TDMA
TITANIUM DIOXIDE MANUFACTURERS ASSOCIATION
for a brighter future

REPORT

21 April 2021

Harmonised classification and labelling of titanium dioxide (TiO_2) Content of particles with aerodynamic diameter ≤ 10 µm Methods and results of analysis

SUMMARY

TDMA carried out a testing programme to measure the content of particles with aerodynamic diameter ≤ 10 µm, one of the two criteria for classification under the Classification and Labelling Regulation (CLP). In the absence of officially designated method, several grades of TiO_2 were tested according to five internationally recognized test methods for dustiness. The results indicate that these methods have minimal variability and are suitable for this application. The data consistently shows that most grades of TiO_2 do not meet the criteria for classification. This report also includes a Q&A section at the end.

INTRODUCTION

Commission Regulation (EU) 2020-217, the 14th adaption to technical progress (ATP) of the CLP introduced a new harmonised classification for certain forms of TiO_2 as a category 2 carcinogen by inhalation. The corresponding entry is shown in Table 1. The ATP was published in the Official Journal of the EU on 18 February 2020, it came into force on 9 March 2020 and applies from 1 October 2021.

Index No	International Chemical Identification*	EC No	CAS No	Classification		Labelling		Notes
				Hazard Class and Category Code(s)	Hazard statement Code(s)	Pictogram, Signal Word Code(s)	Hazard statement Code(s)	
022-006-002	titanium dioxide; [in a powder form containing 1% or more of particles with aerodynamic diameter ≤ 10 µm]	236-675-5	13463-67-7	Carc. 2	H351 (inhalation)	GHS08 Wng	H351 (inhalation)	V, W, 10

Table 1: TiO_2 entry in Commission Regulation (EU) 2020-217.

The new harmonized classification specifies two criteria to determine whether a substance is to be classified:

1. the substance must be in powder form

2. the substance must contain 1% or more of particles with aerodynamic diameter ≤ 10 µm

This report focuses on the second criteria.

There are no methods officially recognized at the EU level to measure compliance with the second classification criteria mentioned above. There are however internationally recognized methods to measure dustiness. Given these uncertainties, the TDMA and its members embarked on an analytical project to review the suitability of these available dustiness test methods for purposes of determining the content of particles with aerodynamic diameter ≤ 10 µm of the various grades of TiO_2 currently in production.

Despite some challenges and delays due to COVID-19, preliminary data are now available.

MEASUREMENT METHODS

The definition of aerodynamic diameter is included in the European Standard EN 481. It takes into account the density and shape of an airborne particle and how fast it will fall compared to a hypothetical sphere with a density of $1000 kg/m^3$. A particle with a lower density and irregular shape will have a larger aerodynamic diameter.

The aerodynamic diameter of a material with irregular shape and density, such as TiO_2, must be determined in air by creating an aerosol. The main method to create an aerosol is by using dustiness methods. Several such methods are available although these tests require some modification to enable them to measure aerodynamic diameter. Table 2 includes National and International standards that have been considered in the evaluation of suitable methods.

EN 15051	Measurement of the dustiness of bulk materials
DIN 55992	Measurement of a parameter for the dust formation of pigments and extenders
EN 17199	Measurement of dustiness of bulk materials that contain or release respirable nano-objects and their aggregates and agglomerates (NOAA) and other respirable particles.
ISO 13320	Particle size analysis — Laser diffraction methods

Table 2: Standards used.

These methods were selected based on the following:

- International acceptability of the test method
- Availability of equipment and laboratory capacity for testing purposes
- Reliability and repeatability of the results, including considerations of aerosolization
- Testing is performed on TiO_2 in the form or physical state in which TiO_2 is expected to be placed on the market and in which it can reasonably be expected to be used, as required by the CLP[1].

The methods are further explained in Table 3 which also describes if a method was originally designed to measure aerosolization as well as equipment and laboratory availability.

[1] There are other methods using aggressive aerosolization devices that are capable of forcibly producing aerosols of very fine particles. These extreme measures are not suitable for the classification of TiO_2. Articles 5.1, 6.1 and 8.6 of the CLP refer to the forms and physical states in which the substance is placed on the market and in which It can reasonably be expected to be used. In particular, Article 8.6 states that *"tests that are carried out for the purpose of this Regulation shall be carried out on the substance or the mixture in the form(s) or physical state(s) in which the substance or mixture is placed on the market and in which it can reasonably be expected to be used".*

Technique	Standardised aerosolization	Equipment vendors	> 5 labs available	Direct <10µm mass% measurement	Comments
Continuous drop EN 15051-3 Also included in EN 17199-1:2019)	Yes	1	No	No (Adaptation possible)	Uses dropping of material against airflow Sample is measured continuously Simulates emptying of bags, silos under standard conditions Included in ECHA Guidance for dustiness of nanomaterials.
Rotating drum EN 15051-2 Also included in EN 17199-2:2019)	Yes	>2	Yes	Yes (Multiple inter-laboratory comparisons ongoing OECD assessment including TiO_2)	Commonly used method, applicable to wide range of sample types. Uses dropping of material perpendicular to air flow. Sample is measured in size increments. Method exists for elemental analysis of collected dust. Represents wide range of handling conditions. Included in ECHA Guidance for dustiness of nanomaterials.
Small rotating drum EN 17199-4	Yes	1	No	No (Adaptation possible)	Allows for smaller quantities of materials to be used. Less familiarity than larger drum. No direct 10µm fraction.
Small rotating drum Modified DIN 55992-1	Yes	1	No	No (Adaptation possible)	DIN standard measures total dust 37 µm and less without differentiation below.
Powder laser diffraction similar to liquid laser diffraction ISO 13320	No	>5	Yes	No (Significant research required for adaptation)	ISO 13320 developed for liquids. No international standard for powders. Highly variable outcome on powders. Does not measure aerodynamic diameter directly, uses calculation.

Table 3: Methods used for analysis.

RESULTS AND CONCLUSIONS

The results for two grades of TiO_2 that were assessed according to the five methods are provided in Table 4. EN15051-2, EN15051-3 and DIN 55992-1 results showed minimal variability although they use different equipment to aerosolize the sample and to measure the aerodynamic diameter of the particles. EN17199-4 also showed a minimal variability although it is less suitable due to small sample size required and the limited laboratories capable to perform the testing. The tests also confirmed that the ISO 13320 powder laser diffraction methodology produced significant variability making it unsuitable for this purpose.

Sample identity	Modified EN 15051-3 Continuous Drop Tower IGF (% wt.)	EN 15051-2 Rotating drum IOM (% wt.)	EN 17199-4 Rotating drum Tech. Univ. of Dresden (% wt.)	Modified DIN 55992-1 Small rotating drum Tech. Univ. of Dresden (% wt.)	Powder laser diffraction depending on equipment Univ. of Dresden (% wt.)
G4–19 pigmentary surface treated	0,0015+/- 0,001	0,01 +/- 0,001	0,04 +/- 0,02	0,03 +/- 0,001	Range of result values: 0 - 99
E 171 food pigment untreated	0,003 +/- 0,001	0,01 +/- 0,001	0,03 +/- 0,02	0,03 +/- 0,001	Range of result values: 0 - 99

Table 4: The content of particles with aerodynamic diameter ≤ 10 µm measured by various methods and including the standard deviation.

In addition, Table 5 shows the results for several grades that were selected and tested anonymously as part of the TDMA Scientific Programme. This included pigmentary, nano and types undergoing various surface treatments. All testing was performed in independent third-party laboratories experienced in dustiness testing. Except for sample G6-3 utilizing the modified DIN55992-1, the data consistently shows that the various grades contain less than 1% of particles with aerodynamic diameter ≤ 10 µm and thus do not meet the criteria for classification.

Sample identity	Type	EN 15051-2 Rotating drum IOM Edinburgh (% wt.)	Modified DIN 55992-1 Small rotating drum Techn, Univ, of Dresden (% wt.)	EN 15051-2 Rotating drum Tech, Univ, of Dresden (% wt.)	Modified EN 15051-3 Continuous drop IGF, Dortmund (% wt.)
G1 - 1	Nano	0,28	0,73	-	0,001
G2 - 5	Nano	0,02	0,27	-	0,003
G3 - 1	Pigmentary	0,01	0,03	-	0,0001
G4 - 19	Pigmentary	0,01	0,03	0,009	0,0015
G5 - 4	Pigmentary	0,01	0,10	-	pending
G6 - 3	Nano	0,38	1,29	-	0,021
G7 - 5	Pigmentary	0,08	0,04	-	0,001
G8 - 2	Nano	0,61	0,73	-	0,012
G9 - 5	Pigmentary	0,03	0,03	-	0,001
G10 - 4	Nano	0,01	0,04	-	0,001
E 171-E	Pigmentary	0,01	0,03	0,011	0,008

Table 5: The content of particles with aerodynamic diameter ≤ 10 µm measured by various methods for a range of anonymous samples.

These results demonstrate that each of the test methods evaluated may be used to measure the content of particles with aerodynamic diameter ≤ 10 µm with reasonable reproducibility, though EN15051-3 results shows consistently lower values. The EN15051-2 method provides the most consistent and repeatable results. EN15051-3 and DIN 55992-1 methodologies are also robust and suitable for use.

Q&A

This Q&A seeks to address the main questions raised by the Commission in connection with the methodology used for measuring the aerodynamic diameter of TiO_2 for classification purposes.

Why are many particles larger than 10 µm aerodynamic diameter?	TiO_2 consists of primary particles bound together in agglomerates due to attraction between the particles. The size of the primary particles of pigmentary TiO_2 typically ranges from 100-250nm and for nano grades from 5-80nm, measured by electron microscopy. The methods described in Tables 2 and 3 measure the aerodynamic diameter of the particles as they are in the air, *i.e.,* the agglomerated particles.
How does this compare to other materials?	TiO_2 is a low dustiness material compared to many other solid substances due to agglomeration.
What happens in a liquid?	Testing TiO_2 in liquids was not part of the scope of the TDMA analysis programme, which focused on TiO_2 grades themselves. As far as we know, there is not a recognized method to measure aerodynamic diameter of particles inside of liquids that become airborne. The type of liquid and application of the liquid will likely also impact such determination.
What is the particle size in animal studies?	Particle aerosols for inhalation toxicity studies are intentionally prepared to be of low particle size around 2 - 4 µm aerodynamic diameter and larger particles are removed. These are extreme test conditions designed to maximise the penetration in the lung.
How does this compare to occupation exposure results for workers?	Exposure monitoring for workers normally measures the respirable fraction of dust present at the workplace, not TiO_2 specifically. That respirable fraction is of similar size to the 1% threshold at 10µm aerodynamic diameter. Workplace measurements show that some dust particles can range below 10 µm aerodynamic diameter, but this is not comparable to the testing conducted for classification criteria for TiO_2 since exposure monitoring measures a mixture of different dust sources such as from factory vehicle movement and exhaust. It should also be noted that all the available epidemiological studies showed no cancer development in workers exposed to TiO_2 containing dusts.
What are TDMA proposing to do?	Classification and labelling is a decision for individual companies. For TiO_2 substances not meeting the criteria for classification, and for which the supplemental EUH 212 labelling is not required, a possible conservative approach would be to use such supplemental label on a voluntary basis. This would provide a practical solution to allow full communication covering all potential exposure scenarios which, as TDMA understands it, the EUH212 supplemental label were designed to address. TDMA are also developing comprehensive information for the safety datasheet (SDS) which could also be used for products not meeting the requirements for classification. Classification and labelling as well as the provision of an SDS for products is the responsibility of individual companies.
How does this compare with the plastics industry approach?	The plastics industry carried out similar dustiness testing on a range of plastic masterbatch which was the basis for excluding these mixtures from classification.

About TDMA

The Titanium Dioxide Manufacturers Association (TDMA) is a sector group of the European Chemical Industry Council (Cefic) and represents the leading producers of titanium dioxide (TiO_2). TDMA is a non-profit organisation established in 1974 and dedicated to promoting the safe use and benefits of TiO_2 to society