Low Migration UV-curable inkjet inks for food packaging

By Frank L. Schelfaut, dr. sc.
Frank is technical writer and principal of External Resources Management specialized in marketing communication projects for hi-tech companies.

August 2013
1. Future trends in package printing

As package converters also became print service providers and package design evolved as a marketing tool for brand owners, the demand for digital package printing has grown substantially since it allows for differentiation and customization in short-runs – two important assets in the competition for maximum visibility on the shelves.

Looking at the trends of printing worldwide, everyone has the feeling that the volume of printed products is declining year after year. This is certainly true for consumer marketing and information print applications where web-based delivery, as provided by e-readers, smart phones and tablets, has a negative effect on the demand for printed products. However, in certain other markets, such as the packaging industry, printing cannot be offset by electronic delivery and while the commercial value of package printing is gaining importance the expected annual volume of package printing will follow suit – as can be seen from the chart below (PIRA, 2011). Due to its high degree of versatility and the potential of printing variable data on several substrates, digital package printing is rapidly closing the gap with conventional printing techniques and moving into mainstream technology.

### Global print market — print products

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>Books</td>
<td>38,715</td>
<td>38,155</td>
<td>36,378</td>
<td>-6.0%</td>
<td>34,902</td>
<td>34,284</td>
<td>32,428</td>
<td>-10.9%</td>
</tr>
<tr>
<td>Magazines</td>
<td>69,430</td>
<td>69,157</td>
<td>66,434</td>
<td>-4.3%</td>
<td>64,655</td>
<td>64,478</td>
<td>64,272</td>
<td>-3.3%</td>
</tr>
<tr>
<td>Newspapers</td>
<td>51,312</td>
<td>50,996</td>
<td>47,411</td>
<td>-7.6%</td>
<td>45,932</td>
<td>44,855</td>
<td>41,447</td>
<td>-12.6%</td>
</tr>
<tr>
<td>Directories</td>
<td>12,772</td>
<td>12,755</td>
<td>12,265</td>
<td>-4.0%</td>
<td>11,837</td>
<td>11,692</td>
<td>11,156</td>
<td>-9.0%</td>
</tr>
<tr>
<td>Security</td>
<td>11,178</td>
<td>10,869</td>
<td>10,393</td>
<td>-7.0%</td>
<td>9,969</td>
<td>9,788</td>
<td>9,430</td>
<td>-9.3%</td>
</tr>
<tr>
<td>Advertising</td>
<td>87,124</td>
<td>86,383</td>
<td>82,599</td>
<td>-5.2%</td>
<td>80,496</td>
<td>79,716</td>
<td>79,011</td>
<td>-4.3%</td>
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<tr>
<td>Office stationery</td>
<td>25,825</td>
<td>22,866</td>
<td>21,149</td>
<td>-18.1%</td>
<td>21,113</td>
<td>20,573</td>
<td>19,326</td>
<td>-8.6%</td>
</tr>
<tr>
<td>Commercial</td>
<td>126,830</td>
<td>128,181</td>
<td>126,334</td>
<td>-0.4%</td>
<td>123,726</td>
<td>124,938</td>
<td>129,300</td>
<td>2.3%</td>
</tr>
<tr>
<td>Packaging</td>
<td>187,375</td>
<td>191,046</td>
<td>186,561</td>
<td>-0.4%</td>
<td>186,978</td>
<td>190,085</td>
<td>203,321</td>
<td>9.0%</td>
</tr>
<tr>
<td>Labels</td>
<td>27,942</td>
<td>27,722</td>
<td>26,562</td>
<td>-4.9%</td>
<td>25,767</td>
<td>25,557</td>
<td>25,148</td>
<td>-5.3%</td>
</tr>
<tr>
<td>Total</td>
<td>684,685</td>
<td>682,485</td>
<td>656,048</td>
<td>-4.2%</td>
<td>643,058</td>
<td>641,066</td>
<td>646,316</td>
<td>-1.5%</td>
</tr>
</tbody>
</table>

Looking at the global market for digitally printed packaging by end-use sector, a recent PIRA study on the Future of Digital Package Printing estimates a compound annual growth rate of 27.8% (between 2009 and 2014) for the food and beverages segment. This is well above the expected average CAGR of 23% across all end-use segments, which also include Pharmaceuticals (23.2%), Cosmetics (20.3%), other consumer products (18.8%) and industrial (22.7%).
Since the food and beverage sector counts for more than 50% of all packed products, it is clear that much of the R&D efforts in digital package printing will be devoted to the specific requirements in this end-use segment. Contamination or tainting of the packaged food, and in particular the safety of the package-printing process, is obviously one of the most important solicitudes.

Today, manufacturers and ink suppliers of package printing systems are still confronted with some regulation uncertainty but legislation has finally started to emerge, strongly supported by industry initiatives. The basis of the current legislations on printed packaging and food contact is always that the ink manufacturers take responsibility for preparing ink formulations in compliance with legislative requirements, and that the printers/converters take charge of securing the appropriate quality of the ultimate food packaging.

As to food package printing inks in Europe there are first of all the guidelines provided by European Printing Ink Association (EuPIA), which involve general guidelines and a negative list of banned compounds. In Europe most of the attention today is going to the Swiss legislation (“Ordinance on Materials and Articles in Contact with Food”, SR 817.023.21), promulgating a positive list of compounds. Many European companies use this guideline today. Germany is preparing a similar type of legislation, which also incorporates a positive list. EuPIA also issues documents on GMP (Good Manufacturing Practices) for the production of packaging inks formulated for use on the non-food contact surfaces of food packaging and articles to come into contact with food1. This GMP guideline describes all the practicalities for formulation, production and control of the inks. The US Food and Drug Administration (FDA) adheres to the no-migration principle and, therefore, does not impose specific guidelines on inks (except for direct food contact).

This white paper focuses on inkjet applications for primary food packaging and attempts to shed some light on the possibilities of keeping contaminating substances, potentially released by UV-inkjet inks, at bay.

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2. Food safety and packaging

Before considering the package printing technologies in relation to food safety it should be emphasized that contamination or tainting of food and beverage is mostly relevant to primary packaging, i.e. the package or wrap that is in immediate contact with the product inside. With the exception of printing on the food itself (think of M&M’s®) where absolutely safe and edible products are used, food package printing is limited to so-called indirect printing on the outside of the packaging, in order to avoid long term contact between the printed substance and the food or beverage. Despite printing on the outside of the packaging substrate, food contamination by ink compounds can still occur in several ways, the most important being migration and set-off. Migration means that ink compounds reach the food product by diffusion through the packaging substrate. Set-off means that ink compounds from the printed layer are transferred to the food-product facing side of the substrate. Set-off can occur when the prints are stacked or rolled up, prior to being used in the package conversion process.

Over the last years several cases of food contamination by ink compounds were extensively discussed in the press. It all started with the so-called ITX case in Italy, whereby baby milk was contaminated with the photo-initiator ITX from UV-curing ink.²

The printing process is, however, not the only source of potential contamination. The packaging material itself may also contain tainting substances. Phthalate plasticizers, for example have attracted a lot of attention in the past and more recent reports involved the contamination of corn flakes by mineral oils from printing inks contained in recycled paper and carton³.

In fact, all measures with respect to the printing on primary packaging materials are just one element of a multi-faceted food safety practice, which starts at the responsibility of brand owners, packaging companies and/or converters to define all relevant parameters of the package design. Food-safe packaging thereby results from a risk assessment that takes into account the food properties, the expected shelf life, the

² http://news.bbc.co.uk/2/hi/europe/4459520.stm
storage conditions and the potential of contamination from all possible sources. The fact that all stakeholders in the product and package chain are becoming increasingly conscientious about the food safety and packaging aspects is seen as a very positive evolution.

Barrier substrates

In the first place, converters will select the adequate substrates and other materials in compliance with the packaging specifications provided by the food industry. These specifications may foresee in barriers to certain gases, liquids, radiation or other substances. The barrier is usually intended to prevent both, penetration of substances from outside and quality loss (taste or smell) of the packaged product inside. Regardless the package printing process that will be used – conventional or digital printing – the substrate itself can act as a barrier that prevents the diffusion of print-related substances through the package wrap. Glass and metal foils typically have a high barrier quality towards ink compounds. When the printed package substrate is stored – as a stack of sheets or rolled up - prior to being used in the conversion process, contamination of the food-facing side remains possible through set-off and other measures need to be taken to eliminate this source of contamination.

Functional barrier layers

A method that is often used in conventional and toner-based digital food package printing is by containment of the printed ink or toner in-between two barrier layers – one on top of the package substrate and one other that is laminated over the printed surface. In order to be effective, the latter must be applied in-line, i.e. before the printed sheets come off the press.

In digital food package printing HP Indigo and Xeikon dominate the market. Their digital presses use primers for the substrate and in-line laminators so that the printed layer is sandwiched between physical barriers in order to prevent tainting substances from reaching the food product. The success of HP Indigo and Xeikon presses in this field of application illustrates the increased acceptance of digital package printing and its functional capabilities surpassing those of traditional printing.

Low migration inks

A third – and obvious – possibility is to develop “low migration inks”, but although the term is widely used in a generic sense, Low Migration (LM) inks as such do not exist. An ink formulation for printing on the outside of primary packaging can only contribute to safe food packaging if the necessary precautions have been taken. Also the conditions of the printing process and the application are extremely important, especially in the case of UV-curable inks. It is important to understand that a specific ink formulation can be developed that is safe for food packaging in combination with certain other variables, such as a given substrate, a specific type of foodstuff under certain storage conditions, to be handled or processed in a given temperature range and over a defined amount of time, etc. But it is not guaranteed that this same ink formulation will be food-safe for all other combinations of substrate, food type, and storage or processing conditions.

Moreover, the qualification of any solution (whether LM ink or other measures) that claims to be a remedy against migration of ink substances doesn’t mean much unless proven in advance. Therefore, the use of migration testing is indispensible during the process of implementing a packaging solution to identify food safety risk from inks, packaging material and process, and is therefore part of the acceptance procedure.
Migration test methods are typically based on the use of a food stimulant, which is contained in the printed food packaging during specific conditions of time, temperature etc., related to the type of food and usage conditions. In Europe, migration test methods are described in detail by European Standards. On the one hand, there is the European Standard EN 1186 for overall migration. On the other hand, there is the European Standard EN 13130 for specific migration testing. Accredited analytical laboratories offer their services for migration testing according to these methods, including Fraunhofer⁴, Intertek⁵ and Fabes⁶.

A key figure in the allowable level of migration and/or set-off for ink compounds is 10 µg/6 dm² (6 dm² is the typical surface area of packaging material for 1 kg of food) per ink compound. This ratio of 10 µg/1 kg of food is also described as 10 ppb and is the rule-of-thumb for the allowable migration limit for an ink compound in the majority of legislations, but this limit can be higher, when substantiated by sufficient toxicological data.

### 3. UV-inkjet in food package printing

In its current status Inkjet printing for the packaging segment mainly focuses on the printing of labels, whose safety risk is at the level of secondary packaging. When moving into primary packaging, many primary food-packaging substrates require the use of UV-curable inks.

The formulation of UV-curable inkjet inks builds on a technology that has already been around for quite some time, e.g. in traditional print processes, such as offset, screen printing and flexography. The UV-curing inks for these printing technologies have substantially higher viscosities in comparison with that of UV-inkjet formulations.

<table>
<thead>
<tr>
<th>Standard UV-inkjet ink formulation</th>
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<tbody>
<tr>
<td>Oligomers</td>
</tr>
<tr>
<td>Monomers</td>
</tr>
<tr>
<td>Pigment</td>
</tr>
<tr>
<td>Additives</td>
</tr>
<tr>
<td>Photo initiators</td>
</tr>
</tbody>
</table>

The liberty to use high-viscosity inks gives the ink formulator much more freedom in the selection of polymerizing compounds. They form the bulk of the ink and are of extreme importance for determining the required ink viscosity. Generally the UV inks for the traditional printing processes contain high amounts of

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⁴ http://www.ivv.fraunhofer.de/load.html?/mainframes/english/service/pc1.html  
⁵ http://www.intertek.com/packaging/testing/migration-for-food-contact-materials/  
⁶ http://www.fabes-online.de/migracell.php?lang=en
oligomers and pre-polymers, along with a lower-molecular weight monomer that is used as the so-called diluent for fine-tuning the viscosity.

For UV inkjet, however, the demand for high ink jet throughput speeds at the highest possible resolution has led to the design of sophisticated print nozzles that require low viscosities in the range of 10 – 30 cps. This requirement is a limiting factor in the selection of viscosity-related ink components and a particular constraint to the choice of polymerizable compounds. In consequence, only a very limited amount of oligomer substance is possible in UV-inkjet inks, the bulk of which will be constituted as a mix of low-molecular weight, hence low-viscosity monomers. In primary food package printing the use of low-molecular weight monomers increases the risk of migration to the food. Migration, however, is not restricted to unreacted monomers but may also involve photo initiators and some additives in the UV-inkjet ink.

4. Migration of UV-inkjet ink components

A standard UV-inkjet ink formulation consists of:

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oligomers</td>
<td>0 – 15%</td>
</tr>
<tr>
<td>Monomers</td>
<td>60 – 85%</td>
</tr>
<tr>
<td>Pigment</td>
<td>3 – 8%</td>
</tr>
<tr>
<td>Additives</td>
<td>1 – 8%</td>
</tr>
<tr>
<td>Photo initiators</td>
<td>6 – 12%</td>
</tr>
</tbody>
</table>

Standard UV-curable inkjet inks (as used in wide format printers for the Sign & Display market) are developed to deliver good image quality, high color gamut and physical properties of the cured inks such as adhesion, scratch resistance, solvent resistance etc.

The use of oligomers in inkjet inks is strongly limited by jetting performance and reliability issues. Oligomers, pre-polymers and polymers in inkjet inks have the tendency indeed to disturb drop formation in the nozzles. Depending on the type and concentration of these compounds, their presence (even sometimes in low concentrations) may even result in a complete failure of drop formation.

The proper selection of the ink components and their concentration is determined by a reconciliation of the above requirements with the cost of the ink formulation. Therefore, formulators will mostly use commercially available monomers, which are often of technical grade and also comprising certain byproducts. Such formulations are perfectly acceptable since migration issues are not relevant for these applications. UV-inkjet for food packaging, however, is another story.

The curing degree of standard UV inkjet inks is typically between 80 and 95% and sufficient for the required specifications in non-food applications. However, the use of inks with low-molecular weight compounds and other substances or byproducts – all prone to migration - may involve risks in applications where food safety is concerned, especially if the degree of ink curing is far from complete.

A seemingly obvious solution could be the containment of migrating ink substances between physical barrier layers, as applied in toner-based digital printing systems.

Migration trough the substrate base could be prevented by means of a primer layer that is applied prior to
inkjet printing, but this solution would jeopardize, or at least compromise, an important advantage of UV inkjet, which is the capability of printing on virtually every substrate surface. A similar caveat holds for the possible application of a laminate on top of the printed layer, which should be done in-line in order to prevent set-off. An in-line laminator would involve a considerable slow-down of the inkjet printing press since the jetting process and the lamination process, both run at a different pace.

In order to preserve the advantages of UV inkjet printing over other digital technologies, a focused development of more fundamental solutions for the migration problem in primary food packaging is required to obtain specific Low-Migration (LM) UV-inkjet ink formulations.

5. **CCT technology**

Using high-purity ink compounds that do not contain by-products – which are typically low in molecular weight and thus prone to migration - is one first step towards LM inkjet inks, but this is not enough.

Agfa Graphics has developed and patented a specific ink technology, denoted as the Complete Crosslinking technology (CCT). By controlling the reactivity of polymerizable compounds, combined with photo-initiators suited for low migration, the polymerization kinetics can be monitored to obtain a degree of crosslinking that is nearly 100% complete.

As opposed to conventional UV-curable inkjet ink formulations, where unreacted acrylate monomers are loosely distributed across the cross-linked network, and thus capable of migrating, the CCT technology delivers a higher degree of crosslinking so that (most) all of the monomers become part of the polymeric network. The mixture of monomers used in the Agfa LM inks results in low ink viscosity, as required for the jetting process, while the CCT technology allows for the highest possible degree of crosslinking.
As explained in Frank Schelfaut’s White Paper Agfa’s CCT technology hinges on special reactivity characteristics of the polymerizable compounds, and the use diffusion hindered photo-initiators.

The selection of the polymerizable compounds is a first crucial component of the CCT technology. The monomer mix needs to be highly reactive to deliver high curing degree but also low in viscosity for jetting through sophisticated inkjet print heads. Therefore combinations are made of monomers of different degrees in reactivity, especially containing a large amount of a unique monomer with two different types of polymerizable groups, which shows high reactivity while being very low in viscosity.

The choice of diffusion-hindered photo-initiators is equally important. There are several ways to impede the mobility of the photo-initiator. One of them is to increase the molecular weight by using difunctional or polymeric molecules so that the diffusion speed is reduced. Another way is to increase the reactivity of the photo-initiators so that they are trapped within the polymerizing network. This can be accomplished e.g. by selecting multifunctional and/or polymerizable photo-initiators.

Diffusion hindered photo-initiators are preferably selected from a group consisting of non-polymeric di- or multifunctional photo-initiators, oligomeric or polymeric photo-initiators and polymerizable photo-initiators. Agfa LM inks do NOT contain ITX, benzophenone, methoxy-benzophenone, and others.

The proper combination of the monomer mix, the photo-initiators, the pigments and the additives allows Agfa to fine-tune their LM ink technology and to formulate LM inkjet, targeted to very specific applications.

This selectivity follows from the mere fact that there is no one-size-fits-all LM ink that is suited for all applications wherein migration risk is at stake. Depending on the use and of the foodstuff package, different requirements may be imposed to the cured UV ink, which makes every LM ink formulation very application-specific. The combination of low migration, high image quality and physical resistance properties (e.g. high scratch resistance and excellent adhesion), can be achieved by a specific formulation tuned to accommodate the specific substrate, printing system and application, but this formulation may be totally inadequate under different circumstances.

Provided intensive R&D, dedicated LM inks can be formulated with maximized performance. This will result in LM inks for different types of applications, but also for different designs of printing systems, e.g. for curing by Hg bulb, pinning with UV LED and final curing with Hg bulb, and even for UV LED curing only (thanks to the development of new high-dose UV LED systems).

Use of the CCT technology in the LM ink, not only keeps the migration of monomers at bay but also prevents the migration of photo-initiators and their break-down products. To do so the Agfa LM inks comprise one or more so called diffusion hindered photo-initiators. These are photo-initiators that exhibit a much lower mobility in a cured ink layer than monofunctional photo-initiators, such as benzophenone.

With the increasing demand for low-viscosity UV inkjet inks that can be used successfully and with good jetting properties in the newest generation of high-speed and high-resolution print heads, the CCT technology is an elegant solution for low migration UV ink formulations that can be safely applied in the most demanding segment of food packaging.

Frank L. Schelfaut