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Assessment of the results of the NanoDefine project with regard to the concrete use of (real life) pigments and fillers and other comparable particulate substances

VdMi was partner in the NanoDefine project especially for the dissemination of the results of the project. VCI has intensively accompanied the project following a long track record of input and feedback to the question how to effectively implement the EC recommendation for the definition of nanomaterial [2011/696/EU].[1] VdMi and VCI acknowledge the progress made by all project partners, particularly the elaborateness of the two-tier approach to determine whether a given material is, or is not, a nanomaterial. The outcome of the NanoDefine Project shows that for most fillers and pigments and other comparable particulate substances, nanostatus assessment and conclusive determination is feasible only with the most labour and cost intensive methods of the second tier. For all other nanomaterials this also is at least a severe hindrance in assessing the regulatory classification with the only exemption of nanostructured materials.

Introduction

- NanoDefine objectives and overall results

The EC recommendation for the definition of nanomaterial [2011/696/EU] requires the quantitative size determination of constituent particles in materials down to 1 nm. Accordingly, a material is a nanomaterial if 50 % or more of the particles in the number size distribution are in the size range 1-100 nm. The fact that materials meeting the criteria of this definition already exist in many industrial and consumer products makes the development of measurement methods that reliably identify, characterize and quantify nanomaterials as such, and when embedded in different matrices especially challenging.
The fact that nanomaterials, that already exist in many industrial and consumer products, have to be measured to meet the requirements of the EC recommendation and require the development of adequate measurement methods to regulatory reliably identify, characterize and quantify their occurrence as substance and in various matrices according to the EC recommendation.

The EU FP7 NanoDefine project [www.nanodefine.eu] has addressed this challenges by developing a robust, readily implementable and cost-effective (but not necessarily low-cost) measurement strategy to obtain quantitative particle size distributions and to distinguish between nano and non-nano materials according to the EU commission recommendation on the definition. Based on a comprehensive evaluation of existing methodologies and intra- and inter-lab comparisons, validated measurement methods and instrument calibration procedures have been established to reliably measure the size of particles within 1-100 nm, including information on shape and chemical composition in industrial materials. Case studies show the potential applicability for various sectors. Progress has also been made in analysing nanoparticles in complex matrices, e.g. consumer products. Another positive result of the project is that progress has been made to bring many supporting stakeholders on a same level of knowledge which might lead to a much better communication between authorities and industry and institutes. The dissemination of the results of the project to NGOs and within industry will be an additional task for the involved partners of authorities and industry.

[1] Also refer to “A tiered measurement strategy to implement the EC recommendation for a nanomaterial definition” by VCI in cooperation with VdMi and Eurocolour, December 2015

- Nano EU Definition and implications for pigments and fillers and other comparable particulate substances:

Pigments are used for the colouring and surface structuring of nearly all products found in our daily life. Fillers, while having a similar wide range of applications, are used as substitutes for cost intensive materials that optimize the performance of cost intensive materials or to improve the mechanical, electrical and handling properties of finished products. They often consist of small particles which in dependence of the solvent are in many cases insoluble (i.e. solubility smaller than 0.1 mg/l) and firmly bound in the application medium (e. g. paints, coatings and plastics). This also counts for other substances that are manufactured in the nanoscale.

Applying the EU Commission Recommendation on the Definition of Nanomaterial of 18 October 2011 [2], most of the traditional pigments and fillers and other comparable particulate substances should be called nanomaterials per definition. Due to the inclusion of aggregates and agglomerates.

- Definition and measuring methods (current status)

In a project together with the Joint Research Centre (JRC), the European association Eurocolour (representing the European pigments, dyes and fillers industry) has comprehensively taken stock of reality, as regards the use of existing measuring methods for pigments and fillers available in practice. The results of the project are summarized in the *JRC Technical Reports „Basic comparison of particle size distribution measurements of pigments and fillers using commonly available industrial methods".* [3]

The major results of the JRC project are:

- Expertise and a sound knowledge of the material(s) 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.
- No single method can be recommended as a standalone solution for identifying a nanomaterial according to the EU definition recommendation.
- Tier 2 methods must be used as confirmed by the NanoDefine project.

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

- The requirement 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 – makes the use of automatic imaging counts difficult in practice, as it is highly challenging to distinguish between primary particles and smaller aggregates and agglomerates.
- The number of particle evaluated with electron microscopy will always be extremely small compared with the whole sample. This leads to very high demands on all the levels of the sample preparation: drawing, preparation and especially the selection of the proper image section.

In conclusion, due to the limited usability of automatic counting, each and every analysis involves high staff input.

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

[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

Evaluation of the usability of the results of the NanoDefine project for pigments and fillers and other substances in the nanoscale

Main outcome of the NanoDefine project is the establishment of an integrated tiered approach including rapid screening (tier 1) and confirmatory methods (tier 2), and a user manual to guide end-users as well as manufacturers, in selecting appropriate methods. Another main product is the "NanoDefiner" e-Tool, supporting the selection of appropriate methods for material classification according to the EU definition.

- Sample preparation
  - It has been confirmed in the NanoDefine project that different materials require adapted SOP's
  - The strong tendency of pigments and fillers to build aggregates and agglomerates leads to specific requirements related to the dispersion of the materials.
  - Broad particle size distributions (at least of organic pigments) make sample preparation very challenging.
  - Sample preparation (especially dispersion) is critical for performing a valid and representative particle size distribution determination.
  - Operators must not only have high competency in sample preparation, measurement processes and evaluation of measurements, but they must also have a specific knowledge of the materials under evaluation and the matrix they are enclosed in.

- Screening methods (tier 1 methods)

With the objective to be robust and easily implementable, different existing measurement methods were evaluated in the NanoDefine project (e.g. analytic centrifugal methods and Dynamic Light Scattering (DLS)). Due to the fact that the evaluated methods do not directly provide number size distributions of primary/constituent particles a safety factor of 2.5 was derived.[4]

  - The required uncertainty factor of 2.5 determines that most pigments and fillers have to be considered as borderline cases.
  - Pigments, fillers and most of the other industrial manufactured nanomaterials in most cases deviate from the spherical shape assumed in several screening methods. Broad particle size distributions additionally complicate the measurement.
  - Considering the problems described above, the use of screening methods for pigments and fillers will only be applicable/workable in exceptional cases.

- Use of VSSA

The results in the NanoDefine project show that under appropriate conditions, the VSSA can be used as proxy to the number based particle size distribution. Therefore, it is proposed as screening technique for the identification of nano and non-nanomaterials in powder form. Based on the limited usability of VSSA (only for non polydisperse, non-porous substances), an uncertainty factor of 2.5 has to be applied. This leads again to the situation that most pigments and fillers have to be considered as borderline cases. Furthermore the BET-method often cannot reliably be used for coated particles. This is a severe limitation of the screening tool.

[4] How reliably can a material be classified as a nanomaterial? Available particle-sizing techniques at work, J Nanopart Res (2016) 18:158 DOI 10.1007/s11051-016-3461-7,

- NanoDefine e-Tool

The NanoDefine e-Tool was developed to support the selection of appropriate methods for material classification according to the EU commission recommendation on the definition. Currently the NanoDefiner release version 1.0.0 is available.[5] For pigments and fillers and also for the majority of other nanomaterials, due to the limited usability of screening methods, the scheme will lead in most cases directly to the confirmatory methods.

- Confirmatory methods (tier 2 methods)

In the NanoDefine project several case studies representing a wide diversity of substances and materials (inorganic and organic materials, nano, non-nano and borderline cases) were performed. Due to the limitation of the screening methods described above and proven by the mentioned case studies for pigments and fillers and most of the other nanomaterials, only electron microscopic methods are suitable to establish whether or not the pigment or filler under investigation is a nanomaterial according to the EU definition.

In typical cases, a size distribution of at least two orders of magnitude has to be characterized. This warrants the counting of a rather high number of particles. Additionally, in the vast majority of cases, the entities visible under the microscope will not be primary particles, but aggregates thereof and/or agglomerates. Consequently, further analysis will be necessary. For pigments and fillers and most of the other nanomaterials, the task is rendered even more difficult by the fact that typically, rather irregular particles are present. Together, this means a substantial effort in time for qualified and experienced personnel.

These factors, namely the identification of constituent particles within agglomerates and aggregates or the irregular shape of the particles, represent challenges for automated TEM evaluation developed in the NanoDefine project. Further intense investigations in this regard are required to get this method ready for the market for pigments and fillers and possible other nanomaterials. At the moment, no automatic procedures are commercially available.

Summary and final conclusion

The NanoDefine project has definitely made good progress concerning the particle size measurements in the nano-range.

Regrettably, despite the progress achieved in the NanoDefine project, from the perspective of pigments and fillers and other comparable particulate substances, this project still fails to achieve the objective to have a readily available, easy to perform and low-cost method to determine whether a given material is, or is not, a nanomaterial according to the EU Commission recommendation.

Pigments and fillers are generally products with a long life cycle as this is a key customer demand. Some of the grades in question have been marketed for decades. In the case of pigments the required coloristic properties determine their particle size which necessarily puts them in the range of several hundred nanometres.

For pigments and fillers and other comparable particulate substances, the main conclusion from the results of the NanoDefine Project is that the use of electron microscopy is unavoidable in order to determine whether or not this kind of substance is a nanomaterial according to the EC recommendation. This necessitates the use of an instrument that is not readily available to most of the industry and probably also to most of the authorities.

[5] http://www.nanodefine.eu/index.php/nanodefiner-e-tool

Additionally the measurement strategy requires dedicated personnel who have not only experience and expertise in running these kinds of analyses but as well specific knowledge of the substance under investigation for producing reliable and reproducible result (as stressed by both the NanoDefine and JRC Eurocolour projects).

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