Key Innovations that allow Low Migration Digital Printing with UV-curable Inks

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Abstract

The advent of digital printing techniques about 30 years ago, announced a new era at first in small scale office and home printing, further has emerged in industrial scale printing in a large variety of wide and super wide format applications and is now being rolled out in even more exciting applications ranging from high speed document printing over (food) packaging to product decoration and shows even strong growth in ceramic tile printing.

This paper focuses on the use of UV-curable inkjet inks for food packaging applications. Agfa has been playing a leading role in Low Migration digital printing with UV-curable inks and is continuously performing necessary research to keep this leading role. As inkjet printing technology evolves, also the inks have to evolve accordingly. Unfortunately for Low Migration printing, one of the trends goes to lower viscosity inks to cope with the newest generations of high speed, high resolution printheads. Even lower viscous monomers have to be used, increasing the migration risk. The current paper covers specific innovations in terms of chemistry to be able to combine low viscosity and low migration: the main focus lies on the use of a primer to capture any migrating monomer molecules.

Introduction

The importance of packaging continually increases: it is no longer just the container to hold and protect the products (food stuff), but the final opportunity for the brand owner to influence consumer buying decisions during the buying process. Brand owners want and need to differentiate their product more and more also by the packaging. Therefore new types of packaging 'formats' and shapes are designed and linked to a brand name. Also the brand image is intensively marketed by the logo (often a specific colour), the packaging and the printing (colours, style etc). Moreover, flexibility is needed because the information or extra additions (often linked to an event or special actions) demands changes of the prints much more often, resulting in drastical drops in run length.

So marketing-wise there is a clear need for digital solutions in the packaging market. The strongest emphasis in the digital printing of packaging lies furthermore in the food, beverage and pharmaceutical packaging markets, where digital printing can bring even more benefits specifically in terms of sustainability of the print on the product.

When considering this specific area of food-related packaging, besides the look of the product and its print as key marketing factors and the increased flexibility to cope with short runs, events, campaigns etc., these requirements are also to be met keeping in mind low migration (LM) quality and food safety as a key prerequisite. The applications within reach of digital printing in the field of food packaging are obviously label and the (foil) packaging material, but it can get even more interesting when also direct object printing becomes available.

Inkjet printing is becoming the most favourable digital printing technique because of the combination of high quality with high speed. Compared to toner based printing, further benefit lies in the fact that printing systems can be built for narrow and wide to super wide print width and printing is possible on a very wide range of substrates, without a coating (depending upon ink class). Inkjet printing in general can be based on different ink classes (aqueous, solvent, oil, UV-curable), but for package printing UV-curable systems are best suited: it is the most reliable method with the highest printing speed and it can be used on most packaging substrates, including rigid and flexible plastics (polyolefines), often even without prior coating.

The technological advantages of UV-curable inks must however meet the LM quality aspect needed for food packaging applications: inks must have low migration levels of their constituents to avoid contamination of the food. In analogue printing with UV curing this can be achieved by using high molecular weight photoinitiators and multi-functional polymerisable monomers or oligomers. For inkjet printing, however, this is not an option, mainly due to viscosity limitations.

The development of LM UV-curable inkjet inks was not established by just hybridizing the technologies from UV-curable inks as known from billboard and signage printing with analogue UV-printing inks designed for food packaging. The convenient use of multifunctional polymerisable compounds and photoinitiators with a relatively high molecular weight in order to limit the risk of migration as used in analogue printing inks does not work in digital inkjet print. Viscosity limitations are the biggest hurdle. The research resulted in a completely new choice of monomers and photoinitiators and the so-called complete crosslinking technology was created, characterized by very low amounts of migrateables and low odor of the printed product. This allows printing of UV curable inkjet inks of low viscosity while meeting the requirements of food and pharmaceutical packaging, but only if proper care is taken with regards to curing, printing speed, inertisation etc: parameters which are all strongly linked to the application. Recklessly printing on food packaging with UV (inkjet) inks is out of the question, that's probably why a lot of big brand owners are the early adopters of the Agfa LM inkjet technology.

While challenges to create low migration inks using UV-curable inks have always been massive, mainly due to the contradictions between reactivity, viscosity and low migration aspects, the latest trends in food packaging and inkjet equipment made it even harder. Indeed, the latest piezo inkjet printheads for UV inkjet are moving towards even lower viscosities to obtain higher print speeds and higher image quality. Besides this, UV curing tends to evolve into the direction of LED sources. And last

but not least, the packaging market is continuously looking for cheaper and simpler packaging materials. It should be clear these combinations pose a new level of challenges to the formulator as on the one hand high speed printing and LED curing have a massive impact on the available cure dose to get all monomers entangled in the network. On the other hand, the low cost substrates add even further complexity in a sense that the low cost is related to a low level of sophistication of the packaging materials and hence relatively lower barrier properties which leads to higher migration risks.

Residual, unreacted, monomers can cause problems in two different ways: set-off and migration. Set-off occurs in roll-to-roll printing or stacking of printed matter where the printed front-side of a packaging material comes into contact with the unprinted back-side (food side) and unreacted monomers are set off on the backside intended for direct food contact. Besides set-off, real migration through the packaging material can also occur and popular packaging materials suffering from such migration are usually olefin based substrates like polyethylene or polypropylene film. Due to the low viscosity of radiation curable inkjet inks, monomers easily penetrate into the substrate before they can be effectively cured.

In the continuing battle against migration, the latest innovation by Agfa is demonstrated: a technology based on the combination of vinylether (meth)acrylate based inkjet inks and a UV-curable blocking primer, making high speed digital printing compatible with low barrier substrates. The chemistry of the ink carrier and the blocking primer are adjusted in such a way that any migrating vinyl ether is covalently captured in the polymerized primer.

Legal background on LM inks

In the introduction, the viscosity requirement was already mentioned as a critical boundary for combining LM with UV inkjet. Because it is so critical, UV inkjet printing of food packaging cannot be considered a black box operation that needs no further attention after implementation: indeed, intrinsically low migration UV inks do not exist, especially for inkjet.

Unfortunately, the criticality was also observed by media and consumers too many times in a negative way in the last ten to fifteen years. A lot of attention was drawn towards UV inks because several ink-related chemicals were found in food stuff, in some cases even in most fragile applications such as baby foods. The main issue was the uncertainty on the toxicological impact of the nature and concentration of the detected compounds. This created an urge in a number of countries and companies to finally develop legislation and regulation in order to avoid this in the future.

What all legislation on printed packaging and food contact has in common is that the packaging ink manufacturers are responsible for preparing compositions meeting the legislative requirements, and that the printers are responsible for delivering the appropriate quality of the final food packaging.

Furthermore, what is also rather general is that materials and articles which are intended to be brought into contact with food-stuffs must not transfer any components to the packed foodstuff in quantities which could:

- endanger human health;
- bring about an unacceptable change in the composition;
- bring about deterioration in organoleptic properties.

In Europe this is part of the so-called "Plastics Regulation" EU 10/2011. This is focused on plastic packaging for foodstuff and covers (at least partially) printing inks for food packaging as well. Although not solely developed for printing inks, the general requirements are already clear: do not allow anything to transfer into food in a dangerous amount, do not induce a change the food and make sure the taste and smell of the food are not impaired by transfer of (ink) compounds. The EU 10/2011 also already describes migration levels for printing ink compounds but only in case they are also listed to be used in plastics: there is no ink-specific raw material listing. There is also no exclusion or positive list for inks in this regulation. In fact, on a European level, only the European Printing ink Association (EuPIA) goes a step further with guidelines mainly describing general compound qualities and a list of banned compounds. The U.S. Food and Drug Administration (FDA) uses the no-migration principle and hence does not impose specific guidelines or laws on printing inks (except for direct food contact). Switzerland is in fact at the forefront of legislation ("Ordinance on Materials and Articles in Contact with Food", SR 817.023.21). There is a positive list of compounds that can be used, with an indication of the allowable specific migration into food [1]. Germany is preparing a similar law (Swiss B-list vs. German Inventory list). The Swiss legislation currently only applies in Switzerland, but is growing to become a global industry standard. A key figure in the allowable level of migration and/or set-off is 10 µg/6 dm² (6 dm² is the typical area of pack-aging 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 specific migration limit for the different ink compounds in the majority of legislations. Provided sufficient toxicological data is available to confirm safe use at higher migration levels, this limit can be higher.

Besides this small selection of regulations (and also a few industry/ ink customer initiatives imposing positive and/or negative lists to suppliers of inks for food packaging) specifically set up for printing inks, there is another part of regulation that applies to inks and the printing process. It concerns the implementation of Good Manufacturing Practices (GMP). The principle of implementing Good Manufacturing Practices (GMP) applies to ink production as well as the printing process and is widely accepted in various legislations worldwide (Europe: 2023/2006/EC, USA: FDA). In the European legislation in fact a specific topic on inks is amended. Due to the fact that also this legislation remains rather vague on the implementation for inks, the EuPIA provided guidelines for implementing GMP in ink production. These documents are available for download on the organisation's website.

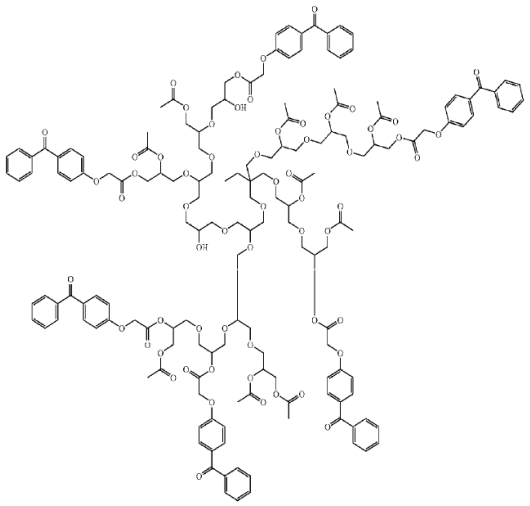
Methods

UV-curable inkjet inks are essentially made up of pigments (stabilised using dispersants) in an energy curable monomer matrix (typically consisting of acrylates, methacrylates etc), one or more photoinitiators that capture the UV light and transfer it into free radicals to start the polymerisation of the monomers. Surfactants, oligomers, polymers and other adjuvants might also be added to improve physical properties. The inks are jetted onto the substrates

by using piezo drop-on-demand inkjet print heads and cured with UV mercury bulb lamps (doped or not) and/or UV LED's.

The majority of a formulation is made up of the carrier, typically a monomer in UV inkjet due to viscosity limitations. In earlier publications [2] it was already revealed that the proprietary monomer VEEA was specifically designed by Agfa to allow low migrating yet low viscous formulations. This is accomplished by designing this highly reactive monomer as part of the complete crosslinking technology, yet having a low viscosity in the liquid phase.

The vast majority of commercial radiation curable compositions contain low molecular weight photoinitiators and co-initiators. When low molecular weight products are not built into the polymer network they are prone to diffuse out of the cured composition and can readily be extracted. There are two types of photoinitiators and the type is determined by the mechanism to generate a free radical: the photoinitiators that undergo Norrish Type I reactions, photolysis through a homolytic fragmentation mechanism of alpha-cleavage and directly form free radicals capable of initiating polymerization. The absorbed radiation causes bond cleavage to take place between a carbonyl group and an adjacent carbon. The photoinitiators that undergo Norrish type II reactions are activated with radiation and form free radicals by hydrogen abstraction or electron extraction from a second compound, a co-initiator or synergist that becomes the actual initiating free radical. A disadvantage of hydrogen abstraction over homolytic fragmentation is the necessity of a bimolecular reaction. Especially type II photoinitiators are a point of concern regarding extractable residues. Indeed, Norrish type I photoinitiators are normally built into the network except when the quantum efficiency for cleavage is less than unity or when side reactions occur yielding extractable degradation products. Norrish type II photoinitiators always require a co-initiator. A co-initiator or synergist is basically a molecule capable of transferring a hydrogen atom to the excited state of the type II photoinitiator. Aliphatic tertiary amines, aromatic amines and thiols are preferred examples of co-initiators. After transfer of a H to the type II photoinitiator, the radical on the synergist initiates the polymerisation. Theoretically the co-initiator is built into the polymer network. However, it is highly unlikely that both the hydrogen transfer and the initiation reaction yields are a hundred percent. Side reactions are likely to occur leaving unreacted synergist and side products in the composition. In food packaging printed upon with such a radiation curable inks, these low molecular weight residues remain mobile and if toxic will cause health risks upon being extracted into the food. Besides a few compounds of known low toxicological concern also high MW, high viscosity polymeric photoinitiators are commercially available and in use in UV inks for LM applications: several manufacturers have focused on polymeric thioxanthone photoinitiators and co-initiators. In LM UV inkjet, preferably high MW, yet low viscosity photoinitiators are used. These are not commercially available, so had to be custom made [3]. An example of such a photoinitiator, called a dendritic initiator, is given in the following figure. The use of it is described in detail in [4].



Generalised representation of a dendritic initiator

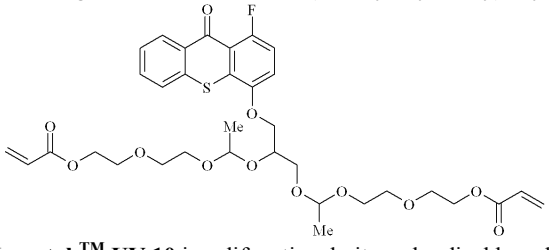
Another approach for creating LM photoinitiator concepts is the use of polymerisable photoinitiators, i.e. photoinitiators that can be locked inside the polymer network of the ink carrier (monomer) [5]. Their use is described in detail in [2] and [4].

In practice, a combination of dendritic, polymerisable [6], (commercially available) polymeric and proven low toxicity photoinitiators will be used.

The combinations of these, together with the proprietary monomer VEEA (based on a vinylether and an acrylate) yield a vast amount of ammunition to tackle the challenges of low migration in digital printing with UV- curable inks for inkjet printing. Due to the rise of earlier mentioned requirements in terms of speed, viscosity, LED curing and low cost substrate materials, these combinations do not seem to be efficient enough anymore to cope with tomorrow's challenges: high printing speeds and LED curing lower dramatically the available cure dose to get all monomers locked in the network. The low cost substrates are furthermore typically also lower barrier substrates properties which leads to higher migration risks.

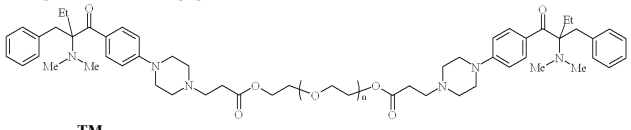
Materials

Thioxanthone-1 is a 22 wt% of a polymerizable thioxanthone according to Formula TX-1 in 2-(2'-vinyloxyethoxy)ethylacrylate:



Irgastab™ UV 10 is a difunctional nitroxyl radical based stabilizer supplied by BASF (Ciba).
Speedcure™ 7040 is a polymeric 4-dimethylbenzoic acid derivative supplied by Lambson.
Quantacure™ EHA is 4-dimethylaminobenzoic acid 2-ethylhexyl ester supplied by Ciba (BASF)
Irgacure™ 819 is phenylbis(2,4,6-trimethylbenzoyl)-phosphine oxide supplied by Ciba (BASF).

Omnipol™ 910 is a polymeric photoinitiator, supplied by IGM, having the following general structure:



Irgacure™ 369 is 2-(dimethylamino)-2-[(4-methylphenyl)methyl]-1-[4-(4-morpholinyl)phenyl]-1-butanone supplied by Ciba (BASF).
Byk™ UV3510 is a polyether modified polydimethylsiloxane, supplied by BYK-Chemie GmbH.
Genopol™ AB1 is a polymeric 4-dimethylaminobenzoic acid derivative supplied by Rahn.
Genopol™ BP1 is a polymeric benzophenone derivative supplied by Rahn.
Omnipol™ TX is a polymeric thioxanthone supplied by IGM.
Irgacure™ 819 is supplied by BASF (former Ciba).
SR9003 is a propoxylated neopentyl glycol diacrylate supplied by Sartomer.
VEEA is 2-(2'-vinyloxyethoxy)ethylacrylate supplied by Nippon Shokubai.
Sipomer™ PAM 100 is a phosphate ester of a polyethylene glycol methacrylate supplied by Rhodia.
Sipomer™ PAM 300 is a phosphate ester of a polypropylene oxide methacrylate supplied by Rhodia.
Genorad™ 16 is a polymerization inhibitor from RAHN AG.

Instrumental

Extraction cells conform EN 1186-1 (cell type B) were used in the migration experiments. Two circles with a diameter of 15 cm were cut from a printed sample. The two circles are mounted in the extraction cells with the non printed side in contact with the extraction solvent. The cells were closed and filled with iso-octane as food simulant. The cells were stored at room temperature for two days (conditions compliant with EC 10/2011, 2002/72/EC, 97/48/EC and 85/572/EEC for testing fatty foods for prolonged storage at room temperature). The extract was filtered over a 0.2 µm filter and analyzed with HPLC for quantification of VEEA.

The chromatographic method used an Altima™ C18 5µm column (150 x 3.2 mm) supplied by Alltech. A flow rate of 0.5 ml/min was used at a temperature of 40°C. A UV-VIS detection at 204 nm was used. The HPLC method used for all samples had an applied gradient with an end run = 38 min as given in Table 1 wherein eluent A was water and eluent B was acetonitrile.

Table 1

Time (min)	% eluent A	% eluent B
0	55	45
6	55	45
11	0	100 (linear gradient)
30	0	100
31	55	45
38	55	45

15 µl of the extract was injected and the VEEA concentration was determined in comparison with a reference sample (5 µl injected from of a solution of 1mg in 50 ml of CH3CN and dilutions thereof). The migrated amount of VEEA is expressed as food ppb. The amount, migrated from the total surface area of each sample in contact with iso-octane, expressed in µg, was recalculated to 6 dm², which corresponds to the surface area of a box containing one liter of a simulant. The recalculated amount of VEEA, expressed in µg corresponds to the amount that would have been migrated through the total surface area of the box in contact with one liter of the simulant. If the simulant would have a density of one, the extracted amount would correspond to the total amount of VEEA expressed as µg in one kilogram of simulant or ppb.

Results

A radiation curable CMYK inkjet ink set was prepared according to Table 2. All weight percentages (wt%) are based on the total weight of the inkjet ink.

Table 2

Ink component	wt% in Y	wt% in M	wt% in C	wt% in K
Dispersion 1	18.00	-	-	-
Dispersion 2	-	-	-	15.87
Dispersion 3	-	-	16.00	1.13
Dispersion 4	-	22.00	-	2.67
VEEA	66.38	30.14	34.98	23.00
Irgastab™ UV10	0.20	0.20	0.20	0.20
Thioxanthone-1	5.00	41.66	41.66	48.63
Speedcure™ 7040	1.42	2.50	1.16	-
Quantacure™ EHA	-	-	-	2.00
Irgacure™ 819	3.00	-	2.50	3.00
Omnipol™ 910	5.00	-	2.50	2.50
Irgacure™ 369	-	2.50	-	-
Byk™ UV 3510	1.00	1.00	1.00	1.00

Three radiation curable liquids Primer 1 to Primer 3 were formulated to be used as a primer in an inkjet printing in accordance with the invention. Their composition is given in Table 3, expressed as weight percentage of the total weight of the primer composition.

Table 3

wt% of compound	Primer 1	Primer 2	Primer 3
Genopol™ AB1	4	4	4
Genopol™ BP1	4	4	4
Omnipol™ TX	3	3	3
Irgacure™ 819	2	2	2
SR9003	67	67	72
Triglycidyl diacrylate	15	15	15
Sipomer™ PAM 100	5	-	-
Sipomer™ PAM 300	-	5	-

Primer 1 to primer 3 were respectively coated on BOPP (a 30 µm biaxial oriented polypropylene supplied as Propafilm RGP by INNOVIA), and on PE (a 50 µm LDPE substrate, supplied by

SEGERS & BALCAEN), using a 10 µm wired bar and cured using a Fusion DRSE-120 conveyer, equipped with a Fusion VPS/1600 lamp (D-bulb), which transported the samples under the UV-lamp of the conveyer until no visual damage was seen when whipping the surface with a Q-tip. This led to four substrates S1 to S4 and four comparative substrates S5 to S6 as defined in Table 4.

Table 4

Substrate	Type
S1	30 µm BOPP primed with primer 1
S2	30 µm BOPP primed with primer 2
S3	50 µm PE primed with primer 1
S4	50 µm PE primed with primer 2
S5	30 µm BOPP primed with primer 3
S6	50 µm PE primed with primer 3
S7	unprimed 30 µm BOPP
S8	unprimed 50 µm PE

A checker board type of pattern according to Table 5 was printed on each of the primed and unprimed substrates, wherein 1 represents a dark grey patch, 2 represents a light grey patch and 3 represents a green patch. The patches were printed, using the different inks of Table 2 using the screen percentages given in Table 6.

Table 5

1	2	3	1	2	3
3	1	2	3	1	2
2	3	1	2	3	1

Table 6

Patch	Color	Screen percentages of			
		C	M	Y	K
1	**Dark grey**	-	-	-	100
2	**Light grey**	60	60	60	20
3	**Green**	100	-	100	60

The patches were printed using a KyoceraTM KJ4A print head at a printing speed of 50 m/min in grey scale mode. The printing order was KCMY and LED pinning at 395 nm was used after printing K, C and M, using a water cooled LED with an output wavelength of 395 nm from Integration Technologies used at 0.75W/cm2 (250 mJ/cm2). The printed image was immediately off line further cured on a Fusion DRSE-120 conveyer using first a D bulb followed by a V bulb at maximum power and a belt speed of 40 m/min.

Two circles with a diameter of 15 cm were cut from each printed sample and the migration was determined.

From Table 7, it should be clear that the primers according to the present invention almost completely block the migration of VEEA through polyolefin type of substrates. It should be stressed that these results have been obtained in very harsh conditions. The printed image was described earlier and it is clear that a choice was made to incorporate all process colours but also stress was put specifically on the use C and K, in general considered to be the toughest colours to cure in depth. Furthermore, the food simulant used was iso-octane. It was used as a replacement for fatty foods. Normally vegetable oils are recommended, but it is known that iso-octane induces typically an even higher migration (often the substrate is weakened as well). The substrates that have been used are also worst case for migration due to their low thickness on the one hand, but also due to their olephinic character on the other hand. These types of substrates are typically characterized by low crystallinity and hence low barrier quality.

Table 7

Substrate	Migrateable VEEA (food ppb)
S1	< 10
S2	12
S3	<10
S4	11
S5	368
S6	181
S7	1086
S8	8207

Conclusions

The design of low migration UV-curable inkjet inks by Agfa has been a specific target and not a "Friday afternoon" experiment. The lack of truly appropriate commercial compounds is probably one of the reasons not many competitors are attempting to tackle this subject. The dedicated research and development of specific compounds such as monomers and photoinitiators led to the leading role Agfa currently holds in this field. Building on these foundations, even further fetched inkjet equipment and packaging applications can get within reach. The ever more demanding inkjet applications involving food packaging still preferably use UV-curable inks, but pose continuously higher risks for migration and put the formulator at the edge of its possibilities. It is shown that a dedicated primer design is capable of supporting the low migration aspect of low viscous high speed UV-curable inkjet printing inks, especially in the case of popular polyolefine substrates.

References

[1] http://www.bag.admin.ch/themen/lebensmittel/04867/10015/index.html?lang=en
[2] R. De Mondt, Closing migration routes, European Coatings Journal, issue 4/2013
[3] US7875698
[4] R. De Mondt, Low Migration UV-curable inkjet printing inks for packaging applications, submitted to Food Additives and Contaminants, 2013
[5] EP2189477
[6] EP2033949

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