Translation / Original: German

VdMi information on the evaluation of unintentional, small-size fragments in pearlescent pigments and in cosmetic products containing those with regard to the nano discussion

Pearlescent pigments are a group of effect pigments exhibiting special colouring properties due to absorption, reflection and/or interference effects. To have this unique colouring properties, a defined platelet structure consisting of several layers of different oxides with clearly defined and controlled thicknesses is needed. In order to achieve brilliant colour effects at consistent quality, the production process is thoroughly controlled and small-size, scattering by-products need to be avoided to the most extent.

Despite tightly controlled process conditions, a small fraction of unintentional small-size fragments may be formed at any stage of the manufacturing process or even during the application of the pigments in cosmetic formulations. Consumer products, including cosmetics, are the focus of many investigations, often commissioned by NGOs claiming improper labelling of approved colour additives. Although there continues to exist ambiguity on many levels, such reports trigger authorities. French authorities are in particular very strict when it comes to potential nanoparticles.

However, such unintentional fragments should not be misinterpreted as free nano particles as they predominantly are tightly bound to the surfaces of the large pigment particles. French authorities, however, argued that these incidental fragments are particles and need to be considered in the assessment of nanomaterials. In case of pearlescent pigments, where these incidental fragments are orders of magnitude smaller than the actual pigment particle, this poses huge challenges for the analytical methods and setups.

Manufacturers of Pearlescent pigments organized within the VdMi decided to conduct a thorough measurement study. The presence of small particles including nanoparticles was analyzed in several pearlescent pigments and cosmetic products containing those pigments by ICP-MS, which enables the detection of sub-micron particles in presence of larger material. This method can be used to obtain number-based particle distributions in combination with the identification of the measured particles. Different labs as well as different ICP-MS methods were compared to allow for informed statements regarding the presence of nanoparticles, the meaningfulness of such measurements, and the resulting consequences for pearlescent pigments.

Our key findings and conclusions:

- Pearlescent pigments exhibit unique colouring properties due to their platelet particles with layer structure. Breaking down this special structure destroys the optical effect.
- Unintentional fragment particles with particle sizes below 500 nm can be detected in pearlescent pigments and product formulations containing those with highly sensitive measurement techniques like sp-ICP-MS methods
- Results from such measurements need to be interpreted carefully due to
  - High influence of the sample preparation method
  - Low inter-lab comparability
  - Intrinsic method errors
- Results from such measurements do not allow for any firm conclusion on the nano status (yes/no) of the pearlescent pigment itself, especially after it has been incorporated into a cosmetic formulation

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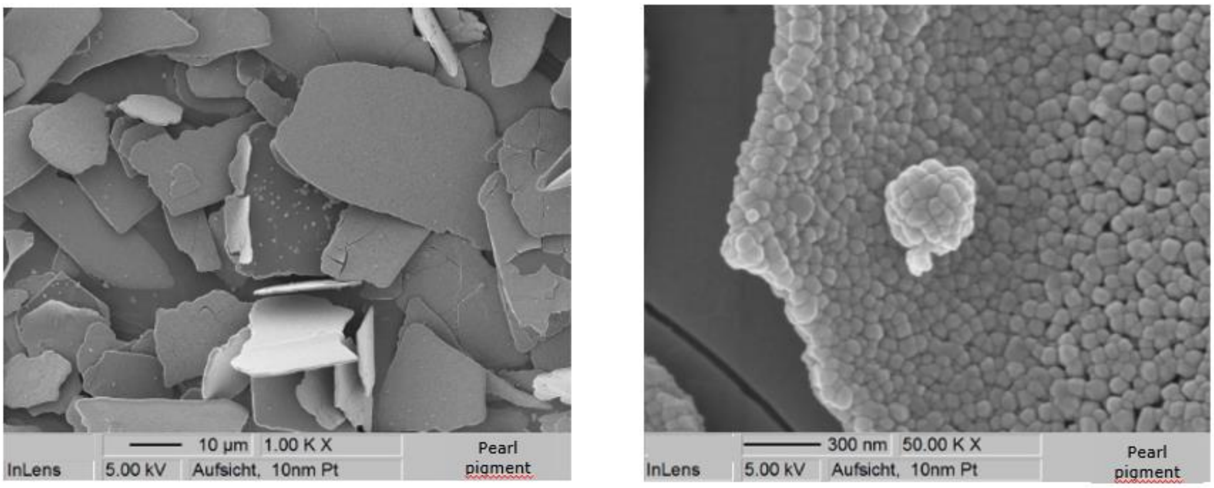
Properties and uses of Pearlescent pigments

Pearlescent pigments consist of platelet-shaped particles with different material layers leading to reflection and/or interference of light. This phenomenon results in different optical properties than spheroidal particles with the same composition. Typical pearlescent pigments use natural mica or synthetic oxides like aluminum oxide, silicon dioxide, or silicates as substrate. The substrate is coated typically with oxides like titanium and/or iron oxides in subsequent layers with a different refractive index. The layer thickness as well as the difference between the refractive indices determine the colour of the effect pigment and therefore needs to be closely monitored during production.

Due to their unique colouring and optical effects, pearlescent pigments are used in various applications. One of the most prominent applications is the use in cosmetic products but in principle these pigments may be used in all kinds of applications – from coatings to food colourants.

Unintentional fragments, incidental particles and the link to the nano discussion



The platelet particles of pearlescent pigments are typically 5-100 micrometers wide and depending on the substrate, several hundred nanometers thick. Accordingly, they do not fulfil any of the current definitions for a nanomaterial[1].

Figure 1: SEM images of a TiO_2-coated mica pearlescent pigment (left: low resolution, right: high resolution).

However, some smaller fragments may be detectable in these non-nano pigments as illustrated in figure 1. These unintentional small-size fragments may be formed during the manufacturing process or during further processing, e. g. incorporation into a cosmetic formulation. As such, imperfections or damage to the platelets comes with a loss of performance, and they are minimized by manufacturers to the best technical extent. Pearlescent pigments placed on the market contain a negligible amount of such incidental particles. During further processing during cosmetic formulation, the platelets may be damaged or broken into smaller particles. Thus, processed products containing pearlescent pigments may have a comparably higher share of such unintentional small-size fragments than the pigments themselves. These unintentional fragments can be detected by image-based methods like SEM or TEM or particle separation techniques like sp-ICP-MS, disk centrifuges etc., whereas the determination of a number-based distribution over several orders of magnitude in one method is not possible until now.

[1] See e. g. Commission's recommendation for nanomaterial definition (download) or definition laid down in the Cosmetics Regulation (Regulation (EC) 1223/2009 (download), see Article 2(k)).

A more detailed discussion is necessary to understand what the analytical challenges are, how they may be overcome, how such results can be interpreted, and what this means for pearlescent pigments in the context of nanoparticles.

Aim of this measurement study

To assess whether a material fulfils a definition for nanomaterials, electron microscopy is still the only method recommended to obtain an unambiguous answer.[2] But these methods are not adequate to analyze a mixture of very large pearlescent pigments particles and in comparison, extremely small fragments. The required size scales are just too different and observed fragments may not be isolated particles, but tightly attached to the large pigment particles. Only by separating the large platelets from the smaller particles, meaningful numbers may be obtained.

On top of fundamental size limitations of measurement techniques, it is always a huge difference whether a material is analyzed as produced or after extraction from a complex matrix like a cosmetic product. The sample preparation and extraction influence the measurement results tremendously.

Due to these reasons, pearlescent pigments' manufacturers organized within the VdMi decided to conduct a detailed measurement study to allow for qualified assessment of such small particles in pearlescent pigments. Two different labs analyzed in total 6 different pearlescent pigments, 3 different lipsticks, and 10 eye shadow formulations. Including additional measurements of different standard materials, more than 70 measurements were carried out. The number-based distribution of particles in the range between 10-500 nm was calculated using sp-ICP-MS[3] measurements and in comparison, using F4-ICP-MS[4]. The sample preparation of the powder samples as well as the extraction from the cosmetic product formulations was not specifically aligned between the two labs beforehand to allow for realistic comparison of different laboratories.

The aim of this measurement study was to evaluate

- the different methods with regard to their accuracy to investigate incidental particles in pearlescent pigments,
- the reproducibility of data from different methods and labs, and
- to investigate the influence of different sample preparations and extraction methods.

Based on the results, an informed statement on the consequences for pearlescent pigments can be made.

Why such approaches have fundamental flaws

The chosen measurement techniques are used to analyze particles with diameters below 500 nm, while micron-sized pearlescent pigment particles cannot be analyzed by these methods. This means that particles larger than 500 nm were cut off during the measurement of sp-ICP-MS. As a result, all measured particles do not refer to the whole pearlescent pigment sample but only to the fraction of small-size fragments below 500 nm. Thus, the reported data do not allow for any statement on the particles size distribution of the whole product, but only on a very limited detectable part of it.

Nevertheless, results from such measurements are often misinterpreted as properties of an independent nano material. As a general analytical principle, measurement data always have to

[2] See e. g. technical reports of the NanoDefine project (link), JRC Technical Reports „Basic comparison of particle size distribution measurements of pigments and fillers using commonly available industrial methods" (download), or ECHA's guidance document on the registration of nanoforms including particle characterization (download).
[3] Single particle inductively coupled plasma mass spectroscopy
[4] Asymmetric flow field flow fractionation inductively coupled plasma mass spectroscopy

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be discussed in context of the respective method limitations and the entire sample. If a technique is used that can only detect nanoparticles or particles in the low micrometer range, by definition, bigger particles are cut off. And if a technique for measuring larger particles is used, nanoparticles cannot be detected. There simply is no comprehensive technique that allows for qualified statements on size detection of particles over 4-6 orders of magnitude.

Why quantitative results need to be treated very carefully

The measurement techniques used in this assessment provide number-based particle size distributions for detected particles in the range 10-500 nm. However, the experimental data raises doubt on the accuracy of the results due to the following observations:

- Standardization on a meaningful size, e. g. detected particles/mass or internal standard, is necessary to allow proper interpretation of the results
- Nanoparticles were detected in blank samples, both eye shadow and lipstick, even though no inorganic material was present in the formulations
- The number of detected particles varies for the same pearlescent pigment when incorporated in different cosmetic product formulations and for different extraction methods from cosmetic product formulation
- The number of detected particles varies for the same cosmetic product samples measured by different labs, whereas the number of detected particles for the pure pearlescent pigments is deviating less

By sp-ICP-MS analysis of an eye shadow sample without any pearlescent pigment, two independent laboratories detected nano-scale titanium dioxide particles in the ppb range allowing to derive a number-based distribution. The reason of this finding remains unclear, contamination can, in principle, result from residual pigment during formulation from previous trials, corrosion of the ultrasound sonde, or residues of the analytical equipment. Even if the identified concentration 3 orders of magnitude lower than the findings in samples that contained pearlescent pigments, such finding can be misleading, particularly if only number sized distributions are reported. To interpret the quantitative results correctly, a baseline from a blank sample needs to be recorded prior to each measurement. This requirement is supported by significant differences between the numbers reported by the two involved labs. While the respective results on the pearlescent pigments powder samples themselves do show quite similar findings, the results for the cosmetic product samples differ by some orders of magnitude.

On using a certified nanoparticle standard in the eyeshadow formulation, a significant lower number of particles was detected compared to the number expected by comparison with powder measurements. A reason for this surprising result may be that some of the particles have been agglomerated during the preparation and were not detectable by sp-ICP-MS. On the other side, investigation of eyeshadow preparations with pearlescent pigment showed that the number of detected particles as well as the particle size was significantly influenced by the ultrasonication used to extract the particles. Higher ultrasonication power resulted in more and in tendency slightly smaller particles. Thus, the extraction method highly influences the degree of fragmentation of pearlescent pigments.

Moreover, the results on the average particle sizes of the different samples differ significantly between the two involved labs. Especially for the investigated pearlescent pigment powder samples, the results differ by a factor between 2 and 4, lying above or below the threshold of 100 nm used in the EU recommendation for the definition of a nanomaterial. Thus, depending on which individual laboratory conditions for detection of unintentional small-size fragments are applied for sp-ICP-MS analysis, the resulting particles may be considered as nanoparticles or not.

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Due to all these reasons, the given number of present particles as well as the average particle size detected by sp-ICP-MS need to be interpreted very carefully. Without detailed knowledge on the sample preparation and experimental set-up, qualified statements are not valid. Additionally, the quantitative results obtained from different labs may differ significantly. In our view, sp-ICP-MS in the current state of the art allows statements on qualitative trends of the amount of sub-micron particles in pearlescent pigments but is not suitable as method *per se* to quantify nano material.

Why results from a cosmetic product cannot be directly transferred to the used Pearlescent pigment

In this study, on comparing the measurement results of the respective pearlescent pigment and an eyeshadow or lipstick formulation containing it, the cosmetic product in general exhibits higher numbers of detected particles and smaller average particle sizes. Thus, the extraction method and preparation of the cosmetic formulation influence the measurement results significantly. Additionally, this is confirmed by the differences between the results from the two labs for the same samples.

The fragments of the pearlescent pigments analyzed in the cosmetic products do not allow for statements on content of sub-micron particles of the original pearlescent pigment. Likely during the formulation process and definitely during the extraction for the sample preparations, a small portion of the platelet particles is forming fragments in the sub-micron range.

What these results mean for Pearlescent pigments with regard to the nano discussion

As pointed out earlier, results from measurements focusing on particles in the lower nanometer range cut out the actual pearlescent pigment particles which are several orders of magnitude larger. Such partial results mostly refer to unintentional fragments, not to the whole product sample. Additionally, the influence of the sample preparation and the differences in the quantitative results of the two involved labs demonstrate, that such measurement studies need to be interpreted carefully, only allowing conclusion on qualitative trends.

The measurement results demonstrate that pearlescent pigments and formulations thereof contain sub-micron particles. Harsh extraction conditions lead to increased small-size fragment numbers. However, a statement on the number-based portion of such small shares in the pearlescent pigment or in the product formulation cannot be made. As a result, such measurements cannot be used to decide whether a pearlescent pigment is categorized as nano or non-nano.

Conclusion

Pearlescent pigments offer unique colouring properties, which are important for various applications. The pigment particles consist dominantly of platelets in the size range of micrometers, but smaller particles including nanoparticles can be detected by sophisticated analytical techniques like sp-ICP-MS or F4-ICP-MS. This finding does however not mean that the pigment itself is considered a nanomaterial as the share of such small fragments is generally low.

Quantitative results need to be interpreted very carefully as the sample preparation as well as several other factors including the measurement set-up have a significant influence on the obtained numbers. Additionally, it is important to point out that the majority of pearlescent pigment particles had to be separated from the small portion of fragments before the measurement due to technical reasons. Such analyses always only refer to a specific particle size range of a minor part in the ppm range, and not the whole test sample. Depending on the used separation technique, different number distributions will be obtained.

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Especially measurement results from cosmetic product formulations bear many possibilities to influence the measurement results. Harsh extracting methods promote the formation of fragment particles. As a result, measurement results on a cosmetic product cannot be transferred to the used pearlescent pigment in the formulation even if the same measurement conditions are used otherwise.

Manufacturers of pearlescent pigments are the best information source for data on their products. Further information on cosmetic ingredients can be obtained by EFfCI as well.

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The Verband der Mineralfarbenindustrie e. V. represents German manufacturers of inorganic (e. g. titanium dioxide, iron oxides), organic and metallic pigments, fillers (e. g. silica), carbon black, ceramic and glass colours, food colourants, artists' and school paints, masterbatches and products for applied photocatalysis.

The VdMi is listed in the Lobbying Register for the Representation of Special Interests vis-à vis the German Bundestag and the Federal Government (Lobbyregister des Deutschen Bundestags, number R000760) as well as in the Transparency Register of the EU Commission (number 388728111714-79).