

Facts on the Nano Discussion in the Pigment and Filler Industry

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Pigments and fillers are used for the colouring and surface structuring of nearly all products found in our daily life. They consist of small particles which are insoluble and firmly bound in the application medium (z. B. paints, coatings and plastics).

Pigments and fillers were not “invented” just recently under nanotechnology promotion programmes; they have been used for centuries or they are the results of industrial research from the past one hundred years.

Applying the EU Commission Recommendation on the Definition of Nanomaterial of 18 October 2011^[1] to pigments and fillers, most of the traditional pigments and fillers should be called nanomaterials. Consequently, pigments and fillers are included in the statistics for nanomaterials.

In Europe, around 100 companies are engaged in the synthetic manufacture of pigments and fillers (ca. 75% of these are small and medium-sized enterprises). These businesses combined achieve sales of roughly 8.1 billion euros and employ around 23,000 staff. Europe accounts for approximately one third of the global market for pigments and fillers.

Definition and measuring methods

Regarding nanomaterial various definitions have been developed by standardisation bodies (e.g. ISO). All of these definitions have in common that a size between 1 and 100 nm is attributed to nanomaterial, even though there is no scientific justification for such borderlines.

The most important definition in Europe is the EU Commission Recommendation on the definition of nanomaterial of 18 October 2011 (in the following: Commission definition), even though it has no legal relevance for the time being.

According to the Commission definition, a nanomaterial means “*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*”.

An alternative definition proposal is provided by the US Environmental Protection Agency (EPA)^[2] where, beside a certain size, a nanomaterial is also required to have new properties compared to conventional substances, due to the particle size.

ASTM E 2456-06 considers only 2- and 3-dimensional nanoscale particles as nanomaterials.

The inclusion of aggregates and agglomerates in the Commission definition turns many pigments and fillers into nanomaterials per definition.

^[1] Commission Recommendation 2011/696/EU (Official Journal L 275 of 20 October 2011)

^[2] <http://www.gpo.gov/fdsys/granule/FR-2015-04-06/2015-07497>

In a project together with the Joint Research Centre (JRC), the European association Eurocolour has comprehensively taken stock of reality, as regards the use of existing measuring methods for pigments and fillers available in practice.^[3]

These are the major results:

- Much expertise and a solid knowledge of the substance in question are needed to obtain reliable results in particle size measurement.
- Sample preparation (especially dispersion) is critical for performing a valid and representative particle size distribution determination.
- Based on the results from this project, it is not possible to recommend one single method for identifying a nanomaterial according to the EU definition.

In the practical implementation of the Commission definition – i.e. the decision whether a material fulfils the requirements to a nanomaterial or not – in particular the following points are crucial:

- The demand of a number size distribution makes the use of electron microscopy inevitable in most cases.
- The inclusion of agglomerates and aggregates – being possibly formed from constituents in a dimension of < 100 nm – excludes the use of automatic imaging counts in practice.
- This much reduces the number of particles that are covered and assessed, which makes it even more difficult to select a sample representative of the material.

This means that each and every analysis involves high staff input. At the same time, these very specific requirements lead to a situation where the existing, partly highly comprehensive knowledge of manufacturers about particle sizes can be used only with strong limitations.

Hazard profile of pigments and fillers

Toxicity

For large parts of the pigment classes and fillers, experimental data were gathered within the REACH registration of industrial chemicals in the European Union or they were newly compiled. Furthermore, studies were carried out to fulfil the registration requirements of countries outside the EU. Also, many data are published in technical literature. The European chemicals legislation^[4] obliges registrants to share available data, to search public databases for relevant information and to review the data for adequacy and reliability. Due to both research activities and ongoing registrations and evaluations of substances, the volume of experimental data is increasing considerably at the moment.

As described earlier in the introduction, many pigments and fillers fall under the Commission definition. Generally speaking, these substances have been placed on the market for decades in the same or equivalent quality. For this reason, huge amounts of experimental data on the toxicity of these materials – especially for safety and environmental assessment – were generated already prior to the discussion about a potential hazard in connection with nano-materials.

^[3] JRC Technical Reports „ Basic comparison of particle size distribution measurements of pigments and fillers using commonly available industrial methods“ <http://publications.jrc.ec.europa.eu/repository/handle/JRC92531>

^[4] Regulation (EC) No 1907/2006 (REACH Regulation)

Consequently, solids with dimensions in the nanometre range are very rarely new and innovative substances. Irrespective of this, publications on some newly developed nanomaterials are triggering fears of exposure to such materials possibly leading to “nano-specific” toxic effects. Therefore, nanomaterials are repeatedly called critical, both in connection with exposure at the workplace and in use by consumers in articles and mixtures.

The results of the manifold investigations by the scientific community and industry over the past years were summarized in a review on the nano-safety issue. As an outcome, for technical nanomaterials there were no unexpected findings that give cause for concern - with a few barely surprising exceptions like fibrous or soluble materials.^[5] Even though the large quantity of research over the past decade focused on nanomaterial safety, no specific nano-toxic effects were identified in animal model systems. To date, there is no evidence of particles in dimensions below 100 nm (the threshold definition of a nanoparticle) showing any step-change in their hazard in comparison to particles > 100 nm (so-called bulk materials).^[6]

For classic materials like pigments and fillers that have been on the market for a long time, the assessment of hazards concerning safety and environment does not change fundamentally – simply because today many of these materials fall under the Commission definition, so that they need to be seen as nanomaterials. In theory, the substances examined so far met the nanomaterial definition already at the time when the studies were conducted. Consequently, such studying and testing already included potential nano-specific toxic properties.

Usually, pigments and fillers are practically insoluble in water and in octanol. In many cases, the measured values are < 1 mg/l. Moreover, pigments and fillers are considered chemically inert. A prerequisite for the absorption of relevant quantities in the organism is solubility in aqueous (e.g. in the gastrointestinal tract) or lipophilic (e.g. to lipid membranes) media. Therefore, it is unlikely that pigments become systemically bioavailable after oral, dermal or inhalation exposure.

As for any material consisting of inhalable dust, inhalation is considered to be the most important route of exposure. This is relevant for industrial workplace exposure.

In a comparison between soluble and insoluble particles, mainly the self-cleansing mechanism of the lungs (mucociliary clearance) transports back insoluble particles towards the mouth where they can be coughed out. The only possibility for an uptake in the body via the lungs is an uptake of solid particles in the cell (phagocytosis) through the so-called big eater cells of the immune system (macrophages). But the dose taken up in this way can be deemed negligible. Health hazards from exposure situations in which more inert particles are inhaled than can be cleared from the lungs by normal body function have long been established. They are the basis for the general exposure limits for inert inhalable dust that exist in many countries. The threshold concentration in Germany is 1.25 mg/m³ for the alveolar fraction (A-dust) at a density of 2.5 g/cm³. The occupational limit value for the inhalable fraction (E-dust) is 10 mg/m³.^[7]

For nanomaterials a lower threshold limit of 0.5 mg/m³ (alveolar fraction) at a density of 2.5 g/cm³ was recently recommended^[8] when other assessment criteria defined in Announcement BekGS 527 are not available.

^[5] H.F. Krug, *Nanosafety Research – Are We on the Right Track?* *Angew. Chem.* **2014**, 126 2 – 19 (*Angew. Chem. Int. Ed.* **2014**, 53, 2 - 18).

^[6] K. Donaldson, C. A. Poland. *Nanotoxicity: challenging the myth of nano-specific toxicity.* *Curr. Opin. Biotechnol.* **2013**, 24, 724 – 734.

^[7] *Technische Regeln für Gefahrstoffe (TRGS) 900 “Arbeitsplatzgrenzwerte”, January 2006.*

^[8] *Announcement (BekGS) 527 „Manufactured Nanomaterials“, May 2014.*

Occupational exposure

Fine particulate materials generally tend to form larger agglomerates. The finer the particles, the more they show this behaviour. Breaking up the thus formed agglomerates takes considerable (dispersion) energy and the ability of the medium to transfer the necessary shear forces to the particles. The achievable dispersion state – and, consequently, the particle size distribution – strongly depend on the medium in which the particles are contained. By using strong shear forces in liquid media, existing agglomerates can be broken up into the primary particles, aggregates or smaller agglomerates. Surface active substances and/or binder systems are additionally needed to prevent re-agglomeration and thus to stabilise the dispersion. In airborne systems, the transfer of strong shear forces and, consequently, the breaking up of existing agglomerates are usually not possible at all or only to a minor extent; this is reflected in the results of workplace measurements.^[9,10,11]

There is also frequently voiced concern that once inhaled, nanomaterials could release nanoparticles which – due to their small sizes – may reach areas of the human body otherwise not accessible to conventional substances, so that they cause damage. Recent works on this area have indicated that a breakdown of nanomaterial aggregates or agglomerates in the lungs, with a release of nanoparticles, does not occur. If anything, research points to the opposite. In lung fluid, nanomaterials come together to form even bigger agglomerates.

In their study Maier et al.^[12] came to the conclusion that lung surfactant does not promote the disaggregation of titanium dioxide aggregates or agglomerates. Creutzenberg et al.^[13] investigated the fate of three different aggregates (including carbon black) after uptake in the lungs and found a tendency of nano-scaled particles to form larger size agglomerates following deposition and interaction with cells of the respiratory tract.

The NanoCare project^[14] in Germany studied and compared the behaviour of nine different nanostructured materials in the presence and absence of lung fluid. These results indicate that contact with serum or lung fluid does not result in nanomaterials breaking down into smaller sized units; rather, the opposite is true.

The NanoCare project used complete lung fluid; therefore, these results are representative of the actual lung environment.

^[9] *Nanoparticle exposure at nanotechnology workplaces: A review*, Thomas AJ Kuhlbusch, Christof Asbach, Heinz Fissan, Daniel Göhler and Michael Stintz, *Particle and Fibre Toxicology* **2011**, 8:22

^[10] Kuhlbusch TAJ, Neumann S, Fissan H. (2004). *Number Size Distribution, Mass Concentration, and Particle Composition of PM1, PM2.5, and PM10 in Bag Filling Areas of Carbon Black Production*. *J Occup Environ Hyg* 1,660-671.

^[11] Kuhlbusch TAJ and Fissan, H (2006). *Particle characteristics in the reactor and pelletizing areas of carbon black production*. *JOEM* **3**, 558-567.

^[12] Maier, M., Hannebauer, B., Holldorff, H., & Albers, P., *Does Lung Surfactant Promote Disaggregation of Nanostructured Titanium Dioxide?*, *Journal of Occupational and Environmental Medicine*, Vol. 48, No. 12, **December 2006**, pp 1314-1320.

^[13] Creutzenberg, O., Bellmann, B., Korolewitz, R., Koch, W., Mangelsdorf, I., Tillmann, T., & Schaudien, D., *Change in agglomeration status and toxicokinetic fate of various nanoparticles in vivo following lung exposure in rats*, *Inhalation Toxicology*, Vol. 24, No. 12, pp. 821-830.

^[14] 39 NanoCare (2009) *Health Related Aspects of Nanomaterials- Final Scientific Report*, http://www.nanopartikel.info/files/content/dana/Dokumente/NanoCare/Publikationen/NanoCare_Final_Report.pdf.

In case of pigments or fillers being the fine particulate material, the particles are bound in a matrix in the final application – e.g. in printing inks, paints and coatings (after curing) or plastics. Usually, these particles cannot be released from the matrix.^[15,16]

Studies on the release of nanomaterials

Release from coatings and plastics

Mostly, end consumers are only in indirect contact with pigments and fillers: through objects that are coated or coloured with them. Here, the fine particulate or nanoscale dispersed particles are bound in a firm matrix. This largely excludes an exposure of end users to free pigment or filler nanoparticles – which has been confirmed recently by scientists from TU Dresden also for the permanent use (ageing) of products.^[17]

Under controlled conditions, coatings and plastics – which contained different fine particulate, organic and inorganic pigments – were exposed to artificial weathering influences, simulating everyday weather over several years. Next, the samples were exposed to several types of mechanical stress. The results show: Often, pigmented coatings and plastics are more stable to weathering influences and mechanical stress than non-pigmented ones.

After mechanical stress on surfaces, no free pigment nanoparticles were found – neither in the airborne state nor in the abrasion. As detected under the microscope the pigment nanoparticles remain firmly bound in the matrix fragments (coatings/plastics), or they mass together to form agglomerates. Consequently, an exposure of consumers to pigment nanoparticles could be largely excluded, also in permanent use or in the ageing of products.

Release from incineration plants

Modern flue gas plants are highly effective. In testing at a waste incineration plant (within the Federal Environment Agency/UBA project on the incineration of nanomaterial-containing wastes “Verbrennung nanomaterialhaltiger Abfälle”) no significant increase in the Ti concentration was found in purified flue gas. It is worth noting that the added quantities of nanoscale TiO₂ (0.28% Ti) were above the concentrations of 0.2% Ti measured in household waste.

Release from wall paints for exterior use („NanoHouse“)^[18]

In weathering tests it was found that the release of TiO₂ nanoparticles from wall paints for exterior use is extremely low. This means that the particles are firmly bound in the matrix.^[19]

Migration of nanoparticles when used in consumer articles

Pigments and fillers are frequently used in plastics, coatings and printing inks in contact with food. Here, it must be ensured that there is no migration into the foodstuff.

^[15] *Nanoparticle emission of selected products during their life cycle*, Dr. Thomas Kuhlbusch, Carmen Nickel, *Environmental research plan of the Federal Ministry for the Environment, Nature Conservation and Nuclear Safety*

^[16] *Expositionsermittlung bei der Herstellung oder Verwendung von Nanomaterialien (Pulver, Lacke, Kompositwerkstoffe)*,

Daniel Göhler und Michael Stintz, *Nano-Tagung der Sächsischen Arbeitsschutz Konferenz*, 19. April 2012, Dresden

^[17] FRiNano Projekt: *Nanoparticle release from nanocomposites due to mechanical treatment at two stages of the life-cycle*, Daniel Göhler, André Nogowski, Petra Fiala and Michael Stintz 2013 *J. Phys.: Conf. Ser.* 429 012045

^[18] <http://www-nanohouse.cea.fr/home/liblocal/docs/Dissemination%20Reports/NanoHouse%20DR3.pdf>

^[19] Al-Kattan et al., *Environ. Sci.: Processes Impacts*, 2013, 15, 2186)

As many pigments and fillers fall under the existing EU Commission Recommendation on the Definition of Nanomaterial, the question is increasingly gaining in importance whether nanoparticles migrate from plastics or printing inks and, consequently, whether they can migrate into foodstuffs.

Based on migration studies from plastics^[20,21] and on theoretical considerations^[22,23] it was possible to demonstrate that a particle migration can be excluded for particles with a size of more than 2 or 3 nm. Then again, because of the strong tendency to agglomerate known for very small particles and due to the prevailing dispersion conditions in plastics, there are practically no free particles sized 1 to 3 nm in plastic materials. This was also shown by comparative electron microscopy. Summing up, it is noted that nanoparticles cannot migrate from plastics into foodstuffs.

In relevant migration studies from printing inks, no migration of nanoparticles was detected either.^[24] Based on the experimental results and as the dried and cured printing ink film is a polymer matrix which firmly binds its pigments and fillers, the conclusion was drawn that no nanoparticles migrate from printing inks into foodstuffs.

Also migration studies of tin oxide (nano-form, with and without surface after-treatment) in plastics have shown that there is no migration of nanoparticles.^[25]

REACH and Nano

In its *Second Regulatory Review on Nanomaterials*^[26] the EU Commission found that “*REACH sets the best possible framework for the risk management of nanomaterials*”.

With this, the EU Commission confirms that nanomaterials are regulated under the European chemicals regulation REACH as a matter of principle, and that the basic text of the Regulation does not require amendment. However, the EU Commission sees the need for more precision on nanomaterials in the Annexes to the REACH Regulation and in the guidance documents.

In late November 2013 the EU Commission issued a document concretizing its ideas for adapting the REACH Annexes (the so-called CARACAL DOC CA/ 53/2013).

In the draft documents so far presented by the EU Commission, the requirements to nanomaterials go far beyond the current requirements to substances already placed or being available on the market.

^[20] *Migration von Nanopartikeln*, Johannes Bott, Horst-Christian Langowski und Maria Wagenstaller, *FORUM WISSENSCHAFT TWB*

^[21] *Scientific Opinion: Statement on the safety assessment of the substance silicon dioxide silanated, FCM Substance No 87 for use in the food contact materials*; *EFSA Journal* **2014**; 12(6):3712

^[22] *Migration potential of nanomaterials in food contact plastics*, Angela Störmer, Johannes Bott & Roland Franz, *1st Joint Symposium on Nanotechnology, Fraunhofer – BfR, Berlin, 5.-6. March 2015*

^[23] *A model study into the migration potential of nanoparticles from plastics nanocomposites for food contact*, Angela Störmer, Johannes Bott & Roland Franz, *Food Packaging and Shelf Life* 2(2) 73-80 (**2014**)

^[24] *Analysis of the migration behaviour from printing ink layers of printed food packaging into the food*, Matthias Henker, Michael Becker, Sarah-Lisa Theisen and Martin Schieß, *DEUTSCHE LEBENSMITTEL-RUNDSCHAU*, 109. Jahrgang **April 2013**

^[25] *Scientific Opinion on the safety evaluation of the substance zinc oxide, nanoparticles, uncoated and coated with [3-(methacryloxy)propyl] trimethoxysilane, for use in food contact materials*, *EFSA Journal* **2015**;13(4):4063

^[26] <http://eur-lex.europa.eu/legal-content/DE/TXT/PDF/?uri=CELEX:52012DC0572&from=EN>

Nano-product registers

So-called nano-product registers have been or are being introduced in some EU Member States and non-EU countries. In the legal area relevant to REACH, this concerns the countries France, Belgium, Denmark, Norway and Sweden. There is no uniform EU register. Furthermore, registers are in place, inter alia, in Canada, Australia or Switzerland.

From the legislators' perspective, the justification for most nano-product registers is that they create transparency for public authorities and consumers as regards the volumes and types of nanomaterials being placed on the market – inter alia, with the goal of being able to respond faster if a new danger emerges.

There are major differences between the various countries in the concrete shaping of the registers. It starts with the definition which varies from country to country and continues with the exemptions from the notification requirement which come in different forms everywhere. For example, it is quite possible that a product needs to be notified as a nanomaterial in country A while it is not a nanomaterial in country B. It also happens in one and the same country that a product requires notification for the nano-product register whereas it is not deemed a nanomaterial in certain, specifically regulated applications (e.g. cosmetics or food). With this, a statement on whether a product is a nanomaterial or contains nanomaterials loses its general validity, so that this question needs to be decided on a case-by-case basis.

France was the first EU Member State to introduce a nano-product register; the definition is closely oriented to the European Commission definition but excludes naturally occurring nanomaterials. The currently available evaluations of reporting from the years 2013 and 2014 are of little informative value and essentially provide only a listing of substances.

The Belgian law, too, defines a nanomaterial based on the Commission definition. It differentiates between substances and mixtures which are registered, and articles or complex products for which a notification is required. Unlike in France, where registration is made for the respective previous year, registration in Belgium is necessary in advance for the following year. Moreover, the downstream users (professional and industrial users) must be stated.

The product register in Denmark comprises solely mixtures and articles which are intended for sale to private end consumers and contain nanomaterials that can be released or whose nanomaterials release cmr-substances or substances dangerous to the environment. The Danish register applies from 30 August 2015, the Belgian one from 1 January 2016 (for substances) and from 1 January 2017 (for mixtures).

Norway has a register of dangerous substances where “nano” is stated as an additional specification. However, a nanomaterial is not deemed dangerous per se.

Sweden is currently carrying out an assessment of potential impacts and will deliberate in early 2016 on the content of a national register.

Outside the EU area, mostly only new substances (not yet included in the countries' inventories) require notification for nanoregisters. Both the VdMi and the European Chemical Industry Council (Cefic) have provided interpretation aids for nanoregisters; these documents are updated regularly.