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ETAD position paper on organic pigments as nanomaterials (update 2018)

What are nano materials?

Nano materials are generally considered as materials of a size of the order of 100 nm or less. Precise definitions may vary under different legislations; however the EU definition ***"a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm - 100 nm"***[1] has the strongest impact on the pigment industry and has been used by ETAD and by other associations as reference for the evaluation of their members' products.

Why is there a nano debate?

Typically mentioned nanomaterials (e. g., carbon nanotubes, fullerenes, gold nanoparticles) are new and technologically advanced; they show novel and useful chemical, physical and biological properties of particles and structures, which do not materialize in macroscopic objects of the same composition. Along with the expected benefits, there is as well the concern that the very small particle size may also give rise to properties which may be hazardous both to humans and the environment. **The ongoing debate revolves around the right approach needed to evaluate and, if necessary, control any potential risk depending on the specific size of these particles.**

Why are pigments part of the nano debate?

Organic pigments are substances which consist of solid particles and are insoluble in the application medium[2]. They are used for coloring purposes in a wide variety of end application media[3]. These applications demand properties which depend both on the chemical composition of pigments and on the size and morphology of their particles. E.g., already in the sixties it was shown that maximum color strength was achieved when the particles in the final application media were approximatively one twentieth of the light wavelength. This size also gives very transparent systems which are desirable, for example, in the printing industry. From this time onward much of the research and development work concentrated on producing very small particles (referred to them as sub-micron particles) while at the same time ensuring that other properties were not too adversely affected.

These sub-micron particles, seen as a crucial component of pigment products, are what we now call "nanoparticles".

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[1] Recommendation on the definition of a nanomaterial (2011/696/EU)
[2] Definition of standard DIN EN 55943
[3] Some application as listed in standard DIN 55944: coatings, both decorative and protective paints for buildings and machinery, plastics, printing inks, candles, paper products, pharmaceuticals, rubber materials, abrasives, soaps, decorative cosmetics, toys, road signs, safety technology equipment and road markings.

Organic pigment powder placed on the market have a wide distribution of particle sizes, from primary nano-size particles whose size maybe as small as 20 nm to clusters of primary particles in the 1 to 5 micron range. It is only during the incorporation (dispersion) step that the clusters are broken down into smaller moieties, ideally to the primary particles, which in most cases cannot be achieved. The dispersion step is very important since the macroscopic behavior of organic pigments, even if chemical properties play a role, is mainly depending on the dispersion state in the application medium. The size distribution (by mass) of the dispersed particles is primarily determining the coloristic properties. The number size distribution is only of minor importance in this regard.

When applying the EU definition to common products on the market, however, the number of primary particles in the nano scale is usually high enough for pigments to be classified as nanomaterials, especially since particles incorporated in agglomerates or aggregates are counted as well. Several size measurement methods exist, however currently there are no officially agreed methods available. Thus, in line with its commitment to Responsible Care and its Code of Ethics ETAD members decided to re-evaluate critically all available information on the hazards of pigments from the point of view of potential nano-related effects.

What is known about the nano toxicity of organic pigments?

When new products are ready to be marketed, their toxicological and ecotoxicological properties have to be evaluated and, especially for new substances, a significant package of data has to be prepared for authorities[4]. Also in order to communicate any potential hazards on any marketed product to downstream users, data has to be obtained in order to prepare the MSDS.

In some cases where inhalation exposure has to be considered additional studies on inhalation, toxicity and environmental monitoring have been undertaken. Testing is carried out on the powder as is, which contains aggregates and agglomerates as well as a larger or smaller nanosize proportion and, **in past studies, no adverse effects have been observed that can be directly attributed to the nanosized component.**

When focusing on potential nano-related hazard, the inhalation route is seen as the most critical. **New results on this specific toxicity were published in a scientific journal in December 2016**[5]: the effects of five well characterized organic pigments were evaluated in inhalation and particle characterization studies. In each case, coarse and fine organic pigments were investigated and compared to coarse and fine inorganic Pigment Red 101. **No nanosize-related toxicological effects were identified.**

Additionally, ETAD companies are currently carrying out similar studies on other organic pigments belonging to different chemical classes. **First results are in agreement with the ones obtained in the above-mentioned study**[6].

[4] In the past: Directive 92/32/EEC in the EU (and similar regulations in other countries with chemical legislation in place), Council Regulation (EEC) No 793/93. Most recently: REACH regulation.

[5] "Comparative short-term inhalation toxicity of five organic diketopyrrolopyrrole pigments and two inorganic iron-oxide-based pigments", Th. Hofmann and others, Inhal Toxicol, 2016; 28(10): 463–479.

[6] Internal results, publication expected in 2017.

Is there a risk for workers in the pigment industry?

The production of organic pigments takes place in industrial-scale plants, where all aspects of occupational health and safety and environmental protection are reliably met. Dust extraction equipment as well as personal protection equipment is standard. Rigorous controls and limits are set here by local authorities to ensure that the plants operate to minimize any adverse risk to humans and the environment.

In downstream uses – e.g. in the production of paints, of inks or master batches - the individual constituents are mostly added in closed systems.

In the final product, the colorant is surrounded by a polymeric or resinous matrix.

What about consumer exposure?

In consumer use, pigments are present in printed matter, painted articles, coloured plastic or as a liquid preparation e.g. a DIY paint. At that stage, pigments are fixed in a solid respectively liquid system and cannot be considered as nano powders.

The lack of migration of nanoparticles from nanocomposites is also confirmed by the first results from ongoing studies on possible release onto dry food simulants[7], a quite sensitive exposure scenario.

Conclusions

Organic pigments have been on the market for several decades now – and already as what we now call nanosize particles. **The experience and the scientific results over this time have given no indication of any adverse effects that can be attributed solely to their very small size**. It would appear that the current regulatory regimes are capable of handling these substances and that the handling measures currently in place are adequate.

[7] "Nano release study – Final results" J. Bott, Frauenhofer IVV presentation held at Cefic (September 2017)