PRINTING INK MIGRATION ANALYSIS IN FOOD & COSMETIC PACKAGING

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ABSTRACT: Materials that come in contact with sensitive contents must fulfill strict legal requirements to guarantee the safety of foods or cosmetics and, in turn, consumers´ health and wellbeing. This includes provisions governing the transfer of substances from the packing into the food or cosmetic product. This transfer of substances (migration) is only permitted in quantities that do not endanger human health, change the food´s composition or negatively impact the food´s organoleptic characteristics (like taste or smell). The risk of substances migrating from the printed to the unprinted side of a so-called "contact material" into the content like foodstuff or cosmetics must be considered before the conformity of a material can be estimated. The main objective of this study is going deeper in the knowledge about the migration of photo initiators and their degradation products into the food. To address this objective, a review about the photo initiators are presented from the food safety point of view, explaining what they are, how they migrate into the food, what is their legislation over the world and which strategies can be followed for their detection (with the problems and peculiarities that this fact implies due to their action mechanism). Following, different analytical approaches have been described for the determination of the photo initiators and their byproducts by multiple techniques, from the classical HPLC-DAD and GC-MS to the novel DART-HRMS. This studies were carried out at all the common temperatures of food storage in all the food stimulants present in the current legislation (except for dry foods), from the polymeric material most used in food packaging, LDPE. Thereby, the mathematical model developed from these data allows the prediction of their migration to the foodstuff almost in any case.

I. INTRODUCTION

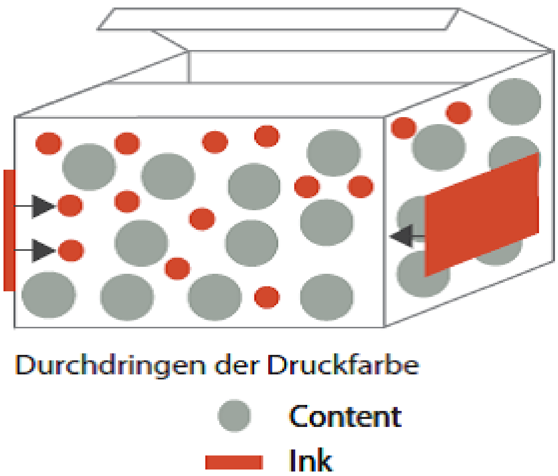
The packaging is the calling card of a product. It's the first visual and tactile impression the prospective purchaser gains in the shop. In addition to the information describing the package contents, the packaging provides lots of other helpful references and tips about the goods inside. It tells the purchaser the price, size, condition and texture of the product, where and when it was made and when it should be used by. Food packaging is an immensely important segment in the packaging sector because it addresses both people's basic needs and quality-of-life issues. It provides the consumer with a range of information that can be of crucial importance to their health: the degree of freshness and ripeness, colour, shelf life, ingredients and nutritional values (such as the number of calories and fat content). But details such as the country of origin, the weight and production methods can also be important factors in consumers' purchasing decisions. Depending on the design, the customer is given suggestions on how to prepare and serve the food, and in what quantities. The packaging also takes on practical functions, such as protecting its contents against damage and preventing them from going bad; it can also play an active role in ripening processes or extend a product's shelf life. Many of the functions above can only be fulfilled by packaging if the packaging has printing ink applied to it. Ink is the often unnoticed information medium that both simplifies and makes our lives safer in many respects. More than 95% of all foodstuffs sold on the Western European market are packaged. Over the past years, the share of direct packaging (with no inner bag) has increased. In this type of packaging, the food comes into direct contact with the unprinted inner side of the packaging material. The situation is different when the contents are packaged in an extra inner bag. Unfortunately, it is frequently and incorrectly assumed that this additional packaging provides the contents inside with an adequate level of protection against substance transfers, but not every inner bag offers such protection. In the last 50 years, the UV-curing inks began to substitute the classical solvent-based inks, obtaining better printing packages, safer for the consumers and with less impact for the environment. Nevertheless, since 2005, when the European food safety authorities have found photo initiators in packaging of milk for babies from these inks, they become in an important food safety issue worldwide. In 2009, the photo initiators benzophenone and 4-methylbenzophenone were found in cereals and milk, increasingly alarming migration issues. Next to primary migrant substances, secondary products can also be formed due to a reaction in the foodstuff. These secondary products can also be harmful and they could possibly have an effect on food too, such as odour, taste, etc. Where printing inks and coatings are separated from the packed food by one or several layers of packaging material, the suitability of the ink or coating system is strongly depending on the barrier properties of the packaging material and the extraction properties of the packed food. Containers such as metal cans and glass bottles represent an absolute barrier, and therefore require no special choice of printing ink, coating or printed label applied to the outside of the packaging. However, there is lack of clarity in the packaging industry today on the ability of a plastic container and / or filmic substrate to function as a barrier. This is due to the infinite number of combinations of food type, packaging material and printing inks/coatings that are possible where the packaging layer might show different barrier functionality. To ensure that the packaging material acts as a functional barrier, preventing migration of components from the printed surface through the packaging material into the packed food, migration tests on the complete packaging construction are recommended. A printer can choose from multiple types of printing ink chemistry, when looking for a food packaging compliant product. Traditionally, solvent based and water based packaging ink formulations have not given any reason for concern, as they have been used historically without any documented issues. When considering UV printing inks and conventional sheet fed inks, it is important to ensure that a compliant product is selected. This often has referred to as "low migration" products. Food packaging compliant inks are based on formulations that are optimized with respect to their migration properties. They are tested under standardized migration test conditions to prove that under these conditions they do not migrate above defined acceptable limits. However, due to the fact that these tests cannot simulate all possible food/ substrate combinations for which the printing inks finally might be used, there can never be a 100% guarantee or warranty that the products will always work, but instead the whole construction should be evaluated and a suitable risk assessment made. Many of the products packaged by the food industry are organoleptically (being perceived by human senses) sensitive. Obviously, the packaging must under no circumstances have a negative influence on the quality of what goes inside it. Changes in smell or taste spoil people's enjoyment of the products and must therefore be prevented at all costs. After all, one of the main tasks of the packaging is to prevent substances from transferring to the food.

How Can Substances be transferred?

There are different types of migration:

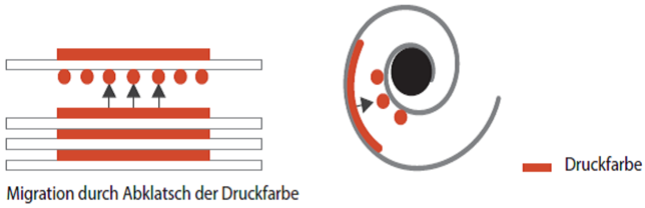
Diffusion Migration

Migration of printing ink ingredients through the substrate Due to their chemical characteristics and molecular size (molecular weight < 1000 Daltons), some substances, known as migrants, are able to migrate from the printed side through the substrate onto the unprinted side. This highly depends on the barrier properties of the substrate.



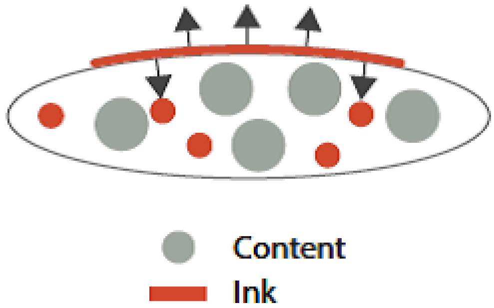
Set-off Migration

Migration of substances from the printed side to the unprinted side of another sheet in a stack, roll or stacked container.



Gas Phase Migration

Migration due to the evaporation of volatile materials by heating food in its original packaging or by steam distillation during cooking, baking or sterilization.



Migration mainly depends on three parameters:

Substrates

For the migration of substances, the barrier function of the substrate is a substantial property. The greater the barrier properties, the lower the risk of migration ("functional barrier"). Materials/substrates which are completely impermeable for substances, like glass or some metals (for example aluminium foil of at least 7 µm) are so called "absolute barriers". A migration of substances through these materials/substrates („diffusion migration") is simply not possible.

Printing Ink

Migration is an issue for all kinds of printing inks. The selective use of high molecular weight substances (e.g. as higher-functional monomers in UV inks), specific selection and purity criteria of the raw materials, as well as tailored production conditions in order to avoid process-related impurities can significantly reduce the amount of migrating substances compared to conventional (not specifically for this application developed) inks.

Process Conditions

Effective drying and curing of the ink film is the prerequisite to minimize the existence of potential migratable substances, like solvents and monomers. Set-off, where possible, must be avoided throughout the entire printing process. The thickness of the ink film and the ratio of printed to non-printed surface area determine the total amount of the potentially migratable substances from the ink. The more printing ink is used, the greater the quantity of substances that can potentially migrate. Even if the printing ink was designed for this purpose, a migration test with the finished product is always essential because other factors in the process chain such as printing parameters, processing conditions and the choice of packaging components also affect the migration risk. Compliance must therefore always be checked with the printed material.

Low Migration
The term “low migration” packaging is commonly used to designate materials used in the packaging structure whose chemicals will not migrate, or move, from the packaging into the product. To qualify as low migration packaging, these materials contained in the packaging structure, including printing inks, coatings and adhesives, must not have any migratory chemicals which would affect the appearance, flavour, odour, taste, or the safety of the product contained within the packaging. Manufacturers in the food packaging segment focus on the highest levels of manufacturing controls in line with the imperative of protecting the consumer. Naturally, food packaging is also the subject of extensive legislation, which applies to all the packaging components of a packaged food – including the label. It is the responsibility of all suppliers in the food packaging value chain to ensure that proper materials are chosen for each package they produce. When considering the choice of inks to use on a package, a printer or brand owner should know if the ink will be used for Direct or Indirect Food Contact.
Direct food contact - is defined as when packages have printed areas that are intended to have direct contact with the food stuff or whereby it can reasonably be expected the printed area will be brought into contact with food or it can be expected the printed area will transfer their constituents to food under normal or foreseeable conditions of use. In these cases, Direct Food Contact ink (known as DFC compliant) must be specified.
Indirect food contact - if the foreseeable usage of the printed package does not result in direct contact between the foodstuff and the print, then a food packaging compliant printing ink can be used. Depending on the industry, these inks are also commonly known as ‘Low Migration’ products.

II. RESEARCH OBJECTIVES

The materials contained in the packaging structure, including printing inks, coatings and adhesives, must not have any migratory chemicals which would affect the appearance, flavor, odor, taste, or the safety of the product contained within the packaging.
In this research we can understand the factors affecting migration and can developed a complete portfolio of inks and coatings for low migration sensitive packaging to support the packaging chain across a range of print processes and technologies. This research will help in educating all partners in the supply chain, from the raw material supplier to the graphic designer to the printer converter through to the brand owner and retailer about compliance, the potential pitfalls, their options, as well as opportunities.
The presence of photo initiators in foods has been a matter of concern in the last years; however, some questions remain unanswered. For this reason, this project and, by extension, this thesis, was focused in this food safety problem. In order to obtain a more in-depth knowledge of this issue, this thesis has three main objectives:
The realization of a comprehensive review about photo initiators in order to understand the peculiarities of this food safety problem. Special emphasis should be placed in two aspects:

- The mechanism of migration of photo initiators into the foodstuffs
- The current analytical methods used for their determination in FCM and foodstuffs.

The development of different methodologies and analytical methods to:

- Identify and quantify photo initiators in FCM.
- Determine the set-off migration of photo initiators, by-products and other print related molecules.

Study the migration kinetics of six model photo initiators, at all the common temperatures of food storage, into water and into the food stimulants present in the current legislation (except for dry foods), from LDPE. The obtained data were applied to a mathematical model, obtaining the migration key parameters: partition and diffusion coefficients. These parameters allow the prediction of the photo initiators’ migration into foodstuffs.

III. RESEARCH METHEDOLOGY

In this research we can analyze the printing ink migration in food and cosmetic packaging and its effect on food and cosmetic products. The experiment will be carried out on different types of packages within a prescribed environmental condition. The overall migration value amount of extractive in ppm or mg/dm2) will be calculated with different ink substrate combination at different environmental condition (that is by varying temperature, humidity, time of exposure…etc.).
Data analysis will be carried out on the basis of relevant methodologies and equations that are adopted for the determination of overall migration value (amount extractive in ppm or mg/dm2).

IV. DATA COLLECTION & result ANALYSIS

Analytical Methods for Determining Photo initiators in Food-Contact Materials
In the past, the main function of food packaging was as a container. Nowadays, the main function of packaging is to protect food and preserve its quality. In this context, food packaging must form an inert barrier to prevent transfer of mass to the foodstuff from outside. However, mass transfer may also occur from the food-contact material (FCM) to the foodstuff, representing a possible hazard to human health.
The packaging sector represents about 2% of the gross national product (GNP) in developed countries, and half of the packaging produced is used for foodstuffs. Any problems associated with the FCM could therefore have serious effects on public health and national economies. The use of printing inks on the external face of food packaging is of particular concern, as many of these are UV-curable inks that contain photo initiators. 12 different photo initiators and one amine synergist were detected in foodstuffs; the notifications

originated in 16 different countries; the migration occurred from/through different types of packaging to reach many different kinds of foodstuffs; and finally, not all the products were seized or withdrawn from the markets. The data gathered indicate that there are many different factors involved in the problem of migration of photo initiators from FCM to foods, making this problem difficult to address.

Photo initiators

Several studies have considered the identification and/or quantification of one or more photo initiators. The technique most commonly used is chromatography, in its different variants: liquid (LC), gas (GC) or high-performance thin-layer (HPTLC), coupled to different detectors: diode array (DAD), fluorescence (FLD), flame ionization (FID), mass (MS), or some combination of these. Other techniques such as voltammetric methods or, the most novel, direct analysis in real time (DART) are also used.

The different analytical methods developed for the determination of photo initiators in food and FCM are described below.

Chromatography

Selection of liquid or gas chromatography should be based on the nature and the properties of the target photo initiators, i.e. liquid chromatography is usually most suitable for photo initiators of low volatility.

HPLC-DAD/FLD

Before the scandal involving the presence of ITX in baby's milk, very few studies involving the determination of photo initiators had been reported and determined 3 different photo initiators (MK, DEAB and DMAB) in different paper and cardboard FCM, using ethanol as solvent in the extraction.

MK, DEAB and DMAB were detected in 10-26 % of the samples at concentrations of respectively 0.05, 0.1 and 0.1 mg kg-1, which are above the limits of detection (LOD), but unlikely to pose a risk to human health.

The photo initiators and amine synergist were detected with DAD at different wavelengths: 246 nm for HCPK, 254 or 256 nm for BP, 256 nm for BDMB, MBB, DEAB, BPAcr, 2-HBP and 4-HBP, 256 or 260 nm for 4-MBP, 290 nm for PBZ, 306 nm for MMMP, 310 nm for EHA and 386 or 256 nm for ITX.

Migration Test

To perform the migration test, the films were cut into pieces of 6 x 1.66 cm, to achieve a total surface of 20 cm2 in contact with the food simulant. These films were placed in contact with 20 ml of food simulant in tubes protected from the light. The food simulants 3 % acetic acid (w/v), 10 %, 20 % and 50 % ethanol (v/v) were selected from the UE Regulation No. 10/2011. Instead of vegetable oil, 95 % ethanol (v/v) was chosen as substitute based on scientific evidences. The migrant assays were also carried out in water, in order to compare the differences between the current simulant for hydrophilic foods (10 % ethanol) with the food simulant of the previous legislation (water). Here, water and 95 % ethanol (v/v) will be named as food simulants, although in the current legislation they are not considered as such. In order to have an experimental approach of the above-mentioned hypothesis, packaging material and food or a food simulant have to be brought into contact as if it were a real packaged food product. A migration cell has been chosen to approach reality as good as possible. This cell is composed of two plates of stainless steel covered with a packaging material of choice. Both plates are clipped onto both sides of a metal ring. A liquid simulant fills the space between the plates and the ring, creating close contact with the packaging material. In order to follow up nitrosation during the heating of nitrocellulose ink, relevant amines are dissolved in water and buffered at an optimal pH. The migration cell is covered by a film homogeneously printed with nitrocellulose ink. This cell is filled with a buffered amino solution and heated during a few hours. After this process and a successive cooling down step, the quantity of nitrosamines in the cell solution is analyzed using the above-mentioned SPEGC-MS determination method.

Experimental migration cell

Analytical Methods for Determining Photo initiators in Food-Contact Materials

The results showed good sensitivity, with limit of detection in the different carton boards ranging from 2.8 μg dm-2 (for BP) to 29.0 μg dm-2 (for PBZ). BP was detected and quantified in 49 % of the 310 samples analyzed, and the other photo initiators, except 4-HBP, were detected in at least one of the samples.

In HPLC-DAD method, determined 5 different photo initiators (ITX, BP, EHA, EDB and HCPK) in beverages and packaging.

In summary, on the basis of the methods reported in the literature reviewed, the following is a suitable and standardized HPLC-DAD method for the determination of photo initiators in FCM and food. By way of example, an HPLC-DAD chromatogram of fourteen photo initiators is illustrated in Figure.

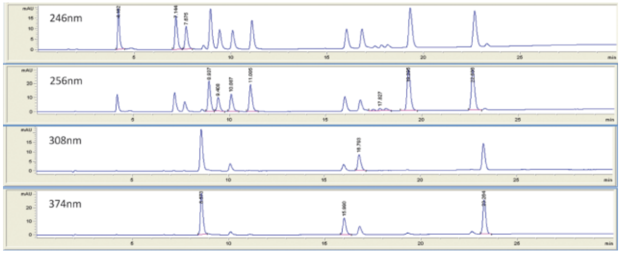


Figure : HPLC chromatograms of fourteen photo initiators and an amine synergist (EHA): HMPP (4.16 min), HCPK (7.14 min), MBB (7.67 min), EDB (8.57 min), BP (8.94min), 2-HBP (9.41 min), DMPA (10.09 min), 4-MBP (11.09 min), PBZ (15.99 min), DEBP (16.79 min), BPAcr (17.83 min), ITX (19.29 min), DETX (22.69 min) and EHA (23.26 min).

V. CONCLUSION

A multimethod for the determination of photo initiators and amine synergists in food packaging has been developed. The described method was simple, reliable and could be useful as a screening tool for the routine determination of fourteen currently used photo initiators and amine synergists, in packaging materials. Furthermore, a LC-MS/MS method allowed the confirmation of the identity of substances in positive samples. The results showed almost 50 % of positive samples, being benzophenone the most common photo initiator in the analyzed samples. The photo initiators reach the foodstuffs mainly by set-off. To determine the magnitude of this mechanism of migration, 2 different techniques (DART-HRMS, GC-MS) have been used in under-cured packages. Moreover, for first time, the HRMS spectra of polymeric PIs have been characterized by DART-HRMS technique. As a result, a total of 110 molecules were identified, with evidence that 30 molecules likely experienced set-off or were present on both sides. Most of the print related compounds detected were not included in the positive list of the European FCM legislation and several were novel PI transformation products. The molecules reported herein can serve as guide for any future assessments of print-related contaminants. Also a small survey in secondary packaging samples were carried out, detecting photo initiators in a 92 % of the samples analyzed, 4 of them presented BP and EDB in their UV curing formulations, but, any of the confirmed photo-products could be detected. Six of the most recurrent photo initiators (BP, 4-MBP, HCPK, EDB, ITX and DETX), were taken as models for the study of the migration kinetics of photo initiators into food simulants. The studies were performed at 4 different temperatures, from -18 to 40oC in order to study also the influence of the storage conditions. The photo initiator source selected was LDPE due to be the most used polymer in the food packaging industry. The following conclusion was extracted from these studies: The migration kinetic in LDPE is highly dependent on the storage conditions (time and temperature), migrant properties (Mw and log Ko/w) and type of food or food simulant (composition and pH).

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