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# GHS – Globally Harmonized System

## Phys.-chem issues

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# ★ Physical hazards in GHS

- Significant change in hazard classification compared to DSD
  - New classes
  - Subdivision into categories
  - Different test methods
  - Extensive test procedures
- Internationally harmonised classification

## ★ Problems in REACH and GHS

- Inconsistency of data
- Data gaps
- Translation of hazard classes from DSD to GHS
- Errors in guidance

# Phys.-chem. data for chemical safety assessment and chemical safety report <sup>1)</sup>

Minimum requirements:

Flammability	⇔	2.6 Flammable liquids 2.7 Flammable solids 2.9 Pyrophoric liquids 2.10 Pyrophoric solids 2.11 Self-heating subst. & mixt. 2.12 In contact w. water emit flamm. gases
Oxidising potential	⇔	2.4 Oxidising gases 2.13 Oxidising liquids 2.14 Oxidising solids
Explosivity	⇔	2.1 Explosives 2.8 Self-reactive substances and mixtures 2.15 Organic peroxides

<sup>1)</sup> REACH Directive, Annex I, 2.2



## Requirements of articles 5 and 6 GHS Directive

- Determination of the relevant information
- by manufacturers, importers and downstream users
- relating to the **forms** or **physical states** in which the substance is placed on the market and in which it can reasonably be expected to be used

## ★ Form and physical state (see ECB1/43/05 )

- Form: The form under which the substance is normally used or may be used ... This covers all physical forms in which the substance is manufactured and placed on the market or all physical forms into which it might be transformed
  - The normal behaviour of the persons that are handling / using the substance : for intended use by general consumers, the normal/ foreseeable behaviour of adults and children shall be taken into account
  - Consideration of foreseeable and realistic accidents
  - Misuse should not be considered
- ⇒ Consequences for registration for REACH !!!

## ★ Form and physical state - consequences

Physical state and form need to be taken into account for classification in many cases, i. e. :

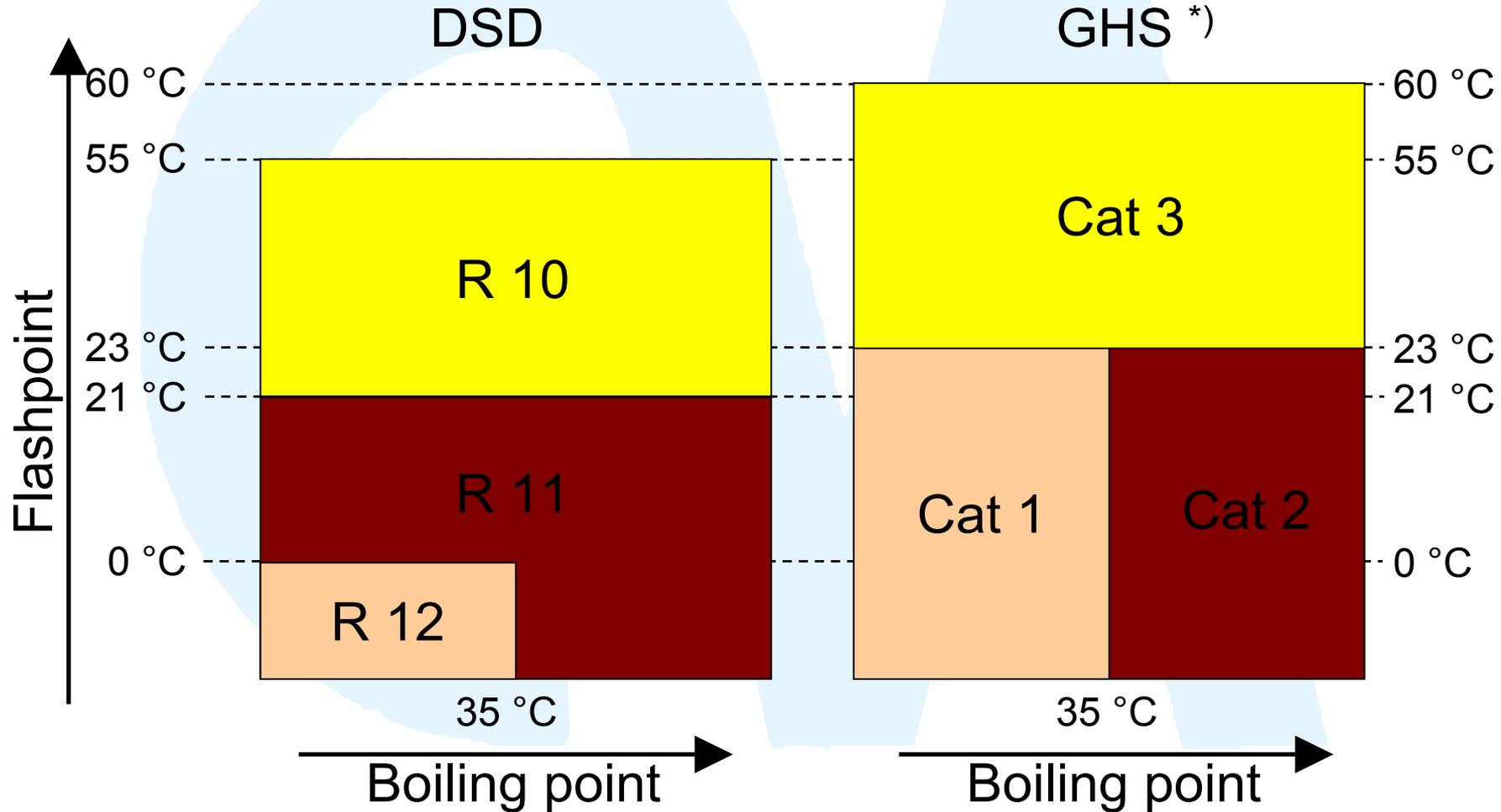
- Powder, pellets, tablets
- Particle size, crystal structure and size
- Moisture, residual solvents
- Surface treatment (i. e. activation, passivation)
- Melting and pumping of substances with low melting point

## ★ Phys.-chem. test methods – general issues

- Methods of UN Test Manual<sup>\*)</sup>
- Quality requirements (Art. 8 (5)):
  - Accreditation according to EN 17025 or GLP
  - from Jan. 2014

<sup>\*)</sup> UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria

# Flammable liquids - Overview



\*) Cat. 4 not implemented in EU GHS



## Flammable liquids – testing

### Test method for flash point:

- Only closed cup allowed
- Selection of method depending on sample composition and properties
- Calculation of flash points only to a very limited extend possible

### Guidance document:

- Double testing for flash points, at least one run with „manual observation“
- Special requirements for viscous substances / mixtures and samples containing halogenated compounds

# Flammable solids



DSD

Test method: EC A.10

R 11

Highly flammable

Metal powders:  
Burning time  $\leq 10$  min

Other subst. / mixt.:  
Burning time  $< 45$  s



GHS

Test method: UN N.1

Cat. 1

Metal powders:  
Burning time  $\leq 5$  min  
Other subst. / mixt.:  
Burning time  $< 45$  s  
Wetted zone does not stop fire

Cat. 2

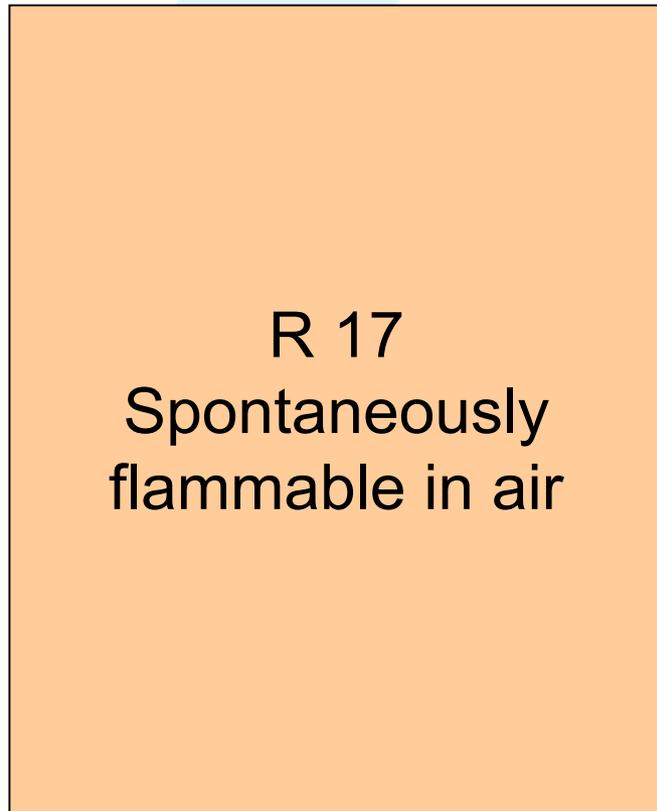
Metal powders:  
Burning time  $> 5$  min and  $\leq 10$  min  
Other subst. / mixt.:  
Burning time  $< 45$  s  
Wetted zone stops fire for at least 4 min

# Pyrophoric liquids and solids



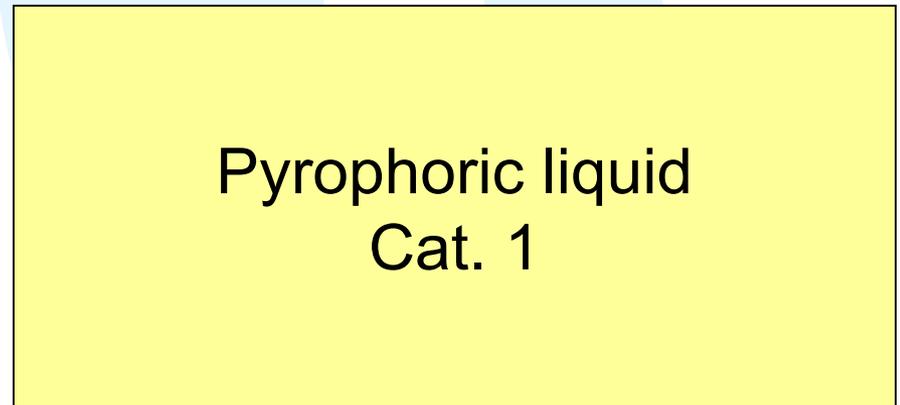
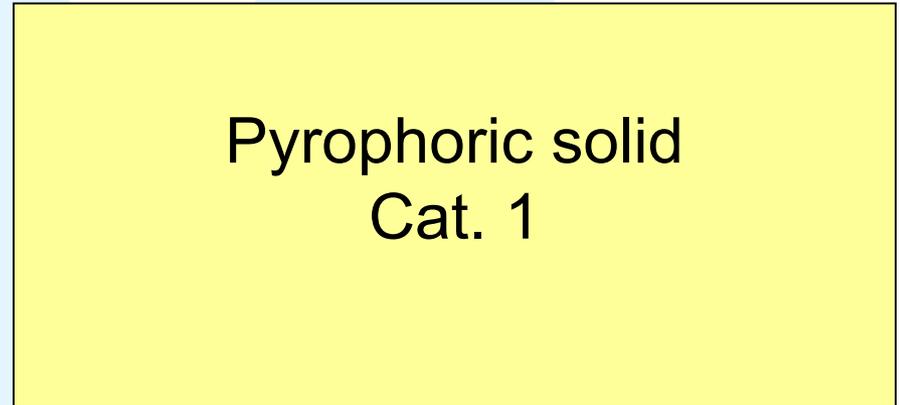
DSD

Test method: EC A.13



GHS

Test method: UN N.2 / N.3



Test methods are very similar

# Substances and mixtures which in contact with water emit flammable gases (1)



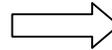
DSD

Test method: EC A.12

**F, R15**

Contact with water liberates extremely flammable gases

gas evolution > 1 l/(kg·h)



GHS

Test method: UN N.5

**Cat. 1**

spontaneous ignition of gas  
gas evolution  $\geq 10$  l/kg over any one minute

**Cat. 2**

gas evolution  $\geq 20$  l/(kg·h)

**Cat. 3**

gas evolution  $\geq 1$  l/(kg·h)

## Substances and mixtures which in contact with water emit flammable gases (2)

### Note:

- According to DSD, for pyrophoric substances and mixtures (F; R17) the test EC A.12 was not to be performed and no additional classification with R15 was required
- However, GHS stipulates an additional classification as a substance and mixture which, in contact with water, emit flammable gases, even for pyrophoric substances or mixtures (F; R17). In case of pyrophoric substances and mixtures, the UN N.5 test shall be executed under nitrogen atmosphere

# Self-heating substances and mixtures (1)



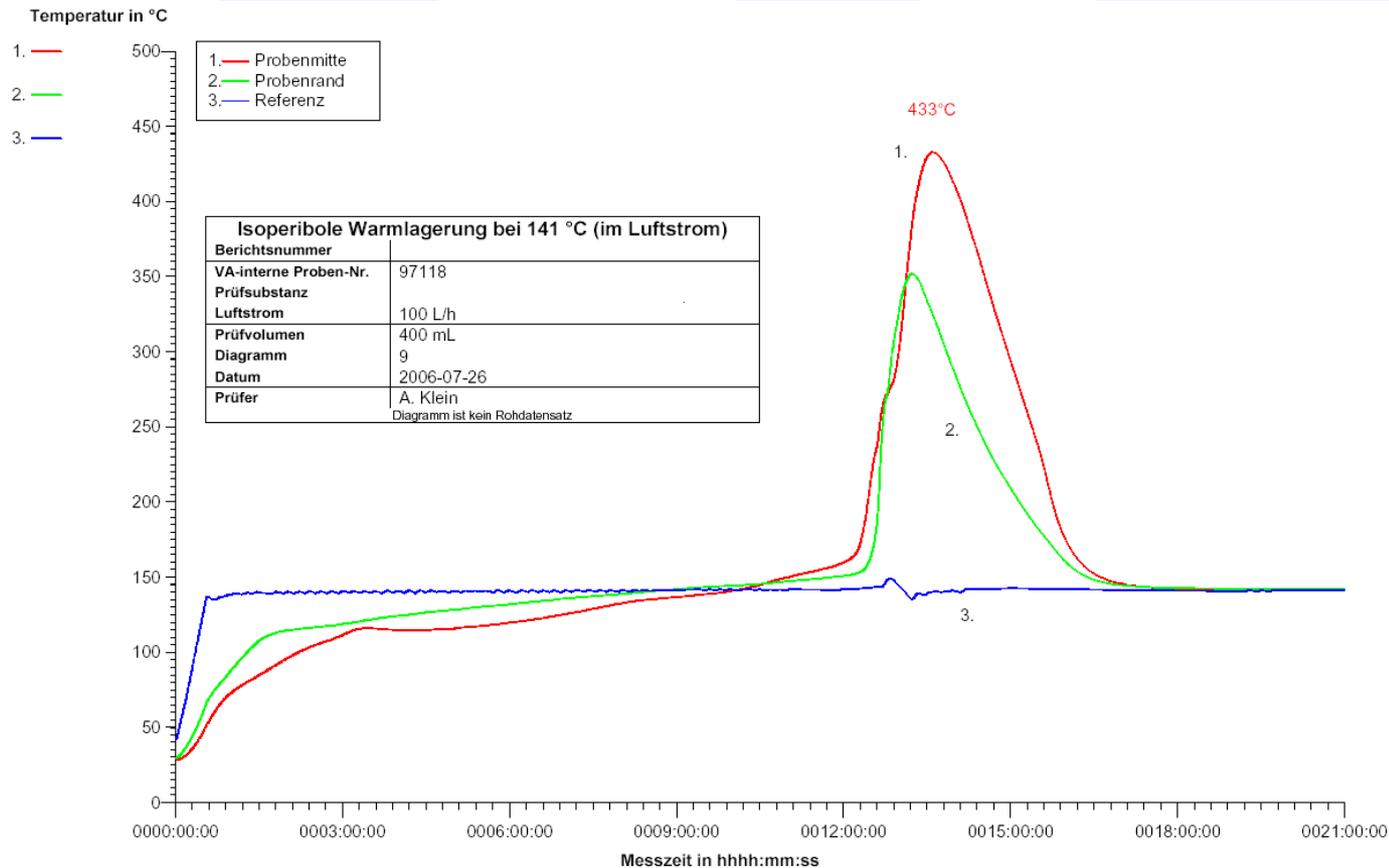
- Substances and mixtures which will self-heat by reaction with air without energy supply
- In general, this effect is relevant in larger volumes and for extended periods of time (especially storage)
- New hazard class without correspondance in DSD

Classification	Category 1	Category 2
GHS Pictograms		
Signal Word	Danger	Warning
Hazard Statement	H251: Self-heating; may catch fire	H252: Self-heating in large quantities; may catch fire

# Self-heating substances and mixtures (2)

Test method: UN N.4 (Bowes-Cameron Cage Test)

Test in air atmosphere at temperatures of 100, 120, 140 °C in 25 mm and 100 mm wire mesh baskets



## Self-heating substances and mixtures (3)

- In general, testing is only required for solids
- Screening tests:
  - Grewer-Ofen-Test<sup>1)</sup> with an onset temperature of 220 °C
  - Bulk Powder Screening Test<sup>2)</sup> with an onset temperature of 200 °C
- Guidance document:
  - No testing required for substances and mixtures if completely (!) molten up to 160 °C

1) VDI Guideline 2263, Part 1

2) N. Gibson, D. J. Harper, R. Rogers, Evaluation of the fire and explosion risks in drying powders, Plant Operations Progress 4 (3), 181-189, 1985)

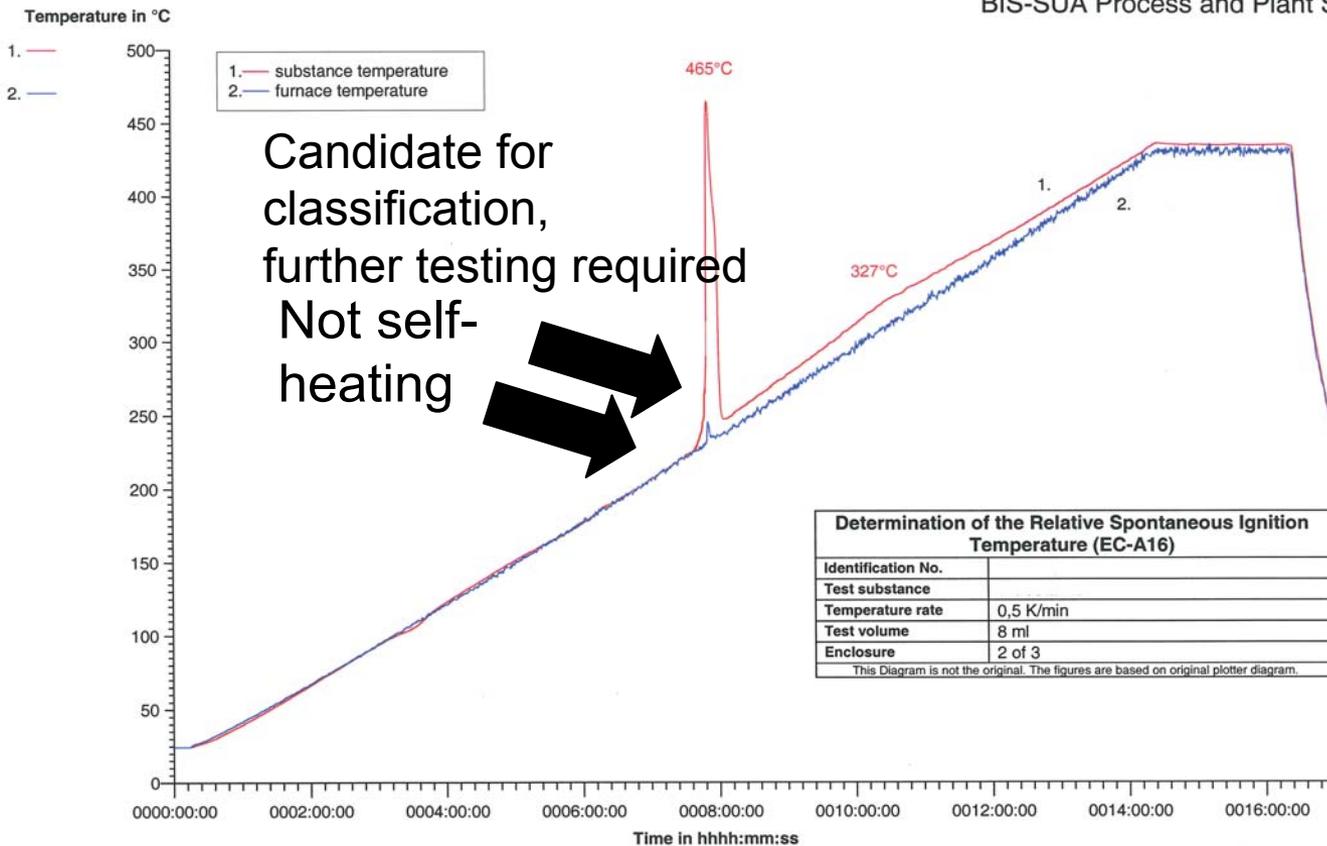
# Self-heating substances and mixtures (4)

Attention: The interpretation of data from A.16 testing can only be done using the measurement diagrams since the evaluation criteria make no sense !



Bayer Industry Services

BIS-SUA Process and Plant Safety





## Oxidising liquids (1)

DSD

Test method: EC A.21

O, R8 or O, R9  
Oxidising

Reference:  
65 % HNO<sub>3</sub> / cellulose

GHS

Test method: UN O.2

Cat. 1  
50 % HClO<sub>4</sub> aq./ cellulose

Cat. 2  
40 % NaClO<sub>3</sub> aq./ cellulose

Cat. 3  
65 % HNO<sub>3</sub> / cellulose

Comparison of pressure rise rates  
sample / cellulose vs. reference mixture

# Oxidising solids (2)



DSD

Test method: EC A.17

O, R8 or O, R9  
Oxidising

Reference:  
BaNO<sub>3</sub> / cellulose  
with max. burning rate  
(ca. 60 % BaNO<sub>3</sub>)

GHS

Test method: UN O.1

Cat. 1  
KBrO<sub>3</sub> / cellulose 3:2

Cat. 2  
KBrO<sub>3</sub> / cellulose 2:3

Cat. 3  
KBrO<sub>3</sub> / cellulose 3:7

Comparison of burning rates  
sample / cellulose vs. reference mixture

## Oxidising liquids and solids (3)

- Small deviations in sample preparation have a strong influence on the outcome of the test
- In the past years, even national reference laboratories have come to the wrong conclusions using the O.1 test
- The tests may be only performed by qualified labs.
- In some cases, false positive test results may be found. Such cases are:
  - Exothermic decomposition (initiated during the test)
  - Substances giving a strong exothermic reaction with the hydroxy groups of cellulose (i.e. functional groups  $-\text{NCO}$ ,  $-\text{SO}_2\text{Hal}$ ,  $-\text{COHal}$ ,  $-\text{CCl}_3$ )
- Translation from DSD: Consider special cases, i.e.  $\text{HNO}_3 \geq 65\%$ :  
Category 3

# Organic peroxides and self-reactive substances and mixtures (1)



- Organic peroxides: solid or liquid organic compounds with bivalent -O-O- structure
- Self-reactive substances and mixtures: liquid or solid substances or mixtures with a combination of high decomposition potential and low thermal stability

Temperature control required (!) when

Self-reactives:           SADT\*)  $\leq 55$  °C

Org. peroxides:       SADT\*)  $\leq 45$  or  $50$  °C, resp.

\*) SADT = Self-accelerating decomposition temperature



# Organic peroxides and self-reactive substances and mixtures (3)

**Table A6.1**    **EXAMPLES OF CHEMICAL GROUPS INDICATING EXPLOSIVE PROPERTIES IN ORGANIC MATERIALS**

<b>Structural feature</b>	<b>Examples</b>
C-C unsaturation	Acetylenes, acetylides, 1,2-dienes
C-Metal, N-Metal	Grignard reagents, organo-lithium compounds
Contiguous nitrogen atoms	Azides, aliphatic azo compounds, diazonium salts, hydrazines, sulphonylhydrazides
Contiguous oxygen atoms	Peroxides, ozonides
N-O	Hydroxylamines, nitrates, nitro compounds, nitroso compounds, N-oxides, 1,2-oxazoles
N-halogen	Chloramines, fluoroamines
O-halogen	Chlorates, perchlorates, iodosyl compounds

**Table A6.2:**    **EXAMPLES OF CHEMICAL GROUPS INDICATING SELF-REACTIVE PROPERTIES IN ORGANIC MATERIALS**

<b>Structural feature</b>	<b>Examples</b>
Mutually reactive groups	Aminonitriles, haloanilines, organic salts of oxidizing acids
S=O	Sulphonyl halides, sulphonyl cyanides, sulphonyl hydrazides
P-O	Phosphites
Strained rings	Epoxides, aziridines
Unsaturation	Olefins, cyanates

# SADT determination

