

Nanoscale pigment particles

Analysis of the migration behaviour from printing ink layers of printed food packaging into the food

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The use of so-called nanomaterials in technical products and consumer goods has been discussed intensively and controversially for several years. On one hand, these materials enable fascinating new material properties (like the famous "lotus effect"), on the other hand the potential effects of these materials on the environment and throughout the food chain are not yet sufficiently known.

In accordance with the second draft of the German Printing Ink Ordinance, nanomaterials in printing inks designed to be applied on food packaging may be used if they are specifically authorised. Without a specific authorisation, nanomaterials may only be used if migration from the printing ink layers into the food is not detectable [1].

In this context, the German Paint and Printing Ink Association (VdL) has organized a working committee to analyse, in collaboration with member laboratories and institutes, the migration behaviour of nanoscale pigment particles from printing ink layers of food packaging into the food.

Print on Food packaging serves the demands for information and product advertising. Packaging inks are complex multi-component mixtures which also contain, amongst others, very small nanoscale pigment particles.

The aim of this study was to answer two questions by means of typical examples:

- 1) Are nanoscale pigment particles present in the wet ink or in the dried ink film, as separate particles?
- 2) Is there any detectable migration of nanoscale particles into food? Offset-printed cartons and gravure-printed polypropylene films have been examined as model cases.



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Definition

The term "nanomaterial" has not yet been defined consistently. The regulation on cosmetic products (EC) No. 1223/2009 [2] defines as nanomaterial an insoluble or biopersistent and intentionally manufactured material with one or more external dimensions, or an internal structure, on the scale from 1 to 100 nanometres.

The intended printing ink ordinance orientates itself on the recommendation of the European Commission on the definition of nanomaterial (2011/696/EU) [3], i. e. materials in printing inks,

a. which are of natural origin, incidentally generated or purposefully manufactured,

b. which contain particles in an unbound state, as an aggregate, or as an agglomerate

c. for which at least 50 % of the particles in the number size distribution, one or more external dimensions is in the size range from 1 to 100 nanometres (article 1, § 2 No. 9).

A particle is a single, isolated particle, agglomerates are a collection of weakly bound particles or aggregates, and aggregates are a collection comprising of strongly bound particles.

In accordance with the definition in DIN SPEC 1121 (DIN CEN ISO/TS 27687) nanoparticles are particles, with all three dimensions in the nanoscale range of 1 to 100 nanometres, nanofibres have two nanoscale dimensions, and nanoplates only have one nanoscale dimension. The term nanobject includes these three types of nanoscale particles.

In this present study it is to be shown that wet printing inks contain

Table 1 Overview of the analysed test specimens

No.	Identification	Analysed material	Ink system	Pigment
1	TD Cyan FD	BOPP film frontal print	NC, PU, Ti complex, ethanol, ethyl acetate	Cu-phthalocyanine
2	TD Cyan KA	BOPP/BOPP film composite	NC, PU, Ti complex, ethanol, ethyl acetate	Cu-phthalocyanine
3	TD White FD	BOPP film frontal print	NC, acrylate, ethyl acetate, two-component cross-linking agent based on isocyanate	Titanium dioxide
4	TD White KA	BOPP/BOPP film composite	NC, PU, ethanol, ethyl acetate	Titanium dioxide
5	Offset Cyan	Printed fresh-fibre carton, coated with water-based overprint lacquer		Cu-phthalocyanine
6	Offset White	Printed fresh-fibre carton, coated with water-based overprint lacquer		Titanium dioxide
7	Offset Silver	Printed fresh-fibre carton, coated with water-based overprint lacquer		Aluminium

TD: gravure printing; FD: frontal print; KA: lamination; BOPP: biaxially oriented polypropylene; NC: nitrocellulose; PU: polyurethane; Cu: copper

nanoscale objects, which are also detectable in the dried ink film, but solidly embedded in the polymer film and therefore, cannot migrate into the food as nanoscale object.

Printing inks

Commercial printing inks have been used in this study. The inks were printed on commercial printing machines and further processed in operational pilot plants.

The film samples (thickness: 30 µm) were gravure-printed roll-on-roll and laminated within 48 hours. The printed or laminated rolls were stored at room temperature until sampling (occurrence of set-off possible). The offset prints on fresh fibre carton were rack-stored. Table 1 gives an overview of the analysed test specimens. Special thanks to Sun Chemical for providing the printed fresh fibre carton samples and Flint Group for the printed BOPP film samples.

Measuring the particle size distribution

For measuring the particle size distribution in the solvent-borne liquid printing inks, analyses have been carried out by means of small-angle X-ray scattering (SAXS) and dynamic light scattering (DLS) [4]. At the same time, results of laser diffraction analyses with a Malvern Mastersizer have been recorded [5]. In addition, the size of the pigment particles have been determined on scanning electron microscopic cross-section images of the printed films [6] as well as with the use of photon correlation spectroscopy (PCS) of the liquid ink samples [7].

Migration analysis

The film samples (No. 1–4) were tested in a standard migration test (simulant 50 % ethanol, 10 days, 40 °C). In the migration study, the content of copper (component of the used cyan pigment) and titanium was determined by means of inductively coupled plasma mass spectrometry (ICP-MS) [8]. In addition, the migration solutions have been analysed for any pigment particles by means of photon correlation spectroscopy (PCS) [7]. The carton samples (No. 5–7) were tested in a modified test for possible migration. This modified test was selected, since for printed carton usually Tenax is used as the food simulant. For Tenax, however, only gas-phase migration is measured, which is unsuitable for solid nanoparticles.

For this modified migration test, sodium chloride was applied on the unprinted side of the samples (25 g salt on 180 cm² of surface) and the samples have been stored for 10 days at 40 °C. In order to achieve an abrasion effect the sample was shaken daily. Subsequently, the salt was dissolved and the solution analysed for copper, aluminium, and titanium [9].

TOF-SIMS and XPS analysis of the surfaces

The printed and unprinted sides of the film samples (No. 1 + 3) have been analysed by means of the surface-specific methods time-of-flight secondary ion mass spectrometry (TOF-SIMS) and X-ray photoelectron spectroscopy (XPS) [10].

In case of the XPS method the surface is exposed to X-radiation, leading to emission of photoelectrons which are then analysed. The analysis



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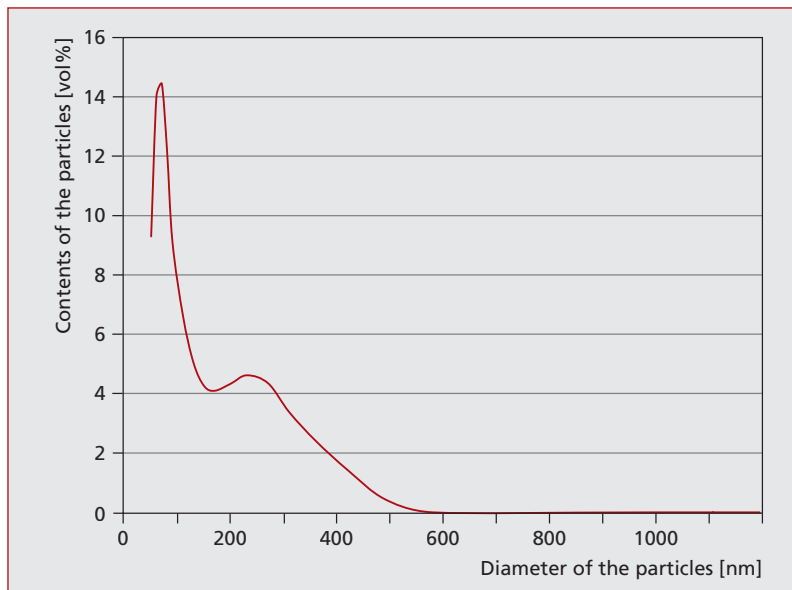


Figure 1 Particle distribution of the used printing ink "TD Cyan KA", determined by means of laser diffraction analysis

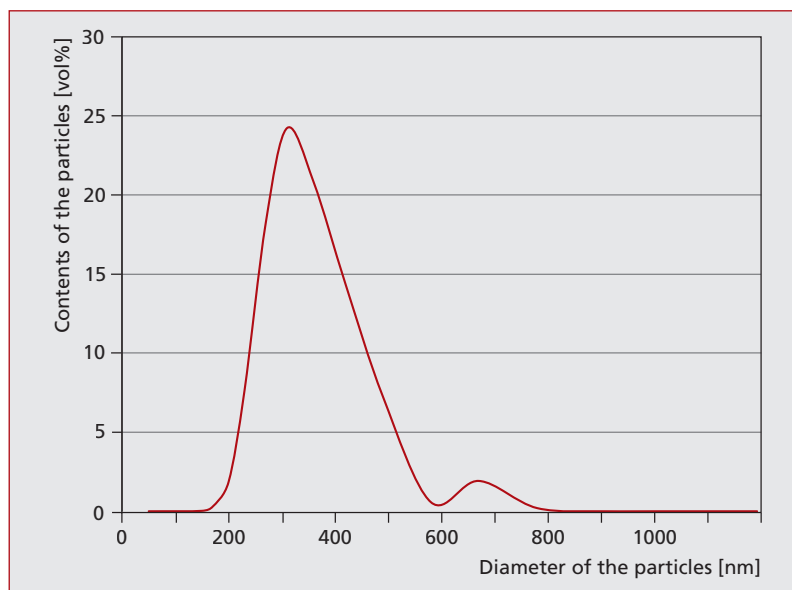


Figure 2 Particle distribution of the used printing ink "TD White FD", determined by means of laser diffraction analysis

depth of this method is 5–10 nm and the limit of detection is around 0,1–1 atomic per cent (At%).

Regarding the TOF-SIMS method the surface is shot with a particle beam, leading to ions separating from the surface which then are analysed in the mass spectrometer. The analy-

sis depth of the method is 1-3 atom layers.

Additionally, any printing ink set-off on printed carton samples has been analysed by means of TOF-SIMS [11]. As reference, pigments used have been examined [12].

Nano-objects in printing inks?

Printing inks consist of four major components: solvents, polymeric binders, additives, and colouring components. Printing inks mostly contain pigments as colouring component. Pigments are insoluble, dispersed particles which absorb a fraction of the visible light and, consequently, appear coloured. Normally, printing ink manufacturers use powder pigments which are finely dispersed and incorporated into the binders during the production process. In order to achieve a high gloss and high transparency of the printed ink films it is necessary to finely disperse the pigments, i.e. the agglomerates and aggregates in the pigment powder must be divided and the formed pigment particles must be stabilized. A dried printing ink film is usually 1–1,5 μm thick, therefore, all of the embedded particles are normally considerably smaller than 1 μm . According to the dimension-specific definition mentioned above practically all printing inks contain nano-objects, even if these materials have not been manufactured specifically for this purpose.

For the analysis of the liquid printing inks by means of small-angle X-ray scattering (SAXS) and dynamic light scattering (DLS) the samples had to be thinned down extremely. It was detected that both methods were un-

suitable for the analysis of the printing ink samples and that the results were not significant [4].

Therefore, laser diffraction analysis and photon correlation spectroscopy (PCS) have been used as methods for the characterization of the particle size distribution in the liquid printing inks. Regularly conducted measurements of the particle distribution on dispersed organic pigments by means of laser diffraction analysis prove that pigments in printing inks contain a considerable percentage in the range of < 100 nm. For example the used printing ink “TD Cyan KA” contains about 50 vol% of the pigment particles with < 100 nm (Figure 1) [5].

In contrast, the respective laser diffraction analysis of the solvent-borne white printing ink TD White FD showed no evidence of TiO₂ particles < 100 nm (Figure 2). This is consistent with the pigment manufacturers’ information that TiO₂ pigments for printing inks are regulated to a range of about 200–400 nm in order to achieve optimal light scattering and, consequently, maximum opacity. The results of the laser diffraction analysis were confirmed by photon-correlation spectroscopic analysis, the measured average particle size was 80–90 nm for Cu-phthalocyanine and 200–300 nm for titanium dioxide.

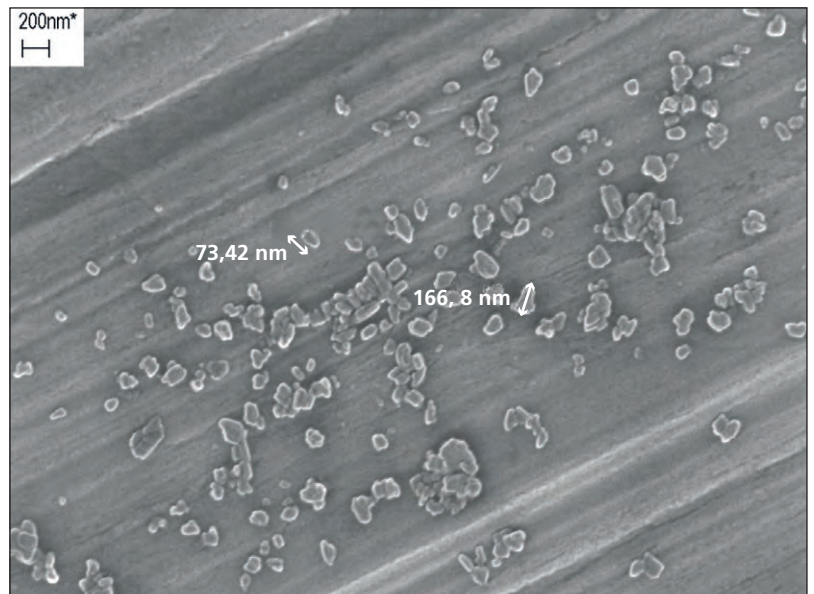


Figure 3 Scanning electron microscopic image of the Cu-phthalocyanine pigment particles in the liquid ink Cyan (magnification 20.00 KX, detector: InLens)

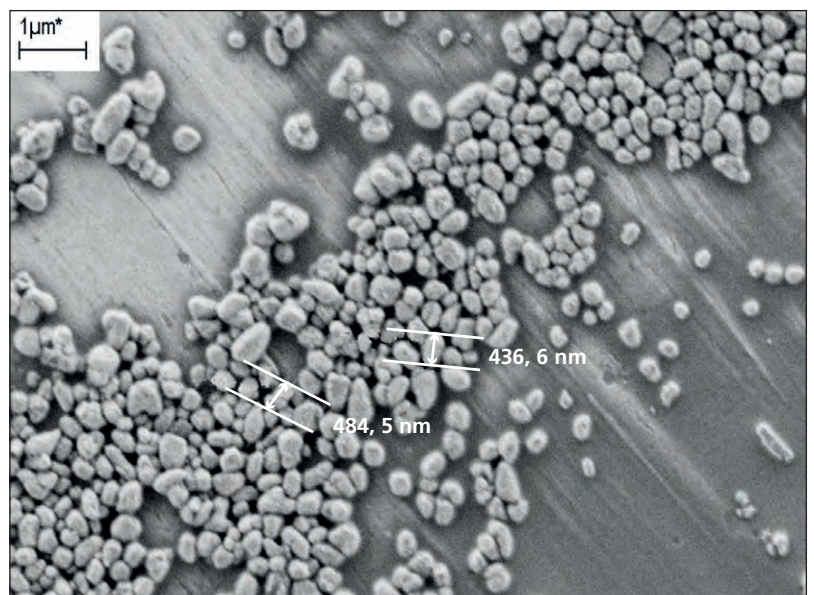


Figure 4 Scanning electron microscopic image of the titanium dioxide pigments in the liquid ink White (magnification 10.00 KX, detector: SE2)

Table 2 Results of the migration analysis on film samples				
No.	Identification	Analysed material	Titanium [μg/L]	Copper [μg/L]
1	TD Cyan FD	BOPP frontal print	< 5	17
2	TD Cyan KA	BOPP/BOPP composite	< 5	18
3	TD White FD	BOPP frontal print	< 5	18
4	TD White KA	BOPP/BOPP composite	< 5	6
	Unprinted	BOPP	< 5	11
	Unprinted	BOPP/BOPP composite	< 5	12

Table 3 “Migration results” on the carton samples

No.	Identifica- tion	Analysed material	Ti	Cu	Al
			[mg/kg salt]		
5	Offset Cyan	Printed fresh-fibre carton, coated with water-based overprint lacquer	< 5	< 5	< 5
6	Offset White	Printed fresh-fibre carton, coated with water-based overprint lacquer	< 5	< 5	< 5
7	Offset Silver	Printed fresh-fibre carton, coated with water-based overprint lacquer	< 5	< 5	< 5
	Unprinted	Fresh-fibre carton	< 5	< 5	< 5

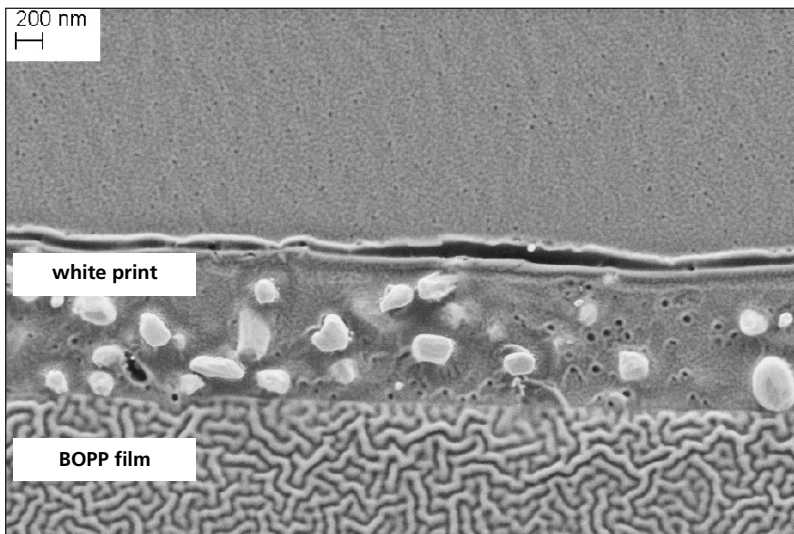


Figure 5 SEM cross section image of sample No. 3 (TD White KA) after migration analysis (10 days, 40 °C, 50 % ethanol; magnification 20.00 KX, detector: SE2)

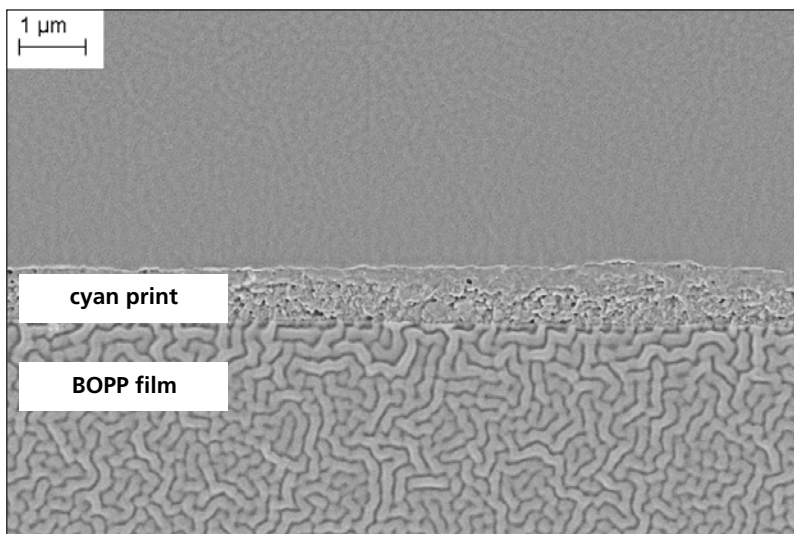


Figure 6 SEM cross section image of sample No. 1 (TD Cyan FD) after migration analysis (10 days, 40 °C, 50 % ethanol, magnification 10.00 KX, detector: SE2)

However, in the scanning electron microscopic cross-section images (Figures 5 and 10) particles in the range of < 100 nm are provable. It can be assumed that TiO₂ pigments normally used in printing inks are not within the scope of the term “nanomaterial” in accordance with the Commission Recommendation [3], but still contain a percentage of nano-objects.

Scanning electron microscopic images (SEM) as well as the results of the photon correlation spectroscopy of the liquid printing inks confirm the ranges of the pigment particles (Figures 3 and 4) detected by means of laser diffraction analysis. The used platelet-shaped aluminium pigments have an average thickness of 30–40 nm and, therefore must also be considered clearly as nanomaterial.

Results of the migration analysis

The pigments Cu-phthalocyanine and titanium dioxide both were selected, since they are among the most frequently used pigments in printing inks and the elements copper and titanium can be easily analysed, both, qualitatively and quantitatively and should not be found in typical packaging material, such as BOPP films.

In the case of the carton samples an aluminium pigment was additionally selected as a typical representative of the group of effect pigments. Due to its structure (nanoplates, only one dimension in the range of 1–100 nm) it is within the scope of the definition nanomaterial [3] and the aluminium is also analytically well-detectable. In Table 2 and 3 the results of the measurements are summarized.

The titanium contents in the migration samples, detected by means of ICP-MS, were below the limit of detection for all of the samples. Copper, however, was found in the migration samples of the printed as well as the unprinted films. The detection of copper in the migration results of unprinted films was confirmed by a check measurement in a different institute. Therefore, it must be assumed that traces of copper are contained in the used film material despite the manufacturers' information that no copper-bearing raw materials were used in the production of the films.

The detected copper contents in the migration results are the same, irrespective of the ink used, i.e. a clearly detectable migration of a copper-bearing cyan pigment from the printed film material into the migrate does not take place.

In order to fully exclude migration of pigment particles, the migration solutions have been analysed for pigment particles by means of photon correlation spectroscopy (PCS). No particles were detected (limit of detection 10 ppm). In order to increase the sensitivity of the determination, in addition, samples were concentrated on a sample holder and examined for particles by means of a scan-

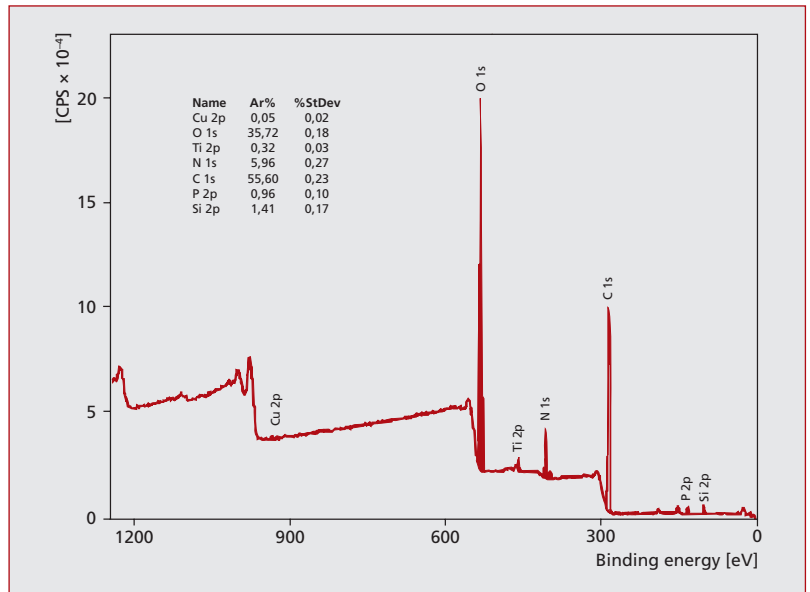


Figure 7 XPS spectrum of the sample No. 1 (TD Cyan FD) with weak copper signal (the signal Ti 2p is caused by the titanium complex which is used as adhesive agent in the cyan)

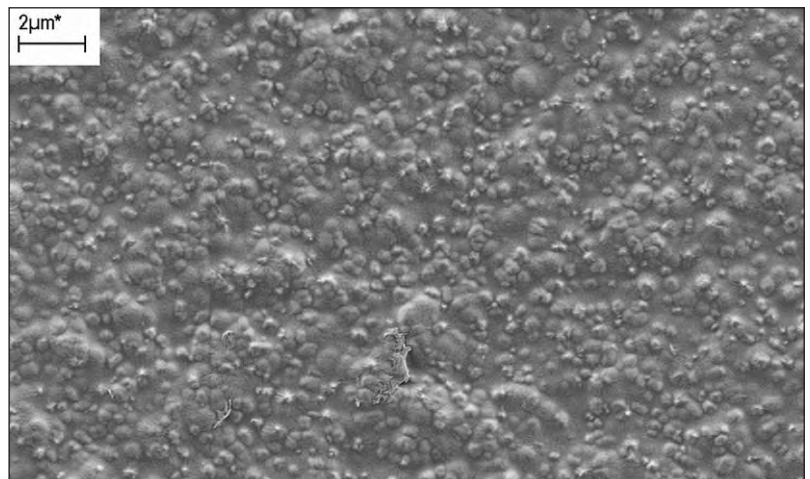


Figure 8 SEM image of the BOPP film surface printed white (No. 3, TD White FD, magnification 5.00 KX, detector: SE2)

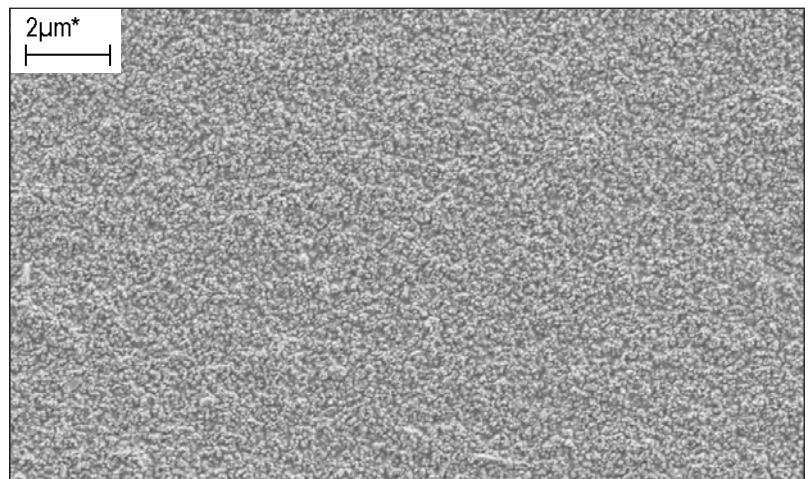


Figure 9 SEM image of the BOPP film surface printed cyan (No. 1, TD Cyan FD, magnification 5.00 KX, detector: SE2)

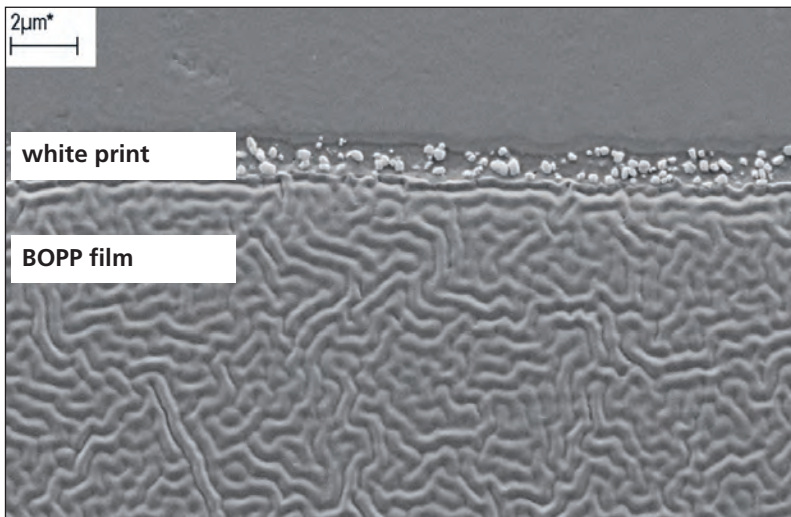


Figure 10 SEM image of a cross section of a BOPP film printed white (No. 3, TD White FD, magnification 5.00 KX, detector: SE2)

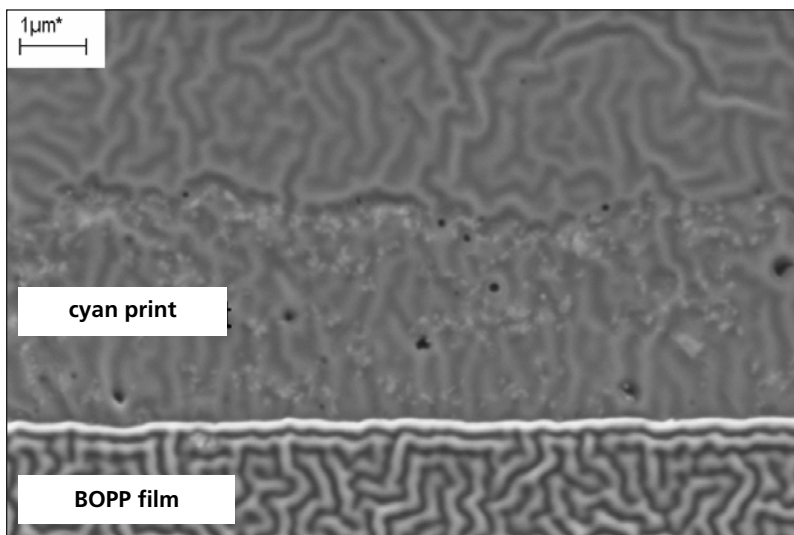


Figure 11 SEM image of a cross section of a cyan-printed BOPP foil (No. 1, TD Cyan FD, magnification 10.00 KX, detector: SE2)

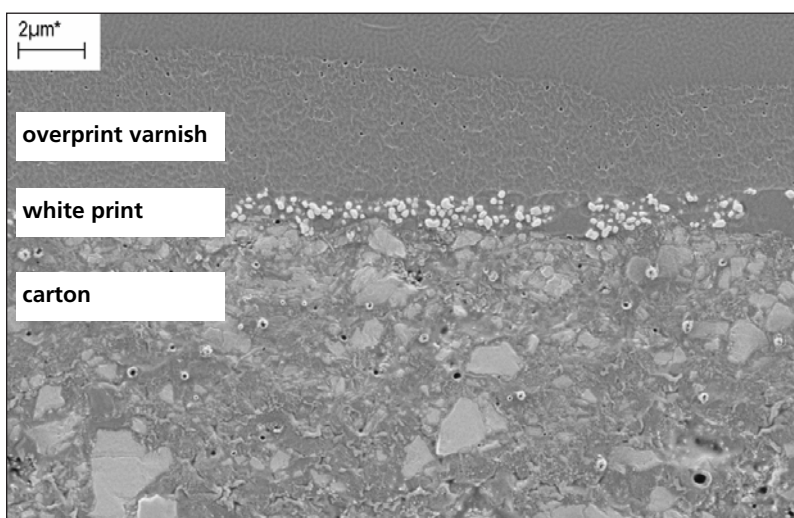


Figure 12 SEM cross section image of a white-printed carton (No. 6, offset white, magnification 5.00 KX, detector: SE2)

ning electron microscope (SEM) – in which case no particles were detected as well [13].

The “migration analysis” by means of salt abrasion on the carton samples was entirely negative, i.e. in this case, a migration of the pigment particles was not detected, too [9].

The printed film samples have been analysed for migration of pigment particles into the BOPP film material prior to as well as after the migration test by means of cross-section images (SEM). A migration of pigment particles from the ink layer was not detected in any case (Figures 5 and 6).

In summary, it was established that the migration analysis on the examined samples provides no indication of a potential migration of pigment particles into a test medium.

Results of the surface analysis

By means of the time-of-flight secondary ion mass spectroscopy (TOF-SIMS) the surface printed film samples (No. 1 + 3) were analysed for “near-surface pigment particles”, referring to pigment particles contained in the first 1–3 monolayers. Up to 25 materials or ions were detected which can be derived from the chemical composition of the printed BOPP film or the printing inks. On the coloured side of the film printed with cyan only a weak copper signal was observed (see Figure 7). By means of X-ray photoelectron spectroscopy (XPS) deeper surface layers of this sample were analysed. The copper content of the upper 5–10 nm measured by means of XPS is around 0,05 At% (error 0,02 At%) and, for this reason, is distinctly below the content of 0,09 At% determined in the volume by means

of energy dispersive X-ray spectroscopy (EDX) [10]. The penetration depth of EDX is considerably above the ink film thickness of approx. 1 µm and, in consequence, the printing substrate is partially analysed, too. Mathematically, the content of copper in the ink layer is approx. 0,26 At%.

Titanium was not detected on the printed side, neither by means of TOF-SIMS nor XPS. The content by volume of 2,18 At% was determined by means of EDX [10]. In regard to the detection of titanium by means of XPS it shall be taken into account, that also during analysis of the powder titanium dioxide pigment the signal lines of titanium are only observed in low intensity. Considerably stronger signal lines occur which can be attributed to aluminium. Titanium dioxide pigments are normally surficially modified in order to ensure an optimal compatibility within the binder system.

The used pigment is modified with aluminium oxide, which causes the aluminium lines. For this reason, these should be more significant for the assessment of the print samples than the titanium lines. Aluminium signals, however, were not detected as well, neither on the printed nor on the unprinted film side. The pigment content in the near-surface area is, therefore, considerably lower than the content in the entire ink layer. The results obtained by means of TOF-SIMS as mere surface method and XPS as method for the near-surface area allow for the conclusion that the pigments in the samples are embedded in the binder film and do not protrude from the surface. On the backsides of the printed films no signals of titanium or copper were found, which is consistent with

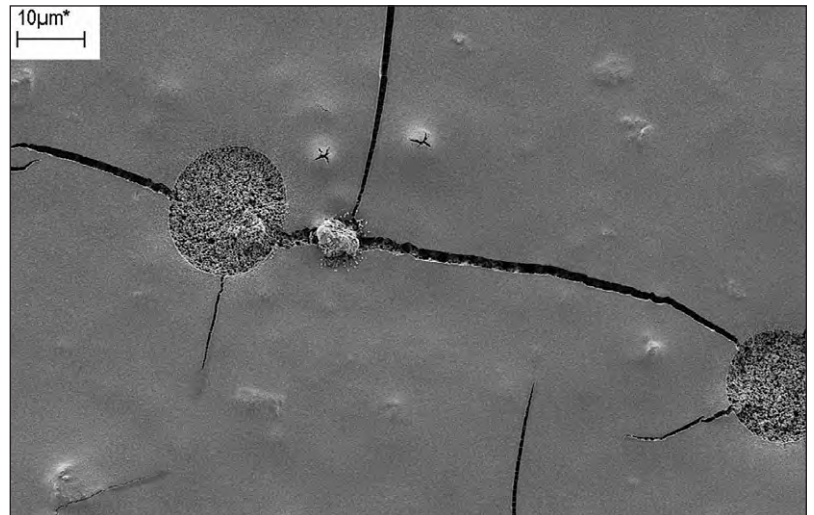


Figure 13 SEM image of a defect in the printed lacquer film (No. 6, Offset White, magnification 1.00 KX, detector: SE2)

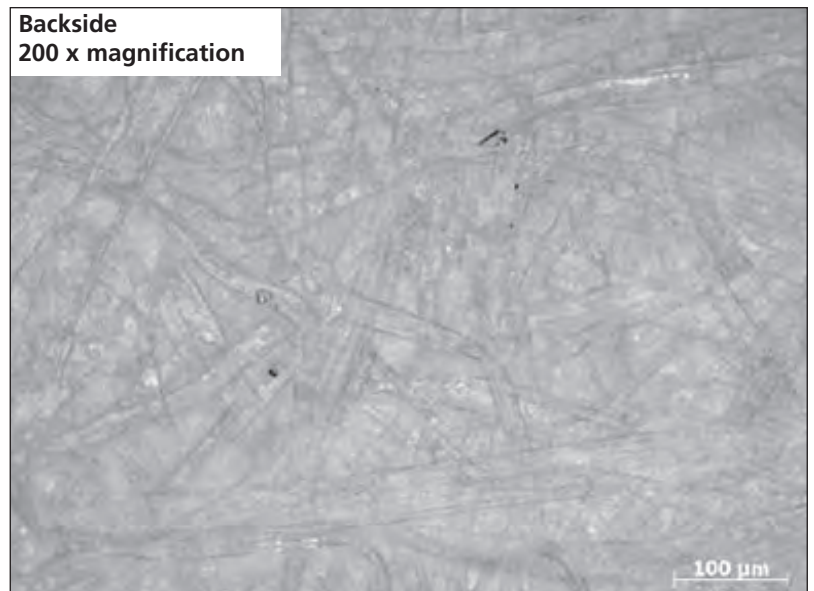


Figure 14 Light microscopic image of set-off on cyan-printed carton sample (no. 5, offset cyan)

the results of the migration analysis. A set-off was not detected on the analysed film samples by means of the applied analysis methods.

The carton samples showed punctual set-off which, for example, is visible under the light microscope (Figure 14). Such an area was analysed by means of TOF-SIMS in order to find out if this is exposed pigment or pigment embedded in the binder. In the respective area pigment (Cu-phthalo-

cyanine) as well as binder substances were detected [11].

Results of the scanning electron microscopic analysis

Figures 8 and 9 show SEM images of the coloured sides of the films printed white or cyan (No. 1 + 3). Clearly visible are the size differences of the pigment particles titanium dioxide and Cu-phthalocyanine embedded in the binder matrix. It is noticeable that no single sharp-edged pigment particles are visible, i.e. the pigment particles are covered by the binder.

Figures 10 and 11 show a cross section of the BOPP films printed white and cyan. Clearly visible are the pigment particles which are embedded in the binder film. Pigment particles in the volume of the printed film sample are not detectable, i.e. migration of pigment particles into the BOPP does not occur.

This becomes even clearer with the example of the printed carton sample (No. 6, offset white) in Figure 12. In the image, the film of the overprint lacquer is clearly recognizable above the ink film. Migration of pigments into this polymeric lacquer film does not occur either. However, the microscopic images of the printed carton samples also prove that cracking of the lacquer film and ink film can occur, resulting in possible set-off. Such set-off points are visible in the SEM and also in the light microscope (Figure 13 and 14).

Summary

Following the wide range of analytical methods used in this study, no mi-

gration of nanoscale pigment particles could be detected from ink layers of printed food packaging into the food. Therefore exposure of the consumer to nanoparticles from the dried and cured ink layers may be excluded. This resulted in a study commissioned by the German Paint and Printing Ink Association.

The printing inks analysed in this project have been found to contain nanoscale objects such as pigment particles and pigment leaves (metal effect pigments). The amount of pigment particles in the nanoscale range varies from pigment to pigment. In the Cu-phthalocyanine based ink more than 50 % of the pigment particles are below 100 nm in size in at least one dimension. The average particle size of titanium dioxide is above 100 nm, but individual particles are smaller than 100 nm. The aluminium based metal pigment particles have a thickness of about 30–40 nm.

Such nanoscale objects are completely embedded in the polymer matrix of the printed and dried ink films, i. e. they are completely covered with binder material. Exposed nanoscale objects on the dried ink surface could not be detected. Migration of single nanoscale objects through a polymeric film or a printed lacquer film has been proven not to take place. Even in case of set-off, no single nanoscale objects are transferred to the unprinted surfaces. Further, any set-off ink transferred, that may contain nanoscale objects, will have such nanoscale objects also embedded in the transferred polymeric binder matrix. ■

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