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Results of Round Robin Study: Determination of the aerodynamic diameter of highly anisotropic particles on the example of pearlescent pigments

Pearlescent pigments with titanium dioxide might fall under the new classification as carcinogen, cat. 2, for specific titanium dioxide containing powders. While the evaluation whether, or not classical pigment powders are affected by the classification is already challenging, pearlescent pigments bring in new challenges due to their highly anisotropic particle form. To assess the applicability of the standard method EN 15051-2 for the determination of the classification relevant aerodynamic diameter of the pigment powders, Eurocolour's Working Group Pearlescent Pigments decided to conduct a comprehensive round robin study.

Summary of the main results of the study:

- *Good reproducibility of each single measurement → EN 15051-2 is also a suitable method for samples consisting of highly anisotropic particles*
- *Good comparability of measurements of the same sample between different labs, absolute deviation typically below 0.01 %*
- *No direct correlation between powder particle size like d50-value and determined aerodynamic diameter*

Pearlescent pigments consist of platelet-shaped particles with different material layers leading to interference of the reflected light. This results in different properties than spheroidal particles with the same composition. Typical pearlescent pigments use natural mica or synthetic oxides like aluminium oxide, silicon dioxide or silicates as substrate. The substrate is coated typically with oxides like titanium and/or iron oxides in a second layer, exhibiting a different refractive index. The layer thickness as well as the difference between the refractive indices determine the colour of the effect pigment.

However, due to Note 10 in the classification entry for titanium dioxide powders, pearlescent pigments coated with titanium dioxide might fall under this classification.

The classification of titanium dioxide in powder form as a suspected carcinogen (Carc. cat. 2 by inhalation) within the 14th ATP of the CLP Regulation was published in the Official Journal of the European Union on 18 February 2020.[1] It is limited to titanium dioxide powders containing 1 % or more particles with aerodynamic diameter ≤ 10 µm or to titanium dioxide containing powders where 1 % or more titanium dioxide is present in particles with aerodynamic diameter ≤ 10 µm. Thus, the aerodynamic diameter of a powder determines whether, or not the classification criteria are fulfilled.

[1] Delegated Regulation (EU) 2020/217, published in the Official Journal of the European Union L44 and L51, respectively, available on EUR-Lex.

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The aerodynamic diameter describes the sinking behaviour of a particle in calm air. Spherical, isolated particles with a density of 1 g/cm³ are assumed. It is important to keep in mind that pigments usually form agglomerates or aggregates and have different densities than 1 g/cm³. Therefore, the aerodynamic diameter of a powder cannot be directly correlated to the physical diameter of the particles within the powder, typically given as a d50-value in the technical data sheet.

Definition of the aerodynamic diameter according to EN 481:

„The diameter of a sphere 1 g cm^{-3} with the same terminal velocity due to gravitational force in calm air, as the particle, under the prevailing conditions of temperature, pressure and relative humidity."

There are several standardized methods available for the determination of an aerodynamic diameter.[2] However, all these methods were developed for OHS issues, not for the characterization of a powder. The transfer procedure of the sample from powder to aerosol form is essential. The platelet-shaped particles of pearlescent pigments as well as the coating material influence the formation of agglomerates and aggregates, thus influence the aerodynamic diameter. Due to these complex interactions, measurements are needed to assess the aerodynamic diameter.

Rotating drum methods have displayed good reproducibility to assess the dustiness of titanium dioxide powders. The TDMA recommends testing as per the standard method EN 15051-2 for determining the aerodynamic diameter, a service that several institutes can currently provide.[3] Assessment as per the newer standard EN 17199-4 is also suitable although not commercially available yet. EN 15051-3 (continuous drop method) and DIN 55992-1 (small rotating drum) for the characterization of titanium dioxide powders with respect to the classification may also be used with some minor disadvantages. Eurocolour's Working Group on Pearlescent Pigments decided to conduct a comprehensive round robin study to assess the applicability of EN 15051-2 for anisotropic particles.

For this, pearlescent pigments producer from all over Europe cooperated. Overall, 32 products were sent to different contract laboratories. The product spectrum covered different substrates, high and very low titanium dioxide fraction, rutile and anatase as crystal structures of the titanium dioxide as well as different amounts and compositions of additional ingredients. The results of the measurements according to EN 15051-2 from the different lab facilities were compared and the following conclusions drawn.

The deviation of the measurements results of the same sample for the different labs is low, typically below 0.01 % in absolute values. This leads to the conclusion that EN 15051-2 is a reliable method for the reproduceable determination of the aerodynamic diameter of highly anisotropic particles like pearlescent pigments. However, influences like the humidity may influence the measurement results as well as the bulk density used for the calculation. Therefore, it is highly important to adhere strictly to the measurement standards to insure comparable results.

[2] For example EN 15051, DIN 55992, or ISO 17199.
[3] See "Harmonised classification and labelling of titanium dioxide (TiO_2) Content of particles with aerodynamic diameter ≤ 10 µm Methods and results of analysis", published by TDMA.

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It is important to note, that there is no direct correlation between the aerodynamic diameter of a powder and the physical diameter of the particles within. The physical diameter often given for example as a d50-value in the technical data sheet refers to the physical dimensions of the constituent particle while the aerodynamic diameter gives information on the sinking behaviour of the particles present in an aerosol, typically agglomerates and aggregates. Therefore, it may very well be possible to have a pearlescent pigment with a d50-value below 10 µm that does not fulfil the classification criteria for titanium dioxide powders.

The round robin study confirms EN 15051-2 as a suitable method to characterize pearlescent pigments with regard to the classification criteria of titanium dioxide powders. However, other methods may as well lead to reasonable results. Based on such measurements, manufacturers can assess to which extent their individual products are affected by the classification and label their products accordingly if need be.

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About Eurocolour:

Eurocolour e. V. is the umbrella association for the manufacturer of pigments, dyes, fillers, frits, ceramic and glass colours and ceramic glazes in Europe.