REACH-CLP-Biozid Helpdesk

Quick Guide from the German national helpdesk

Characterisation of nanomaterials

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This brochure is intended to provide advice to potential registrants of nanomaterials. The guide is considering the particular situation that nanomaterials are not specifically regulated under REACH at present and there are in consequence no specific dossier requirements. It shall be clarified what information should be included in the registration dossier especially regarding the characterisation of nanomaterials.

REACH-CLP-Biozid Helpdesk

National Helpdesk of the Federal Agencies

Three regulations – one helpdesk

established at the Federal Institute for Occupational Safety and Health (BAuA)

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1. Cover note

Until now the REACH Regulation (EC) No. 1907/2006 does not explicitly address nanomaterials. Indeed specific requirements taking into account the special character of nanomaterials will have to be included into the Regulation in the future. But since nanomaterials are considered to be substances in terms of REACH manufacturers and importers of nanomaterials have to fulfil their REACH obligations already today.

This practical guide is a first attempt to give hands-on advice to registrants who are preparing a registration dossier until concrete assistance is available in one of the ECHA guidance documents.

The guide focuses on the presentation of in-house data as a basis for the characterisation of a nanomaterial. However, if the in-house data are not considered to be of sufficient quality or if there are data gaps it is necessary to generate new data, as it is needed for any other substances under REACH.

2. Background

In October 2011 a Commission recommendation on the definition of nanomaterials has been published.[1] Although this definition has not yet been implemented in REACH registrants should take it into account when preparing for the next registration deadline in 2013 and for updating registrations.

[1] Recommendation of the Commission of the 18th of October 2011 on the definition of nanomaterials please refer to: http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2011:275:0038:0040:EN:PDF

Essential statement of the recommendation:

0. '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.

   In specific cases and where warranted by concerns for the environment, health, safety or competitiveness the number size distribution threshold of 50 % may be replaced by a threshold between 1 and 50 %.

1. By derogation from point 2, fullerenes, graphene flakes and single wall carbon nanotubes with one or more external dimensions below 1 nm should be considered as nanomaterials.
2. For the purposes of point 2, 'particle', 'agglomerate' and 'aggregate' are defined as follows:
   a) 'particle' means a minute piece of matter with defined physical boundaries;
   b) 'agglomerate' means a collection of weakly bound particles or aggregates where the resulting external surface area is similar to the sum of the surface areas of the individual components;
   c) 'aggregate' means a particle comprising of strongly bound or fused particles.

Already for the registration deadline in 2010 dossiers containing information on nanomaterials were submitted to ECHA. However, an evaluation of these dossiers[2] showed that, there is no consistency in presenting nanomaterial specific information, although this could in many cases easily be done by using already available in-house data and the structural conditions in IUCLID. However, for the registration deadline in 2010 manufacturers or importers of substances which may be considered to be nanomaterials on the basis of parameters like particle size or surface dimension in fact did not know whether their substances may be covered by a future nano definition or not. In view of the registration deadline in 2013 the situation has been improved insofar as the recommendation of the Commission offers a preliminary standard to companies to decide whether they manufacture or import a nano substance or not.

The basic substance information for the identification of substances is given in annex VI of REACH, e.g. spectral data like UV/VIS, IR, NMR, purity, impurities etc. However, for this

[2] Nano Support Project (http://ec.europa.eu/environment/chemicals/nanotech/)

type of information no nano specific methods are required. But, in order to characterise nanomaterials this information is of limited value.

Therefore, in this practical guide the awareness of manufacturers and importers of nanomaterials shall be raised with respect to the upcoming registration deadline 2013 and at the same time give hands-on advice for an appropriate characterisation of the materials as a starting point for the description of possible risks and the determination of risk management measures. It is not the scope of this guidance to go into further detail in view of the demands according to annex VI of REACH.[3] Chapter 1 of this guide is thus dealing with the morphologic characterisation of nanomaterials and available analytical standard methods.
In chapter 2 advice is given which and respectively where nano specific information should be provided/presented in the registration dossier.

Nevertheless, this guidance cannot replace the necessary adaptation of the REACH legislation for nanomaterials.

[3] Additional guidance documents are summarized in Annex I of this guide

3. Morphologic characterisation of nanomaterials

With the definition recommendation of the Commission in place, the registrant should provide information on whether the registered substance is a nanomaterial. However, to be able to take into account substance specific properties it is important to have well characterised substances. This applies to nano as well as to bulk materials.
Compared to bulk materials nanomaterials may exhibit changed or additional properties, which are based e.g. on their increased surface to volume ratio or quantum physical effects.
In order to cope with these modified properties it seems reasonable to characterise nanomaterials by the following parameters:

- shape, size of primary particles, aspect ratio
- degree of aggregation and agglomeration
- size distribution
- specific surface
- surface chemistry (e.g. surface charge, functional groups, catalytic activity)
- crystal structure
- surface modification (chemical composition, type of modification)

It is very likely that much of this information is generated by the manufacturer by default during the development phase of the nanomaterial or during the production process e.g. for quality management purposes and consequently many demands can be covered by already available in-house data. This is simply due to the fact that a manufacturer or importer needs to know whether the material was synthesised or imported with the desired feature. It is in the own interest of every manufacturer or importer of a nanomaterial to have an answer to the question how a desired feature can be established before the material is synthesised or imported independently from the REACH requirements. Additionally, he should know the relevant tools for proving that the desired features are achieved. For example, if it is required to have nano particles of a defined size, it is mandatory to choose a suitable analytical method.
In case the in-house data indicate any justified concern or any data gap it is in the responsibility of the registrant to either generate additional data to show that there is

actually no concern or he will have to give advice against a specific use of the nanomaterial.
This is a general obligation of REACH and therefore valid for bulk as well as for nanomaterials.

Next to using available data for the generation of the registration dossiers the understanding of nanomaterials, their characteristics and resulting properties, can be increased significantly by describing the idea on which their design is based. To know for which use and under which conditions a material was developed not only helps to understand the characteristics of a substance but also to make a statement regarding any potential risks. The following questions could help to further characterize the material:

- What is the intended use of the material?
- What specific properties of the nanomaterial are needed for that use?
- Are specific surface properties intended like hydrophobic or hydrophilic properties, surface charges etc.?
- Are there functional groups?
- Is the aim an amorphous or a crystalline nanomaterial?
- Should specific forms be manufactured like fibres or spherical particles?
- Is the aim the production of primary particles or aggregates/agglomerates?
- Is there information about differences concerning the properties of nano and bulk material?
  If yes, what are the differences?

This information is very valuable with respect to the obligations set by the REACH Regulation.

Until now, there are no standardized analytical methods which can be used for the characterisation of nanomaterials. Furthermore, it can be concluded that there is no single method which can be used for every type of nanomaterial. Based on e.g. its shape and / or surface properties the set of analytical methods will have to be chosen on a case by case basis. Moreover, a characterizer can be described by different methods. Since until now no standardized methods are available for nanomaterials, every scientifically suitable method can be used. Therefore, it is important not only to present a measured value for an endpoint, but also to give detailed information on the applied method, the sample preparation and any adaptations which became necessary to conduct the test. An experimental result can only adequately be evaluated if it is embedded in a robust

description of the used method. An **exemplary list** of methods is given in Annex II of this document.

Finally, it should be pointed out that next to the usage of in-house data for the characterisation of a nanomaterial all other available information should also be incorporated into the registration dossier in association to the corresponding nano form. This concerns available information regarding e.g. physico-chemical, eco- or toxicological properties.

4. Required nano specific information and where to present it

4.1 Characterisation of nanomaterials

As indicated above the following characterisers have been identified to describe nanomaterials properly. In this context robust study summaries of available in-house data could be used for the characterisation.

The information for the characterisation of nanomaterials should be presented in the IUCLID file.

Where to provide information that the registered substance or parts thereof are considered to be a nanomaterial in the IUCLID	1.1 Type of substance and 1.2 Constituents - Remark
	2.1 GHS, state/form of the substance
	4.1 Appearance, Result and discussion - form

Characterisation	**Where to provide the information in IUCLID**
shape, size of primary particles, aspect ratio	1.4 Analytical information and 4.1 Appearance
aggregation and agglomeration	1.4 Analytical information
size distribution	4.5 Particle size distribution
specific surface	4.23 Additional physico-chemical information
surface activity	4.23 Additional physico-chemical information
surface charge (zeta-potential)	4.23 Additional physico-chemical information
crystal structure and	1.4 Analytical information
structure modification	1.4 Analytical information

Next to this, a brief description about the design and the desired feature of the nanomaterial could be given in the dossier, e.g. in chapter 3.1 Technical process. Here also information about surface properties could be described, if present at all.

4.2 Physico-chemical properties

Physico-chemical properties are included in Annex VII of the REACH Regulation and are already part of IUCLID (Section 4). Even though these information requirements are not set explicitly for nanomaterials they can – in many cases – be used for a proper description of the physico-chemical properties of nanomaterials.

However, since bulk and nanomaterials can be covered within one registration dossier it is likely that information on physico-chemical properties of both forms are available. In this case it is recommended to create a separate robust study summary for each form. To avoid any confusion it is important to clearly indicate within each robust study summary to which form of a substance it applies.
On the other hand, if one single robust study summary is applicable for all forms of a substance (bulk and nano), a brief justification of its applicability for all forms should be given. An example for this is the determination of the boiling point. The test sample will be liquefied during the measurement which, in case of a nanomaterial as test sample, would lead to a loss of the nanospecificity. Therefore a single endpoint study summary is valid for both the bulk and the nanomaterial (see table below).
In case the registration dossier is covering a nanomaterial only, it is a REACH requirement -even today - to provide information for the endpoints given in Annex VII – XI of the regulation. Thus, coming back to the example above, if information on the boiling point is available for the bulk material as test sample, this information could be used in the registration dossier of the nanomaterial. However, it should be clearly indicated in the robust study summary that the bulk material was used as test material. Next to this, if it is e.g. scientifically not appropriate or justified to conduct a study a waiving argument should be provided.

In the table below the physico-chemical properties requested under REACH are listed. Column 2 of the table lists problems which might occur during adaptation to nanomaterials and also general remarks.

Standard information requirement acc. to Regulation (EC) No 440/2008	**Problems, which might occur during adaptation / general remarks**
7.1. State of the substance at 20°C and 101,3 kPa	
7.2. Melting/freezing point	The melting point of nanomaterials is influenced by the particle size. Based on a case by case decision it may be acceptable to use the value determined for the bulk material.
7.3. Boiling point	Not required if information on bulk material is available. This is due to the fact that the liquefied material, which itself is no longer a nanomaterial, will be transferred to the gaseous phase.
7.4. Relative density	
Standard information requirement acc. to Regulation (EC) No 440/2008	**Problems, which might occur during adaptation / general remarks**
7.5. Vapour pressure	Normally not required, if e.g.: • the substances have a very high melting and boiling point • the liquefied material, which itself is no longer a nanomaterial, will be vaporized (dynamic method)
7.6. Surface tension	Only required if the water solubility is sufficiently high. If information for the bulk material is available this value is also valid for nanomaterials. This is due to the fact that the test material will be dissolved for the determination of the surface tension and is therefore no longer a nanomaterial.
7.7. Water solubility	
7.8. Partition coefficient n-octanol/water	Only required if the water solubility is sufficiently high. The determined value for the bulk material is also valid for nanomaterials. This is due to the fact that the test material will be dissolved for the determination of the partition coefficient and is therefore no longer a nanomaterial.
Technical characteristics: • dispersibility /-stability • dustability	
7.9. Flash-point	Methods should be adapted (e.g. to the test material quantities available)
7.10. Flammability	
7.11. Explosive properties	
7.12. Self-ignition temperature	
7.13. Oxidising properties	

In general it is advisable to consider some principle issues before conducting a test:

- Is the result obtained by using a nanomaterial as test item likely to differ from the one obtained for the bulk material?
- Does the sample need to be liquefied for conducting the test? If the answer is yes, the value obtained for the bulk material might be acceptable for the nanomaterial, too.
- Is the nanomaterial in the test sample a newly synthesized material? How long has it been stored? Has the surface been modified by ageing processes? Is it aggregated or agglomerated?
- Is the obtained result therefore representative for the nanomaterial in general?

In case those considerations were made it is recommended to also communicate them in the registration dossier.

4.3 Description of the use of nanomaterials and information to be presented in the chemical safety report (CSR)

It is a general objective of REACH to improve the protection of human health and the environment. Therefore, manufacturers and importers have to describe how a substance can be used safely. Furthermore, they must communicate the risk management and protective measures within the supply chain. This of course also applies to nanomaterials.

Therefore, the following questions should be addressed in the registration dossier:

- for which use was the nanomaterial designed?
- which conditions of use and
- which exposure scenarios have to be taken into account?

In order to answer these questions the procedure established for bulk materials could be used. But the specific characteristics of the nano forms should be taken into account and be described transparently.

5. Final note

This practical guide applies until concrete assistance is available in one of the ECHA guidance documents. However, even if nanomaterials are not yet implemented in REACH the registrant is obliged to guarantee a safe use and give appropriate risk management measures for the nanomaterial he is manufacturing or importing.

Annex I

Additional guidance documents:

- Guidance on Registration, ECHA (May 2012)
  http://echa.europa.eu/documents/10162/13632/registration_en.pdf
- Recommendations for nanomaterials as appendices to Chapter R7a, R7b, R7c, R8, R10 and R14, ECHA
  Guidance on information requirements and chemical safety assessment.
  Appendix R7-1 *Recommendations* for *nanomaterials* applicable to: Chapter R7a Endpoint specific guidance Draft
- Final reports of RIP-oN 1, 2 and 3, DG ENV
  http://ec.europa.eu/environment/chemicals/nanotech/
- IUCLID user manual, ECHA
  http://iuclid.eu/index.php?fuseaction=home.documentation
  The manual will be updated in August 2012.

Annex II

Exemplary list of available analytical methods for the determination of nanomaterials

Characterisation	**Analytical method (exemplary)**
shape, size of primary particles, aspect ratio	Atomic Force Microscopy (AFM) Transmission Electron Microscopy (TEM) / Raster Electron Mikroscopy (REM) Small Angle X-Ray Scattering (SAXS) UV-VIS Spectroscopy Raman-Spectroscopy
aggregation and agglomeration	Dynamic Light Scattering (DLS) Brunauer-Emmett-Teller-Method (BET) Transmission Electron Microscopy (TEM) Small-Angle Neutron Scattering (SANS)
size distribution	Dynamic Light Scattering (DLS) Scanning Mobility Particle Sizer (SMPS) Field Flow Fractionation (FFF) Small Angle X-Ray Scattering (SAXS) Nanoparticle Tracking Analysis (NTA) Ultra Centrifugation
specific surface	Brunauer-Emmett-Teller-Method (BET) NMR Small Angle X-Ray Scattering (SAXS) Ultra Centrifugation
surface activity	Auger-Elektronen-Spectroscopy Ultraviolet Photoelectron Spectroscopy (UPS) FT-IR Chemisorption
surface charge (zeta-potential)	Isoelectric Point (IEP) Particle charge sizer (PCS) Dynamic Light Scattering (DLS) Electrophoresis
crystal structure and	X-Ray Diffraction (XRD)
Surface modification	TEM+FT

If you have any questions concerning REACH, CLP or Biocides, do not hesitate to contact us by phone from Monday through Thursday between 8 a.m. and 4.30 p.m, on Friday between 8 a.m. and 1.00 p.m.

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