STATE-OF-THE-ART REPORT

Nanotechnology in the Construction Chemicals Industry

1st Edition, November 2009

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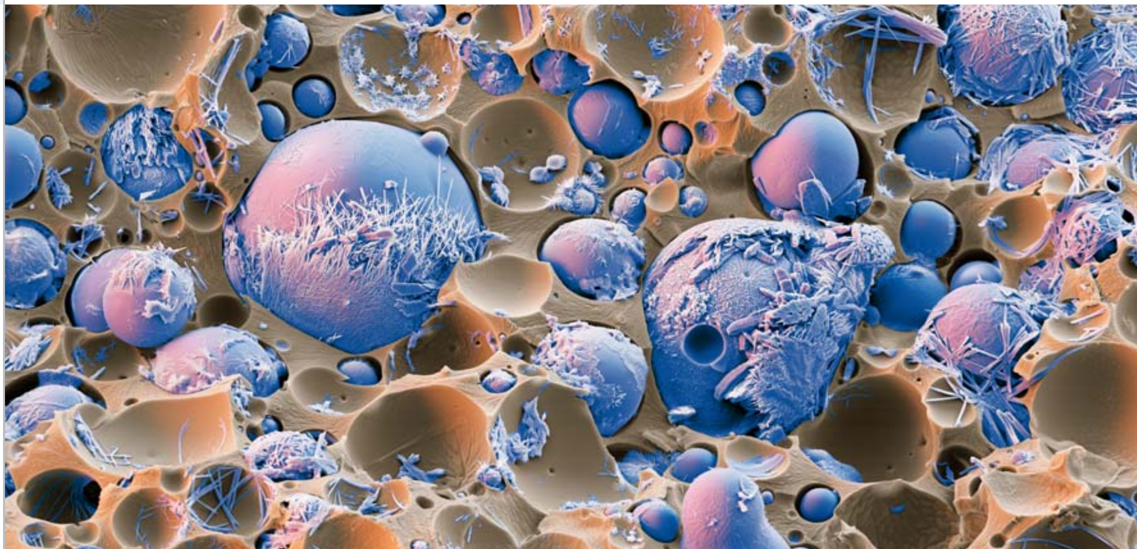


1 NANOTECHNOLOGY BETWEEN MARKETING AND INNOVATION

„Always smaller, always faster“ is the motto of nanotechnology which is deemed a future technology with an enormous range of applications. As a result of the specific properties of nanomaterials, nanotechnology utilises these special properties to improve products. New findings in basic research have already been implemented in practice and respective products have established themselves on the market. Nanotechnology is deemed a key technology that will be an essential factor in the future competitiveness of important branches in industry (including the construction chemicals industry). This also explains the rapid increase in the number and reputation of companies that focus on nanotechnology. At present, Germany has taken the leading role in Europe.

It would be very difficult, however, to describe the nanoproducts that are available on the market. Since uniform terms have not yet been established, the general public is not always able to conclude what type of product is concerned from the conventional designations and advertisements presently used. With this in mind, Deutsche Bauchemie recommends that products should only be advertised as nanoproducts if they actually have these outstanding properties that were achieved through nano-structured materials or through selectively produced and utilised nano-objects. The objective of this report is to show not only the significance but also the variety of forms of nanotechnology in the field of construction chemical products.

2 DEFINITION OF NANOMATERIALS

When looking at nanomaterials, an important first step in understanding is a generally recognised definition. According to the definition given in „ISO/TS 27687:2008 Nanotechologies – Terminology and Definitions for Nano-objects – nanoparticle, nano-fibre and nanoplate“ issued by the ISO Technical Committee 229 „Nanotechnologies“ which was also adopted as a working definition by the „OECD Organisation for Economic Cooperation and Development“, nanomaterials are understood as either nanostructured materials or so-called nano-objects. Nanoscale is understood as a dimension of approximately 1 nm to 100 nm. Nanostructured materials have an inner nanoscale structure or a nanoscale surface structure.

But the materials themselves are larger. Typical representatives of nano-objects are composites, aggregates and agglomerates.

Nano-objects are materials which are confined in one, two or three dimensions at the nanoscale; typical representatives are nanoplates, nanofibres and nanoparticles. Some examples of nano-objects for our purposes are silica sol (a dispersion of nanoscale silicon dioxide) or the substance class of sheet silicates (phyllosilicates).

In nature, nanostructures are responsible for a variety of colours and resistance to soiling

Nanofoams

3 CONSTRUCTION CHEMICAL PRODUCTS

The group of construction chemical products consists only of preparations/mixtures (products in liquid, paste and powder form) that are produced using a relatively large number of substances and preparations.

Examples of construction chemical products:
Concrete and mortar admixtures
Hydrophobizing agents (silanes, siloxanes)
Modified, mineral mortar systems
Plastic modified bitumen emulsions and bitumen solutions for waterproofing buildings
Reactive resin coatings (EP, PU, acrylates, etc.)
Wood preservatives and fire protection agents

4 NANOTECHNOLOGY IN THE VALUE CHAIN

There are three areas in the value chain of construction chemical products. The raw materials for the products, the ready-to-use products and the result of their application (e.g. coated surfaces, laid tiles). From this it can be concluded that there may be different reasons for the decision to call a product a nanoproduct. According to our understanding today, gold ruby glass can also be designated a nanoproduct because its colour is attributed to colloidal gold.

As in the case of gold ruby glass, nanoscale particles and structure elements are used in modern working materials where they provide new or at least enhanced properties. But it is still difficult to draw the line up to which point you may and can speak of a nanoproduct. It is quite normal to designate a varnish that has been optimised by an additive as a nanoproduct even if the particles are worked into a conventional varnish matrix.

The positive effects and properties achieved through nanotechnology are not always apparent to the consumer because sometimes they have played a role at another point in the value chain. If nanotechnology is used to improve working properties, for example, the system can no longer be distinguished from conventional systems after curing.

Examples from the value chain:	
Raw material	nanoscale silicon dioxide
Product	sealant
Result of application	building element with a scratch resistant coating

5. NANOTECHNOLOGY IN THE CONSTRUCTION CHEMICALS INDUSTRY

The feet of the Tokay Gecko can cling to practically anything: An example in nature for universal adhesion

5.1 Products and Technologies

Nanotechnology in the construction chemicals industry includes the use of nanomaterials and the application of technologies for the production of nanomaterials.
In the field of construction chemical products, the following types of nanoproducts are found:

a. Nanoproducts that do not contain solid nanoparticles but do have or form nanostructures to achieve particular properties. The nanomaterials that have been used in the construction chemicals industry so far have been mainly nanostructured materials or emulsions that contain nanoscale liquid drops. Some examples of this are dried paints with nanostructured surfaces and micro-emulsions (internal structures).

b. Nanoproducts selectively produced by using nanoparticles to achieve specific new product properties. In newer developments, selectively produced nanoparticles are used, e.g. special photocatalytic concrete (with nanoscale titanium dioxide).

But, of course, there are also conventional products that were not purposely developed as nanoproducts but may contain nanoscale particles (e.g. loam render).

5.2 Nanoanalytics to Optimise Products

Nanoanalytic methods can be used to follow the formation of nanoscale objects or structures during the development and production process. Examples of nanoanalytics in the construction chemical area are modern microscopy methods (electron microscopy, atomic force microscopy).

Specially mentioned here are product developments, the special properties of which are based on chemical or physical effects in the nanometre range which can only be produced with the aid of modern analytical techniques. In the case of nano-optimised materials, you could designate every type of cement binder as a nanostructured material in the widest sense (strength through the formation of crystalline structures on a nanometre scale). Additional modern variations are, e.g. ultra high performance concrete (UHPC) and polymer modified, high performance mortar (flexible cements, repair mortars).

5.3 Examples of Nanotechnology in the Construction Chemicals Industry

Findings in nanotechnology are selectively implemented in the formulations and manufacturing processes of construction chemical products to optimise their performance parameters and properties. In the following you will find several examples for the utilisation of nanotechnology in the construction chemicals industry.

Optimising workability
Nanoscale additives influence the rheology of formable or flowing capable construction materials. For example, they optimise the flow behaviour of single and multi-component liquid resins and thus the workability of the products. Coating resins flow by themselves on horizontal surfaces in a defined layer thickness and cure into optically pleasing surfaces. Nanoscale additives can lend other construction products a paste to stable consistence. In the uncured state, these mortars and resin mixtures can be shaped in exactly fitting forms.

Improved Durability

Nanotechnology can also lead to improved properties in the cured state after the product has been applied. For example, through the formation of nanostructures or through the use of nanomaterials, resistance to frost and de-icing salt and the strength of cement bound construction elements can be increased. Both these properties have a positive effect on the durability of the structure.

Improved surface properties of coatings

The most well-known nano-effect is found in the area of surface technology. Because of nanostructured surfaces, coatings, for example, can be made highly scratch resistant, extremely durable and even clean themselves. The water repelling effect of nanostructured surfaces is the most well-known. This effect is based on the combination of hydrophobicity and micro-structurization that was copied from the surface of the lotus leaf. Drops of water run off the lotus leaf, taking particles of soil with them. This is what keeps the lotus leaf free of dust and dirt (the „lotus effect").

Shelf-life and pot-life of construction chemical products

The mode of action of nanoscale structures or nanoscale additives is not always as obvious as with the lotus effect. For example, it is thanks to nanotechnological effects that construction chemical products can be stored for longer periods. The example of water emulsified synthetic resins readily shows this property. Since the reactive ingredients form a micellar structure in the liquid phase, the resin components remain workable over a long period. This also increases the pot-life of the product which allows it to be worked properly at the building site. Because of this, the content of solvents and other active chemical ingredients in formulations can be reduced and, in some cases, it is even possible to dispense with them completely.

Biocides and the catalytic action of construction chemical products

Nanostructured silver in wall paints prevents the growth of micro-organisms. Through the fine distribution of silver particles, sufficient quantities of silver ions are available. When the silver ions come in contact with germs, they block the enzymes that transport nutrients and prevent the growth of the germ.

Photocatalytic active facade paints with metal oxides in the nanostructured surfaces of wall paints destroy pollutants in the air. That is how coatings and other building materials used in indoor as well as outdoor areas contribute to keeping the air clean.

Tunnel with nano-coated guard rails on the side to reduce their tendency to soil and make them easier to clean

5.4 Nanotechnology in the Life Cycle of Construction Chemical Products

In principle, construction chemical products are divided into paste/liquid and powder form products.

5.4.1 Paste/Liquid Construction Chemical Products

Typical paste/liquid construction chemical products are, e.g. primers, coatings, paints, adhesives, reactive foams, sealing compounds and agents used to protect buildings.

Production

The production of all paste/liquid construction chemical products is carried out in the liquid phase.

The most various raw materials (emulsions, dispersions, polymer solutions) are used as initial materials. These are mixed with fillers, pigments and additives and adjusted to the required application properties.

Nanoscale structures are found not only in the raw materials but can also be selectively created in the final product. The products are then filled into tightly closed containers for storage or for use at the building site.

Working

Liquid or paste form construction products are applied by pouring, filling, brushing or by similar means of application. Nanoparticles are not released during application. If chemical construction products are sprayed, the fineness of the sprayed mist depends on the spraying technique used. The conditions for use and measures for managing risk given in the Safety Data Sheets should be observed.

Utilisation

After drying, the physical and/or chemical properties of the binders have changed. They have either formed a film, cross-linked, cured or set. This can take place by purely physical processes (drying, diffusion and adhesion) or in conjunction with the formation of chemical bonds. The ingredients of the construction chemical product are tightly bound into the working material matrix. After the reaction is concluded, there are no free nanoparticles.

Subsequent mechanical processing, recycling and disposal

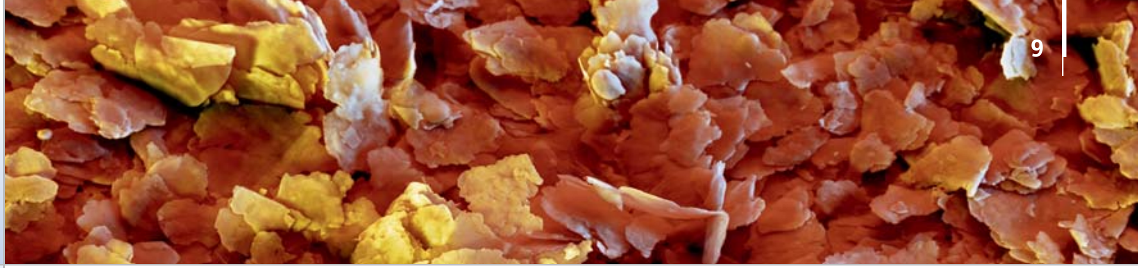
When subsequently processed mechanically or recycled, no nanoparticles from the products are released for the applications described above. All substances that have been added are tightly bound in the binder matrix. Even selectively used nanoparticles are not released as such.

Cured products can be disposed of as normal building rubble.

5.4.2 Construction Chemical Products in Powder Form

Typical construction chemical products in powder form are especially dry mix mortar.

Scanning electron microscopical photographs of agglomerated, cubic nanoparticles



Production
The raw materials used in dry mix mortars are predominately cements, lime and/or gypsum as binders, powdered limestone, sand, micro-silica or pyrogenic silicic acid as fillers and dispersible polymer powder as well as other polymers as functional additives. A few dry mix mortars also contain pigments. For the production of dry mix mortars, the raw materials in powder form named above are fed from silos in a closed system through metering equipment into a mixing aggregate and mixed dry. The finished product is filled through metering and filling equipment into silos, bags or other containers. The powder-form raw materials typically have a mean particle size in the micrometer to millimetre range. Since the sizes of the particles follow a distribution curve, there can be very small quantities of powder in the lower micrometer or in the upper nanometre range.

During the production of dry mix mortars, work place limit values (dust limit values) can be maintained through utilisation of closed plants and, if required, by exhaust systems.

Working
When using dry mix mortars, particularly when mixing the mixed powder with water and when opening the powder bags, there may be exposure to dust. Work place limit values can be observed by taking suitable measures and using protective devices (e.g. ventilation). If values that exceed the work place limit occur, workers must wear respiratory protection. It is technically possible to produce low-dust, dry mix mortars in which dust formation is reduced by up to 90 %.

Minimisation of exposure to dust when working conventional dry mix mortar manually has been the subject of investigations for years. Decades of experience with the products have shown that they can be worked safely at all times.

However, the selective use of nanoscale particles in dry mix mortars would have to be investigated in each case in regard to the exposure to be expected and eventual risk. If necessary, personal protective measures that comply with the „VCI Guidelines for Handling and Use of Nanomaterials at the Workplace" (section III, 4) would have to be taken.

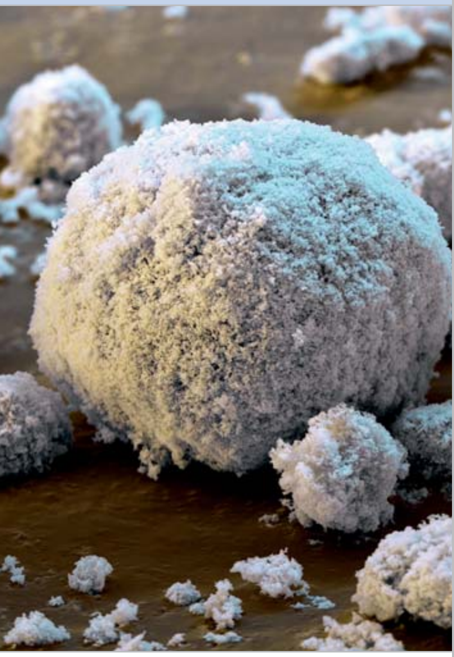
After mixing, i.e. in the form of a paste-like, fresh mortar, as well as after setting, there will not be any emission of dust.

Utilisation
After setting, the form of the binders has changed chemically into a solid structure. Set cement, for example, is in the form of calcium silicate hydrates that form a spacious, three-dimensional network. After setting, all of the fillers, additives, etc. are either tightly bound in the mineral binder matrix or they have undergone a chemical reaction during setting and the reaction products have, in turn, been bound into the binder matrix. Thus, powder form or dusting materials are no longer present and consequently exposure is not possible.

Subsequent mechanical processing/recycling
Mortars that have hardened after setting have properties that are similar to natural or synthetic stone or building materials. All of the substances that have been added are tightly bound into the binder matrix. Even selectively used nanoparticles can no longer be released as such. Instead, depending on the type of mechanical processing, non-specific dust fractions form.

Hardened mortar can be disposed of as normal building rubble.

6 OUTLOOK

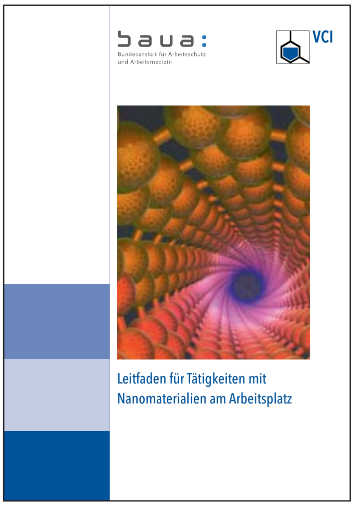


The use of nanotechnology offers many possibilities for developing products with outstanding properties. In the future, this technology will be increasingly used for the development of construction chemical products to further enhance their performance and to expand application areas. As when using conventional raw materials, manufacturers will not only pay attention to technical properties when developing products using nanotechnology but, to the same degree, will also make sure that neither employees in the production plant nor workers at the building site, do-it-yourself consumers or the environment will be harmed by the products.

In the on-going discussion on nanotechnology, Deutsche Bauchemie will endeavour to make sure that uniform definitions are established throughout Europe to ensure more clarity and transparency for all concerned. To build trust in this pioneering technology, the companies that use these products in the building trade and construction industry as well as private consumers must be given clarity based on unambiguous definitions so that they know what type of nanoproducts they are dealing with.

7 GUIDE

Deutsche Bauchemie recommends the application and observance of the following guidelines which can be downloaded at: http://www.vci.de.



Implementing Responsible Care® for a Responsible Production and Use of Nanomaterials.

Requirements of the REACH Regulation on Substances which are Manufactured or Imported also as Nanomaterials.

Guidance for a Tiered Gathering of Hazard Information for the Risk Assessment of nanomaterials.

Guidance for Handling and Use of Nanomaterials at the Workplace.

Guidance for the Passing on of Information along the Supply Chain in the Handling of nanomaterials via Safety Data Sheets.

The „Strategy Paper of the German Chemical Industry on the Standardisation of Nanomaterials" explains which aspects should have priority for the international standardisation of Nanomaterials.

As far as the chemical industry is concerned, these should also include terminology and measuring technology. An overview of the most important research projects on safety and environmental aspects of nanomaterials is given in the „Roadmap for Safety Research on Nanomaterials" and the paper, „Environmental Aspects of Nanomaterials".

8 VALID LAWS AND REGULATIONS

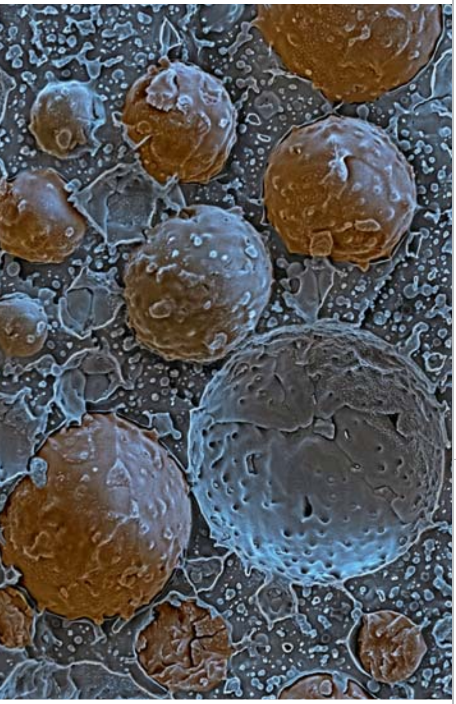
The rules given below taken from the general German law on chemicals and the specific laws on construction products formulate requirements and protection goals that also include eventual risks attributed to nanomaterials in construction chemical products.

a. Production and Marketing of Preparations
REACH Regulation EC No. 1907/2006
CLP Regulation EC No. 1272/2008
EC Dangerous Preparation Directive 1999/45/EG
EC Dangerous Substances Directive 67/548/EWG
EC Restriction Directive 76/769/EC (until June 1, 2009)
German Chemicals Law
German Chemicals Prohibition Ordinance
EC Decopaint Directive 2004/42/EG
German Solvent Based Paint and Varnish Ordinance
EC Biocidal Products Directive 98/8/EG
German Law for the implementation of directive 98/8/EG

b. Industrial Processing
EC Council Directive on Health and Safety at Work 89/391/EEC
EC Agents Directive 98/24/EG
German Law on Occupational Safety
German Ordinance on Hazardous Substances

c. Utilisation Phase
EC Construction Products Directive 89/106/EG
German Law on Construction Products
German State Building Regulations (LBOs)

d. Recycling and Disposal
German Commercial and Industrial Waste Management Act (KrW-/AbfG)



EPILOGUE

This State-of-the-Art Report „Nanotechnology in the Construction Chemicals Industry" which was prepared by Project Group 6.7 „Nanotechnology in the Construction Chemicals Industry" is intended as a source of information for member companies and qualified members of industry.

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