

**Nano**

**The Measure of all Things**





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## **Foreword**

Pigments and fillers are used for colouring and creating surface effects on nearly all products found in our daily life. They consist of small particles, which are insoluble and are firmly bound in the respective application media.

The pigments and fillers described in this booklet have existed for many years, in some cases centuries, and are, therefore, not considered new materials.

If the EU-Commission recommendation of 18.10.2011 on the definition of nanomaterial is applied to pigments and fillers, the majority of them will be considered as nanomaterials.

This booklet presents an outline of the measurement and assessment of pigments and fillers in the context of the “nano” discussion.

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Eurocolour

## Introduction and Summary

### **The Economic Importance of the Pigments and Fillers Industries**

In Europe some 100 companies are engaged in the manufacture of synthetic pigments and fillers. These companies – around 75% of them are small and medium-sized enterprises – generate sales of ca. 8.1 billion euros and employ around 23,000 staff. Europe represents about one third of the global pigments and fillers market.

Pigments and fillers were not developed under programmes to exploit nanotechnology: they have been in existence for centuries or are the results of industrial research activities over the past 100 years. The present definition of nanomaterials includes these substances which have been known for a great many years. Therefore, pigments and fillers will be included in the statistics for nanomaterials and become part of the assessments of the success of promotion programmes.

The concern regarding the risk analysis of nanomaterials is partly attributable to the fact that new substances, which are designated as nanomaterials, are solid particles. Unless they are bound in a matrix, they can give off dust and – if they are also of a suitable particle size and form – they can enter the body through the lungs. However, for many years, this has been the subject of discussions about respirable fine dusts so that there was no need to resort to, or introduce, the term “nanomaterial” in relation to this type of exposure. Pigments and fillers are manufactured industrially and frequently delivered in low-dust forms to the supply chain.

After incorporation into printing inks, paints, plastics, rubber, ceramics and other materials, pigments and fillers are firmly bound and can no longer give off dust. Therefore, the fine dust problem is restricted mainly to workplaces at manufacturers and processors of pigments and fillers.

In view of political intentions to cover nanomaterials and their uses in nano-product registers, it should be pointed out that practically all products used in our daily life contain pigments and fillers. This would mean most, everyday products being listed ad absurdum in a nano-product register. For the above reasons, an explicit exemption of traditional pigments and fillers from the nanomaterial definition is the obvious choice.



## 1 What do pigments have to do with nanotechnology products?

### Important terms and their definitions

#### *Nanoscale and nanomaterials*

The prefix “nano” comes from the Greek word *nanos* = *dwarf* and means “a billionth”. In consequence, one nanometre (1 nm) is one

billionth of a metre:  $1 \text{ nm} = 10^{-9} \text{ m}$ . Conversely, one billion ( $10^9$ ) nanometres equals one metre:  $10^9 \text{ nm} = 1 \text{ m}$ . In other words, the following can be said to better visualize the size of one nanometre: one nanometre corresponds to one millionth of a millimetre or one thousandth of a micrometre.

Thus one speaks of “nanoscale” where the objects in question – here: the primary particles of the pigment – are sized between one and one hundred nanometres.

### *Pigments*

Pigments are defined as coloured – possibly black, white, fluorescent or metallic – solid particles, which are of organic or inorganic nature and insoluble in the application medium.

The respective media of the printing ink and paint or the polymer do *not* have any colour themselves. Only the addition of pigments provide the desired colouring effect.

Different colour shades – in particular mixed colours – can be achieved only by mixing different pigments.

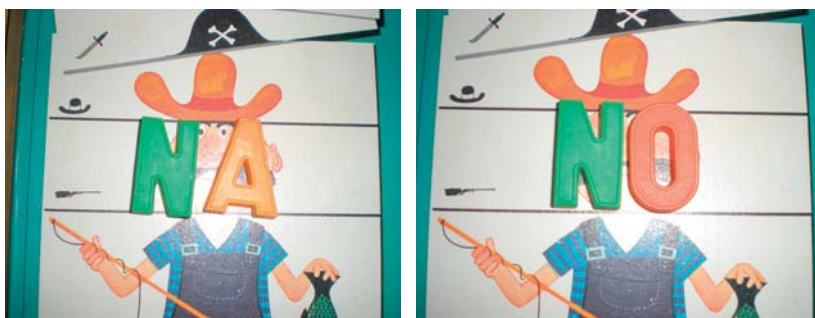
The colour-providing properties of a pigment occur when the pigment particles interact with visible light. The human eye sees light with a wavelength between ca. 400 nm (violet) and 700 nm (red). Most pigment particles are sized between 200 nanometres and some micrometres (i.e. some thousands of nanometres). The colour of a pigment can be brought about in two different ways, depending on the individual particle size which, beside the material properties, is a major factor for the colour effect of the pigment:

- The pigment molecule absorbs certain fractions of visible light so that the colouring effect is of the complementary colour; for example, a yellow pigment absorbs the blue fraction of incident light.
- Depending on the particle size in the pigment (see chapter 3) the light is scattered with different intensities.



Given the very wide range of different uses of pigments, specific, individual properties are required, e.g. dispersibility, colour intensity, light- and weather-fastness, mechanical resistance, colour shade, transparency or opacity/hiding power. These properties depend on both the chemical composition and sizes and shapes (morphology) of the pigment particles.

To be effective in their applications, the pigments need to be finely dispersed into binders. Examples are the manufacture of printing inks, coloured coatings, polymers or other materials. Pigments maintain their crystalline particle structure throughout the entire dispersion process, and they are practically unaffected physically or chemically by the binder, i.e. the medium into which they are dispersed.



The particle size range of the pigment powder prior to incorporation into the medium is a decisive characteristic in this context. Further details on this feature can be taken from the following section and in particular from chapter 3.

As mentioned above, one pigment consists, inter alia, of a large number of small to very small particles, which are generated in comminution processes in mills or comparable powdering devices. Ideally it is desirable for all particles to be of similar sizes, but this

is never possible. Therefore, differently sized particles are invariably obtained in the manufacture of pigments, with the so-called particle size distribution stretching from very fine to coarser particles (see chapter 3). In milling processes for classic (established) pigments, nano-particles are not generated on purpose but are bound to occur.

### *Fillers*

Fillers are used mainly for their technical properties and less for providing colour. They need to be distributed as homogeneously, i.e. as evenly, as possible in the application medium (e.g. the paint to be applied).

Most fillers are very fine particulate solids. The thickness of a paint layer depends solely on the technical properties necessary for the respective application.

### *Applications of pigments and fillers*

Pigments and fillers are found in all consumer goods, which would be inconceivable without them. They have functional, decorative, protective and safety-technical functions. Colour effects are of great importance for consumer goods; they also influence buying decisions of users.

Improving the application properties has always been the primary focus for the pigments and fillers industry. Classic pigments and fillers are available in a wide range of particle size distributions in the micrometre range and in various particle shapes (morphologies).

Pigments and fillers are mainly used for the colouring and filling of coatings, decorative paints or anti-corrosion paints for buildings and for the colouring of, for example

- abrasives
- candles
- ceramics
- concrete
- cosmetics
- device casings
- emulsion paints
- foodstuffs
- glass products
- paper
- pharmaceuticals
- polymers
- printing inks
- rubber
- soaps
- sunscreens
- textile fibres
- toys
- traffic signs



## 2 Manufacture of pigments and fillers

As stated briefly in chapter 1, the industrial manufacture of pigments and fillers aims to produce small and insoluble particles. Various manufacturing processes have been developed to achieve this aim.

### Inorganic pigments

#### *Synthesis*

For inorganic pigments, synthesis generally takes place through heat treatments (thermal processes) in rotary kilns or in other calcining processes. The colour palette of pigments can be influenced by variations in the way the reaction is controlled.

Depending on the choice of the raw material, there can be combinations of precipitations and thermal processes where different colour shades or certain optical effects need to be achieved. One of the oldest white pigments is calcium carbonate which is obtained in several stages starting with the calcining of limestone.

### *Precipitation*

At the beginning of the precipitation process, solid raw materials – e.g. inorganic salts or oxides – are dissolved and blended with each other. Depending on the manufacturing method, further substances may be added, for example, acids or bases. All these substances in the liquid react with each other and create the desired, new substance which forms as a solid.

Crystals of this solid start to form on so-called nuclei ( tiniest particles in the solution or wall irregularities). Crystals grow on these nuclei and can then be separated from the solution, e.g. by way of filtration.

After separation from the liquid, the solid particles are washed and dried, using e.g. spray driers or belt driers. Where the particle size is required to be as homogeneous as possible, the material is processed, for example, through a classifier. Depending on intended uses of the pigment, further purification or processing steps can follow.

The processes described are used in the manufacture of e.g. inorganic colour pigments, including iron oxide (red, yellow or black), bismuth vanadate (yellow), ultramarine pigments or iron blue pigments. The same goes for titanium dioxide (a white pigment with good hiding power for a very wide range of applications) and synthetic amorphous silica.

Precipitation onto a substrate is one variation of the precipitation process: prior to the chemical reaction intended to lead to precipitation, minute insoluble particles are introduced into the solution. Next, the desired crystals accumulate in a thin, defined layer

on the surfaces of these particles. As soon as the desired layer thickness is reached on the carrier particle, the reaction is stopped and the solid is separated from the solution.

### **Metal effect pigments**

The basic material for the manufacture of metal effect pigments is the respective metal or can also be an alloy. Important starting materials are aluminium, copper and zinc, with the latter two frequently being alloyed into gold bronze (a type of brass).



**Flamespraying:** The molten metal is squeezed through a nozzle and as the jet cools, a granule with particle size dimensions in the micrometre range (i.e. above nano-range) is formed. This granule is ground into thin, platelet-shaped pigment particles to bring about the desired properties of the pigment.

**Grinding:** The duration and intensity of the grinding process influence the particle size distribution (see chapter 3) as well as particle thicknesses and improve other properties required of the pigments. Either during grinding or subsequently, the particles of the pigment are polished – i.e. a layer is applied to prevent caking or welding together. Metal pigments are placed on the market almost exclusively in dust-free forms, e.g. pastes or suspensions.



## Organic pigments

Organic pigments are manufactured in chemical syntheses which frequently comprise several process steps, where starting materials react with each other to form a new compound.

Even very complex structures can be produced in relatively few stages. Where necessary, these structures are additionally modified chemically – e.g. to bring about a different shade of the same colour or to optimise certain properties of the pigment for its intended use.

The processes result in the formation of small, solid pigment particles. As described in the previous section, after the reaction these pigment particles need to be separated from the solution. For this purpose, solvents may be used, other treatments added or, quite simply, the solid can be filtered out – depending on the substance class. Subsequent processes (drying, grinding etc) will be similar to those described under "Precipitation".

All the manufacturing methods described here can be followed by further process steps to optimise the technical properties of the pigment needed for its application especially dispersibility and hiding power but also colour shade or weather-fastness.



For organic pigments, after-treatment can take the form of heating in the presence of solvents and/or chemical additives.

### **Delivery forms**

Products manufactured according to the methods described above are fine particulate powders with certain particle size distributions (see chapter 3). Granules, fine granules or pastes can be produced from these powders, in order to reduce dust formation and/or to make further processing easier.

## **3 Particle sizes and their distributions**

Particle sizes of pigments before further processing stretch from some 10 nanometres to some thousand nanometres, i.e. some micrometres. However, in practice there is never just one single particle size, quite the contrary, there can be a very wide range of particle sizes in one pigment sample.

Normally, the particle size distribution comprises at least one order of magnitude; this means that the smallest particles are at least 10 times smaller than the largest ones. Reasons for differences in particle size are the technical limitations of manufacturing processes and of subsequent production and processing steps.

The optical and technical properties required for an application are usually more favourable where particle sizes do not vary too widely. Therefore, a narrow particle size distribution is sought in manufacture and development, and hence is an important characteristic of the resulting pigment sample.

Consequently, when *measuring* particle sizes not only the mean particle size but also the entire distribution needs to be determined in order to get the full picture.

### **Measuring of particle sizes**

A description of measuring methods would go beyond the scope of this text so that only a brief overview can be given here. This overview does not focus on the theoretical bases of the equipment used but on those aspects which are required for a correct interpretation of results.



The most obvious method to measure the particles is in an electron microscope image, because the smallest pigment particles,



with nano-scale dimensions, are not detectable in a light microscope because of their very small size.

However, on closer examination this method has major disadvantages: in order to determine the mean particle size and, in particular, the particle size distribution at least 2,500 to 10,000 particles need to be assessed. As counting is only partially automated, at best, this method is too labour-intensive and time-consuming for routine activities. Moreover, there is the basic problem that viewers invariably see only a two-dimensional projection of any three-dimensional particle. Nevertheless, there is the advantage of obtaining information about particle shapes and morphology.

Standard instruments for measuring particle size distributions are, on the one hand, centrifuges and, on the other, devices that use the diffraction of light by small particles.

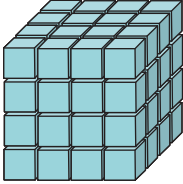
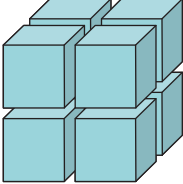
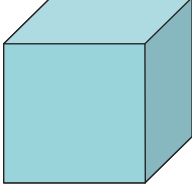
In the evaluation of the results of measurements, particles are generally assumed to be spherical.

Centrifuges usually have the advantage of high separation efficiency. Furthermore, when using centrifuges the various distributions within one mixture of particles can be imaged individually too.

## **Volume distribution and number distribution**

One point, which frequently gives rise to misunderstandings, is the distinction between *volume distribution* and *number distribution* in a given pigment sample. This difference will be illustrated by means of a highly simplified distribution.

The model of the pigment sample consists of 64 small cubes with edge length  $d$ , 8 cubes of twice the edge length, and 1 cube of four times the edge length. The chart shows the respective values for the solids volumes of these particles.

64 cubes with edge length $d$	8 cubes with edge length $2d$	1 cube with edge length $4d$
		
Volume: $64d^3$	Volume: $8 \cdot (2d)^3 = 64d^3$	Volume: $1 \cdot (4d)^3 = 64d^3$

### *Volume distribution*

The total volume of the pigment sample is

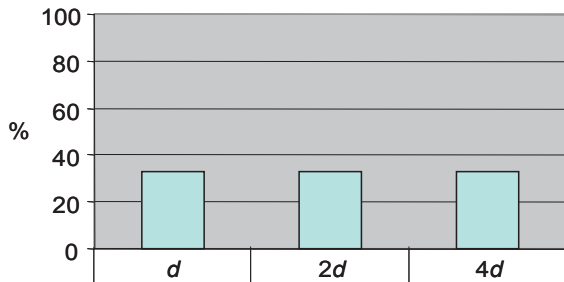
$$64d^3 + 64d^3 + 64d^3 = 192d^3$$

This results (rounded to whole percentage figures) in the following shares in the total *volume*:

- small particles:  $64d^3/192d^3 = 33\%$
- medium-sized particles:  $64d^3/192d^3 = 33\%$
- large particles:  $64d^3/192d^3 = 33\%$

The above can be depicted in a histogram:

Volume distribution as a function of edge length



### *Number distribution*

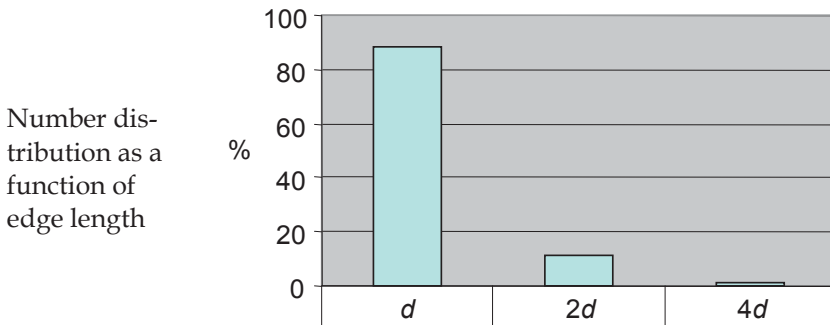
The total number of particles in the pigment sample is

$$64 + 8 + 1 = 73$$

This results (rounded to whole percentage figures) in the following shares in the total *number* of all particles:

- small particles:  $64/73 = 88 \%$
- medium-sized particles:  $8/73 = 11 \%$
- large particles:  $1/73 = 1 \%$

The resulting histogram looks as follows:



It is obvious that the same facts lead to quite different conclusions. This also applies, of course, for all real material samples containing many small particles: at times, a relatively minor share (here  $1/3$ ) of the total *volume* – and thus in the total amount – will result in a very high share of the *number* distribution, as is the case here for small particles.

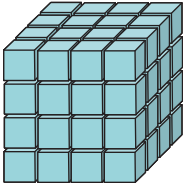
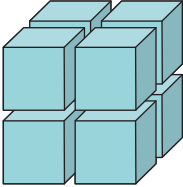
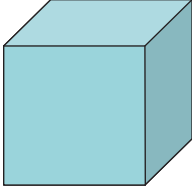
When interpreting such diagrams it is essential not to give an incorrect impression.

## Total surface of the particles

An indirect but very common method for determining the particle size is to measure the *specific surface*, i.e. the *surface per mass unit*.

Applying this method to the simple model of a pigment sample used previously results in the values shown in the following chart.

A pigment usually consists of one homogeneous (uniform) material, therefore the distribution based on volume can also be based on mass. In other words: the volume and mass of any particle are proportional, so that here the relative total mass, 64, can be taken as a parameter instead of the total volume  $64d^3$ .

64 cubes with edge length $d$	8 cubes with edge length $2d$	1 cube with edge length $4d$
		
Volume: $64d^3$	Volume: $8 \cdot (2d)^3 = 64d^3$	Volume: $1 \cdot (4d)^3 = 64d^3$
Relative mass: 64	Relative mass: 64	Relative mass: 64
Surface: $64 \cdot 6 \cdot d^2 = 384d^2$	Surface: $8 \cdot 6 \cdot (2d)^2 = 192d^2$	Surface: $1 \cdot 6 \cdot (4d)^2 = 96d^2$

(The factor of 6 in the calculation of the surfaces is required as a cube has 6 square faces with edge length  $d$ .)

Here, the *specific surfaces* have the following relative values:

- small particles:  $384d^2/64 = 6$
- medium-sized particles:  $192d^2/64 = 3$
- large particles:  $96d^2/64 = 1,5$

Clearly for samples of the same material and the same solids volume: the smaller the particles, the larger the total surface.

Frequently, the specific surface is measured by introducing the purified, dried pigment sample into a certain gas, followed by measuring of the amount of gas that accumulates on the surfaces and in accessible pores of the particles (adsorption). Various methods, which cannot be described in this text, are available for this purpose.

## 4 Consumer Protection and Occupational Health and Safety

### General observations

During dispersion into application media – e.g. paints or polymers – nanoscale entities cannot be ruled out, depending on the strength of the shear forces applied and the shapes and particle size distributions of the starting materials. However, in the end products the fine particles are firmly bound in the respective matrix, i.e. there are no free particles.

For this reason, end consumers – i.e. private users – have no contact with pigment powders, granules or pastes, because these materials are only used in industrial processes using suitable protection.

To keep subsequent processing steps as straightforward as possible, pigments are manufactured in such a way that they are easily dispersible. Most of the dispersion processes take place in closed systems so that exposure in the workplace is largely excluded. In order to avoid dust formation, powders are frequently delivered in

paste form or dispersed into a liquid during the manufacturing process. Closed systems or exhaust ventilation systems are used when transferring powders between containers.



### *Exposure in manufacture*

In medicine, exposure is understood to mean the effect of the respective substance, e.g. in the form of dust or gas, on the human body. Substances can enter the human body through the respiratory tract (by inhalation), the mouth (oral) or the skin (dermal). Depending on the type and concentration of the substance as well as the duration and frequency of the effect, one speaks of acute or chronic exposure. Toxicological examinations are performed to find out whether the actual exposure leads to pathological changes in the organism.

### *Discussion about a possible carcinogenic effect through non-toxic, poorly soluble, respirable dusts*

In animal tests carried out as early as in the 1990s with inert, non-toxic fine dusts of different chemical compositions – amongst oth-

ers carbon black and titanium dioxide – inhalation or direct administration in the trachea throughout the lifespan of the animals led to chronic inflammation, lung scarring and some tumour formation.

Their extremely low solubility in the aqueous medium and their respirability are of great importance for the toxicological and ecotoxicological assessment of these pigments. Therefore, under comparable test conditions in animal experimentation similar results cannot be excluded for other poorly soluble and non-toxic pigments.

***The risk of a carcinogenic effect in humans through pigments and fillers can be excluded at workplace concentrations***

Animal tests with carbon black and titanium dioxide were carried out at very high concentrations that do not occur in the workplace,



neither during manufacture nor in use. The extremely high dust concentrations used in the animal experimentation caused a “lung overload” where normal pulmonary purification mechanisms do

not function. In these tests, tumour formation was found only in rats but not in mice and hamsters. Influences of the animal species, the type of fine dust and the mechanism of tumour formation are not, as yet, fully explained. More exhaustive scientific epidemiological studies on carcinogenic effects are only available for some representative pigments and fillers.

Mortality studies in former workers in carbon black production in England, Germany and the USA show no correlation between a carbon black exposure and the formation of lung cancer. There are comparable results for titanium dioxide. The International Agency for Research on Cancer (IARC; part of the World Health Organization/WHO) confirmed this in 1996 in their assessment of carbon black (industrial/pigment soot). Studies in large groups of workers from the carbon black manufacturing industry provided insufficient evidence of a carcinogenic effect in humans.

In view of the results (tumour formation) of tests in rats, IARC classified carbon black (1996/2006) and titanium dioxide (2006) in category 2B ("possibly carcinogenic"). Also based on the animal tests described above, the German Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area (MAK Commission) - who proposes science-based thresholds for hazardous substances and assesses substances in respect of their carcinogenic potential - classified carbon black (1999) and titanium dioxide (2008) as "möglicherweise krebserzeugend" (possibly carcinogenic).

Against this backdrop, a classification by the IARC of other poorly soluble, non-toxic materials in dust form cannot be ruled out.

Fine-particulate pigments and fillers are manufactured exclusively in industrially operated plants (see chapter 2) which meet all the requirements of occupational health and safety and environmental protection. A study has shown that concentrations of nanoparticles inside the production plant are not any higher than in the ambient air. Consequently, no additional exposures of humans and



the environment were found. Furthermore, filters used in exhaust ventilation systems or when transferring powders between containers are maintained to standards which are “state-of-the-art”.

The risk of developing lung cancer for humans, at exposure concentrations in workplaces and when complying with the protection measures stated in the safety data sheets, can be excluded.

### *Exposure in further processing*

As described earlier, breathing in (uptake by inhalation) of pigment powder during manufacture and further processing is only possible if processes do not take place in closed systems.



When taken up by inhalation, non-toxic pigment powders behave like all other poorly soluble fine dusts. If any fine dusts are breathed in over very long periods of time and in high concentrations, a health hazard cannot be excluded: coughing, secretion and impaired lung function can occur as a consequence. Therefore, safety measures advised in the relevant safety data sheet and, as a

matter of principle, applicable thresholds for workplace exposure need to be observed to protect workers.

In further processing – e.g. in the manufacture of a coating – the individual components are usually dosed and added automatically. In a paint, the solid particles of pigments and fillers are enclosed in a liquid matrix. For this reason, emissions of fine-particulate substances are only possible in pouring powders between containers where, however, such emissions are prevented by extraction systems. When applying an automotive coating in industrial plants, emissions are minimized by strictly complying with existing regulations and laws for the protection of workers and environment.



### *Threshold values for dusts*

Regarding general threshold values for dusts, a distinction is made between A-dust (alveolar dust) and E-dust (respirable dust). According to the current (autumn 2011) guidelines in Germany, the maximum admissible concentration in air is  $3 \text{ mg/m}^3$  for A-dust and  $10 \text{ mg/m}^3$  for E-dust. In view of the most recent publication of revised dust threshold values by the MAK Commission, the above concentrations are likely to be reviewed shortly and then lowered

by the Committee on Hazardous Substances (Ausschuss für Gefahrstoffe/AGS) at the Federal Ministry of Labour and Social Affairs (BMAS).

In other European countries different workplace thresholds apply than those stated above.

### *Exposure to nanoparticles*

At present, determining exposure to nanoparticles is not part of the routine controls in industry. However, over recent years various scientific studies on fine dust exposure have been carried out in Europe and in the USA, with a focus on carbon black pigments. For example, for carbon black pigments with particles sized less than 400 nm, no additional release, which would go beyond the exposure during the application or handling of these pigments, was found at or near the workplaces. Workplaces for the manufacture of other nanomaterials were examined within the “NanoCare” project, which is supported by the German Federal Ministry of Education and Research (BMBF). Results confirm the findings described previously.



### *Exposure of end consumers*

In most cases, contact between end consumers and pigments and fillers is only indirect – namely, through articles coated and/or col-

oured with these products. Here, fine-particulate or nanoscale dispersed particles are firmly bound in a solid matrix or in a liquid preparation. Because of this fact, exposure of end users or consumers is extremely low, as has been mentioned earlier.

Under the research project FRINano, at Dresden University, tests were performed on weathered paint and polymer samples which contained various fine-particulate, organic and inorganic pigments. Samples were weathered in controlled conditions, simulating outdoor weathering roughly over a 5-year period. Next, samples were exposed to several forms of mechanical stress (suction, abrasion, grinding).



These studies were intended to find out whether nanoparticles are released from weathered paint and polymer samples, leading to a possible exposure of humans and/or the environment. Pigmented paints and polymers turned out to be more resistant to weathering influences than non-pigmented ones. Furthermore, pigmented paints and polymers are more stable mechanically (to

abrasion). Given these results, any additional burden on the environment – through a release of nanoparticles from coloured, everyday articles – is negligible.



Thus, published studies, to date, on finished paints and polymers show that abrasion does not cause any additional burden on the environment due to nanoscale pigment and filler particles.

### *Pigments and Nanoparticles*

In the industry where pigments are manufactured or processed, the handling of chemical substances is adequately regulated by a number of laws and regulations. Regular control measurements ensure compliance with legal provisions. As an extra step, the German chemical industry association Verband der Chemischen Industrie e.V. (VCI) and the German Federal Institute for Occupational Safety and Health (BAuA) published in 2007 the *Guidance for Handling and Use of Nanomaterials at the Workplace*.

Pigments and fillers have particle size distributions (see chapter 3) which are always product-specific. Consequently, every pigment or filler invariably has a certain fraction of rather coarse particles and one of rather fine particles. The rather fine particle fraction

comes in the form of aggregates (i.e. more or less regular clusters of particles). These aggregates are dimensioned in the micrometre range, i.e. clearly above the nano-range. Nano-particles in free form have not been detected in significant quantities in pigments and fillers.



In toxicological tests, for data in safety data sheets, the pigments used include their possible nanoscale fraction. Toxicological results always comprise effects of the aggregated nanomaterial, which can be present in the pigment or filler. In view of this, potential toxicological effects of the aggregated nanomaterial present are inevitably also covered.

Taking into account what has been said, we ask for confirmation that pigments and fillers where these substances are firmly bound in a matrix or in a paste in consumer-related products are not considered as being within the scope of legal regulations. This approach can prevent an overload of the nanoproduct register.



Eurocolour – pigments, dyes and fillers  
and its member associations

- Asociacion Nacional de Fabricantes de Fritas, Esmaltes y Colores Ceramicos (ANFFECC), Spain, [www.anffecc.com](http://www.anffecc.com)
- British Colour Maker's Association (BCMA), Great Britain, [www.bcma.org.uk](http://www.bcma.org.uk)
- Syndicat des Fabricants d'Emaux, Pigments, Sels et Oxydes Métalliques (EPSOM), France
- Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers (ETAD), Switzerland, [www.etad.com](http://www.etad.com)
- Associazione Nazionale colorifici ceramici e produttori di ossidi metallici (Ceramicolor), Italy, <http://ceramicolor.federchimica.it>
- Verband der Mineralfarbenindustrie e.V. (VdMi), Germany, [www.vdmi.de](http://www.vdmi.de)
- Verband TEGEWA e. V., Germany, [www.tegewa.de](http://www.tegewa.de)

