Printing inks and Plastic Recycling – Q & A

▪ Are your inks recyclable?

Today recycling of printed packaging or publication print focuses on the recovery and reuse of the main structural component (e.g. paper, plastics, glass, metal, …). Therefore, the recyclability has to be evaluated for the final printed product. From a recycling perspective, the main purpose of the printing ink is to not interfere with the recycling process of a packaging or a publication print product. Different institutes and associations published recycling guidelines for plastics to evaluate recyclability, amongst these CEFLEX with their D4ACE-Guidelines, PRE (Plastic Recyclers Europe) with their RecyClass tool, Ellen McArthur Pioneer Project Barrier "Recyclability Guidelines for Plastic-Based Flexible Barrier Packaging", Cyclos HTP and many others. Unfortunately, they are not harmonised yet. Where printing inks are mentioned the requirements can be summarized as the following:

1. Printing inks should comply with the EuPIA exclusion policy.

2. The guidelines recommend applying as less ink as possible resp. limit the share of ink to <5% by weight for easy recyclability.

3. There is a preference for lighter shades.

▪ Can you provide inks with lighter shades only?

Printing ink manufacturers can provide ink for almost every application and packaging design, in every colour density and colour shade. However, it is not the ink manufacturer who decides on the packaging and print design. The packaging designer decides if the packaging is made with light or strong colour shades. Consequently, the packaging, which requires strong, or dark colours, and which is fully printed on the surface may not be well-designed for recycling. Nevertheless, it is important to note, that there are differences between rigid packaging, which may carry a printed separable sleeve and a flexible packaging film forming the packaging as such.

▪ What can you state about heat stability of inks/components of inks in the temperature range between 200 – 270°C?

At temperatures above 160°C NC is unstable and in situations where nitrocellulose (NC) containing inks are included in plastic that is recycled in extruders at temperatures of over 200°C this can result in gel-particles in the recyclate or gassing during the extrusion process. Other ink components also start to become unstable at temperatures exceeding 170°C. Whilst this does pose potential problems if the recyclate is re-used in a Food-Contact-Material application it typically does not dramatically affect the properties of the recyclate in non-sensitive applications. There may be a small amount of (typically brown) colouration due to this decomposition occurring. One situation where there is a known problem is when Poly-Vinyl-Chloride (PVC) resin containing inks are used, as this resin decomposes at temperatures exceeding 200°C found in the extruders releasing hydrochloric acid which then corrodes the metal parts of the extruders. Many customers and brand-owners are now specifying that PVC containing inks should not be used.

▪ Why is it, that we observe gassing at mechanical recycling?

Mechanical recycling typically involves an extrusion process, which either produces pellets from the sorted and washed post-consumer plastic waste or directly produces films from recycled plastics. In order to melt the recycled plastics and achieve good flow characteristics temperatures of 250°C on average would be applied for polyolefines, in case of PE (polyethylene) a temperature of 220°C may be sufficient, for PET (polyethylene-terephthalate) even higher temperatures of up to 270-300°C would be regarded as typical.
Given the fact that the plastic waste material to be extruded usually is containing coatings, inks and adhesives, in addition to the substrate polymer, also these materials are subjected to these high temperatures. It is a matter of fact, that some of the ingredients in inks are not stable under these conditions and start to degrade. Nitrocellulose (NC) is the most common binder in inks for flexible packaging, it starts disintegrating at 160°C by forming nitrous gases, which then would be observed as gassing phenomenon. The more NC is available, the more gassing is observed. Gassing could interfere with the film-forming process, however, problems could be avoided when using extruders with degassing units.
There are other ink systems based on different binders, which will not show a similar gassing behaviour but which are equally decomposing under the extrusion temperatures. To be mention-ned here to the best of our knowledge are inks based on polyurethanes, acrylates, polyvinyl acetales like PVB (Polyvinyl butyral) and other cellulose esters like CAP (cellulose acetate propionate).

▪ Why is it, that PCR (Post Consumer Recyclate) shows black to brown colour stain?

The brown colour stain observed in mechanically recycled polyolefins can be attributed to the presence of pigments in the printing inks, if there is no deinking step before extrusion, which can still impart colouration even in a small amount to a transparent film. Additionally, the thermal decomposition of some printing ink ingredients, like for instance some binders indicated in the questions above, may result in brownish substances which contribute to the overall colour of the PCR material. Also, some pigments (e.g. Azo-Pigments) may undergo thermal decomposition, which breakdown products may also contribute to the darker shade of the PCR. To date, the exact mechanism of thermal degradation of printing inks raw materials is not completely known and other conclusions may be drawn thanks to further investigations.

▪ Do printed black surfaces prevent from proper sorting?

In most plastic sorting processes a Near-Infra-Red (NIR) method is used to distinguish between different types of plastic to ensure that different kinds of plastic are sorted into different waste streams so that each can be recycled to maximize its value. If the NIR beam can only see an area covered with an area coloured with carbon black (Pigment Black 7) then the NIR beam is absorbed and the lack of a reflected signal means that the plastic cannot be correctly sorted. In most cases this means that the plastic is burned with thermal energy recovery, which potentially wastes some of the recyclate's value. In situations where packaging is printed with black ink the design rarely contains such a high percentage coverage of black that the NIR beam cannot find an area without black and sort the plastic based on the reflected NIR signal. There is a problem in situations where a plastic is mass-coloured such that there are no non-black areas. In situations where a very high coverage of black ink is required for a design or where a mass-coloured black plastic is required then there are alternative black pigments which can be used and which are transparent to NIR allowing for effective sorting.

- **Do printed metallic surfaces prevent from proper sorting?**

Printing inks constitute a very thin layer on flexible packaging, therefore the contribution of metallic printed surfaces to the total weight of the packaging is normally minimal, even if the printed surface may be wide. So far for NIR based sorting as well as for tracer based sorting no negative impact from metallization is known. Since the metallic pigment used in printing inks are non-ferromagnetic, this leads to the conclusion that sorting mechanisms based on magnets should not be negatively affected by packaging printed with metallic inks. Some recyclers report that sorting techniques based on eddy current or metal detection may detect large-area metallic printed surfaces as “metallic items” and therefore calibration procedures may be needed to adjust the results of the sorting process.
Although metallization of flexible films is not obtained via printing process, it may have the same interfering effects described for large-area printed metallic surfaces metal detection and eddy current, due to the large surface area of the metallization, despite the negligible weight increase on the total film weight.

- **Can we get rid of inks before recycling?**

In principle, the answer is yes. To avoid problems with inks during the recycling processes wash-off or deinking may come into consideration. Whilst wash-off solutions are already existing on the market especially in the labels segment for PET bottles, so-called deinking solutions did not yet make it to the post-consumer recycling market. However, certain pilot installations are utilizing either solvents or caustic aqueous solutions, which are working well with defined packaging waste material qualities, ideally from post-industrial sources. A further effort has to be put on the development of this methodology to demonstrate universal deinking effects on all kinds of printed plastic materials as well as economic feasibility. To complete this, there are also de labelling solutions available on the market based on printed primers, which enable getting rid of printed labels before the PET bottle recycling process.
To complete this overview, the so-called solvolysis, which is utilizing different solubilities of polymers from laminate structures in organic solvents, has to be mentioned. It is a proven fact, that in pilot installations inks from post-consumer waste could be widely separated, thus giving the recycled polymers a higher market value.

- **Is there a contribution of hazardous components from inks, which would interfere with intended uses of PCR material?**

The answer depends strongly on the ink system used in the post-consumer feedstock, but also on the definition of hazardous components and the intended uses of PRC.

Concerning hazardous components, EuPIA members formulate inks in accordance with EuPIA Exclusion Policy, therefore CMR cat 1 substances along with substance classified as Acute tox cat 1, 2, 3, STOT RE 1, STOT SE 1 are not used. Since long time, the raw material selection process of EuPIA members also ensures that toxic heavy metals (Hg, Pb, Cr, Cd) stay below 100 mg/kg in printing inks.

Non-sensitive applications, for example the ones requiring compliance with RoHS and Toy Safety Directive, appear non problematic, because the residual printing inks in the PCR are not an obstacle for this compliance, due to the known low content of toxic heavy metals and the general absence of polybrominated compounds from printing ink formulations.

On the contrary, sensitive applications, e.g. where PCR materials are intended to be used as food contact materials (FCM) are regulated today by Commission Regulation (EC) No 282/2008, whilst so far there is only authorization for processes on post-consumer recycled PET. Further legislative updates on other PCR plastic materials are expected to come.

Depending on the ink technology, different substances may be generated by thermal decomposition. To date, the exact mechanism of thermal decomposition of printing inks raw materials is not completely known and other conclusion may be drawn thanks to further investigations. Here some examples based on current information:

1. The thermal stability of binders differs considerably throughout the technologies, and so vary the potentially cleaved substances. Some of them, like nitrocellulose and PVC binders may decompose, were already mentioned in the above sections. For other binder system, the following considerations can be offered:
    a. PVB-binders can create some unsaturated derivatives because of water elimination. The toxicology of these components is mainly not well reported.
    b. Polyurethanes (PU) have different thermal stability depending on composition: aliphatic PU are expected to have higher thermal stability, whereas aromatic PU could more easily undergo thermal decomposition. The resulting decomposition products are depending on the chemical environment in which the decomposition happens.
    c. Polyesters are expected to be quite thermally stable and survive the temperature of the recycling process, unless in strong acidic or alkaline environment, which could promote cleavages. The same consideration applies for polyamides, which in the condition mentioned above could cleave in substances not fully characterized (an example could be caprolactam).
    d. Styrene-Acrylates and pure acrylic binders could undergo thermal decomposition, yielding a variety of unsaturated components and aromatic compounds. For most of the substances potentially developed no toxicological data are available, although for very few (styrene, acrylic acid and respective esters) more data are available
2. Some pigments (e.g. PY 13) could thermally cleave in a complex substance mixture creating potentially hazardous components like primary aromatic amines (PAAs) and NOx-containing aromatic components.

- **What is the average ink contribution (in % of weight) on printed plastics?**

The total amount of printing ink is depending on ink coverage, i.e. grams per square meter applied and also on the ink type applied. But, as general rule, a maximum amount of ink between 2-4 % in weight can be taken into consideration.

EuPIA Plastics Recycling Task Force

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