

**Committee of Experts on the Transport of Dangerous Goods
and on the Globally Harmonized System of Classification
and Labelling of Chemicals**

2 December 2015

**Sub-Committee of Experts on the
Transport of Dangerous Goods**

Forty-eighth session

Geneva, 30 November – 9 December 2015

Item 10 (h) of the provisional agenda

**Issues relating to the Globally Harmonized System
of Classification and Labelling of Chemicals:
miscellaneous**

**Sub-Committee of Experts on the Globally Harmonized
System of Classification and Labelling of Chemicals**

Thirtieth session

Geneva, 9 – 11 December 2015

Item 3 (d) of the provisional agenda

**Classification criteria and related hazard
communication: nanomaterials**

GHS informal working group on nanomaterials

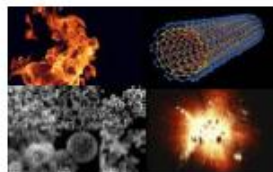
Transmitted by the expert from France

1. An informal working group on Nanomaterials is scheduled on Wednesday 9 December, 2015 during the 30th session of the Sub-Committee of Experts on the Globally Harmonized System of Classification and Labelling of Chemicals.
2. The expert from France is submitting the attached presentation in appendix as supporting information for discussion during the informal working group. It appears to be also interesting information for both plenary sessions of TDG and GHS sub-committees. Based on comments from the other experts, France may come back with a more detailed review of test descriptions and screening procedures if needed and proposals on their adaptations to fit with nanomaterials.
3. Of course this is also links to a more general discussion on what belongs to the terminology of nanomaterials.



NANOMATERIALS

Important issues on assessment for TDG/GHS classification for physical hazards



Synthetic Nanomaterials

Nano-objects (ISO 80004-2)
Particules with 1, 2 or 3 external dimensions
of less than 100 µm



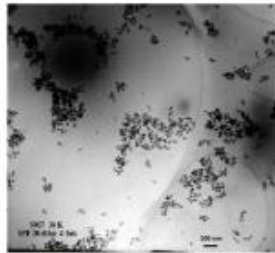
Nanoplate
Clay, graphene



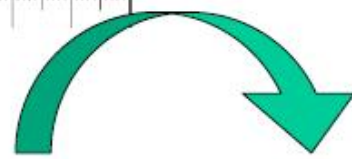
Nanofibre
Carbon, Silicium



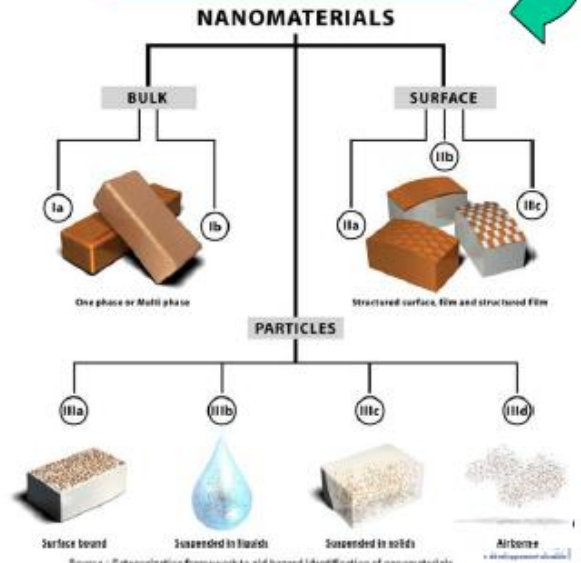
Nanoparticle
Carbon black, TiO₂



TiO₂ dans crème solaire diluée



*Nano-Objects,
agglomerates and
aggregates*



Source : Categorization framework to aid hazard identification of nanomaterials
S. F. HANSEN, et coll - Nanotoxicology 2007, 18

Nanomaterials have very specific properties

New materials with new properties → *polymers, metals, ceramics, paints, ...*

- Associated benefits for mechanical strength, thermal or electrical conductivity, corrosion, abrasion resistance, surface properties...

Challenges for classification related to physical hazards

- For physical hazards test based classification should be suitable whatever the form of the substance is.

However:

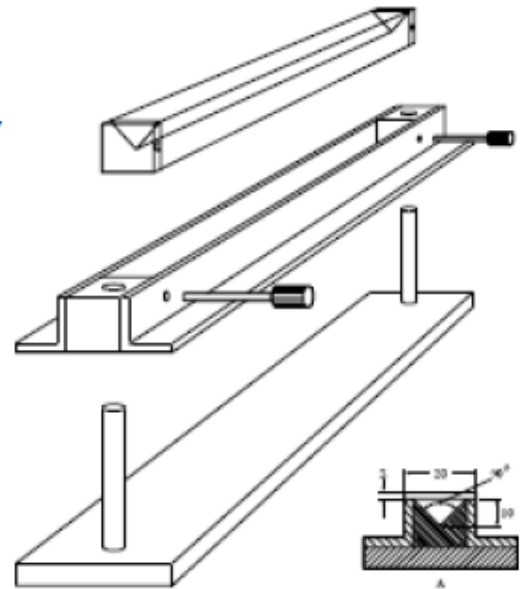
- Are the existing UN test methods applicable?
- Safety at work place issue to be considered

Example of problems are illustrated hereafter

UN Test N.1 "Test method for readily combustible solids"

"The powdered or granular substance, in its commercial form, should be loosely filled into the mould. The mould is then dropped three times from a height of 20 mm onto a solid surface"

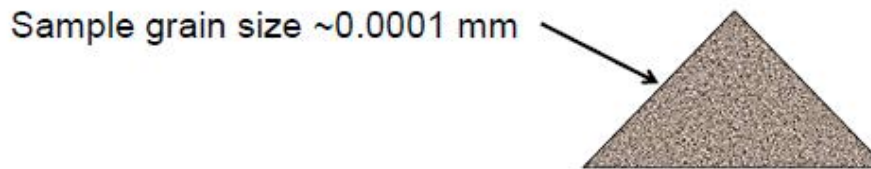
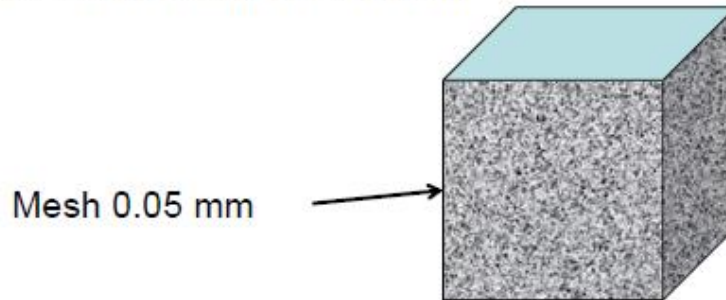
"Any suitable ignition source such as a small flame or a hot wire of minimum temperature 1 000 °C is used to ignite the pile at one end"



- => Very fine particles such as nanomaterials tend to behave as liquid, which do not allow to form the train as foreseen
- => Difficulties to ignite the train as a flame will blow the sample

UN Test N.4 "Test method for self-heating substances"

The sample is placed in a cubic container, made of stainless steel net with a mesh opening of 0.05 mm.



=> How to keep the sample in the container as it is too small compared to the mesh size



UN Test O.1 "Test for oxidizing solids"

The test sample is mixed with dried fibrous cellulose in a given ratio and the mixture is formed as a defined truncated conical pile.

The cellulose has a fiber length between 50 and 250 μm and a mean diameter of 25 μm .

- => How to make a correct mixture between the cellulose and the sample particles with such difference in size
- => Volume of sample required due to low density of some of nanomaterials does not allow to fit the sample mixture in the defined cone

Conclusion

| Test ref. | Physico-chemical property | Issues identified |
|-----------|---------------------------|---|
| UN N.1 | Flammability | <ul style="list-style-type: none">- Sample preparation- Sample ignition |
| UN N.4 | Self heating | <ul style="list-style-type: none">- Containment of the sample- Large variation of density from one material to another- Increased reactivity (safety issue) |
| UN O.1 | Oxidizing | <ul style="list-style-type: none">- Volume of material required- Quality of mixture with reference material |
| UN N.2 | Pyrophoric | <ul style="list-style-type: none">- Dispersion of the material- Safety at work place |
| UN N.5 | Water reactivity | <ul style="list-style-type: none">- Preparation of the test (filter paper, position on the liquid surface...)- Addition of water drop wise on the sample |