Attention please

Safety Assessment of Cleaning and Maintenance Products, which contain Nanomaterials and/or Form Nano-Layers

This Safety Assessment of Cleaning and Maintenance Products, which contain Nanomaterials and/or Form Nano-Layers is no release from the obligation to comply with legal regulations. This Safety Assessment of Cleaning and Maintenance Products, which contain Nanomaterials and/or Form Nano-Layers was developed with the utmost care. However, the authors and IKW do not accept any liability for the correctness of information, instructions and advice given in this Recommendation and they do not accept any liability for misprints. For these reasons, no claims can be made against the authors and/or IKW in respect of potential consequences. This does not apply if damage was caused intentionally or by gross negligence by IKW or by parties assisting IKW.

Safety Assessment of Cleaning and Maintenance Products, which contain Nanomaterials and/or Form Nano-Layers

Status: April 25, 2008

Introduction

The »Recommendation for the Safety Assessment of Detergents, Cleaning and Maintenance Products« (1) describes general steps to be observed in the development and marketing of safe products of these types. The present paper highlights essential points for safety assessments of cleaning and maintenance products, which contain nanomaterials and/or form nano-layers. This paper was elaborated by the IKW expert committee »Cleaning and Maintenance Products«. The committee consists of experts from various competing manufacturers. This ensures the neutrality of the committee.

■ General description

Some cleaning and maintenance products for private consumers (e.g. certain products for the cleaning and/or care of floorings, vehicles and surfaces of glass or leather) are advertised with claims such as e.g. »*nano effect*« (2). These products are intended to endow surfaces with new, positive properties (e.g. water or dirt repellent or anti-fogging). Furthermore, the performance of cleaning products can be improved; this makes cleaning easier for users.
Most products are applied onto surfaces in the form of aqueous solutions. They are sprayed on or applied with the help of sponges or cleaning cloths.

■ Definitions

Nanomaterials are understood to be either *nano-objects* or *nanostructured materials* (3). Nano-objects are materials which are confined in one, two or three dimensions at the nanoscale (approximately 1 – 100 nm). Nano-objects with three dimensions at the nanoscale are *nanoparticles*. Nanostructured materials have an internal structure at the nanoscale. Typical examples are *aggregates* and *agglomerates* of nano-objects. Aggregates are assemblies of primary nanoparticles, e.g. in the form of chains or clusters. Agglomerates are assemblies of aggregates (4).
Usually, highly sophisticated chemical and physical processes are needed to manufacture nanomaterials as nanoparticles in isolated form. However, in most products currently manufactured commercially in larger volumes, nanoparticles do not come as individual particles but as aggregates and agglomerates of various particles. Without major energy input, a release of nanoparticles from these aggregates and agglomerates is often not possible (5).
Nano-layers have a thickness of under 100 nanometres (nm), but they have much larger diameters in both other directions. Depending on product type, nano-layers on surfaces can form either *with or without* the use of nanomaterials.
Nanotechnology is a collective term for a wide range of technologies, which are dedicated to the research, processing, production and use of materials and structures in sizes of less than 100 nm. In some cleaning and maintenance products for private consumers, nanotechnology serves to systematically use the effects of nanomaterials and/or nano-layers.

■ Active substances in cleaning and maintenance products, which contain nanomaterials and/or form nano-layers

In the following, the term »active substances« is used for those ingredients of cleaning and maintenance products, to which the »nano effect« is attributable. For example, the below listed active substances are used:

- Aluminium oxide, silicon dioxide and titanium dioxide as dispersions
- Fluorocarbon resins
- Nanoscale wax dispersions
- Silanes

■ General characterisation of ingredients

All ingredients of cleaning and maintenance products are characterised by means of their trade name, manufactur-

er name, CAS and EC nos., classification and labelling (cp. 1); where necessary, details are given on further fields of application and descriptions of their occurrence in nature.

Extra safety for formulations, which contain nanomaterials and/or form nano-layers

The German Chemical Industry Association (Verband der Chemischen Industrie e.V. – VCI) published »Guidance for the Passing on of Information along the Supply Chain in the Handling of Nanomaterials via Safety Data Sheets« (5).
In particular, the following must be ensured for safety data sheets (SDSs) of nanomaterials:

- Under heading 3 (Composition/information on ingredients) it must be stated whether – and if so, in what way – the surface of the concerned substance has been modified;
- The details given under heading 2 (Hazards identification), heading 8 (Exposure controls/personal protection), heading 9 (physical and chemical properties), heading 11 (Toxicological information) and heading 12 (Ecological information)
  - must refer expressly to the nanomaterial and not to the same substance in larger dimensions;
  - for surface-modified nanomaterials, the above-mentioned details must refer to these materials and not to non-surface-modified materials.

Due to their versatility, an individual assessment of nanomaterials used as inputs is necessary – with a special view to the intended use in households (e.g. spraying or application in aqueous solutions). Therefore, in particular for those formulations, which contain nanomaterials and/or form nano-layers, the recommendation is given to additionally answer the following questions within safety assessments. If one of these questions is answered in the affirmative, it is recommended to carry out the subsequently described steps:

1. **Is a raw material used, which contains nanoparticles, aggregates or agglomerates in sizes of < 100 nm?**

   If the answer is yes, assessments of risks of the active substance and of the preparation become necessary:
   - due to chemical properties (where applicable, including limit values of TRGS 900 or MAK values [TRGS = Technical Rules for Dangerous Substances of the German Hazardous Substances Ordinance; MAK = Maximum Workplace Concentrations], natural uptake quantity)
   - due to nano-dimensions of the active substance (relevant for occupational health and safety: Inhalation, where applicable also fine dust limit values, consequences of systemic exposure).

2. **Do nanoparticles, aggregates or agglomerates in sizes of < 100 nm form in the formulation or when applying the product?**
   If the answer is yes,
   a) the following types of exposure must be differentiated and estimated, in respect of the formulation:
   - inhalation, during application
   - inhalation, during subsequent post-application phase
   - dermal exposure
   - oral exposure

   b) the following risk assessments must be carried out, in respect of the formulation:
   - risk through uptake by inhalation
   - risk through dermal uptake
   - risk through oral uptake

3. **Can nanoparticles be released into the environment in the manufacture or in the intended use of the cleaning or maintenance product?**
   If the answer is yes, an ecological assessment (risk assessment) of the formulation is carried out – considering the hazard potential and by means of an exposure estimation:
   - taking into account the chemical properties of the non-nanoscale material of the same chemical composition (where applicable, in comparison with the concentration occurring in nature and/or the release from other sources)
   - taking into account the nano-dimensions of the active substances

4. **Can nanoparticles be taken up by the human body in the manufacture or in the intended use of the cleaning or maintenance product?**
   If the answer is yes, the following points must be taken into account:

   Uptake by inhalation
   According to the present state of science, inhalation is the most likely pathway for the uptake in nanoparticles in the human body, where spray applications are concerned. Therefore, it is imperative – e.g. when using nanomaterials in sprays – to measure and to assess the droplet size distribution in the spray mist.

   Dermal uptake
   According to currently available scientific findings, healthy non-injured skin constitutes a sufficient barrier against the uptake of titanium dioxide nanoparticles in the human body. In individual cases, it must be examined whether e.g. findings from the NANODERM Project can be transferred to other settings. (NANODERM = EU-funded project regarding the quality of skin as a barrier to ultrafine particles)

   Oral uptake
   Where oral exposure is possible in the intended or foreseeable use, safety can be determined by means of toxicological data.

Where the risk assessment shows that – in the reasonably foreseeable use of cleaning and maintenance products, which contain nanomaterials and/or form nano-layers – nanomaterials are taken up by humans, the manufacturer of such cleaning and maintenance products must ensure that no damage is caused to the health of consumers.

Activities involving nanomaterials at the workplace

Regarding such activities, the German Federal Institute for Occupational Safety and Health (BAuA) and the German Chemical Industry Association (VCI) jointly published in August 2007 the »Guidance for Handling and Use of Nanomaterials at the Workplace«. This document is available on the internet (http://www.vci.de/default~cmd~shd~docnr~121306~lastDokNr~122306.htm).

Literature

(1) IKW, Sicherheitsbeurteilung von Wasch-, Pflege- und Reinigungsmitteln, SÖFW-Journal 133, 10-2007, Seite 53-69

(2) The syllable »nano« stands for one nanometre, i.e. one billionth of a metre (0.000 000 001 m or 10^{-9} m); the Greek word »nanos« means dwarf.

(3) These terms are used according to the definitions in the draft of the Technical Committee 229 »Nanotechnologies« of the International Organization for Standardization (ISO), which were taken over as working definitions by the Organisation for Economic Co-operation and Development (OECD).

(4) European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC), JACC No. 51 (Synthetic Amorphous Silica), Brussels, September 2006; ISBN 0773-6339 51, p. 24, according to DIN standard 53206.
The report states the following: »*The British Standards Institution has defined the term aggregate as used by DIN 53206 as agglomerate, and agglomerate as aggregate (BSI, 2005). In this report, the German definitions are used*«.

(5) German Chemical Industry Association (Verband der Chemischen Industrie e.V. – VCI), »Guidance for the Passing on of Information along the Supply Chain in the Handling of Nanomaterials via Safety Data Sheets«, status of the English version: 6 March 2008; available on the internet at www.vci.de (under »Nanomaterialien«).

(6) TRGS = Technical Rules for Dangerous Substances of the German Hazardous Substances Ordinance/Technische Regeln für Gefahrstoffe; TRGS 900 (http://www.baua.de/de/Themen-von-A-Z/Gefahrstoffe/TRGS/TRGS-900.html?__nnn=true&__nnn=true)

(7) MAK = Maximum Workplace Concentration, http://www.dfg.de/dfg_im_profil/struktur/gremien/senat/kommission_ausschuesse/senatskommission_pruefung_arbeitsstoffe/

(8) http://www.uni-leipzig.de/~nanoderm/

(9) http://www.vci.de/template_downloads/tmp_VCIInternet/LeitfadenNano_engl_FINAL~DokNr~121306~p~101.pdf

Industrieverband
Körperpflege- und Waschmittel e.V.
(German Cosmetic, Toiletry, Perfumery and Detergent Association)
Referat Wasch-, Pflege- und Reinigungsmittel
(Section Detergents, Cleaning and Maintenance Products)
Mainzer Landstrasse 55
60329 Frankfurt am Main
Germany