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[IJ2-03] Pigments for Inkjet Food Packaging Printing

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With inkjet printing showing strong and steady growth in packaging and industrial printing, there are rising concerns over the suitability and compliance of inkjet inks for sensitive applications such as food packaging, where the inks – and thereby the primary ink components like pigments, resins and additives – need to meet stringent requirements in terms of their toxicological profile and migration behavior. This paper reviews pigments for inkjet food packaging printing, in the light of the latest changes in legislations and recommendations by the competent authorities, particularly the EU authorities.

Pigments for Inkjet Food Packaging Printing

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This paper reviews organic pigments that are suitable for inkjet food packaging printing, in the light of the latest changes in legislations and recommendations by the competent authorities, particularly the EU authorities.

1. Digital Packaging Printing

Digital printing (inkjet and electrophotography) has become a significant print technology for all kinds of applications, including publication, commercial and industrial printing.

The well-known benefits of digital printing, like variable data printing and print customization, short-run efficiency, print-on-demand, minimal set-up and switchover time and costs, are also of high value for packaging printing applications. For example, there are many trends in packaging that lead to a decrease of the average print run length. Packaging is critical in establishing brand identity and serves as an advertising medium, and there are more and more specific, seasonal or regional packaging designs. This is resulting in shorter run lengths and the need for a better management of the packaging supply costs, which are negatively impacted by long lead times and high stock levels. Thus, it comes as no surprise that digital printing is on the rise in the label and package printing sector, to the detriment of the conventional packaging printing technologies such as flexography, gravure and offset.

An increasing number of products around the world are adopting digital printing. According to a recent Smithers-Pira study, in 2017 all digitally printed packaging amounted to some $13.2 billion sales, which is about 3.33% of all printed packaging. The labels sector is currently the most advanced in its adoption of digital print. Through 2022, the value of the digital packaging sector will grow at 11.2% CAGR to $23.2 billion, accounting for nearly 5.3% of packaging by value, while print volume will reach the equivalent of 334 billion A4 prints (some 3.2% of the total print area output). This projected growth is driven mainly by new, highly productive corrugated inkjet and electrophotographic presses, with additional contribution from cartons and other segments, such as flexibles, rigids and metals.

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2. Food Packaging and the Food Contact Regulatory Landscape

Packaging has always served a critical role in the food supply chain and roughly 90% of all foodstuffs are packaged, at least in mature countries. Considering that the value share of food and beverage packaging is approximately 70% of the overall consumer packaging market, food packaging printing is obviously a primary target market for all players in the digital printing value chain, from raw material suppliers to OEMs and converters.

Besides design and sustainability, a major topic for food packaging relates to consumer health and food-safe packaging, including the printing of food packaging. This is reflected in the increasing regulation of food packaging materials and the printing inks used to print on them, which is aiming to guarantee food safety and human health through use of appropriate packaging materials and printing technologies.

Guidelines and regulations for food packaging differ from region to region, and even from country to country, but the underlying principle is that the packaging should not endanger human health, change the composition of the foodstuff or alter its organoleptic properties.

Amongst the guidelines and regulations that pertain to food package printing inks for indirect food contact (i.e. inks for use on the non-food contact surfaces of food packaging), there are few which are particularly important and enforced. For example, the EU Framework Regulation (EC) No. 1935/2004 which – in substance –

states that food contact materials shall be safe. Also, the GMP Regulation (EC) No. 2023/2006, which lays down the general rules for all business operators in the food packaging value chain, and specifies that quality assurance and control systems are established and implemented. The more recent EU plastic packaging regulation (EC) No. 10/2011 is relevant for food package printing inks too, since printed plastics are also in scope. A lot of attention is also going to the Swiss Ordinance SR 817.023.21, since it was officially enacted in April 2008. SR 817.023.21 comprises positive lists of chemicals that are allowed to be used in inks for food packaging printing. List A comprises substances that have been thoroughly evaluated in terms of their health and safety risk and have a stated Specific Migration Limit (SML) or have to comply with the Overall Migration Limit (OML). List B comprises substances for which there is insufficient information currently to define a SML, but are allowed for use provided they comply with a migration threshold of maximum 10 ppb. EuPIA (European Printing Ink Association) provides general guidelines, including directions on Good Manufacturing Practice, and a negative list of banned ink chemicals. Worth mentioning, is the fact that the EU commission started activities to adopt a new Union legislation on printed food contact materials, including printing inks and commonly printed materials such as paper and board, in 2018.

In the US, the FDA concerns itself with food additives and direct food contact, and does not provide a regulation for inks for indirect food contact applications (no-migration principle).

In Japan, under the Food Sanitation Law, the inertness of food packaging must be ensured and the Japanese Printing Ink Manufacturers Association has issued recommendations on food packaging inks.

Also, some brand owners (e.g., Nestlé) have defined their own guidelines for food packaging printing, which have to be complied with by their packaging suppliers.

As far as pigments are concerned, the primary concern of regulations which pertain to food packaging pigments is to define upper limits for impurities such as traces of heavy metals, Primary Aromatic Amines (PAAs), Polychlorinated Biphenyls (PCBs) or dioxins. In Europe, the most relevant recommendations concerning the colorants for food packaging are the European Resolution AP (89) 1 (1989) and the German BfR IX (2015).

3. Ink Migration

A major concern with printed food packaging, when it comes to food safety and consumer health, is ink migration. All printing inks have the potential to migrate from the printed side of the packaging to the food-contact side and contaminate the food. At this point, it must be emphasized that ink migration into the packaged foodstuff is not only a function of the ink itself, but also largely depends on the other packaging components (print substrate), the printing and processing conditions, and also on the nature of the packaged food (e.g., fatty foodstuffs are more prone to absorb ink migrants). In the end, it's the entire printed packaging together with its content that must be compliant with regulations to ensure consumer safety, not just the ink. Ultimately, the responsibility therefore lies with the converter and the brand owner.

As a general rule, it is always recommended to use barrier substrates such as glass or metal or implement functional barrier layers (aluminium laminated cardboard, for example), even though this doesn't resolve the set-off migration issue. Also, low-migratory ink components should be selected whenever possible, and if migrating substances cannot be avoided, comprehensive toxicological data must be available and migration levels must be below the defined SML.

Ink migration and thereby food contamination can occur in different ways. The most common migration mechanisms are set-off, diffusion and gas phase migration. Set-off might occur when the prints are stacked or rolled up after printing and before conversion. In that case, ink components might transfer directly from the printed side to the reverse side of the packaging and later be in direct contact with food. In case of diffusion migration, ink compounds might reach the food by diffusing through the packaging substrate (e.g. thin-walled PE pouches). Gas phase migration might occur during strong heating (e.g., microwave-ready meals).

Examples of ink components with high migration potential include low molecular weight photoinitiators and monomers, as present in UV-curable inks, solvents, plasticizers, as well as any other low molecular weight substances (< 1'000 $g.mol^{-1}$). In general, ink components like binders, inorganic materials (e.g., fillers, silica matting agents) and organic pigments have no or extremely low migration potential and are usually not regarded as migrants. That said, aforementioned non-migrants might contain impurities which could migrate and contaminate food. In case of organic pigments, such impurities often consist of substances with significant toxicity and human health risks such as Primary Aromatic Amines (PAAs) or Polychlorinated Biphenyls (PCBs).

4. Azo Pigments and Primary Aromatic Amines (PAAs)

Azo pigments still reign supreme amongst organic pigments and represent more than 50% of the worldwide organic pigment production by volume. They are used in all kind of industries and applications, in particular in printing inks.

All azo pigments can potentially contain traces of PAAs, which are relatively small, mostly hydrophobic aromatic molecules that are prone to migrate, unlike the pigment itself (due to its particulate, crystalline nature). This is related to the azo pigment manufacturing process, which always starts with the conversion of a primary aromatic amine into a diazonium salt in the 1st synthesis step (the so-called diazotization). In addition, the coupling component introduced in the second step – while not being a PAA itself – might also contain PAA residues. Considering possible PAA residues originating from the coupling component and unreacted PAA from the diazotization step, the final azo pigment might contain residual PAAs at its surface or embedded into the crystal lattice (even after thorough washing). On top of that, certain non-azo pigments are also made from PAAs and can also potentially include PAA impurities. All in all, there are numerous pigments, mostly azos but some non-azo types as well, that are potentially contaminated by PAA residues, especially yellow, orange, red and magenta pigments (cyan and green pigments of the copper-phthalocyanine type or DPP red pigments, for example, are not concerned).

Issue with PAAs is that most of them exhibit acute or chronic toxicity, and a number of them are suspected human carcinogens. Actually, at least 22 PAAs are recognized and classified as CMR (Carcinogenic, Mutagenic, Reprotoxic) substances and are not allowed to come into contact with food at all. Examples of CMR-classified PAAs include 3-3'-Dichlorobenzidine (used in the synthesis of PY 13, PY 83 and other diarylide pigments) and o-Anisidine (used in the synthesis of e.g. PY 74). Both PY 83 and PY 74 are very popular yellow ink pigments, also widely used in inkjet inks and electrophotographic toners.

5. PAAs in Printed Food Packaging Materials

5.1 Regulatory Landscape

Older regulations and recommendations about PAAs are usually dealing with PAA content of the pigment itself (e.g. AP (89) 1 (1989) or EuPIA 2011), whereas for more recent regulations like BfR IX (2015) or (EC) No. 10/2011, it is the final packaging item that is in scope and it is PAA migration to food which is defined and regulated. For instance, under European Resolution AP (89) 1 (1989), the maximum threshold limit for PAAs in pigments is 500 ppm in total and 10 ppm for 3 specific PAAs (singly and in total). In the German BfR IX recommendation from October 2015, limit values for PAAs are no longer defined for pigments but for migration from final article, with a migration limit of 10 ppb in total and only 2 ppb singly for 22 specific PAAs that are recognized as CMR substances.

According to BASF Colors & Effects' worst-case assessment, aforementioned migration limits for PAAs translate into PAA content requirements for pigments which are significantly lower compared to the 500 ppm limit as recommended under AP (89) 1 (1989) or the old BfR IX recommendation from 2010. Thus, maximum PAA content of the pigment should now be less than 100 ppm singly and in total and 20 ppm singly for 22 PAAs classified as CMR.

5.2 New Analytical Method for PAA Analysis

Following the recent change in BfR (IX) recommendation regarding PAAs, and considering similar European regulations which are also focusing on PAA migration, there was an urgent need for a new analytical method to accurately identify and quantify PAAs as single substances in organic pigments. The established method from ETAD (Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers), ETAD No. 212, became obsolete since it didn't anymore fulfil the criteria regarding sample preparation, PAA extraction, selectivity and detection limit, as required by latest recommendations and regulations pertaining to PAA migration. Since no industry-wide feasible and accepted analytical method existed that complies with the newly required benchmarks, during 2015/2016 BASF developed a new test method for the exact qualitative and quantitative analysis of PAAs in pigments. BASF promoted the test method at ETAD, who had it validated by a round robin test within ETAD members. The method was subsequently published as ETAD Method No. 212 revised, edition May 3rd, 2016. As a released ETAD method, industry-wide acceptance is ensured and conversion into a norm is intended. All ETAD members, which include all major pigment and dye manufacturers, have the right to use the method free of charge, while non-ETAD members can purchase the method.

6. Conclusion

Digital printing enjoys increasing popularity for packaging printing applications. Food packaging is a strongly regulated field and Primary Aromatic Amine (PAA) impurities commonly present in organic pigments and thereby in printing inks, are of particular concern with regard to food safety and human health. Indeed, many PAAs are toxic and may endanger consumer health in case of migration from the printed packaging into foodstuff. To control PAAs in digital printing inks for food packaging, it is advisable to use pigments not relying on PAAs for their synthesis and therefore free of PAA impurities or breakdown by-products.

In case PAAs are used in pigment manufacturing, only pigments from reliable sources that are strictly monitored for PAA content should be used.

BASF Colors & Effects is analyzing its pigments with a new method to accurately identify and quantify PAA impurities. A pigment selection for digital food packaging printing inks which is meeting all relevant EU (incl. latest German BfR IX (2015)), Swiss Ordinance SR 817.023.21, as well as US and Asia-Pacific regulations, is available from BASF Colors & Effects.

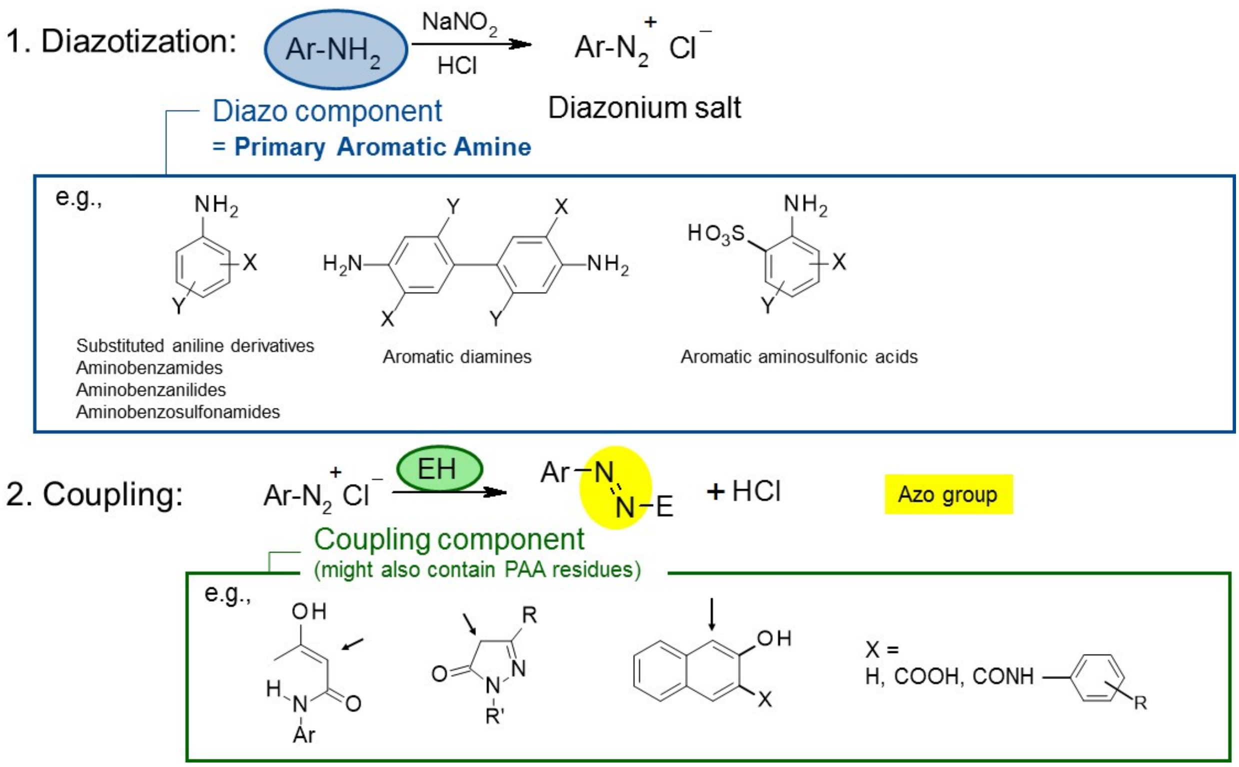

Fig.1 Azo pigments synthesis.

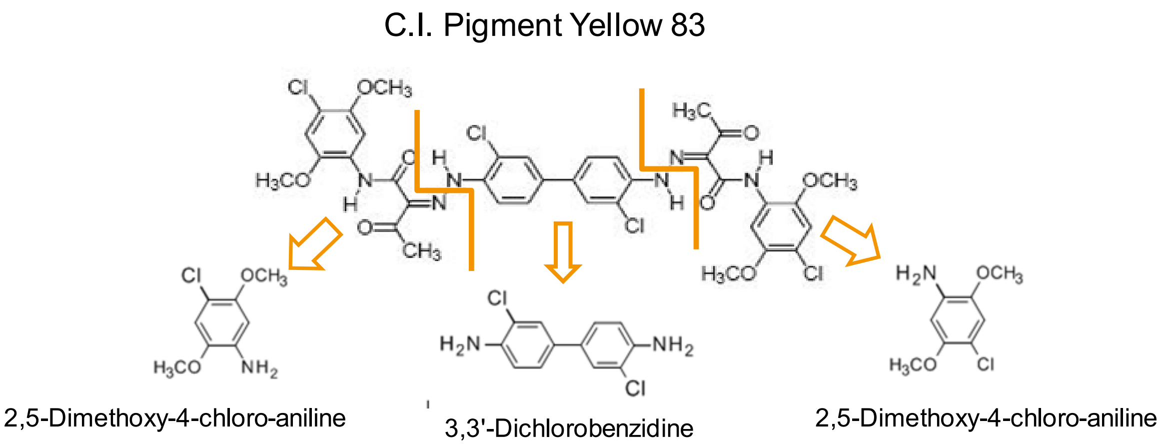

Fig.2 Possible PAA contaminants in P.Y. 83.