Is titanium dioxide without alternative?

published in Beauty Forum 2023 (3), 96-98

Titanium dioxide was banned in food in August 2022 because a carcinogenic effect cannot be completely ruled out. Since then, substitutes for the pigment have been under discussion, among others in cosmetics, pharmaceuticals and emulsion paints. In sunscreens, titanium dioxide still plays a dominant role as an alternative to the chemical-synthetic filters.

Both the absorption of titanium dioxide (E171) via the lungs and the absorption via the gastrointestinal tract are classified by the EFSA (European Food Safety Authority) as no longer safe and potentially carcinogenic. The German Federal Institute for Risk Assessment (BfR) has concurred with this. The possible absorption was the criterion for the ban in food by the European Commission in 2022. However, the European Court of Justice recently annulled the classification of TiO_2 in powder form by the EU Commission as "carcinogenic".
The extent to which the amounts absorbed by the body are actually relevant for carcinogenesis in humans cannot be conclusively assessed from the data currently available. Although no further bans are yet in sight in areas outside of food, the hint of risks has, however, already led to preventive thinking about a replacement that will be necessary in the future. This is because aerosols from hair styling aerosol cans and paint mist from spraying dispersion paints also enter the lungs.

Nano- versus non-nanoscale pigment

The uptake of titanium dioxide from sunscreens by the skin was already discussed as long as it was still a matter of using nanodispersions, but these have now completely disappeared from the market. In contrast, the non-nanoscale pigment is still in use for this purpose.

No universal replacement

The use of the excipient in lipsticks, toothpastes and decorative as well as light-protective coatings of tablets, hard gelatine capsules, soft gelatine capsules and other pharmaceutical products is equivalent to the risk in food. They are swallowed unintentionally or intentionally.
Its properties as a white pigment with the code CI 77891 (CI = Colour Index) combined with high stability towards the other substances with which it is used in mixtures make the universal replacement of titanium dioxide practically impossible at present. Therefore, different substances come into question depending on the objective. Apart from some biodegradable, organic representatives, most of the substitutes are inorganic pigments.

Biodegradable substances

As far as food products in powder form are concerned, which are consumed or processed as such, it is obvious to use digestible, white natural substances. Polysaccharides such as starch from wheat, rice or bamboo and their derivatives are suitable. Polysaccharides, however, are more or less limited to powdered foods and cosmetic powders - including intermediates that are supposed to look appealing but are used for further processing. The optical qualities, however, do not come close to those of titanium dioxide. The humidity-dependent stickiness can also be a disadvantage.
One advantage of starches over non-degradable inorganic pigments, however, is the much lower risk of pulmonary fibrosis from dusts, which depends on the particle size, and the associated possible carcinogenesis.

Dust

The risk from dusts is relevant when the lungs are exposed to prolonged, constant stress in specific work areas, for example in production, construction and mining. This does not usually apply to the sporadic use of cosmetic powders in everyday life. Nevertheless, efforts are being made to eliminate even minor risks. One example is the elimination of talcum (CI 77718), which may contain asbestos, from powders.
Sometimes it depends on the crystal modifications whether and how strongly a substance has a fibrogenic effect and how well it is degradable in the lungs. Ingestion, e.g., when using lipsticks, is not a problem with all inorganic pigments. Toxic substances, such as the formerly used white lead (CI 77597), a compound of lead carbonate and lead hydroxide, were included in the banned list of the European Cosmetic Regulation.

Inorganic pigments

When pigments are applied topically in the form of powders, the reaction with skin components must be taken into account. Calcium carbonate (CI 77220; INCI: Calcium Carbonate), magnesium carbonate (CI 77713; INCI: Magnesium Carbonate) and to a lesser extent magnesium oxide (INCI: Magnesium Oxide) and the zinc oxide (CI 77497; INCI: Zinc Oxide) sometimes found in sunscreens tend to bind acids on the skin surface and thus disrupt the barrier.
The consequences are dry skin and, with extensive use, eczematous phenomena. When processing these compounds in creams, chemical instabilities must also be expected, as triglycerides, for example from native oils, and other fatty acid esters are attacked.
While the carbonates and oxides are insoluble in water, calcium sulphate (CI 77231; INCI: Calcium Sulphate) has a low solubility in water and can thus attack the skin barrier even more easily. Destructive lime soaps are formed in the process. One reason, by the way, to plan for an oil- or fat-containing separating layer between the skin and the mask mass in the institute when using hardening face masks containing calcium sulphate.
The toxicity of an element, such as barium, also depends on its solubility in water. Thus, soluble barium salts are generally prohibited in cosmetics, whereas the completely water-insoluble barium sulphate (CI 77120; INCI: Barium Sulphate) can be used without restriction. Therefore, it can also be used as an oral X-ray contrast agent.
Prohibited toxic elements such as the heavy metal lead can occur in traces in other pigments and are not critical as long as they are firmly bound. This is typical for natural kaolin (CI 77005; INCI: Kaolin), a raw material for the porcelain industry ("china clay"), which is used both as a pigment and filler, among other things in cosmetics. Here we speak of undesirable but technically unavoidable contents that are harmless to health.
The legislator only stipulates that the quality with the lowest heavy metal content is to be used in the case of different provenance. Kaolin is contained in make-up preparations and enzyme peeling masks. Mineral mica (INCI: mica), a pearlescent pigment that may be coated with silicon dioxide ("silicic acid"), serves similar purposes.
Silicon dioxide, in its cristobalite modification, is characterised by high colour saturation and reflection. The pigment is used, among other things, in dental restorations, sealants and fine plasters. Like other silicates, especially aluminosilicates, it has the disadvantage of a high fibrosis potential. In this case, one speaks of "silicosis". Accordingly, there are detailed protective regulations for handling cristobalite and quartz dusts in general.

Other pigments

A long-known mixture of barium sulphate and zinc sulphide is lithopone, which is used in more technical areas, with zinc sulphide (INCI: Zinc Sulphide) registered in the CosIng register of cosmetic ingredients as an agent for hair removal.
There are also a number of other substances that can be used in cosmetics, including boron nitride (INCI: Boron Nitride), bismuth chloride oxide (CI 77163; INCI: Bismuth Chloride Oxide). Calcium aluminium sulphate (satin white) should also be mentioned as a white pigment for liquid plasters and dispersion paints, as well as dicalcium phosphate as a generally suboptimal titanium dioxide alternative for the pharmaceutical sector.

Opacity

In addition to the health and ecological aspects of the substitutes, the opacity, which depends on the highest possible refractive index, and the associated lower layer thickness of the white pigments are of decisive importance for decorative cosmetics and sun protection.
The listed substitutes all have to be used in much higher concentrations than titanium dioxide or, like calcium carbonate, are only suitable as fillers. In the case of technically suitable alternatives such as zirconium dioxide (CI 77990), the high price is the exclusion criterion. A really useful substitute for titanium dioxide in cosmetics is therefore not yet in sight.

Still titanium dioxide

In the case of emulsion paints, it has been agreed that products that still contain titanium dioxide will carry warnings if they contain more than 1% titanium dioxide. In addition, reference is made to the potentially carcinogenic effect and precautionary measures to be observed during use. The declaration also applies to solid, powdery products with particle sizes of ≤ 10 micrometres

Dr Hans Lautenschläger