator package resulting in the lowest possible migratable monomer was determined to be 4.8% (w/w) Genopol TX, 2.5% Irgacure 819 and 0.7% Genopol AB1. When an ink was prepared with this photoinitiator package and cured, the levels of migratable DPGDA and Mon-1 were found to be below the detection limit (1.0ppb) of the analytical method.

HPLC-MS analysis of the extracts from the contact migration testing indicated that the amount of each individual migratable photoinitiator was below the detection limit of 6ppb.

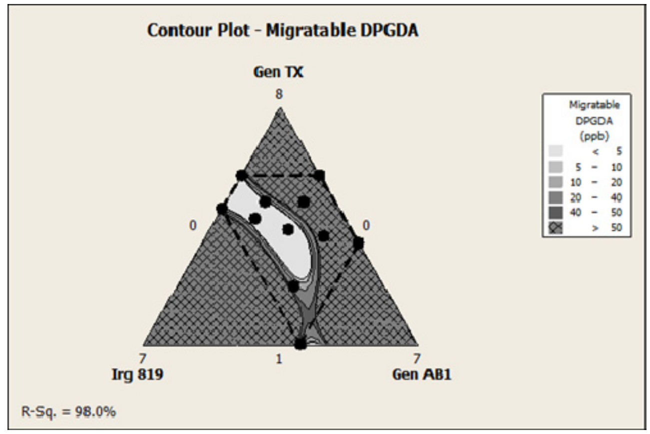

Figure 4: Contour Plot for migratable DPGDA emanating from 8µm ink films cured on PET film, in air, at 225mJ/cm^2

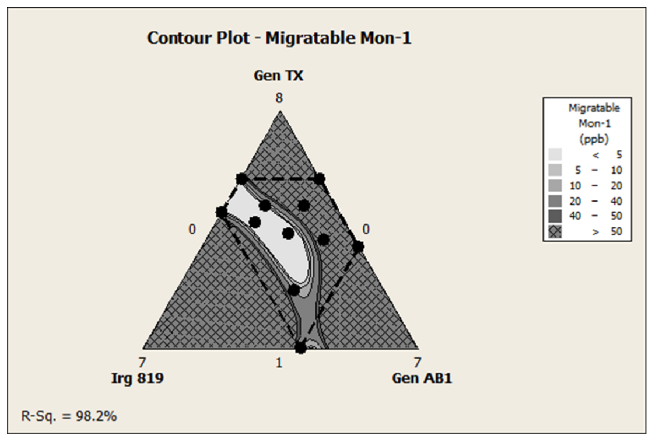

Figure 5: Contour Plot for migratable Mon-1 emanating from 8µm ink films cured on PET film, in air, at 225mJ/cm^2

Migratables and Extractables from Cured Films of Fully Optimised Inks

Inks formulated on the basis of the output from the mixtures DOE described here and from further (unreported) DOEs have excellent cure responses and can produce cured ink films with even lower levels of contact migratables. Figure 6 provides the results for the analysis of contact migratables for a cyan ink, prepared accordingly, at UV-doses between 150 and 250 mJ/cm^2. Even at the lower dose level the cured ink film produced significantly less than 10 ppb of each migratable component analysed, and only at the lower dose level did the amount of migratable monomer exceed the detection limit (1.0ppb). Similar results were found with the yellow, magenta, black and white inks of this set. Where two or more ink films were applied, i.e. 2x, 3x 8µm, and the migratables determined at cure doses of 200mJ/cm^2, the levels of migratable monomer remained below the detection limit of the GC-MS method (1ppb). The amount of migratable mesitaldehyde tended to increase in proportion to the amount of ink laid down. However, it has been subsequently found that the level of migratable mesitaldehyde can be reduced significantly, by a factor of 2 or more, by slight changes to the ink formulation.

Figure 6 also provides the results for the extracted component from an 8µm cyan ink film, cured at 200mJ/cm^2. The amount of extracted DPGDA and Mon-1, which represents the material which has failed to react into the cured network via either of the acrylate groups, is very low at less than 2ppb for each monomer. These levels are very much lower than those which have been reported in the literature for other low migration potential inkjet products, by more than 2 orders of magnitude [10] .

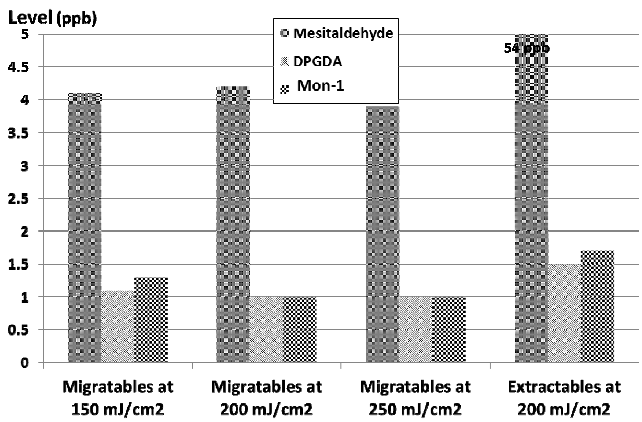

Figure 6: *The Migratables and Total Extracted Material from 8µm UV-cured optimized Cyan Ink Films*

Migratables from Commercially Produced Prints

The migratables for a CMYK set applied to both PP and PE label stock at speeds between 20 and 50 m/min have been determined and in all cases (100% lamp power) the level of individual monomer migratables was less than 3.0ppb. The level of migratable mesitaldehyde from these prints was between 3 and 8 ppb and no migratable photoinitiator was detected (HPLC detection limit = 6ppb). These results have been corroborated by a second analytical lab.

Conclusion

By employing statistical design-of-experiment methodologies, UV-curable inkjet products with low migration potential and suitable for the printing of the non-contact surface of food packaging have been developed. These inks use only those materials that are approved for the printing of the non-contact surface of food packaging under the guidelines provided by EUPIA. When inks with optimized monomer and photoinitiator packages were prepared it was possible to produce printed material using acceptable UV-doses (less than 250 mJ/cm^2) under atmospheric conditions, resulting in contact migratables of less than 10ppb for each analysed ink component. Inks prepared using the findings from this work have now been successfully run on commercial presses, producing printed label stock in which the levels of set-off migration are significantly below the 10ppb level.

References

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Author Biography

Derek Illsley gained his PhD in Polymer Chemistry in 1990 and during the early part of his career worked on non-migrating photoinitiators. He then developed a number of radcure and waterbased resin technologies for the graphic arts market prior to his leading projects on nanocomposite gas barrier coatings for food packaging. Derek joined the SunJet division in late 2011, as Principal Scientist, working on ink technology platforms for the packaging and publication markets.