

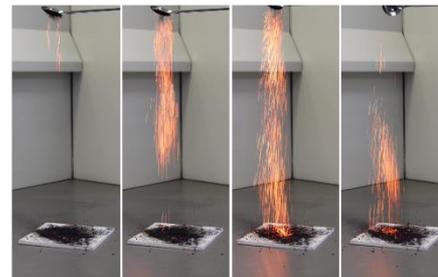


Some considerations when evaluating physico-chemical hazards of nanopowders

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Bundesanstalt für
Materialforschung
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maîtriser le risque |
pour un développement durable

Assessment of physical hazards

Regulatory framework

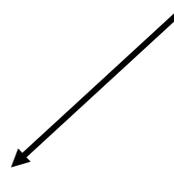
- European framework
 - CLP (Classification, Labelling and Packaging)
 - Reach
 - SEVESO III
- International framework
 - UN : regulation on transport of hazardous goods
 - GHS : Globally harmonized system

Risk assessment framework

Fire and explosion risk assessment

- Heat release rate & Self heating risk
- Ignition sensitivity (e.g. MIT, MIE)) and explosion severity (P_{\max} , K_{St})
- Release of hazardous gases (flammable, toxic)

Main object of research in the past 10 years in ENM related process safety



Some issues regarding specific ENM properties

New materials  often no comparable reference

Some specific issues with ENMs

- Dustiness (lower/higher depending on the formulation)
- Suspected to be hazardous to health
- Very low apparent density (till ~30 g/L)
- Strong influence of particle size on hazardous properties
- High cost of combustible ENMs

Test protocols need to be applied with special care

What nanomaterials are concerned ?

Combustible	Not combustible
Carbon Black	Metal oxides (TiO_2 , CeO_2 ...)
MWCNT	SiO_2
SWCNT	ZnO
Carbon nanofibre	
Metals (e.g. Cu, Al, Fe...)	Al_2O_3
Metal carbide/nitride	Iron oxides (Fe_3O_4 , Fe_2O_3)
Si, SiC	Zirconium oxide (ZrO_2)
MoS_2	Nanoclay
Organic ENMs (e.g. polymers, Nanocellulose)	(Provided that they are not coated with combustible material)
Metallic alloys (e.g. Co-Cu, NiFe, Co-C, Co-C-Au ...)	
Polymer or carbon coated metal oxides (?)	

The UN test series

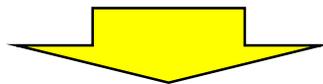
Described in the UN test and criteria manual

Flammability tests

- N1 : easily flammable substances (Reach A.10)
- N2 : pyrophoric substance (Reach A.13)
- *N3 : pyrophoric liquids*
- N4 : self-heating materials
- N5 : materials which in contact with water produce flammable gases (Reach A.12)

Robust and simple tests in order to be performed anywhere around the world requiring simple laboratory equipment.

BUT...presenting some practical limitations in the case of non conventional materials, among which nanopowders

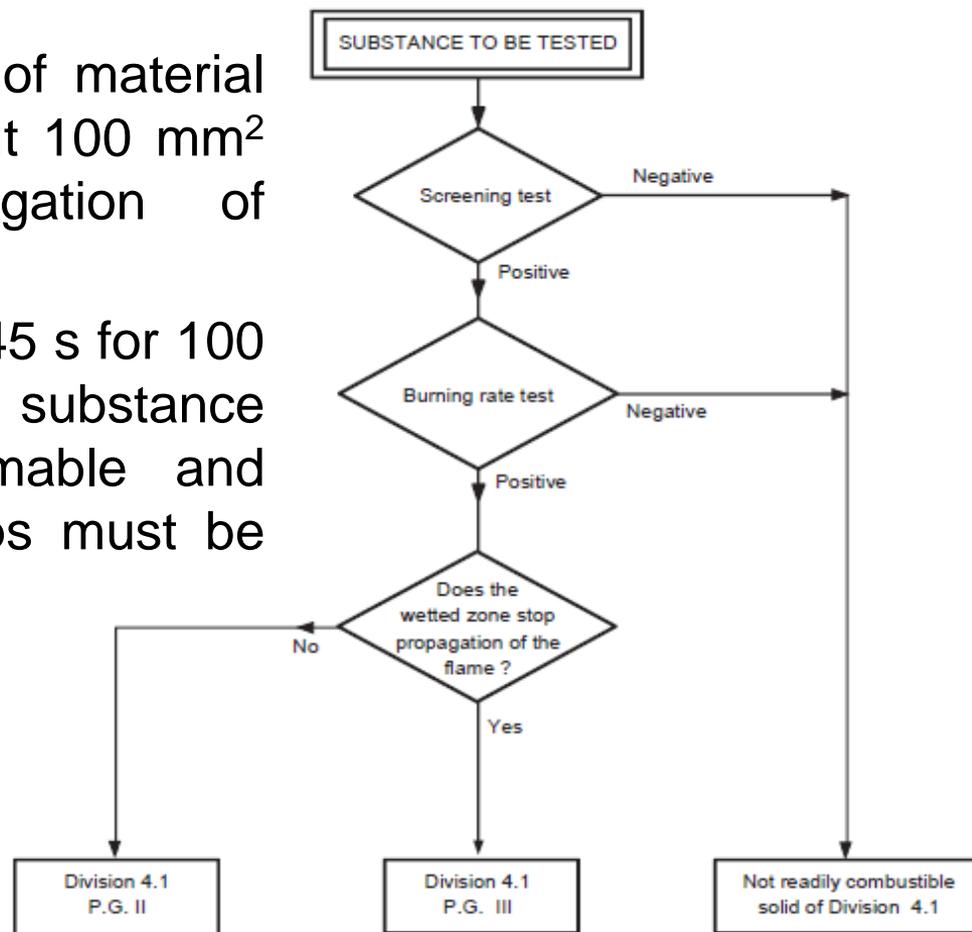
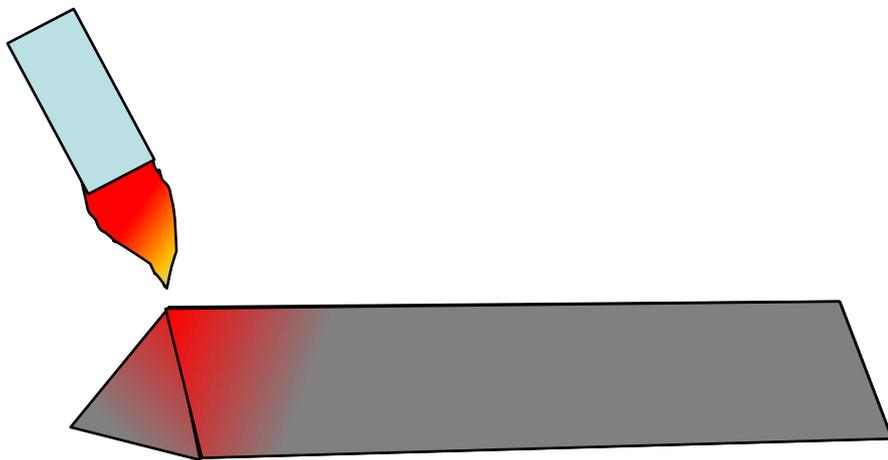


Risk of false negative tests leading to hazardous situations

N1 test : easily flammable solids

Principle :

- Ignite a 250 mm long train of material with a cross section of about 100 mm² and monitor the propagation of combustion
- If propagation in less than a 45 s for 100 mm or (10 minutes for metal) substance is considered easily flammable and appropriate packaging groups must be used



N1 Test : Identification of difficulties on ignition source



Ignition of the powder train with sparks moved by the flame of the burner while being approached



Blowing of the powder while approaching the burner



The powder deviates at the approach of the hot wire
=> No ignition whereas a flame would ignite

Other difficulties



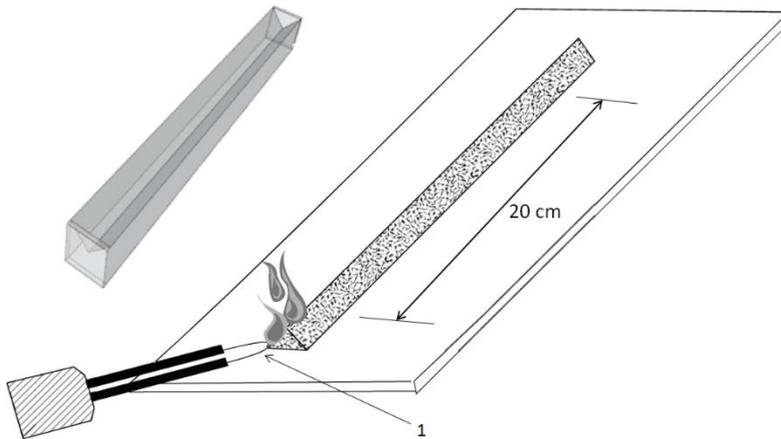
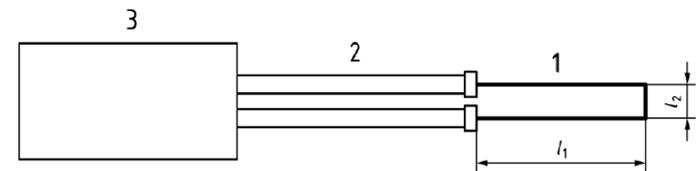
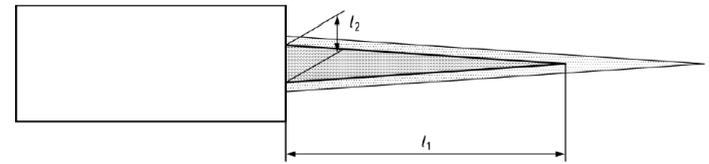
« Collapse » of the powder train



Destruction of the powder train during humidification

Future work : adaptation of the ignition source

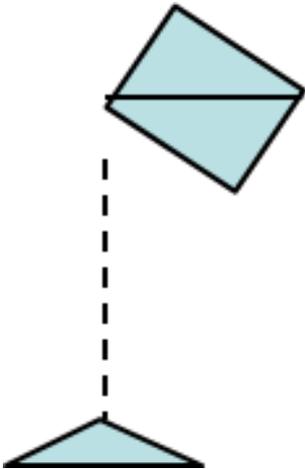
- Test other sources of ignition (eg. spark ignition, hot spot, chemical ignition) and estimate if their temperature is adequate with ONU N1 (<1000°C)
- **Validate at UN level the use of alternative ignition source**



UN N2 Test: pyrophoric solids

Principle :

- drop 1 or 2 ml of the substance from 1m and observe if it ignites during fall or within 5 min after fall.



Some practical issues :

- very dusty material, may not fall as a pile
- Potential influence of the surface on which material is poured (thermal conductivity)
- What about very sensitive substances (low MIE sensitive to friction) ?
- What about self-heating substances that require only a few g (10 to 100 more than the test requirements) to self-ignite at room temperature ?
- Flammable and pyrophoric ? (packing under inert)

33.3.1.1.2 The test procedures are intended to identify two types of substances with spontaneous combustion properties:

- (a) Substances, including mixtures and solutions (liquid or solid) which, even in small quantities, ignite within five minutes of coming in contact with air. These substances are the most liable to spontaneous combustion and are called pyrophoric substances;
- (b) Other substances which, in contact with air and without an energy supply, are liable to self-heating. These substances will ignite only when in large amounts (kilograms) and after long periods of time (hours or days) and are called self-heating substances.

Some alternative approaches to pyrophoric property assessment

Use of theoretical models such as Glassmann or Vorzhtsov theory to assess a priori the pyrophoric character

- support for critical interpretation of test results and potential sensitivity to fluctuations of characteristics
- use for safe by design approach

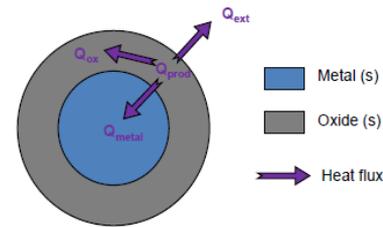


Figure 35 : Heat balance performed on a pyrophoric particle

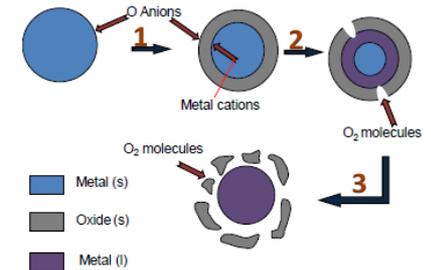
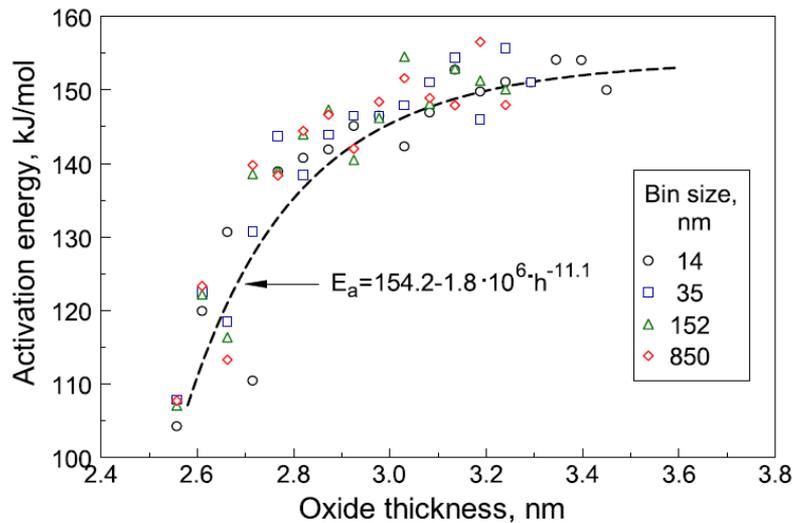
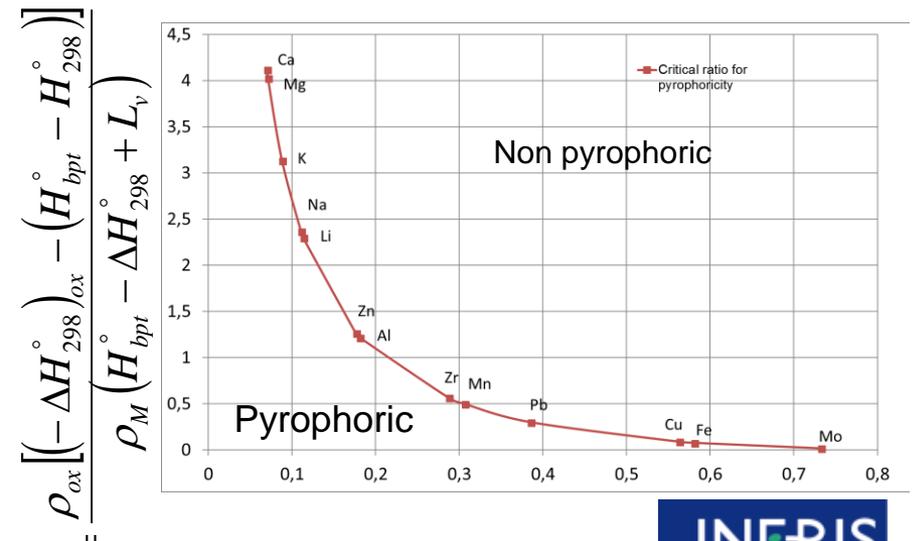


Figure 36 : Sketch describing the steps in pyrophoricity phenomenon



Activation Energy vs oxide thickness

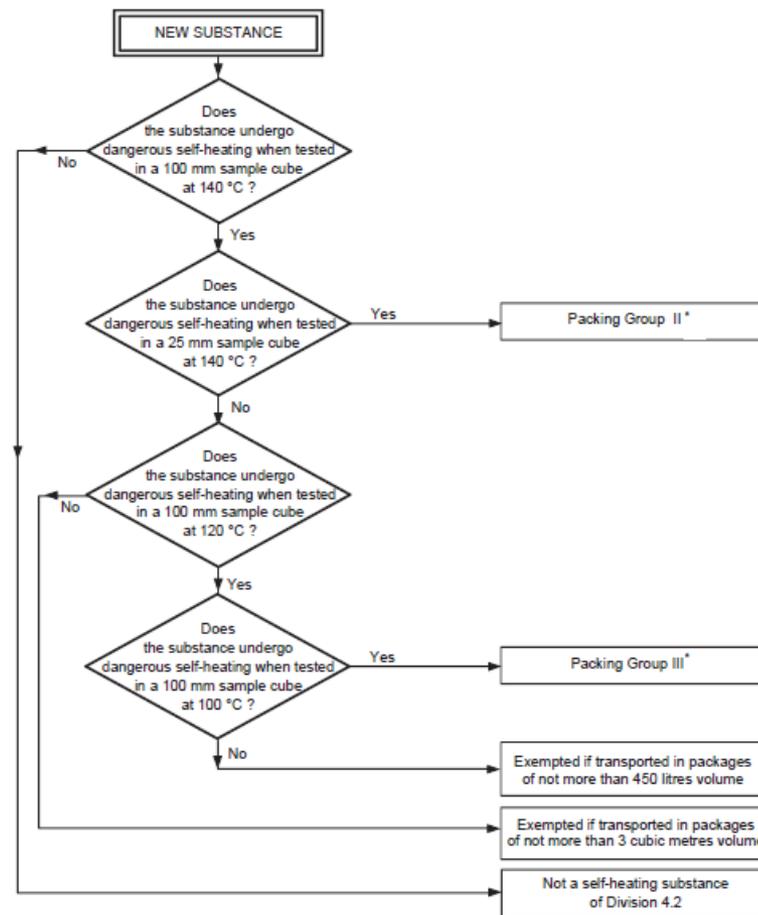
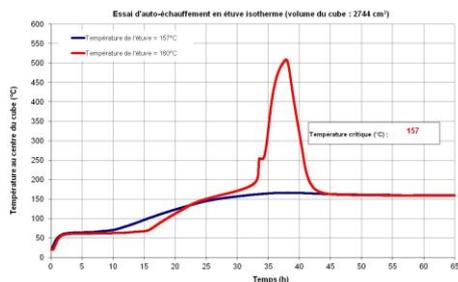
[Vorozhtsov, 2017]



N4 test: Self heating

Principle of the test :

Maintain a given volume (253 mm³ and 1003 mm³) of the material in an oven at the test temperature (100°C, 120°C, 140°C) and monitor the sample temperature. If it increases more than 60°C then the material is considered as self-heating.

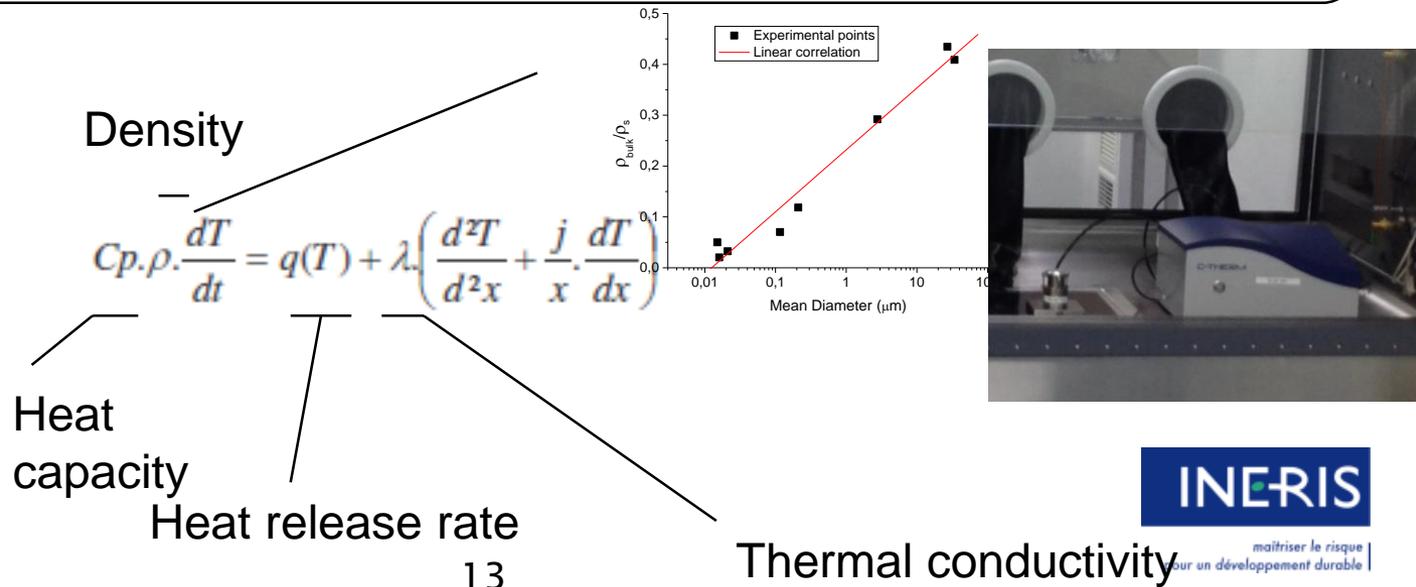
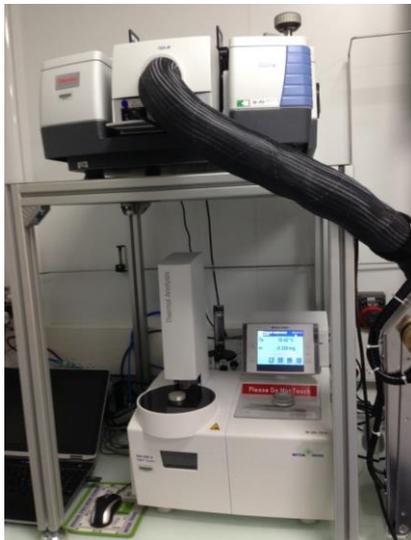


N4 test: Examples of difficulties and perspectives

- Applying the nanosafety principles to the test
- Avoiding leaks of the basket
- Burning a large amount of valuable nanopowder
- Huge effect of density on thermal conductivity
 - rate of compaction needs to be considered



Development of alternative methods based on combination of calorimetric tools/TMI in layer (El-Sayed, 2018) and getting the parameters of the FRANCK-KAMENETSKII model...



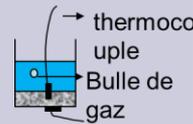
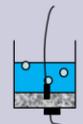
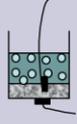
N5 test : materials which in contact with water produce flammable gases

Principle:

- Introduce material in a drop funnel
- Pour water over it
- Follow the gas production flow rate for 7h
- If increasing or erratic, extend the test for 5 days

Difficulties :

- recognised gas rate measurement technique (present one requires to be present during 5 days and alternative techniques are not recognised by UN)
- Induction time can be longer than 7 hours (sometimes days)
- Influence of the type of water

Time	Day 1	Day 2, 12 h	Day 2, 16h
			
Temperature evolution	+ 0,3 °C	*	T _{max} = 27 °C
Gas emission	Weak	Moderate	Fast
Appearance of the water solution	clear	clear	troubled

INERIS proposed the use of a new gas counting device, not yet accepted by UN

Conclusion

1. ENM low density/small particle size and related high surface area induces practical difficulties when implementing flammability tests
2. So far, most efforts were put on explosivity test protocols
 - To assess if the tests were adapted to ENMs (TC 352/WG3/PG3)
 - To investigate more fundamental aspects (combustion, flame velocity...)
3. The UN test series for regulatory classification of hazardous substances was less studied and yet also present practical difficulties
4. Several alternative are being proposed or under study
5. Major challenge to come : make these alternative methods accepted at UN level