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Information sheet on the classification of TiO₂ used as raw material for producing “frit, chemicals”

The classification of titanium dioxide powder forms containing 1 % or more of particles with aerodynamic diameter $\leq 10 \mu\text{m}$ 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. This harmonised classification refers exclusively to TiO₂ in certain powder forms and it does not cover any other titanium-containing substances. It becomes legally binding in the supply chain on 1 October 2021, following an 18-month transition period.^[1]

Titanium dioxide is an inert inorganic compound that is used in many applications and industrial sectors. These applications include the manufacture of frits, where titanium dioxide gives certain physicochemical properties to the final substance created, but also to the production process itself.

During the manufacturing process, exposure to titanium dioxide dust can occur. However, both at EU and national level, there are regulations on dust exposure and worker protection. Historically, no correlation has been found between workers exposed to titanium dioxide and the risk of lung cancer.

Ceramic frits are amorphous vitreous materials formed from inorganic chemical oxides. The definition of ceramic frits described as a differentiated substance is found under CAS 65997-18-4 and EC 266-047-6, where they are defined as a “mixture of inorganic chemicals obtained from the fast cooling of a melted complex combination of materials, by which the chemicals become insoluble vitreous compounds appearing in the form of scales or granules”.

The raw materials for the manufacture of ceramic frits can be either natural or synthetic, and TiO₂ is one of the oxides that might be used. Depending on the characteristics of the final product, frits may have different compositions expressed in % (in weight) of the respective oxides.

During the manufacturing process, chemical bonds of the raw materials are broken, and the elements are rearranged and ionically interdiffused within the vitreous lattice (amorphous structure). This means that once the substance is produced, the presence of TiO₂ in powder form no longer exist in the new vitreous matrix created.

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

https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=uriserv:OJ.L_.2020.044.01.0001.01.ENG&toc=OJ:L:2020:044:TOC

Bearing in mind i) the particularities linked to the hazard classification of the TiO₂ in powder form and ii) the role that the frit production process plays on the components used as starting materials, as well as on the characteristics of the final substance formed, we consider that the classification of TiO₂ in powder form containing 1 % or more of particles with aerodynamic diameter ≤ 10 µm, does not apply to the industrial sector of frit manufacturers, since TiO₂ classification and its subsequent route of exposure is clearly related to the particle size and not to the intrinsic tox and/or eco-tox properties of the TiO₂ as such.

In addition to this, it is also important to highlight the fact that it is demonstrated, by use of relevant bibliography, and by studies performed, that titanium is part of the glassy structure created without the presence of free TiO₂.

We would also want to stress the possibility that when the TiO₂ in powder form used for producing frits does not meet the criteria for being classified as hazardous, entry 11 of Annex V could be applied, so the use of TiO₂ in our industrial sector would not have any impact either.

Frits with Ti-content might be used by downstream users to produce enameled products. In this scenario, during the manufacturing of the enameled product, a precipitation of the ironical Ti-compounds can take place so that TiO₂ particles which are embedded in the solid enamel layer are formed. These TiO₂-particles are firmly embedded into the glass matrix, therefore, the hazardous classification proposed by inhalation does not apply 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.