

VdMi Information on the influence of the production of powder mixtures with titanium dioxide on the applicability of the classification of titanium dioxide powders

On 18 February 2020, the classification of titanium dioxide powders in the CLP Regulation as a suspected carcinogen (carcinogen, category 2) was published.¹ What is special about this entry in CLP Annex VI is not only the justification based on non-specific particle effects, but also the complex implementation with various requirements and notes. Therefore, manufacturers of powders containing titanium dioxide are faced with the challenge of identifying whether their products meet these classification criteria. The decisive factor here is the aerodynamic diameter of the particles - a parameter that has not been used so far to characterise a powder product.

The test results of the titanium dioxide manufacturers show that the majority of the products do not meet the classification criteria. Users of these powders, who in turn also produce powder mixtures, are thus in a dilemma: First of all, the information provided by the suppliers of titanium dioxide powders is the first reliable source of information for users. However, the users have to show that the production of the mixture does not result in any changes in the aerodynamic diameter. Otherwise, their products could fall under the classification.

In order to show that the mixing process has no significant influence, the manufacturers of various powder mixtures in the VdMi decided to conduct a series of measurements. Various mixing partners, mixing processes and parameters were systematically investigated. The results are presented in this paper.

Key factors at a glance

- The VdMi measurement study systematically investigates the influence of the mixing process on the aerodynamic diameter of powders, as powdered mixtures with ≥ 1 % titanium dioxide may be affected by Note 10 of the classification.
- The test results prove
 - No significant influence of mixing on the aerodynamic diameter
 - Total amount of particles with aerodynamic diameter ≤ 10 μm are several orders of magnitude below 1 %
- **Conclusion:** powder mixtures with titanium dioxide not subject to classification have a very high probability of not meeting the classification criteria

¹ Delegated Regulation (EU) 2020/217, published in the Official Journal of the European Union L44 and L51

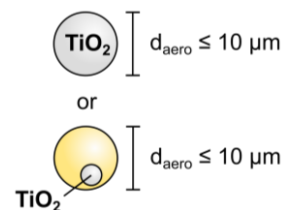
Powder mixtures affected by the classification

The classification entry for titanium dioxide provides for several conditions and has been supplemented by three additional Notes. With regard to powder mixtures, Note 10 is of great importance. It states that not only pure titanium dioxide powders are covered by the classification, but also powder mixtures if they contain particles containing titanium dioxide that are suspected of causing damage in the lungs.

Note 10:

„The classification as a carcinogen by inhalation applies only to mixtures in powder form containing 1 % or more of titanium dioxide which is in the form of or incorporated in particles with aerodynamic diameter $\leq 10 \mu\text{m}$.“

The aerodynamic diameter was chosen as the criterion and 1 % as the limit value. The aerodynamic diameter describes the sinking behaviour of particles in air, not their physical size.² It was also clarified, that for powder mixtures it is irrelevant whether the titanium dioxide is present as individual particles, as shown opposite, or whether it is embedded in other particles.



Powders that meet this criterion must be classified and thus in future be labelled with the warning H351, the signal word “Danger!” and the hazard pictogram GHS08.

No classification of titanium dioxide powders

The measurement results of the titanium dioxide manufacturers have shown that the majority of their products do not meet the classification criteria. However, this does not necessarily mean that powder mixtures containing such unclassified titanium dioxide do not have to be classified. The mixing process could change the aerodynamic diameter of the titanium dioxide particles contained. Thus, manufacturers of such powder mixtures have for the time being not obtained clarity on the potential classification of their products.

In its guide on dealing with the classification³, ECHA recommends relying on the information provided by one's supplier. The German BAuA takes the same view in its FAQ document on the classification⁴, but does not rule out the possibility that the mixing process may have an influence.

Therefore, the manufacturers of titanium dioxide containing powder mixtures organised in the VdMi have used this test study to investigate the influence of the mixing process more closely in order to be able to make a substantiated statement.

VdMi measurement study on the influence of the mixing process

For the measurement study, various mixtures with titanium dioxide were prepared and tested by independent test laboratories according to common measuring methods⁵ recommended by the titanium dioxide manufacturers. Different, partly surface-modified titanium dioxide powders were used, which do not meet the classification criteria.

By producing different model mixtures, the influence of the mixing partner, the mixing ratio and the selected mixing method could be investigated specifically. In addition, various RAL colour shades with a more complex composition were selected as practical examples. Comparative measurements on mixtures without titanium dioxide were also used to prevent misinterpretations. The processes and mills used to produce the mixtures always corresponded to the standards used in large-scale production. A total of 31 samples were analysed.

² See also VdMi Information „Differences between the physical particle size and the aerodynamic diameter of a particle – two sizes, two different worlds“, ([Download](#))

³ See also [information ECHA \(Download Guide\)](#)

⁴ See also [information BAuA \(Download FAQs\)](#)

⁵ For example DIN EN 15051-2 or DIN EN 15051-3.

Measurement results provide clarity for powder mixtures

None of the samples tested had a share of particles with an aerodynamic diameter of $\leq 10 \mu\text{m}$ of 1 % or more. Therefore, the mixtures, like the titanium dioxide used, do not meet the classification criteria according to the entry in CLP Annex VI.

Typical values were in the range of 0.001 % up to 0.003 %. The values for the next largest fraction, which represents particles with an aerodynamic diameter of up to $20 \mu\text{m}$, were also in the range of less than 0.04 %. It should also be noted that the comparative measurements showed that the proportion of these particles does not result exclusively from the titanium dioxide used, but that the mixing partners also contain such fine particles. The proportion of titanium dioxide in the fraction of these small particles is therefore even lower.

In principle, there is no significant influence of the mixing partner. Neither hard, inorganic compounds nor softer mixing partners such as carbon black or organic pigments increased the proportion of fine particles. It was also shown that the mixing ratio has no influence. Only mixtures with a titanium dioxide whose surface is hydrophobic tended to show higher values than when using a hydrophilic titanium dioxide. However, these values were also in the range of clearly less than 1 %.

Since different forces act on the pigment particles depending on the mixing method, various techniques were investigated. Among others, ploughshare mixers, high-speed mixers and an edge mill were used. However, there was still no discernible influence on the fines content. Regardless of the mixing method, no significant increase in the share of particles with an aerodynamic diameter $\leq 10 \mu\text{m}$ was found.

Conclusion

The comprehensive investigations of the VdMi member companies were able to show that the production of various mixtures with titanium dioxide did not significantly increase the share of particles with an aerodynamic diameter of $\leq 10 \mu\text{m}$. Neither the titanium dioxide used, nor the mixtures produced with it fulfil the classification criteria according to the CLP Regulation.

Particular emphasis was placed on the fact that the mixing processes used correspond to the standard processes. The measured values were several orders of magnitude below the limit value of 1 % relevant for classification. However, since no significant influence was found regardless of the mixing partner, mixing ratio or the method used, it is reasonable to conclude that the measurement results can also be transferred to other mixtures. Powder mixtures with titanium dioxide that does not have to be classified therefore do very probably not meet the classification criteria either.

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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 colorants, artists' and school paints, masterbatches and products for applied photocatalysis.