Cradle to Cradle Perspective on UV Printing, especially UV / LED

1. Introduction

In the context of the healthy printing initiative the question arose how to view UV/LED printing in the Cradle to Cradle framework. UV curing for stationary printers requires special equipment for UV-light sources. The following paper summarizes simplified facts about UV curing for printing inks.

As „light catching“ ingredients, „photoinitiators“ play a crucial role in UV printing processes. These photoinitiators are toxicologically relevant, therefore this is described in some detail.

This statement also includes results of discussions with experts from print shops and ink producers. Finally, advantages and disadvantages of UV resp. UV/LED printing are summarized and the Cradle to Cradle perspective is applied, resulting in recommendations to different players.

2. UV Printing Inks

In principle, printing inks for UV curing („drying“) do not differ much from printing inks for other mechanisms of drying like coldset or heatset. However, those differences change the properties of the ink and have a certain influence on workers' protection and recycling.

Generally, printing inks consist of the following groups of ingredients:

- Binders (resins, or in UV inks: monomers)
- Pigments
- Auxiliaries (e. g. photoinitiators in UV inks)
- Solvents (not in UV inks)

The UV curing process is based on a photochemical reaction, using light instead of conventional curing with heat. Liquid monomers and oligomers are mixed with a small percentage of photoinitiators and are exposed to UV-light as energy source. The ink hardens instantly. This hardening is triggered by photoinitiators, which absorb light of certain wavelengths and transfer this energy to the binding system molecules. As photoinitiators, there is a wide range of products in the market as the applications are different and require suitable mechanisms for „light catching“. The term LED describes the source of the UV light and does not change the mechanism of curing. The wavelengths of UV light are appr. 200 – 400 nm.

UV curable inks were created as an alternative to solvent-based products. Conventional heat- and air-drying inks work by oxidation and evaporation of solvents. In UV curing inks there is no solvent to evaporate [1] [2] [3].

Traditionally, UV inks are used for printing on non-absorbent surfaces like plastics.

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3. UV-Curing of Printing Inks

Currently UV resp. UV/LED printing is used in the following areas:

- Inkjet printing (mobile LED lamps)
- Offset printing (stationary UV lamps)
- Flexo printing (stationary UV lamps)

As light (=energy) sources for UV printing typically medium pressure mercury lamps, pulsed xenon lamps, LEDs or lasers are used. Mostly, medium pressure mercury lamps are in use, which provide emission maxima mainly as line outputs at wavelengths of appr. 254 nm (weak), 313, 366, 404 and 436 nm.

For UV offset printing, the UV-lamps (incl. LEDs) are stationary. In case LED lamps are used for inkjet printing they have to be lightweight parts in order to follow the ink drops for rapid cure. LED UV lamps emit radiation in a small wavelength range in the longwave UV range at 365 and 395 nm.

As photoinitiators, chemicals are needed which absorb light of the wavelengths provided by the light source. A typical photoinitiator like thioxanthone (or a derivative) has an absorption spectrum which picks up the emissions at 366 and 404 nm - typical emissions of medium pressure mercury lamps - and can therefore act as an initiator for photochemical reactions like UV curing of printing inks. For LED printing, different photoinitiators are needed since LED works in the longwave range of 365 and 395 nm.

3.1. Advantages and disadvantages of UV Curing from the Perspective of a Print Shop

From the perspective of the users UV curing provides several advantages but also some disadvantages, which overlap partly with advantages/disadvantages in terms of C2C.

The following points outline criteria as they are communicated in several sources, reflecting also different opinions of particular players on some points [4] [5] [6]. Discussions are still ongoing.

Advantages:

- Less input of ink necessary.
- Curing within seconds, no subsequent drying necessary.
- Fast processing in general due to immediate processing.
- Suitable for quick double sided printing.
- Long service life of the UV lamps.
- High mechanical durability of print.
- High quality printing results (e.g. brilliance).
- Suitable for substrates that are sensitive to heat, like films.
- No powdering necessary (in sheet offset needed to separate the printed sheets).
- No solvent (VOC)- or mineral oil containing inks.
- Less maculation/printer’s waste, but this kind of waste has to be separated and disposed separately (see also below).

- In some sources, UV printing is communicated as suitable for many types of paper and PE- as well as PP films, whereas other experts see this method only as suitable for non-absorbing surfaces [7].
- Some sources highlight energy savings compared to conventional printing. However, this may be misleading (see [6]) since LEDs are less energy consuming than UV mercury lamps, but this does not include comparison to conventional printing

Disadvantages:

- Only a few optimized systems available.
- UV printing inks are harmful prior to application, workers' protection needed.
- Paper waste from UV printing to be separated in the print shop, possibly even to be disposed of as hazardous waste, because de-inking in paper recycling is still problematic.
- Possibly higher prices for UV inks compared to conventional printing.
- Higher prices for the UV-equipment.
  Remark: Within a UV system, LED equipment is possibly more expensive compared to mercury UV source. Energy balance for a particular print shop has to be calculated individually.
- Uncertainty whether 100 % curing occurs, resulting in residual monomers and residual photoinitiators, which may be toxic.

3.2. Mechanism of the UV Curing Process [8]

UV-coatings and printing inks need a binder like an acrylate monomer (sensitizing in uncured state), which has to be initiated for starting the polymerization. This can be achieved by photoinitiators, which form radicals under UV light and convert this energy to the binder.

During the polymerization reaction the active radical becomes part of the polymer.

In general two types of photoinitiators are used for curing of printing inks:

Type 1 Photoinitiators: Substances, which produce radicals under UV light themselves.

Type 2 Photoinitiators (sometimes called photosensitizers): Substances, which are activated under UV light and convert this energy to a co-initiator (often amines). The co-initiator is the radical forming agent, which initiates the polymerization.

4. Photoinitiators in printing inks and possible migration

In order to achieve a successful curing process, high concentrations of photoinitiators are often used and only part of the material is consumed. This means that a significant amount of unchanged photoinitiator might remain in the polymer.

Studies with printed food packaging have shown that especially small molecule photoinitiators can migrate from the surface of the cured ink into the contact material. The majority of commercial photoinitiators have molecular weights between 200 and 350 and hence are suitable for migration, like isopropylthioxanthone (ITX) and benzophenone (BP).

However, it has been shown that materials with a molecular weight of around 500 will lead to low migration and such with molecular weight of 1000 (polymeric) will show practically zero migration.

5. Polymeric Photoinitiators

Consequently, polymeric photoinitiators were developed, mainly of type 2. A polymeric photoinitiator combines solving the migration issue with reasonably fast reactivity.

Typical polymeric Type 2 photoinitiators contain structure elements of benzophenone or thioxanthone but carry a „backpack“ of unreactive material, so polymeric photoinitiators require to be present in higher concentrations in a printing ink recipe.

For the formulation of a printing ink it has to be taken into account that polymeric photoinitiators differ in their properties from conventional photoinitiators. Their higher viscosity is a challenge for the formulation of UV flexo and inkjet inks, which need to be modified by additives in order to achieve a consistency, which allows processing.

6. Toxicological Properties of Photoinitiators

During curing processes of printing inks, photoinitiators are consumed or remain partly unchanged, as described above. In scenarios like food packaging or skin contact, there is the possibility for exposure by migration of photoinitiators or their decay products into food, or simply by skin contact with printed products.

Example benzophenone:

As benzophenone is a widely used chemical with several applications but also a well-known and frequently used photoinitiator, it was investigated in terms of toxicological evidence, including some studies, which also analyzed byproducts formed under UV-light. Benzophenone in its function as a photoinitiator can migrate from cardboard into food through the vapour phase. Benzophenone itself was reported to be possibly carcinogenic to humans (Group 2B), but there is no classification in the German MAK-list [9] [10].

Example ITX:

In 2008, ITX was found in beverages, originating from UV printing inks. In a statement the German BfR stated that ITX was only poorly investigated in terms of toxicology. The conclusion was that it was not possible to assess these substances – and other photoinitiators in discussion at that time – in terms of human health [11].

Applying the precautionary principle of Cradle to Cradle it can be assumed that still many of the hundreds of photoinitiators in the market are not fully assessed and so a qualified rating is not always possible. Own research of EPEA (confidential) supports this assumption and reveals e.g. sensitizing properties of several photoinitiators.

7. Legal Situation

There is no detailed legal requirement for the formulation of printing inks yet. The European Printing Ink Association says [12]:

> *„Even if printing inks are applied on the non food contact surface of packaging... they must not prevent the final package from meeting the requirements of Regulation (EC) No 1935/2004 concerning materials and articles intended to come into contact with foodstuffs. This Regulation requires that no food contact material (whether printed or not) should endanger human health, change the composition of the food or alter the organoleptic properties of the food. This Regulation repealed Framework Directive 89/109/EEC and, as a Regulation, immediately came into force in the Member States on 3 December 2004.“*

In 2011 Switzerland was the first country to issue lists of „permitted substances“ (starting 2008 with an amendment to the Swiss Ordinance on Materials and Articles (SR 817.023.21)) for the formulation of printing inks. These included binders, dyes, pigments, solvents, additives and photoinitiators, updated 2017 [13]. The substances were classified according to the quality of evaluation – mainly in terms of migration. Compared to the Cradle to Cradle perspective it can be stated that the listed substances, esp. photoinitiators, are not evaluated in depth sufficiently according to the ABC-X assessment methodology of EPEA.

In Germany a Printing Ink Ordinance is still remaining in the status of a draft, meanwhile notified by the EU [14]. It provides a long list of allowed substances for the formulation of printing inks. However, as expected, this list includes also substances, which would be regarded as problematic from a Cradle to Cradle perspective.

8. Cradle to Cradle-Perspective

As UV-, especially UV/LED printing, is a growing printing technique the goal of this paper is to formulate an opinion on this method applying the Cradle to Cradle-Perspective. The following points focus mainly on material properties but also touch on the after-use scenario.

Compared to conventional printing inks the photoinitiators, which are essential for UV- and UV/LED printing, were identified as a crucial point. Due to toxicological properties and possible migration issues it is recommended to use polymer photoinitiators (preferred type 2) wherever possible instead of typical small molecules like benzophenone or thioxanthone (or derivatives).

For printing on plastics and non-absorbing surfaces in general UV printing is widely accepted as a standard method. This can apply for printed materials like plastics or labels on packaging, which after use follow other pathways than typical paper recycling.

Assuming printed paper goes into paper recycling, the issue is what happens to the UV printing inks. Unfortunately, it is known that UV printing inks as well as inkjet inks usually cause problems in the de-inking step due to their hydrophilic properties and the comparatively big particle size during breakdown in the recycling process. In the flotation step of the paper recycling process currently only hydrophobic materials can be separated. Hence UV printing inks stay in the water phase, are transported to the following process steps and may cause a grey colour of recycled paper. For example, benzophenone as a typical photoinitiator is difficult to remove during paper recycling [15]. Some research about this issue is going on. Recent activities and results show that it seems to be basically possible to design de-inkable ink jet UV inks [16] [5]. As this depends on the recipe of the printing ink, further research would be necessary by the printing ink industry and paper recyclers to develop suitable UV inks which can be removed during de-inking in paper recycling.

For paper or cardboard, which does not go through de-inking steps, the UV printing substances remain in the pulp, and can principally be designed in a way that they do not pose a risk from a C2C perspective.

Here are, summarized, the positive and the problematic properties of UV resp. UV/LED printing:

Positive

- No mercury in the UV sources when using LEDs.
- Several advantages in application for the print shops (see above).
- Minimal or zero solvent content of the inks, resulting in less emissions and better air quality in the company.
- Available: Photoinitiators, which are non-migrating due to high molecular weight.

Potentially problematic

- UV resp. UV/LED printing is communicated by several sources as suitable for offset and flexo printing of several surfaces like paper and also polyolefines. However, some experts doubt that UV printing is a suitable method of choice for printing of paper due to lack of quality of the printed matter and non-convincing energy savings. About the de-inking issue see above.
- Acrylate binders in uncured status are strongly sensitizing. Workers' protection is needed in order to avoid skin contact.
- De-inking of printing products produced with UV seems still problematic.
- Migration of photoinitiators with lower molecular weight into food possible.
- Toxicological properties of photoinitiators are in many cases only partly assessed, therefore hazards partly unknown.
- Paper waste from UV printing has to be separated in the print shop, possibly to be even disposed as hazardous waste (see also 3.1).

After evaluation of literature and expert discussions about UV printing, several advantages and disadvantages of this method were identified. For printing of non-absorbing surfaces like plastics there is wide acceptance in the market.

Regarding printing on paper, EPEA still sees issues as outlined above, as long as the recipes are not optimized and the after-use scenario requires de-inking according to current practices.

These problematic topics currently seem to outweigh the advantages. Therefore a wide scale application of UV-inks in the mass print market for paper and cardboard cannot be recommended from a C2C perspective.

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