

Low-Migration, UV-Curable Inkjet Printing Inks for Packaging Applications

By Roel De Mondt

For packaging applications involving food or beverage, food safety is very important. In analog printing technologies, UV-curable inks are used for indirect food contact applications. These UV-curable, low-migration (LM) inks are typically based on using multifunctional polymerisable compounds and photoinitiators with a relatively high molecular weight, thereby limiting the risk of migration.

For inkjet printing, however, this ideal scenario does not work, mainly due to viscosity limitations. The development of LM, UV-curable inkjet inks was not established merely by gently redesigning analogue printing inks. A low-viscous ink formulation was developed based upon the use of a combination of specific polymerisable compounds and photoinitiators, resulting in a very high degree of crosslinking and low amounts of migratables.

Introduction

Packaging is increasingly important because it is not just the product “container.” It is also the brand owner’s final opportunity during the buying process to influence consumers’ buying decisions. Brand owners use the packaging to differentiate their product. Therefore, new types of packaging “formats” and shapes are designed and linked to a brand name. Also, brand images are intensively marketed through the logos (often

a specific color), packaging and the printing (colors, style, etc). Moreover, flexibility in packaging printing is needed because the information or extra additions (often linked to an event or special actions) can demand making changes to the printings—often resulting in drastic drops in run length.

So 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—which are strongly regulated regarding compound migration and odor.

Inkjet printing is becoming the most favored digital printing technique because of the combination of high quality and high speed. Compared to toner-based printing, further benefit lies in the fact that inkjet 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 types can be based on different ink classes (aqueous, solvent, oil, UV-curable), but UV-curable inkjet printing systems are best suited for packaging printing because they offer the most reliable method with the highest printing speed and can be used on most substrates for packaging, including rigid and flexible plastics (poly-olefines), without a coating.

Legal Boundaries

A large number of packaging applications involves food or beverage packaging where, obviously, food safety is of outmost importance. After several incidents with inks in food packaging the last 10 years in Europe and the U.S., legislation has finally started to catch up, strongly supported by industry initiatives. Besides the above-mentioned technology-based restrictions for the inkjet printing process, these legislations constitute another restriction to LM inkjet ink development.

What the legislative mandates for printed packaging and food contact have in common is that the packaging ink manufacturers are responsible for preparing compositions in accordance with the legislative requirements and the printers are responsible for delivering the appropriate quality of the final food packaging.

In Europe, the European Printing Ink Association (EuPIA) provides a guideline for food packaging printing inks that describes mainly general compound qualities and includes a list of forbidden compounds. The U.S. Food and Drug Administration (FDA) employs the no-migration principle and, hence, does not impose specific guidelines or laws on printing inks (except for true food contact). Switzerland is, in fact, at the forefront of legislation with its “Ordinance on Materials and Articles in Contact with Food” (SR 817.023.21) that includes 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. The Swiss legislation is actually only applicable in Switzerland, but is growing to become a global industry standard.

Another part of regulation applies to inks as well as the printing process and concerns the implementation of Good Manufacturing Practices (GMP).

This is a widely accepted principle throughout the different legislations worldwide—i.e., Europe: 2023/2006/EC—and the same obligation applies for the U.S. FDA.

Even though there is only one country with a specific ink legislation, there is a general concern throughout different legislations regarding food contact materials. Materials and articles which are intended to be brought into contact with foodstuffs must not transfer any components to the packed foodstuff in quantities which could:

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

The latest European regulation applicable (at least partly) to printing inks for food packaging is the so-called “Plastics Regulation.” The Plastic Regulation (European Union Commission Regulation 10/2011) is the most comprehensive of the specific directives/regulations. This regulation came into force on May 1, 2011 (transitional until Dec. 31, 2015).

A key figure in the allowable level of migration and/or set-off is $10 \mu\text{g}/6 \text{ dm}^2$ (6 dm^2 is the typical packaging area for 1 kg of food) per ink compound. This ratio of $10 \mu\text{g}/1 \text{ kg}$ 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 throughout the majority of legislations. Provided sufficient toxicological data are available to support safe use in higher migration levels, this limit can be higher.

Experiment

Curing Speed

The percentage of the maximum output of the lamp was taken as a measure for curing speed—the lower

the number, the higher the curing speed. A sample was considered fully cured at the moment scratching with a Q-tip caused no visual damage.

Total Extraction

A sample of 3 cm in diameter was taken from each coated-and-cured ink composition. The sample was put in a beaker and extracted with acetonitrile using ultrasound for 30 minutes. The reference compounds were introduced as a 10-fold dilution of a solution of 10 mg in 50 ml. acetonitrile. High-performance liquid chromatography (HPLC) analysis was performed to determine the amounts using the total peak area compared to the peak area of the reference samples. This yielded the amounts of co-initiator extracted.

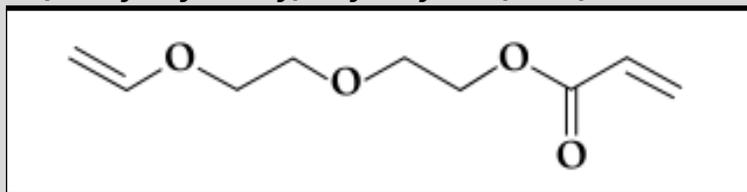
What is a Low-Migration Ink?

It should be clear that, although the current paper and several other publications on the market mention the term, there is no such thing as “LM inks.” An ink can only have intrinsically beneficial properties for LM or can be expected to be able to yield a safe food or pharma packaging if the necessary curing precautions (i.e., dose, UV type, inertization, etc.) have been taken.

Furthermore, an ink may yield a safe food packaging in combination with a given substrate, for a given application of foodstuff in a certain storage and processing temperature range and during a defined amount of time. It is perfectly possible for an ink to be considered LM for direct printing on a Polyethylene Terephthalate (PET) foil to wrap fresh vegetables and not appropriate as an LM ink to wrap chocolate in a printed PP foil. In these cases, there is a big difference in the simulants and the temperatures used for testing. The intrinsic migration potential is also a lot different for PET in comparison with poly-olefines (related to the amount of crystalline phase in the polymers).

FIGURE 1

2- (2-vinyloxyethoxy)ethylacrylate (VEEA)



What is Needed to Create an LM Ink?

An LM-UV ink differs from a regular UV ink not so much in the compounds used (i.e., for billboard printing), yet it differs in the nature of the compounds. At first, the compounds should be of high purity or the contaminants should be identified. The monomers should preferably be poly-functional, highly reactive or high in molecular weight (MW). Ideally, they should be a combination of these three aspects. In inkjet, due to the printhead requirements, this is narrowed down by viscosity limitations to only the highly reactive compounds. In the Agfa LM-UV inkjet inks, 2- (2-vinyloxyethoxy)ethylacrylate (VEEA) is one of the key ingredients (Nippon Shokubai) (Figure 1).

This molecule lacks high functionality and high MW, but is very

reactive. As an example, two black inks on a polyester substrate have been tested for total extraction with acetonitrile. The one ink contained VEEA (50 w/w%) in combination with di(propyleneglycol)di-acrylate (DPGDA) (30 w/w%), a common di-acrylate of relatively low viscosity and the other contained only VEEA (80 w/w%) as a monomer. Bar coating of identical amounts of ink onto a PET substrate was followed by curing using one LED-curing lamp (395 nm, 4W, Phoseon). The following total extraction results were obtained on these prints (Table 1).

It is clear from Table 1 that, although the amount of VEEA was raised in the formulation from Ink 1 to Ink 2, the amount of extractables remained in the same order of magnitude. Moreover, as DPGDA was removed from Ink 2 in comparison

with Ink 1 (obviously resulting in no extraction of DPGDA) this resulted in the total amount of extractable monomers to be reduced by one-third.

Besides the monomers, the next crucial ingredient is the photoinitiator (package). When developing something as innovative as LM, UV-curable inkjet inks, it is important to follow a clear strategy that is, as mentioned, restricted by legal boundaries. This means the Swiss legislation is definitely a starting point for new developments. There are several categories of photoinitiators that can be distinguished in the Swiss legislation. EuPIA has summarized these types in a very clear document which is available on the organization's website. This can be used as a first guideline.²

There is a clear distinction between appropriate LM photoinitiators that are, on the one hand, implicitly less sensitive to migration because of their MW that is above 1,000 Da. There are, on the other hand, photoinitiators that are not that bulky and, hence, are more sensitive to migration, but are supported by sufficient toxicological data to allow relatively high amounts of the photoinitiators to migrate into the food (provided no organoleptic changes occur).

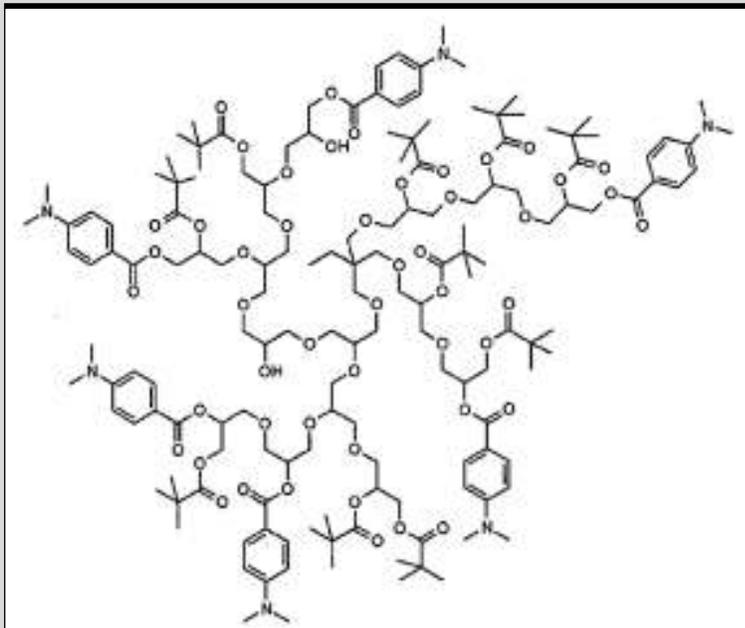
TABLE 1

Amounts of ink components (in ppb on 1 kg of food) determined by high-performance liquid chromatography (HPLC) after total extraction of the ink constituents with acetonitrile for 30 minutes

Migration in 'ppb'	Ink 1	Ink 2
VEEA	3,000	2,800
DPGDA	1,500	0
Photoinitiator 1	20,000	20,000
Photoinitiator 2	14,000	14,000
Photoinitiator 3	12,000	9,000

FIGURE 2

Generalized representation of dendritic amine co-initiator, basis for compounds I to V



because of specific properties. This is, of course, mainly triggered by the viscosity limitation and preferential intrinsic LM properties. As said, the high MW, high-viscosity polymeric versions are commercially available and in use in UV inks for LM applications. Several manufacturers have focused on polymeric thioxanthone photoinitiators and co-initiators.

Beyond commercially available compounds, a next step would be to create high MW, yet low-viscosity photoinitiators. An example is given in Figure 2. This is a dendritic photoinitiation co-initiator to be used in combination with a Norrish Type II photoinitiator.³

A series of similar co-initiators has been produced with the main difference between them being the polyglycidol core and the type of acylating compound. The structural parameters are described in Table 2.

They can all be used in high enough amounts to create inks in the typical viscosity range of inkjet inks. All compounds were tested in identical formulations (see Table 3) in comparison with 2-ethylhexyl-p-dimethylaminobenzoic acid (EHA) (structure, see Figure 4), a common low MW amine co-initiator. The inks were coated in a thickness of 10 μm

Legislation such as the Swiss legislation is beneficial in terms of formulating new inks. It means the rules of the game are clear—everyone knows what can be used and to what amounts every given compound can migrate. However, in the long term, such positive lists should never be closed, as they would limit innovation. There should always be the possibility

to add compounds to the list, as is the case in the Swiss legislation.

How to Innovate in the UV-LM Inkjet Inks?

In addition to using existing legislative boundaries, photoinitiator concepts can be built that are beyond the scope of general LM-UV inks but which are crucial for inkjet applications

TABLE 2

Structural parameters for five dendritic co-initiators for LM-UV inkjet printing inks

	Polyglycidol core	Average number of OH acylated with dimethylamino-benzoic acid	Average number of OH acylated with pivalic acid	Number average MW
Compound I	15 OH-groups	4.1	10.9	2,500
Compound II	36 OH-groups	9	27	6,200
Compound III	8 OH-groups	4.9	3.1	1,500
Compound IV	15 OH-groups	7.5	7.5	2,760
Compound V	36 OH-groups	16.8	19.2	6,700

TABLE 3

Ink formulations produced using the reference amine co-initiator EHA and the dendritic co-initiators compounds I to V

w/w %	Ref ink	Ink 1	Ink 2	Ink 3	Ink 4	Ink 5	Ink 6	Ink 7	Ink 8	Ink 9	Ink 10
DPGDA	41	52	52	44	44	50	50	42	42	42	42
SR351	41	30	30	30	30	30	30	30	30	30	30
IC500	10	10		10		10		10		10	
Benzophenone			10		10		10		10		10
EHA	8										
Cpd I				16	16						
Cpd II								18	18		
Cpd III		8	8								
Cpd IV						10	10				
Cpd V										18	18

using a bar coater on PET and cured using a D-bulb at 20 m./min. The dendritic co-initiators all yielded similar or higher curing speeds than the EHA-containing formulations, as can be seen in Table 3 for the different compounds. Additionally, they have the benefit of intrinsic LM properties due to their high MW above 1,000 Da, whereas EHA with an MW of 277 Da has a high migration potential.

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).⁴ In Figure 3, three examples are shown of polymerisable compounds (two initiators and one co-initiator). Their “regular” counterparts that were used as a reference are shown in Figure 4.

The different co-initiators were tested in identical ink formulations of which the composition is given in Table 5. The dibutylphthalate was added as an internal standard to be able to compensate for eventual differences in layer thickness between the coatings.

Table 6 shows the results of the curing speeds and extractables that can be recovered from the cured samples on PET (cured at 200%, 20 m./min, D-bulb). The results show that the polymerisable compounds create an ink formulation that yields lower amounts of extractables than their “regular” counterparts (shown in Figure 4), while maintaining comparable cure speeds with an

ink viscosity in the range of inkjet applications.

A final concept to create LM inks would be to use electron beam (EB) for curing of the layers instead of UV light. There are some intrinsic benefits to EB such as the technology’s independence of layer thickness and color. A drawback is the sensitivity of some substrates to EB radiation, especially thin foils such as those used

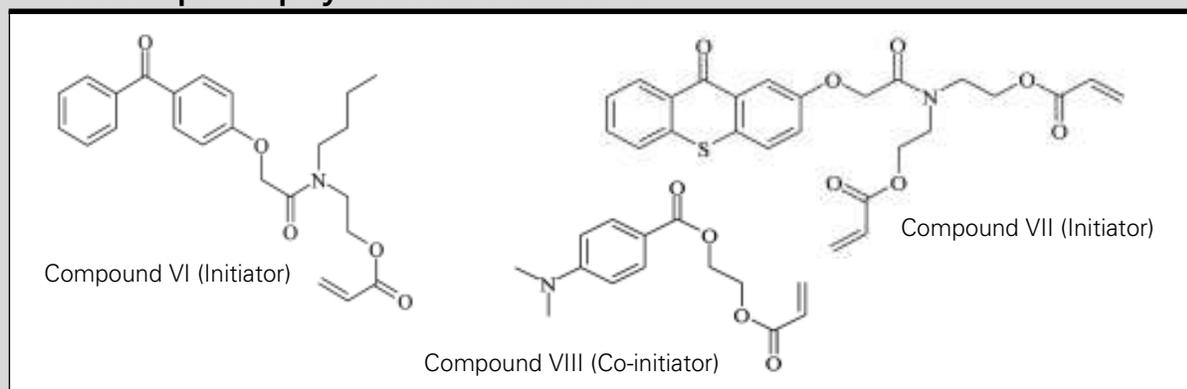
TABLE 4

Comparison of cure speeds for the different ink formulations with compounds I to V as dendritic co-initiators, in comparison with EHA as a co-initiator

Ink formulation	Curing speed % of maximum output
Reference ink	80
Ink 1	45
Ink 2	50
Ink 3	40
Ink 4	100
Ink 5	50
Ink 6	80
Ink 7	50
Ink 8	65
Ink 9	40
Ink 10	50

FIGURE 3

Three examples of polymerisable co-initiators



in food packaging. Currently, there are no Agfa inks based on or designed for EB applications.

The above-mentioned influence of the type of the photoinitiators on the aspect of migration is one thing. The other is, of course, their working mechanism (i.e., Norrish type I or II) and their sensitivity to specific UV-light wavelengths. This is especially true for the growing market of LED-curable inks. In Figure 5, an example is shown for two different polymeric thioxanthone derivatives to be used in food packaging inks. It is clear that the compound used in Figure 5A exhibits UV absorbance in the region of 395 nm, the region of typical UV-LED

emission; whereas the UV absorbance of the compound in figure 5B drops down to about zero, right before the wavelength of 395 nm is reached. It is clear there is a great difference in UV-LED (395 nm) sensitivity for both compounds, thus limiting their application.

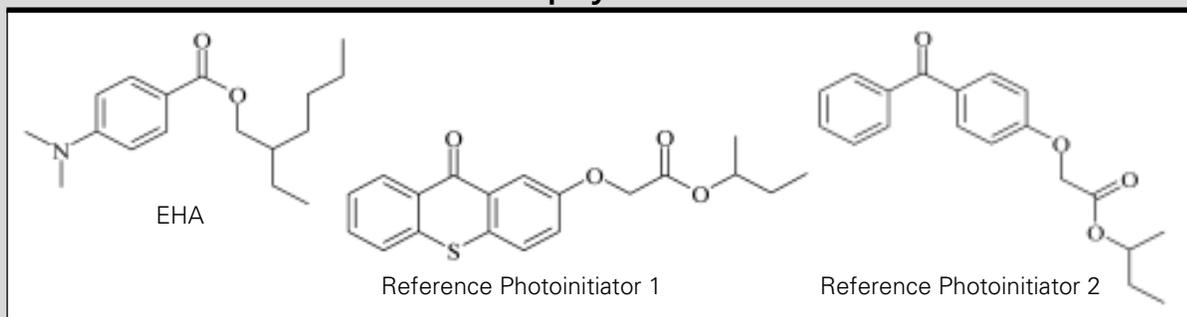
This concept of spectral limitation has to be further expanded down to the pigments and the UV lamps used. While the output wavelengths of LEDs are rather focused to narrow bandwidths, most typical UV Hg-bulb lamps exhibit a series of maxima in the UV region. The position of the maxima depends on the doping elements in the lamps, of course,

but they should be chosen as a function of the susceptibility range of the photoinitiators. The example of polymeric thioxanthones already made clear a minor shift in chemical structure can cause a huge difference in the print applications that can be covered by the choice of the photoinitiators.

Furthermore, the transmission range of the pigments is also of great importance.⁵ The pigments further narrow down the available range of combinations of photoinitiators and curing lamps. Typically, the following wavelength domains are to be considered as the areas of highest transmission by pigments used for

FIGURE 4

Structures of the three reference non-polymerisable co-initiators



cyan (C), magenta (M), yellow (Y) and black (K) inks (Table 7).

By combining these three factors—pigment transmission, photoinitiator susceptibility range and lamp output range—it is possible to create the highest sensitivity in the inks. This sensitivity is necessary to create LM inks that have enough room available to maintain LM output in practical applications where not always ideal conditions (such as in the lab) can be met.

Besides the monomers and photoinitiators, all other compounds (such as pigments, surfactants and other additives) should at least meet the purity criteria. However, their direct impact on migration is rather

low. It is, nevertheless, important to assess eventual reaction products of all used compounds, especially after UV-light irradiation. Any reaction product might induce smell or off-tastes, or even create low-MW compounds which might migrate.

Conclusion

The development of UV-curable, LM-inkjet inks has been a specific goal, demanding specific knowledge and chemistry. It is possible to create jettable, LM-ink formulations based on commercial compounds. However, the use of these compounds brings the formulator to the edges of allowable viscosity for inkjet applications mainly due to the fact that often high MW

or highly functional compounds are used. As a source of information, it is advisable to start from the legal boundaries, such as the Swiss legislation on printing inks for food packaging, where mainly such solutions would arise. We have gone further down the road of reducing viscosity and maintaining LM quality. This can be achieved by the right choice of monomer and innovative inventions on the photoinitiator and co-initiator side. A specific low-viscosity monomer is used which exhibits very high reactivity. Furthermore, dendritic or polymerisable photoinitiator compounds have been shown to yield highly reactive ink formulations with low extractables. Moreover, these

TABLE 5

Ink formulations tested for cure speed and extractables

w/w %	Ink 11	Ink 12	Ink 13	Ink 14
DPGDA	42.5	41.5	45	43.5
TMPTA	40	40	40	40
Cpd VI	10			
Cpd VII		10		
Ref PI 1			7	
Ref PI 2				7.5
Cpd VIII	5.5	6.5		
EHA			6	7
Dibutylphthalate	2	2	2	2

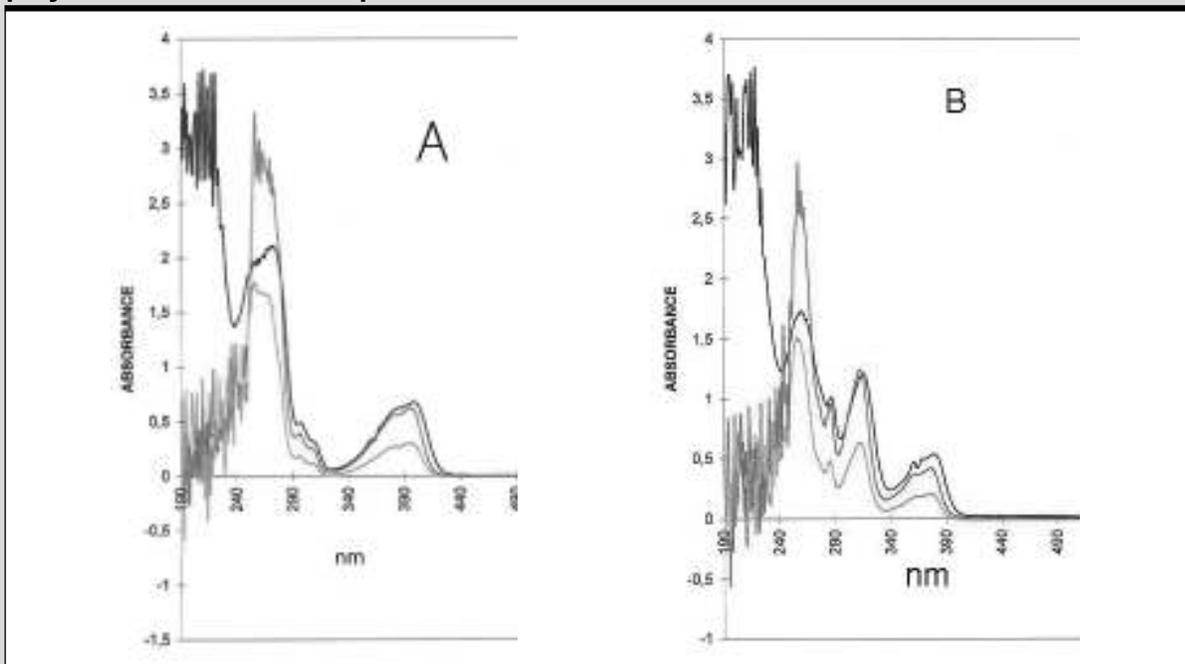
TABLE 6

Viscosity, curing speed and amount of extractables from the ink formulations with regular and polymerisable co-initiators compound VI, VII and VIII

	Viscosity (mPa.s)	Curing speed % of max. output	Extractable initiator (mg/m ²)	Extractable co-initiator (mg/m ²)
Ink 11	37	160	0	0
Ink 12	35	180	0	0
Ink 13	31	110	19	2
Ink 14	30	130	39	13

FIGURE 5

Comparison of UV absorption spectra for two similar, yet slightly different polymeric thioxanthone photoinitiators



compounds introduce less viscosity in the ink formulations than their polymeric analogs, which is specifically beneficial for inkjet applications. In this way, by combining these specific photoinitiator compounds with low-viscosity monomers, enough room remains available for additional compounds to tune the ink's functionality. Furthermore, as the trend of inkjet moves into the direction

of higher resolution (using print heads that need even lower viscosities), the low viscosity will also be of benefit for these future applications. Hence, in this area, the Agfa developments will also find their place.

Finally, it should be clear that the development of LM-UV inkjet inks requires getting the maximum out of the formulation. Every degree of freedom on the migration side has to

be maximized by choosing the right lamps, pigments and photoinitiators. This allows creating trustworthy formulations that, if combined with a highly efficient printing engine, can create a reliable printing solution for safe food packaging. ▀

References

1. www.bag.admin.ch/themen/lebensmittel/04867/10015/index.html?lang=en
2. www.eupia.org
3. EP1616922
4. EP2033949
5. W. Arther Green, *Industrial Photoinitiators: A Technical Guide*, CRC Press, (1st edition, 2010), ISBN: 1439827451

—Roel De Mondt is project manager for Inkjet Inks at Agfa-Gevaert N.V., in Mortsel, Belgium.

TABLE 7

Typical transmission ranges in the UV spectrum of commonly used colors in printing (CMYK)

	Optimal UV transmission range
C	380-400 nm
M	350-400 nm
Y	300-380 nm
K	Generally low transmission of UV light, best region around 400 nm