Development of UV-Curing Inks for Food Packaging Applications

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Abstract

Web printing systems are now being developed which will allow digital production of packaging with ink jet. Within the very diverse range of packaging applications, food packaging is in particular attracting much interest. The commonly accepted benefits of the digital process – i.e. cost effective short run printing, inventory reduction, versioning etc are the main drivers for the activity. The usual conventional print processes being displaced are flexography or gravure, often with solvent based inks or for some markets UV-Curing.

With ink jet printing, UV-curing is the leading technology in developing this application, because of the excellent reliability of UV-Curing inks in the single pass web printing systems. There are, however, considerable challenges in developing suitable inks for these food applications, due to the necessity of meeting various odor, taint and extractables requirements. The difficulty of meeting these requirements with ink jet is heightened due to the low viscosity and consequently high monomer content and the high photo-initiator content of ink jet inks.

This paper will examine the requirements in the applications currently under development and the ink considerations in this work.

Introduction

Energy curable inks (UV and EB) are relatively small in terms of overall market size, when compared to traditional solvent and water based printing inks. These technologies though have found widespread use in everything from coating magazine covers to printing currency to printing mobile phone covers. One key area where energy curable inks have found favour is that of indirect food packaging. In the UK for example, 80% of energy curable printing ink is sold into this sector. The reason for the strong position in this sector is the unique balance of properties available for the ink system. The most important of the factors though is the ability to process jobs faster, due to avoiding the need to allow time for printed stacks of packaging to "air", which is commonly carried out with conventionally (solvent etc) printed items. This airing allows retained solvents to be dissipated and so the odor of the print to diminish.

When considering ink jet printing of packaging UV-Curing ink is an attractive technology option, due to the good nozzle stability (due to its low volatility) and hence greater reliability compared to solvent or water based inks. This becomes a deciding factor when considering single pass (as opposed to scanning) printing, due to the need for extremely high nozzle reliability and the greater complexity of maintaining the printheads. It is also worth considering here, that with solvent based DOD ink jet, the issue of retained solvent from solvent based inks would be considerably more severe than in conventional flexo or gravure etc, due to the slower drying solvents that would inevitably have to be used in an ink jet system.

Although generally UV-Curing products are superior to solvent based inks regarding issues of odour and taint, there are certainly issues to be addressed. There has been increasing concern over the nature and quantity of materials that can migrate into the packaged foodstuff and legislation is increasing in this area. In Europe new directives are in preparation and in the meantime the European Plastics directive has been enforced in inks and coatings, which sets SML's (Specific Migration Limits) and TDI's (Tolerable Daily Intakes) for various materials that can migrate into the foodstuff.[1]

It is generally clear that with the development work currently in progress and that envisaged, migratables materials from UV-Cured inks will decrease. This paper looks at some of the work as it relates to ink jet printing.

Sources of Migratable Material

Migration of ink components is undesirable for two main reasons: firstly the components can cause taint/odour in the packaged food or secondly will lead to unacceptable intakes (ingestion) of materials when the food is consumed. There are two main causes of migration: - poor cure or the use of inappropriate raw materials. The issue of poor cure is in itself complex and can be caused by a variety of factors:

- Insufficient UV energy – due to incorrect UV lamps, old lamps, lamps with dirty reflectors etc

- High film thickness – with poor through cure in the thicker ink areas
- Inadequate reactivity in the ink
- High levels of low functionality monomer present in low viscosity ink jet inks

Whilst EB (electron beam) curing will not be considered in detail in this paper, it is true to say that these problems are mostly an issue in UV-curing systems and would not be as significant in EB curing systems. EB curing equipment, whilst becoming more reliable and cost effective is still in many applications too bulky and expensive to consider.

Poor cure of the ink film can lead to migration of un-reacted monomer. This is undesirable due to the ingestion of the chemicals, but it is less often the cause of taint and odor problems, which are more usually due to the photoinitiators employed.

The migration of species from the photoinitiator can be either the photoinitiator itself or breakdown products from the photolysis by UV light. How much migration actually occurs will depend on various factors: photoinitiator used, type of packaging, printed area relative to pack size, food type being packed, quality of cure etc. The routes by which migration can occur in indirect food packaging are summarized in Table 1.

Table 1. Routes for Migration

Migration Type	Cause
Set-Off Migration	Rolls of printed material will have cured ink in contact with what will become the inside of the food pack.
Through-Migration	Migratable species move through from the outside to the inside of packaging.
Vapour Phase Migration	In cook-in or microwave packaging, species transfer in the vapour phase into the food.
Condensation Extraction	In microwave food packs, steam from the food can effect an extraction of migratable species from the back of the printed area.

Reducing Migration – Photoinitiator Chemistry

One of the key approaches to reducing the potential of photoinitiator or photoinitiator breakdown products to migrate is to limit their mobility. This will then lessen their tendency to migrate out of the ink film and into the back of the rolled up print (set-off migration) or transfer through the substrate (through-migration). One way to decrease mobility of the photoinitiator is to increase its molecular weight, although this is not the preferred approach due to the difficulty of incorporating such materials into inks (low solubility/high viscosity) and their relatively low reactivity. More recent work has focused on multifunctional photoinitiators (MFPI).[2]

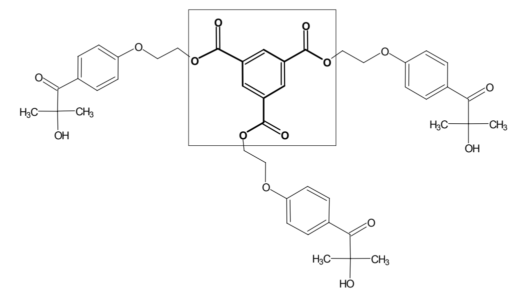

Figure 1. Example of a simple Multifunctional Photoinitiator. Esterification Product of a 1,3,5-benzenetricarboxylic acid "core" and the photoinitiator Irgacure 2959

These MFPI molecules have several photo-initiating groups attached to a small "core". If during the curing process one of these groups reacts it will effectively become bound into the cured ink film, thereby inhibiting migration. The higher number of photo-reactive sites on the molecule makes it statistically more likely for an MFPI to be bound in compared to a single functionality molecule. It is this factor as well as the larger molecular size of MFPI versus conventional photoinitiator, which makes these an attractive option for the reduction of migration.

Various MFPI's (see Figure 2) have now been developed and incorporation of them into pigmented UV-Curing inks is a commercial possibility.

The excellent low migration potential of these materials has been demonstrated. Black inks based on SiMFPI and MFPI-TX showed very low levels of migration into polyethylene. Results shown in Table 2.

Table 2. Results of Migration into PE from SiMFPI and MFPI-TX based inks

Photoinitiator	Migration into Polyethylene (ppb)
SiMFPI	<1
MFPI-TX	3

In this test prints were stacked with a polyethylene acceptor layer, under a pressure of 10 tonnes for 72 hours. The polyethylene was then extracted with acetonitrile and analyzed for the relevant photoinitiators. The migration levels were assessed using the standard EU food model of one kilogram of food being wrapped by 600cm^2 of print coverage.

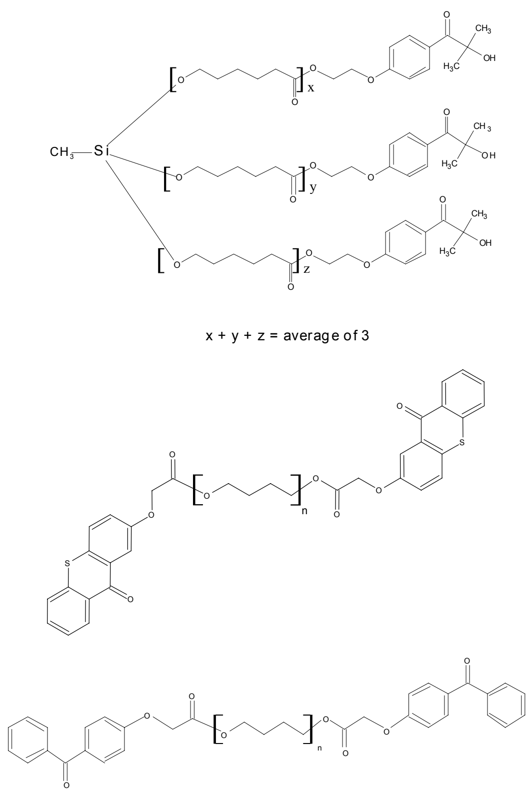

Figure 2. MFPI's based on a) Irgacure 2959 (SiMFPI) b) ITX (MFPI-TX) c) Benzophenone (MFPI-BZP)

The MFPI initiators do in general have lower reactivity (weight for weight) than their monomeric counterparts, but with the correct ink design, adequate cure speed can be obtained.

An ink formulated as follows:
7% Photoinitiator
8% Amino-acrylate synergist
25% Epoxy acrylate oligomer
60% GPTA

was printed and cured at 100m/minute with a 140W/inch medium pressure mercury arc lamp.

As can be seen from Table 3, the ink formulated with the MFPI showed comparable reactivity to the monomeric benzophenone. Thus in this case the benzophenone, which is known as having extremely poor migration performance, could be replaced with the MFPI. In cases where reactivity would not be high enough, curing with reduced oxygen or inerted atmosphere will be a possible route forward.[3]

Table 3. Cure speed attained with MFPI "benzophenone" versus conventional benzophenone

Photoinitiator	No. of passes to achieve full cure
Benzophenone	4
MFPI-BZP	5

Reducing Migration – System Issues

The reduction of migratables can also be greatly influenced by factors other than ink chemistry. Some of these critical factors will now be considered.

Ink Viscosity

Lower viscosity ink jet inks contain greater levels of low functionality monomers. In such inks there will be a greater tendency to have un-reacted monomer remaining, which can then migrate. The result of this is that more viscous inks or jetting at elevated temperatures may be advantageous to lowering migration of monomeric materials, because of the ability to incorporate higher levels of multifunctional monomers and/or oligomer. These multifunctional materials will have both greater tendency to react and also higher molecular weight, and so overall a lower tendency to migrate.

Nitrogen Inerting

Reducing the oxygen level above the print as curing takes place can be particularly effective at reducing migration and odor/taint problems. The nitrogen inerting can help in two ways: 1) Improvement of cure efficiency by lessening or eliminating oxygen inhibition effects 2) Allowing lower levels of photoinitiator to be used. Work has been carried out in some areas to show that very reduced levels of photoinitiator can be used.[3] Table 4 shows how even for a "standard UV-Curing product" (i.e. conventional photoinitiator levels) the odor can be reduced by use of nitrogen inerting. In this case, the improvement is chiefly ascribed to improved cure efficiency.

Table 4. Improvement in "Taint" by use of nitrogen inerting at cure station

Curing Condition	Taste Panel Assessment of Packaged Water 5=Significant taint, 1=no taint
20 % Oxygen, 200 W/cm Mercury Lamp	4
0.16 % Oxygen, 200 W/cm Mercury Lamp	3
0.16% Oxygen, 200 W/cm (Iron doped)	2

Print Design

Migration into packaged food and taint/odor will be proportional to the area of print around each pack. Limiting the printed area coverage is therefore a legitimate means of controlling migration/odour problems. Of course the commercial acceptability of this means would have to be considered.

Over-Coating or Reverse Printing

Over-coating the print, or encapsulating it by a reverse print process can significantly reduce or completely eliminate migration of the set-off kind. It will still be necessary though to ensure that through migration does not occur through the over-coat or encapsulating layer. Generally this is a less attractive approach due to the extra cost of such processing, although there are many types of food packaging printed by conventional printing that is handled in this way. In some cases the additional benefits of the digital ink jet process may be great enough to warrant such an additional process step.

Conclusion

Ink Jet printing of indirect food packaging will be an important market area as the technology matures. There are clearly challenges in meeting the requirements of this type of packaging with ink jet, but is likely that through new innovative chemistry and careful consideration of total system design the issue of migration and taint can be controlled adequately.

References

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Biography

Nigel Caiger received his Chemistry degree from Oxford University in 1985. He joined SunJet (formerly Coates Electrographics) in 1989 and is now Technical Manager, overseeing the activities of a development and customer support team, working on various ink jet technologies including UV-Curing, phase change, water, oil and solvent based inks. He has several patents in the field of jet inks.

Shaun Herlihy graduated in Applied Chemistry from Trent polytechnic in 1987. He joined the Group Research Department of Coates Lorilleux in 1989 and has been completely dedicated to the field of radiation curing ever since. He completed his PhD from the University of Kent in 1997, in the field of photoinitiator chemistry. He is now a Principal Scientist within Coates Lorilleux, St Mary Cray Research – Science Group.