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Nanoscale pigment particles

Investigations on the migration of nanoscale pigment particles from printing ink layers to food during transient direct contact

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Nanomaterials may be present in food contact materials. In 2018, the European Union Observatory for Nanomaterials (EUON) published a comprehensive literature study on nanoscale pigments in consumer products and their safety during processing [1]. This study also lists virtually all pigments used in printing inks for food packaging as potential nanomaterials.

The study highlights the problems and gaps in the definition of nanomaterials, analytical detection and toxicological evaluation of such materials. Nanomaterials can be absorbed in the gastrointestinal tract under certain circumstances. However, these particles usually pass through the digestive tract unchanged after oral absorption and are excreted again. In general, the toxicity of nanoparticles after oral uptake is considered to be low due to the very low human exposure. The study shows, that further investigations on nanomaterials and their potential release are necessary to be able to conduct a realistic risk assessment.

In a previous work [2] the migration behaviour of nanoscale pigment particles from printing ink layers printed on the non-food-contact-side of food packaging was investigated. It could be shown, that nanoscale pigment particles are embedded in the polymeric matrix of the printing inks, but that a migration of the pigment particles from the printing ink film through a polypropylene film does not take place. In printing ink residues that undesirably stick to the reverse side of a print stored in a roll or stack (set-off), the pigments are also bound in the polymeric material and are not present as isolated nanoscale pigment particles.

In this study published by the "Verband der deutschen Lack- und Druckfarbenindustrie e. V. (VdL)" the aim was to investigate the migration behaviour of nanoscale pigment particles from printing ink layers that are in transient (i.e. short-time) direct contact with the food.

Printing inks used

Water-based printing inks based on styrene-acrylic copolymers were used for the investigation. The binders and additives contained in the printing inks correspond to

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commercially available ink systems used for printing on paper in short-term food contact. After various preliminary tests, the pigments used were Pigment Blue 15:3 (copper phthalocyanine), nanoscale titanium dioxide and nanoscale iron oxide (Pigment Red 101). Nanoscale titanium dioxide or iron oxide pigments are not normally used in printing inks, but in the context of this study, special (transparent) pigment dispersions were used to study the migration of such nanoscale pigment particles.

Papers used

The tests were carried out with different paper qualities. To avoid misinterpretations, e.g. by paper coatings containing titanium dioxide, a smooth (calendered, 30 g/m²) but uncoated paper was selected.

Prints

The papers were printed with the inks produced in the laboratory on a pilot installation in flexographic printing reel-to-reel under conditions similar to those in practice. The amount of ink applied was approx. 1.5 g/m² dry and thus corresponds to the usual ink layer thicknesses in practice.

We would like to thank the following companies for their support in the implementation of the project

- *Company Follmann Chemie GmbH & Co KG, Minden* for the production of the printing inks and the press proofs, as well as for the colour fastness tests according to EN 646
- *Company Harold Scholz & Co GmbH, Recklinghausen* for the provision of the nanoscale iron oxide dispersion
- *Company Flint Group Packaging Inks Germany GmbH,* Willstätt for carrying out the examination of the printed paper samples by means of optical microscopy (incident light, microtome sections).
- *ECKART GmbH,* Hartenstein for carrying out a wide range of analyses of the samples with SEM.
- *Company KRONOS TITAN GmbH,* Leverkusen for the execution of the TEM investigations and the provision of a nanoscale TiO_2 sample.
- *Fraunhofer Institute for Process Engineering,* Freising for the execution of migration investigations and many preliminary investigations (including the AF4-MALS method)

Colour fastness test according to the EN 646 standard

The colour fastness of printed paper is usually determined according to the EN 646 standard (determination of colour fastness of dyed paper and cardboard). In this test, the test specimen is placed between two glass fibre papers soaked with the test liquids and, after contact time at room temperature, the bleeding of the colourants onto the glass fibre paper is evaluated. The test was performed with the printed papers for 4 hours.

Migration tests (immersion tests)

The migration tests were carried out in accordance with the European Standard EN 646. As simulants, ultrapure water, 3 % acetic acid, an alkaline solution of 4.2 g/L Na_2CO_3, 0.5 g/L NaCl, and 0.2 g/L K_2CO_3 as well as isooctane were used.

In contrast to EN 646, 1 dm² of the test specimens were immersed in 30 mL simulant liquids for 10 min at 23 °C. The migration samples were then examined by ICP-MS for the elements copper, titanium and iron.

The immersion of the test specimens in the simulants simulates a worst-case scenario, since in the case of the aqueous simulants the paper fibres swell up considerably. With isooctane as simulant, this swelling effect should be avoided. As the printed papers swell very quickly in the aqueous simulants and then dissolve, it was not possible to simulate longer contact times.

In the case of isooctane as a simulant, the migration samples were first reduced until dry with a nitrogen stream and resuspended with 10 mL 3 % nitric acid. The other simulants were measured directly via ICP-MS.

Unprinted paper, paper printed with pigment-free ink and samples printed with the pigmented inks white (nanoscale titanium dioxide), cyan (partial nanoscale copper

phthalocyanine) and red (nanoscale iron oxide) were examined.

Optical microscopy and scanning electron microscopy (SEM)

In order to examine the quality of the ink film on the printed paper surfaces, microtome sections of the printed papers were made and examined with an optical microscope.

The papers were examined by SEM before and after the migration test. Both the surface structure and microtome sections were examined. An SE2 detector was used for analysis.

Transmission electron microscopic examination (TEM)

To demonstrate the nanoscale nature of the pigment particles used, TEM investigations were carried out on the ink films. Due to problems in sample preparation, these investigations could not be performed on the printed papers. The inks were applied to the side of a metal plate coated with a white primer using a spiral doctor blade (number 2, approx. 6 µm wet layer, or approx. 2 µm dry layer) and then dried. Microtome sections of 200 nm thickness were prepared from these lifts and then examined.

Nanoscale character of the pigments used and their embedding in the ink film

The TEM images of the ink films clearly show the nanoscale character of the pigments used.

Figure 1 shows the ink film of the printing ink with nanoscale TiO_2. In figure 1A, the white TiO_2 pigments from the white coating of the metal plates can be seen as black-grey particles on the right side of the picture. The average pigment size is about 200–300 nm, as

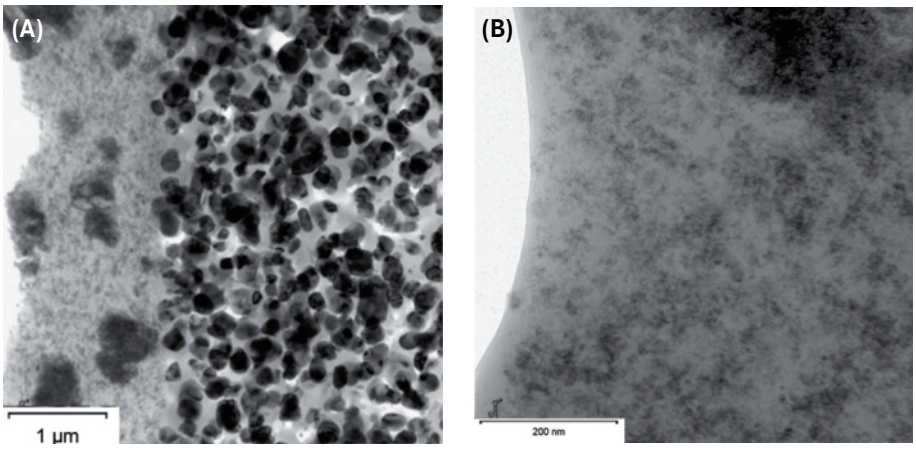


Fig. 1 Ink film with nanoscale TiO_2

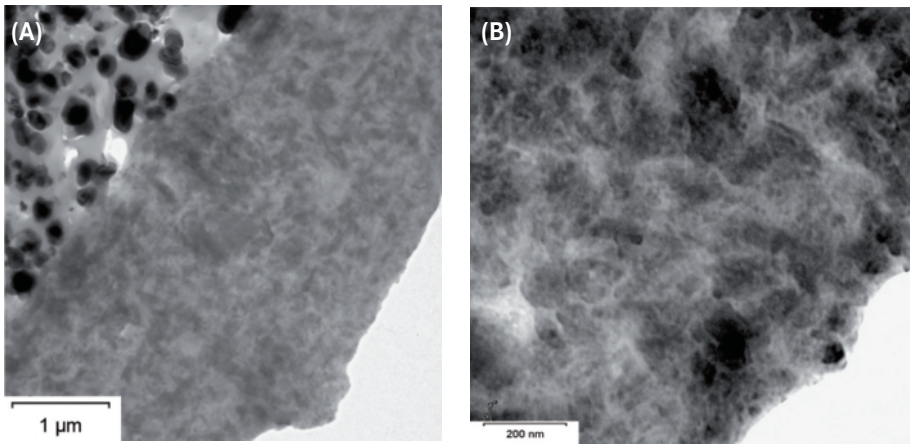
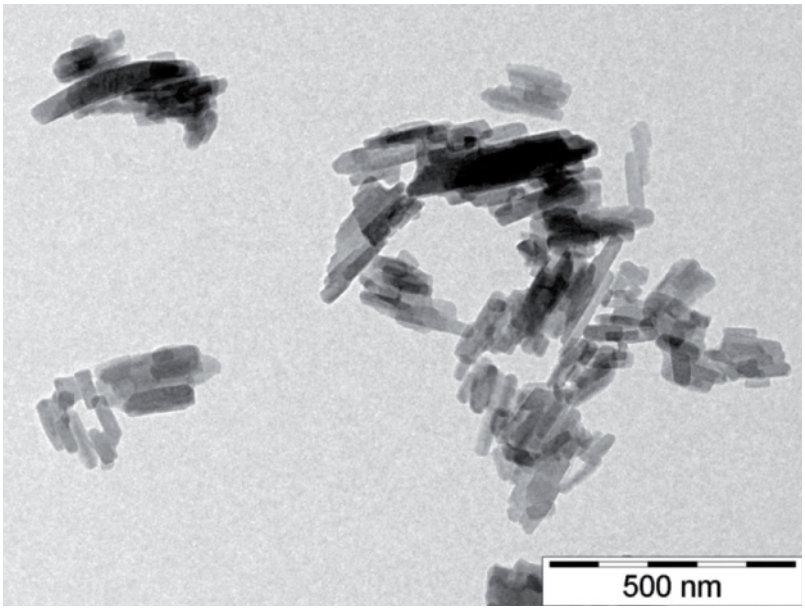


Fig. 2 Ink film with nanoscale cyan pigment

Fig. 3
Electron microscope image of a copper phthalocyanine pigment



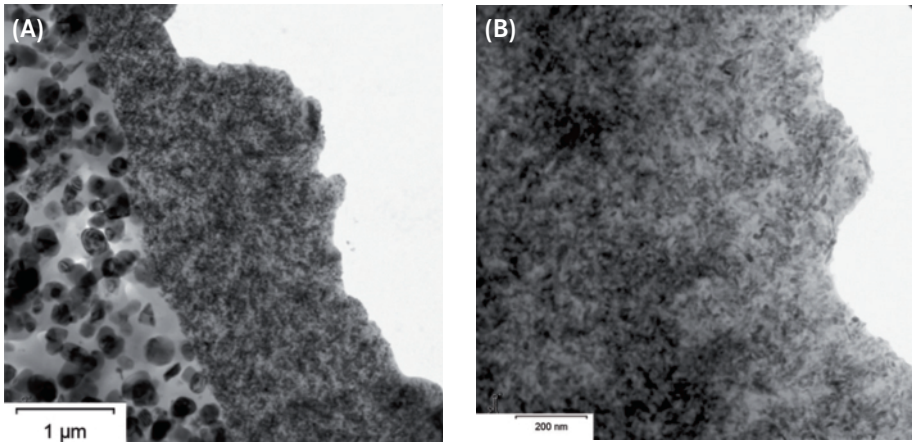


Fig. 4 Images of an FeO_x pigment under investigation

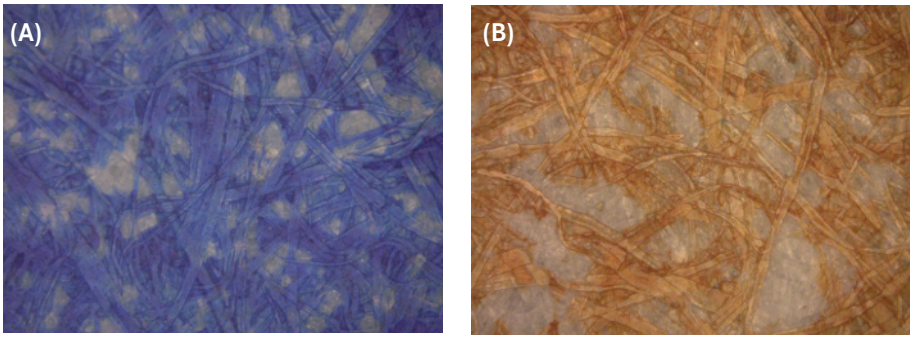


Fig. 5 Photomicrograph of a paper printed with cyan (**A**) or FeO_x red (**B**)

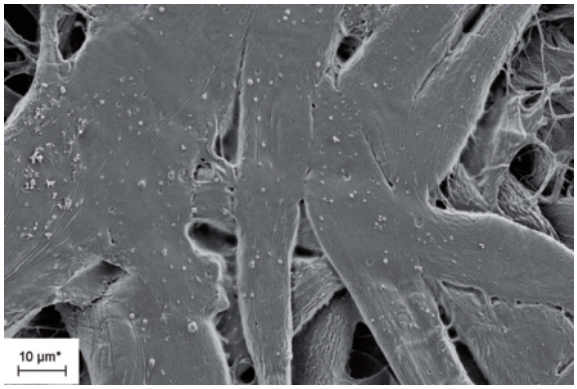


Fig. 6 SEM image of the paper used for the migration experiments

Figure 2 shows the analog images for the nanoscale cyan pigment. In figure 2A, the TiO_2 of the coating of the metal plate is again visible in the upper left corner, to the right of it the ink film can be seen. The cyan pigment consists to approximately 90 % of the elements C, H, N and therefore gives only a weak contrast to the acrylate polymers of the ink layer.

Electron microscopic examinations of a typical copper phthalocyanine pigment show the typical rod shape (Fig. 3) of this pigment. The primary particles have a length of 70–300 nm and a diameter of 25–39 nm. These rods can be found on printed paper surfaces in SEM images. However, since other paper grades were used, these images are not shown here.

Finally, Figure 4 shows the images of the FeOx pigment under investigation. The pigment particles are also very small (estimated < 20 nm).

Besides the nanoscale character of the pigments used, the TEM images of the ink films demonstrated, that the pigments are homogeneously embedded and firmly fixed in the polymeric matrix of the ink films. No accumulation can be seen on the upper side of the ink. Although a different substrate and application method was used for the TEM investigations, it can be assumed, that the pigments in the ink films behave analogously on the paper surfaces.

» The nanoscale character of the pigments used was checked and confirmed by electron microscopic examinations. «

it is the case for TiO_2 normally used in printing inks. To the left of this, the ink film in which the nanoscale TiO_2 pigments are embedded is depicted. The small grey dots are individually dispersed particles, the large grey areas represent incompletely dispersed agglomerates of the nanoscale TiO_2. Figure 1B shows a detail enlargement. The images clearly show, that the individual TiO_2 particles are very small (estimated < 20 nm).

Characterization of the printed paper surfaces by means of optical microscope images and SEM-examinations

Although a smooth calendered paper has been used, the paper surface is still very rough. Only the paper fibres are smoothed on the surface by calendering, but the open-pored fibre structure is retained. Light mi-

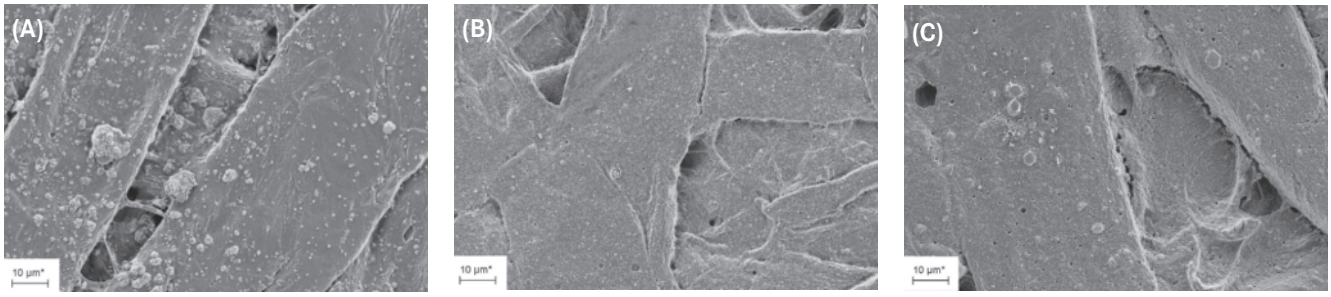


Fig. 7 SEM view of printed paper surfaces with differently pigmented printing inks: (**A**) white (TiO_2), (**B**) red (FeOx), (**C**) cyan

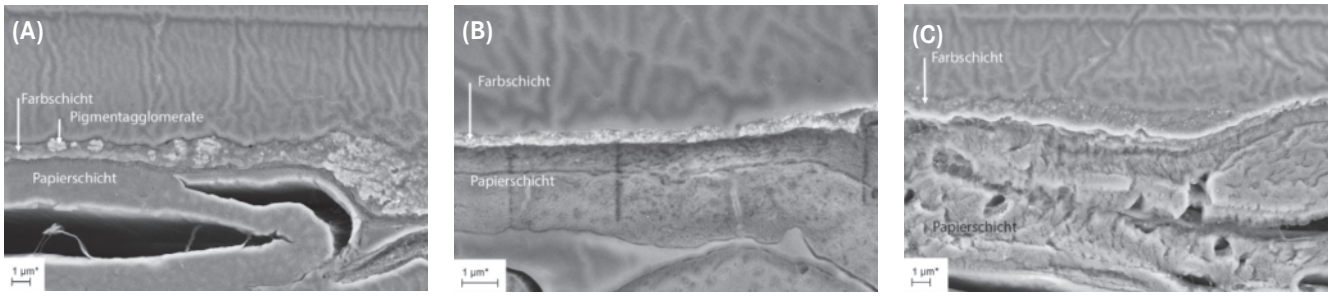


Fig. 8 SEM images of the microtome sections of the printed papers: (**A**) white (TiO_2), (**B**) red (FeOx), (**C**) cyan

croscope images (magnified 250 times) of the printed paper show, that only the smoothed paper fibres located on the surface are wetted by ink (Fig. 5).

Figure 6 shows the surface of the paper used for the migration tests, which was printed with a pigment-free extender. The extender (like the pigmented ink films) is not able to completely close the pore structure, as the optical microscope images have already shown. The small particles on the paper fibres are probably wax particles, which are needed to achieve sufficient rub resistance.

Figures 7A-C show the surfaces printed with the colours white (TiO_2), red (FeOx) and cyan. In the sample printed with the nanoscale TiO_2, the pigment agglomerates already observed with TEM are clearly visible on the surface. At this point it should be emphasized again that the permanent stabilization of such nanoscale TiO_2 pigments is very difficult and the used ink formulation (in real printing inks no nanoscale TiO_2 is used) obviously does not sufficiently support this. However, on the surfaces of the samples printed with red and cyan such agglomerates are not found.

In the microtome section (Fig. 8) of the printed papers, the polymeric ink films on the paper surface are clearly visible in each case. On the planar paper fiber surfaces, the printing inks form island-shaped zones with a largely closed ink film. The pigments are homogeneously embedded in these ink films, as shown in the TEM images.

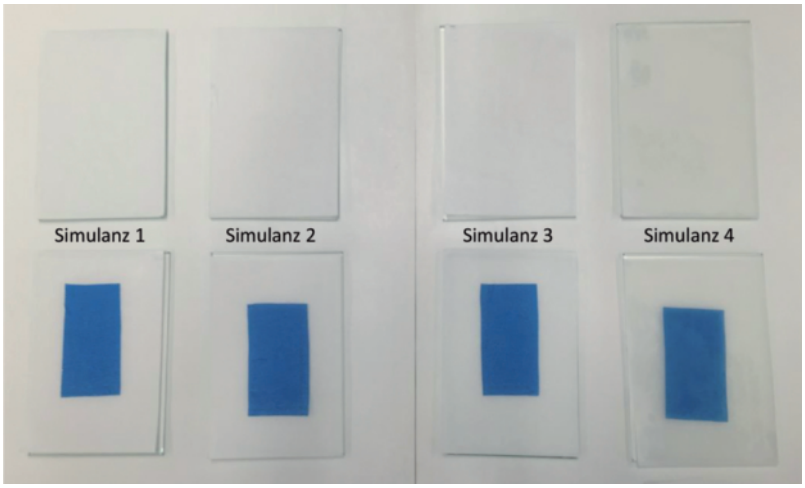


Fig. 9 Colour fastness test according to EN 646 with blue print samples: simulant 1 (water), simulant 2 (alkaline salt solution), simulant 3 (3 % acetic acid) and simulant 4 (isooctane)

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Colour fastness test according to EN 646

In the colour fastness test (Fig. 9) of the prints according to EN 646, printed samples are soaked with the simulants and brought into close contact with a filter paper for 4 hours. This test did not reveal any visible colour transitions, i.e. all printed samples are conform to EN 646.

However, this method is not suitable for testing whether individual pigment particles have migrated. For this reason, the method was modified to a dipping test. The simulants were analysed for the elements typical of the respective pigments. If these elements were detectable in the simulants, it was planned to check their particulate or ionic character in further investigations, e.g. with AF4-MALS analysis. The results of the immersion tests are summarised in Table 1.

The detection limit of the ICP-MS method was 5 ng/mL in the simulants. Related to the respective pigments and assuming the EU cube model for packaged food (1 kg food in 6 dm^2 packaging), the following detection limits for the pigments can be derived from this

- Titanium dioxide: 1.5 µg/kg (ppb)
- Iron oxide: 2.4–2.7 µg/kg (ppb)
- Copper phthalocyanine 7.7–9.1 µg/kg (ppb)

With the exception of 3 % acetic acid as simulant, no pigment-specific elements were found in the sample solutions. However, in the case of acetic acid elevated values of iron (pigment printed samples up to 32.2 ng/mL) were found. With acetic acid, values of 10.9–13.1 ng/mL were found for iron on the sample printed with pigment-free blends and on the unprinted paper, respectively, due to the fact, that the acetic acid used was contaminated with 10.2 ng/mL iron. Since iron oxide dissolves in acetic acid and no values above the detection limit were found with any other simulant, it can be assumed that this result is due to dissolved iron ions.

Slightly elevated values of copper (printed sample, 9.1 ng/mL) were also found using acetic acid. The complex bound copper in the pigment is not soluble. However, commercially available copper phthalocyanine pigments may contain very small residual amounts of ionically bound and thus acid-soluble copper due to the synthesis process, which is the reason for the very low copper content of the sample solution in the case of acetic acid [3]. At approx. 20 ppb, based on the EU cube model, the copper values found are a factor of 250 below the limit value of 5 ppm specified in the plastics regulation (EU) 10/2011.

Conclusion

In this study the migration of nanoscale pigment particles in direct contact with test simulants was investigated. Since the pigments used in commercially available printing inks only partially contain nanoscale particles, nanoscale pigments were specifically

Tab. 1 Migration studies of samples printed with titanium dioxide, iron oxide and Cu-phthalocyanine pigments

Simulant	TiO_2 [Ti, ng/mL]			Iron oxide [Fe, ng/mL]			Cu-phthalocyanine [Cu, ng/mL]		
	Paper	Without pigment	Printed	Paper	Without pigment	Printed	Paper	Without pigment	Printed
Ultrapure water	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Alkaline salt solution	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
3 % Acetic acid	< 5	< 5	< 5		13.1	32.2	< 5	< 5	9.1
3 % Acetic acid				10.9*	10.9*				
Isooctane	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5

* Separate determination; blank values 3 % acetic acid: Ti (< 5 ng/mL), Fe (10,2 ng/mL), Cu (< 5 ng/mL)

incorporated in a commercially available water-based ink system (suitable for printing on paper). The nanoscale character of the pigments used was checked and confirmed by electron microscopic examinations. The pigments are homogeneously distributed in the ink film, an accumulation on the surface was not detected. The migration of the pigments was investigated by testing in accordance with EN 646 and by brief (10 min) immersion in the simulants. According to the results of this study, a migration of nanoscale pigment particles from printing ink films that are in short-term direct contact with food can be excluded. The pigments are firmly incorporated in the polymeric binder matrix, which creates a more or less closed ink film on the papers. However, it should be mentioned, that the colourants and ink films must of course be inert to the foods in direct contact and must for example not be dissolved by them. To test this colour fastness testing according to EN 646 has proven to be suitable in practice for many years. The results of the study are thus in line with other tests on polymeric coatings that come into direct contact with food [4,5].

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» A migration of nanoscale pigment particles from printing ink films that are in short-term direct contact with food can be excluded. «

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