

Food Safety and Digital Printing

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April 2012

Food safety is hardly ever out of the news. Moreover, it is not only about the hygienic production, processing, and storage of food. There is more to food safety than avoiding bacterial contamination. In 2005, isopropyl thioxanthone (ITX), a photoinitiator used in UV-curable inks, was found in baby milk. In 2009, other photoinitiators were detected in breakfast cereals packed in polyethylene pouches inside cardboard boxes that were only printed on the outside. More recently, in 2011, mineral oils from liquid printing inks were discovered in recycled paper-board used for food packaging. If it had not done so already, the packaging industry now realized that substances used in printing inks could contaminate food even without direct contact.

With digital printing gaining acceptance in the packaging market, this paper aims to provide a better understanding of how different digital printing technologies compare as far as food safety is concerned.

Packaging includes folding carton, flexible packaging, and labels. The discussion is limited to indirect contact between printed matter and food – few packaging applications require print on the inside in direct contact with food. For the sake of brevity, contamination from the packaging materials is not considered either. However, the reader should be aware that there are regulatory restrictions on these materials.

Rules, Requirements, and Restrictions

Different stakeholders apply different requirements regarding food safety. The only legally enforceable rules are those imposed by regulatory authorities. However, organizations and interest groups, certified laboratories, and, not least, brand owners have established requirements as well.

Regulatory Authorities

Countries worldwide have their own regulations. In Europe, the European Commission issues directives and regulations, but member states have some leeway on local implementation. While there is a framework regulation on materials and articles intended to come into contact with food, which is applicable to all food packaging, there is not yet any specific European legislation concerning printing inks for these applications. Nevertheless, some European countries may have explicit requirements for packaging inks. Switzerland, for example, has issued restrictions on the components used in inks for food packaging applications. The Swiss Ordinance on Materials and Articles in Contact with Food lays down a list of permitted substances, i.e. the only substances that may be used in the manufacture of food packaging printing inks marketed in Switzerland. This Ordinance is by far the most stringent in Europe and has gained international recognition.

In general, European legislation defines authorized substances, for which it imposes contamination limits (see below). Extensive testing by accredited laboratories is required to demonstrate whether a specific application is 'safe for purpose'. In the US, FDA regulations apply.

Organizations and Interest Groups

In the absence of harmonious European – not to mention global – legislation, several organizations and interest groups have each tried to streamline the existing regulations. For example EuPIA, the European Printing Ink Association, has developed guidelines for its members, based on the current European framework regulation, and provides detailed recommendations on how to formulate inks that will comply with this regulation.

Certified Laboratories

Several independent laboratories test inks and printed matter and issue declarations of conformity and product certifications. Well-known examples are Isega, Intertek, and Eurofins. The findings and advice of these laboratories inevitably influence the consensus.

Brand Owners

Increasingly brand owners are issuing guidelines, including lists of authorized and non-authorized substances. The Nestlé Guidance Note on Packaging Inks, for example, stipulates that only components that are listed in the Swiss Ordinance on Materials and Articles can be used for packaging inks, but it also explicitly excludes some of these (e.g. certain photoinitiators, acrylates, and solvents). Like the Swiss Ordinance, it is increasingly used as a reference. Moreover, while the restrictions imposed by Nestlé are not necessarily required by other brand owners and/or for other applications, there is definitely a market advantage in being able to claim compliance with Nestlé's guidelines.

It is worth noting that food safety, like many health-related issues, is as much about perceived safety concerns as it is about actual concerns. Brand owners increasingly opt for the most stringent rules possible. Printers, designers, and marketers have no option but to comply, as food safety has a significant impact on brand image.

Migration and Food Safety

As pointed out, the cases mentioned above show that substances from the printed layer on the outside of food packaging could contaminate food, even without direct contact. The mechanism that causes this contamination is known as migration.

Migration and Migration Thresholds

Migration refers to the transfer of substances from the packaging to the food. Migration is a diffusion-controlled process, i.e. it involves a net transport of molecules (known as migrants) from an area of higher concentration to one of lower concentration.

The transfer of ink components¹ from the printed layer can occur via penetration of the migrants through the packaging material, via set-off (see below) or through gas-phase migration. Migrants are substances that have sufficient migration potential due to their chemical composition and/or size.

Migration depends on several factors:

- Size of the migrant molecule – the larger the molecule (the larger its mass), the lower its mobility, and therefore the less its tendency to migrate.
- Temperature – all things being equal, migration is a thousand times faster at 100°C than at room temperature.
- Nature of the food inside the packaging – migration of most organic molecules is more pronounced into fatty foods than into dry foods.
- Nature of the packaging material – see below.
- Type of coating applied onto the printed surface – especially important to avoid set-off migration (see below).

With a view to limiting the risk, legislators have defined migration thresholds or limits. Based on toxicological evaluations, the EU authorities have compiled positive lists of 'evaluated substances' that are part of the existing packaging regulations. These lists provide acceptable migration thresholds for individual substances, i.e. specific migration limits (SML). The SML is the maximum permitted amount of a given substance that can be released from a material (packaging material and/or printed layer) into food. Migration limits are typically expressed in ppm or ppb². As mentioned earlier, in the EU, printing inks are generally not explicitly regulated, but many evaluated substances are used in printing inks and therefore have to comply with the SML determined by the EU. Non-evaluated substances for which no toxicological data is available should not be detectable. A generally accepted definition of 'detectable' is 'below 10 ppm'.

The Swiss Ordinance explicitly imposes thresholds for substances in food packaging inks. It includes a list of permitted substances (part A) that have been toxicologically evaluated and for which an SML has been established. A second list (part B) includes non-evaluated substances for which the default SML has been set at 10 ppb.

1 As stated above, this paper does not discuss the migration of substances from the packaging material itself.

2 ppm and ppb: parts per million and parts per billion. Both are measures of concentration by volume or by mass. 1 ppm is equivalent to 1 mg/kg; 1 ppb is equivalent to 1 µg/kg. 10 ppm is a migration level that complies with most international safety laws on food packaging. To put things in perspective, 1 ppb is equivalent to 3 seconds in a century.

Set-off

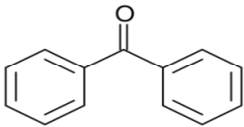
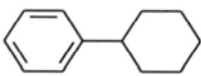
Set-off migration is the unintentional transfer of printing ink components from the outer printed surface to the food contact surface on a reel (reel-to-reel printing), in a stack or during storage (e.g. stack of printed paper cups). Note that contamination due to set-off migration can occur even in the presence of a functional or near-perfect barrier (see below).

Functional Barrier

One way to prevent migration is to apply a perfect barrier that is impermeable to any gaseous, liquid, or solid substance and does not itself release any substances. However, perfect barriers do not exist.

A functional barrier is a barrier consisting of one or more layers that reduces the migration of authorized substances into food below their specific migration limit and also reduces the migration of non-authorized substances to a non-detectable level. This functional barrier can be an additional inner pouch (e.g. as used for the packaging of cereals inside cardboard boxes) or the printed substrate. Whether or not a material is a functional barrier depends on (1) its defined conditions of use, (2) the nature and concentration of the substance for which it should act as a barrier, (3) the nature of the food inside the packaging, and (4) storage time and conditions (e.g. temperature). Solid layers like glass or metal are supposed to act as a functional barrier under all normal circumstances. For plastics, it is impossible to state that any type or thickness will act as a functional barrier under all circumstances.

The table below shows diffusion data for benzophenone, a model molecule for a photoinitiator, and phenyl cyclohexane, a model molecule for a solvent, through different polymers at 40°C.

Polymer	Benzophenone	Phenyl cyclohexane
		
	-log (D)	-log (D)
HDPE (high-density polyethylene)	8.3	8.3
LDPE (low-density polyethylene)	7.6	7.8
LLDPE (linear low-density polyethylene)	8.3	8.1
PP (polypropylene)	9.4	9.3
PVC (polyvinyl chloride)	8.5	8.4
PET (polyethylene terephthalate)	16.0	18.0
EVA (ethylene vinyl acetate)	7.5	7.3
EVOH (ethylene vinyl alcohol)	9.9	
PA (polyamide)	10.5	10.9
PS (polystyrene)		15

-log (D): Diffusion coefficient, a measure of how quickly the molecule can diffuse through the polymer. The higher the number in the table above, the slower the diffusion. A difference of 7.7 (almost 8) between high-density polyethylene and polyethylene terephthalate (a form of polyester) translates to a difference in diffusion speed by a factor of 10^8 (diffusion through polyester is slower by a factor of 10^8 than diffusion through HDPE).

Source: A. Feigenbaum et al., 'Functional Barriers: properties and evaluation', Food Additives and Contaminants, Volume 22, Issue 10 (2005): 956-967.

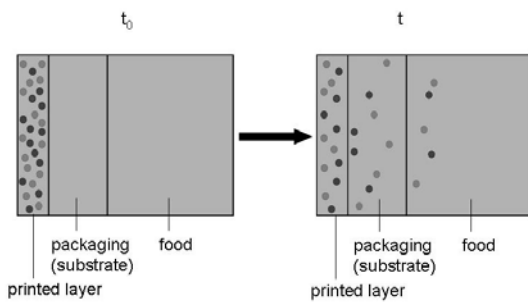


Fig 1 Diffusion migration through permeation

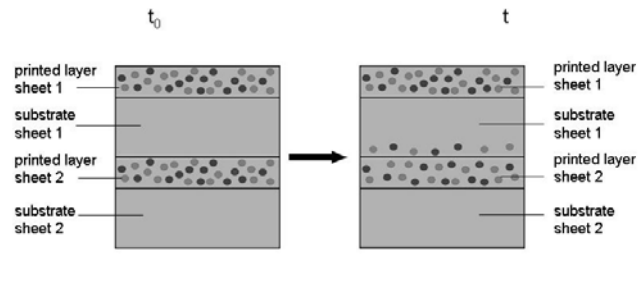


Fig 2 Set-off migration

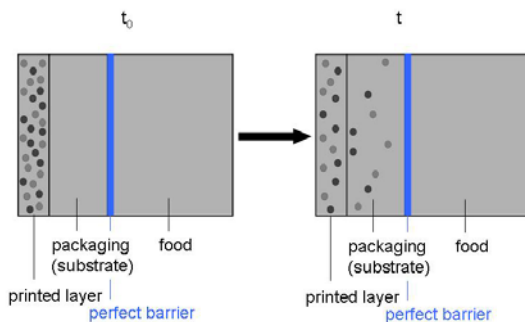


Fig 3 Perfect barrier

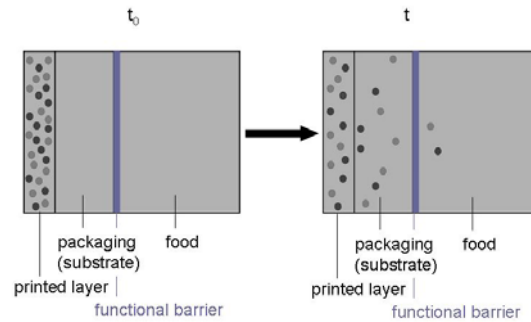


Fig 4 Functional barrier

Not all Technologies are Equal

How do different digital printing technologies compare as far as food safety is concerned? To help answer this question, it is important to understand how they compare with regard to migration. First, a brief description of three commonly used digital technologies explains how they differ in the way in which print is applied to a substrate.

Digital Print Technologies - Basic Principles

Dry Toner Electrophotography

During electrophotographic printing, electrically charged toner particles are transferred to a substrate by an electrostatic field to form the printed image. The colorant used to produce dry toner is a pigment. Surrounding the pigment particles is a polyester resin, which is a polymer with a high molecular mass. Charge-controlling agents are dispersed in the resin to either speed up or – if necessary – slow down the charging rate and maintain the charging properties of the toner. Once the image is transferred to the substrate, heat is applied to fuse the toner to the substrate: Heat causes the toner particles to coagulate (i.e. the resin melts), forming a homogeneous, solid polyester film.

Liquid Toner Electrophotography

Liquid toner electrophotography differs from dry toner electrophotography in that the pigment particles are slightly smaller³. Surrounding the toner particles is a polyethylene-like resin, which, like polyester, is a polymer with a high molecular mass. The amount of resin surrounding the pigment is much less than in dry toner. The electro-

³Pigment particle size dry toner: 7 microns; pigment particle size liquid toner: 2 microns.

static transfer of liquid toner involves a 'carrier liquid', a mineral oil that is partly dissolved inside the pigment-resin system. In the final step of the printing process, prior to the transfer of the image to the substrate, heat is applied. The toner melts and most of the carrier liquid evaporates. The toner particles coagulate, forming a homogeneous, flexible polyethylene film on the substrate. After the image transfer, the evaporation process continues. Any residual carrier liquid should have evaporated within a few days.

Inkjet

In the inkjet printing process, liquid ink is 'jetted' through nozzles directly onto the substrate to form the printed image. The colorant used to produce the high-performance inks is a pigment, as in toner. The solid pigment particles are dispersed in a carrier liquid to form a fluid. Surface treatment of the pigment particles with dispersion agents ensures a stable colloidal solution.

In water-based inkjet, the carrier liquid is water. Heat is applied to dry the image and the water simply evaporates. This printing technique is rarely used for packaging applications, since adhesion to polymeric substrates is problematic. Instead, packaging applications rely on UV-curable inkjet ink, which can be used on a wider variety of substrates, including polymeric substrates.

In UV-curable inkjet, the ink is not dried but cured with ultraviolet light to fix the ink film to the substrate. The carrier liquid in UV ink is a reactive solvent containing monomers (e.g. acrylates) and photoinitiators. A monomer is a chemical with a simple molecular structure that can combine with other similar molecules to form a polymer. Under the influence of UV light, the photoinitiators form free radicals that react (cross-link) with other ink components (the monomers) to form a polymerized (cured) film. The ink is 'dry' when the cross-linking reaction is complete, i.e. when all components have been cross-linked.

Digital Print Technologies Compared

The table below compares three commonly used digital printing technologies with regard to migration of ink components.

It is clear that some technologies are more prone to contamination caused by migration than others are.

	Dry toner electrophotography (polyester-based)	Liquid toner electrophotography	UV-curable inkjet
Fixation	fusing	fusing and evaporation (transfusion)	curing with UV light
Carrier	air	mineral oil and conductivity agents	acrylic monomers and photoinitiator (~7%)
Molecular mass of carrier ⁴	not relevant	160-170	400-600
Pigment capsule	polyester polymer with high molecular mass	polyethylene polymer with high molecular mass	dispersing agent – cross-linked polymer to be formed during curing
Molecular mass of resin	high	high	high, provided curing is complete
Potential migrants from ink layer (worst case)	low molecular mass polyester resin fragments, some toner ingredients (e.g. charge-controlling agents)	residual mineral oil, low molecular mass polyethylene resin fragments, some toner ingredients	unreacted monomer molecules, photoinitiator fragments, disper- sing agent
Thickness of ink layer	4 microns	1.5 microns	5 microns
State of layer at room tempera- ture	solid	flexible	flexible
Chemical composition of layer	polyester	polyethylene	polyacrylate
Tendency to migrate out of ink layer at room temperature	low	low, provided evaporation of the carri- er liquid is complete	low, provided curing is complete

From a migration point of view, green indicates properties that slow or impede migration, while orange indicates properties that favor migration.

Potential Migrants

As outlined above, migration depends on several factors, a major one being the size of the potential migrant molecule: The larger the molecule, the lower its mobility, and the less its tendency to migrate from one layer to another.

The potential migrants differ depending on the digital print technology. Pigments are large, solid molecules that are not considered migrants. Migrants stem from the other ink components, one source being the pigment capsule, a polymer. Polymerization generally leads to a mixture of polymer molecules of different lengths and different mass. Indeed, the mass of a polymer is not fixed, but distributed around a mean value⁵. In dry and liquid toner, the pigment particles are encapsulated in a high molecular mass polyester or polyethylene resin. In practice, there will be trace amounts of low molecular weight fragments present as well. The same holds for UV-curable inkjet ink where unreacted monomers or photoinitiator fragments may remain. The migration speed of acrylic monomers is a billion times faster than that of polyester resin fragments⁶. Therefore, from a food safety point of view, it is crucial that the curing be complete. Among the potential migrants are not only low molecular mass fragments of the polymer pigment capsules, but also additives

⁴Molecular mass, often used as a synonym for molar mass, the mass (in grams) of 6.022×10^{23} particles (1 mole) of a specific molecule.

⁵The average molecular mass of dry toner polyester polymers is 6,000, i.e. the mass distribution is centered on 6,000 with the lowest mass fractions at 2,000 and the highest at 10,000.

⁶A difference in mass of a factor of 10 translates to a difference in migration speed of a factor of 10^9 .

Dry Toner is One Step Ahead

There are many aspects to food safety. Dry toner per se does not guarantee that the printed food packaging is safe for purpose. The toxicology of the toner components plays a role as well. However, with migration being of pivotal concern, dry toner does have an intrinsic advantage over other digital technologies. Further acceptance of digital printing for packaging applications will depend on specific developments to broaden the application area. Accurate color reproduction, color consistency, and lightfastness are equally important. Xeikon leads the way with its QA-I dry toner, which has been developed and formulated specifically with lightfastness and food safety in mind.

More Information

European Framework Regulation

Regulation (EC) No 1935/2004 of the European Parliament and of the Council of 27 October 2004 on materials and articles intended to come into contact with food and repealing Directives 80/590/EEC and 89/109/EEC is available on the EUR-Lex website <http://eur-lex.europa.eu/en/index.htm>.

Swiss Ordinance

Can be found at www.admin.ch

[EuPIA](http://www.eupia.org): www.eupia.org

Nestlé Guidance Note on Packaging Inks

Can be downloaded at www.xeikon.com/downloads

such as charge-controlling agents (dry toner), conductivity agents, mineral oil fractions (liquid toner), and dispersing agents (UV-curable ink). Evaporation and curing will eliminate these substances in liquid toner and UV-curable inkjet, provided the evaporation and curing processes are complete. However, there are many factors affecting the evaporation and curing process and most are beyond a printer's control. The result may be different and difficult to predict, depending on the substrate, the printing conditions and printing speed, the age of the UV-curing lamp, the coating, the use of in-line or off-line finishing, and the time elapsed between the printing and the packaging of the food.

Tendency to Migrate

Given the inevitable presence of potential migrants, how likely is it that these actually migrate out of the ink layer?

Both the state and the chemical composition of the layer are important. At room temperature, dry toner forms a thick, solid layer from which virtually nothing can escape. Due to their lower polymer content, liquid toner systems produce a thinner, slightly flexible ink layer. UV-curable inkjet produces a thicker, but equally flexible layer. The table listing the diffusion data through different polymers at 40°C (see above) also illustrates the tendency to migrate from these printed layers, with dry toner, liquid toner, and UV-curable inkjet forming polyester, polyethylene, and polyacrylate layers, respectively.

Dry toner clearly has an intrinsic advantage over the other two digital technologies as far as migration is concerned.

For more information check on www.xeikon.com or contact info@xeikon.com