Science For A Better Life

Physical Hazards in CLP

Classification of Mixtures

Dr. D. Heitkamp

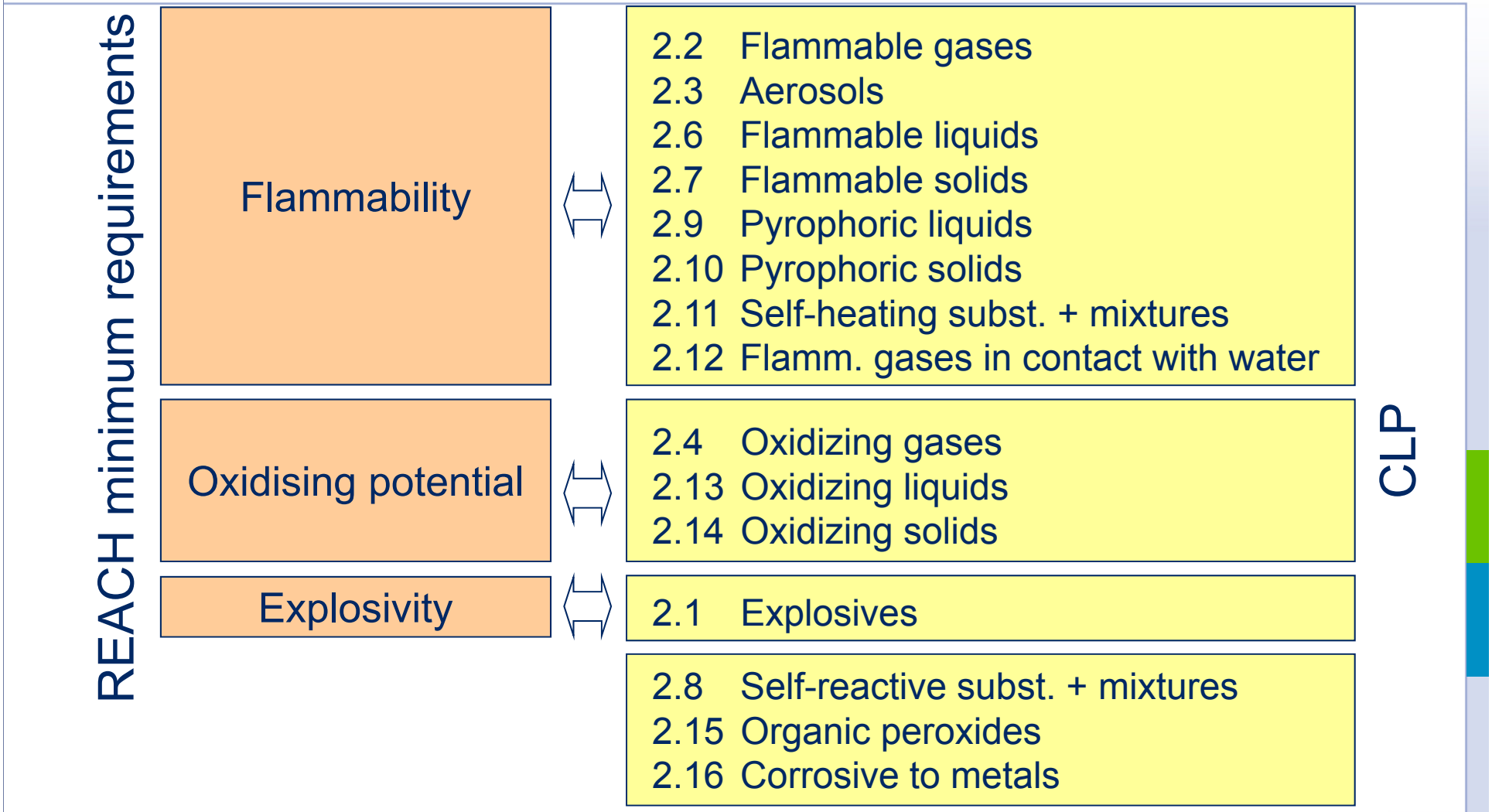
Physical hazards (GHS)

- 2.1 Explosives
- 2.2 Flammable gases (incl. unstable gases)
- 2.3 Aerosols
- 2.4 Oxidizing gases
- 2.5 Gases under pressure
- 2.6 Flammable liquids
- 2.7 Flammable solids
- 2.8 Self-reactive s.+m.
- 2.9 Pyrophoric liquids
- 2.10 Pyrophoric solids
- 2.11 Self-heating s. + m.
- 2.12 S. +mixt. which, in contact with water, emit flammable gases
- 2.13 Oxidizing liquids
- 2.14 Oxidizing solids
- 2.15 Organic peroxides
- 2.16 Corrosive to metals

Problems in REACH and CLP

- Inconsistencies of data
- Data gaps
- Translation of hazards from DSD to CLP
- Inconsistent guidance

Physicochemical data for chemical safety assessment and chemical safety report[1)]



[1)] REACH Directive, Annex I, 2.2

Gathering information (CLP articles 5 + 6)

- Obligation for manufacturers, importers and downstream users
- To determine the relevant available information
- In relation 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 - consequences

The aggregation state and the physical form are to be considered for classification, e.g.:

- Powder, pellets, tablets
- Particle size, crystal structure and crystal size
- Moisture, solvent residues
- Surface treatment (e.g. activation, passivation)
- Melting and pumping of solids with a low melting point

Generating new information for substances and mixtures (CLP, article 8)

Obligation for manufacturers, importers and downstream users

- Health and environmental hazards:

  New tests *may be performed*, provided that all other means of generating information have been exhausted (including application of rules as set out in section 1 of Annex XI, REACH Directive)

- Physical hazards:

  New tests *shall be performed*, unless unless there is adequate and reliable information already available.

Physical testing – general requirements

- Application of test methods as given in the UN Test Manual *)

- Quality requirements for testing laboratories (Art. 8 (5)):
  - Accrediation acc. to EN 17025 or application of GLP
  - At the latest from 1 Jan. 2014

*) UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria

Definitions (aggregation state) for substances and mixtures

Gas:

- Vapour pressure > 300 kPa (absolute) at 50 °C or
- Completely gaseous at 20 °C and 101,3 kPa;

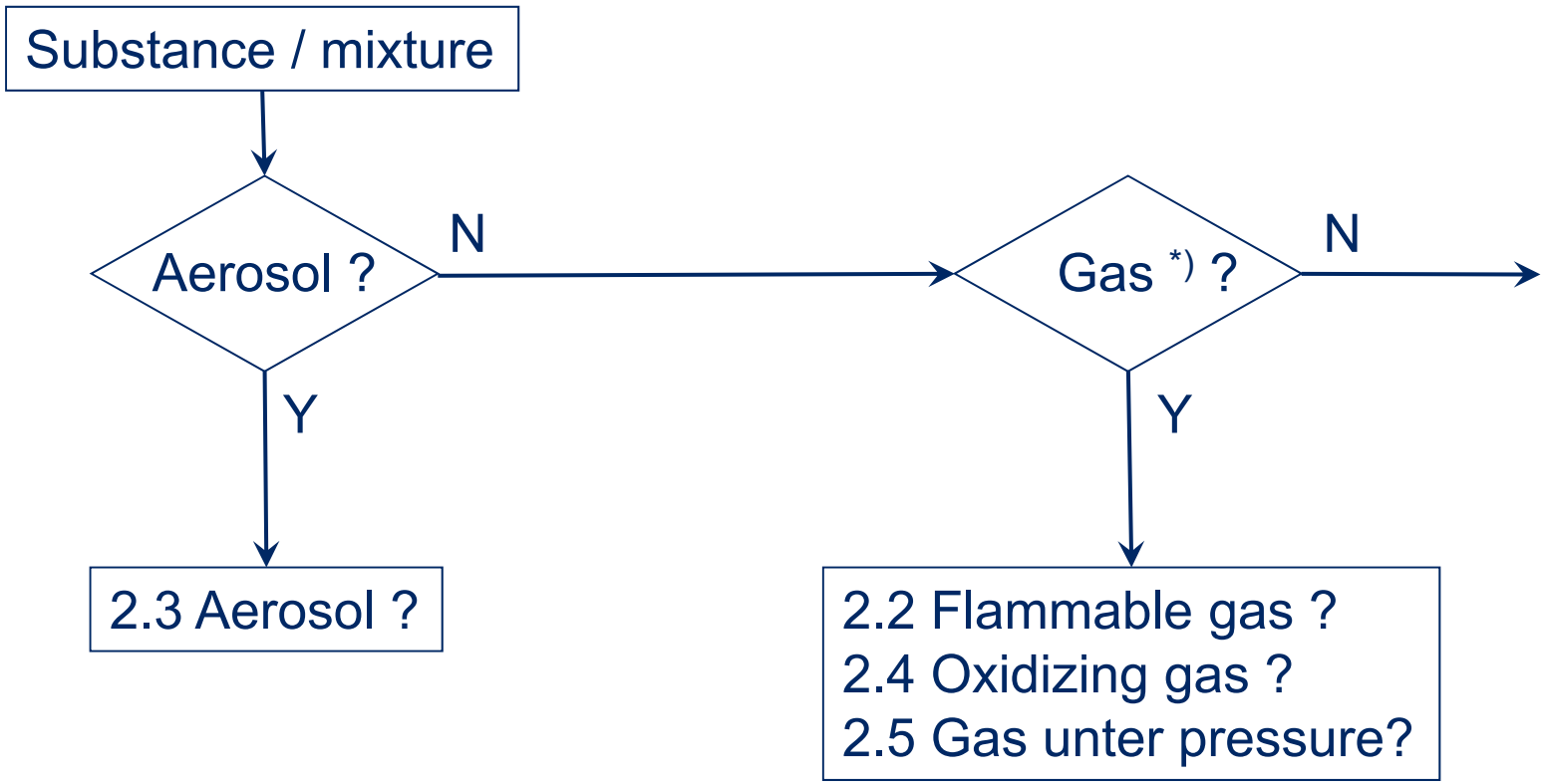
Liquid:

- Melting point or initial melting point of ≤ 20 °C at 101,3 kPa;

Solid:

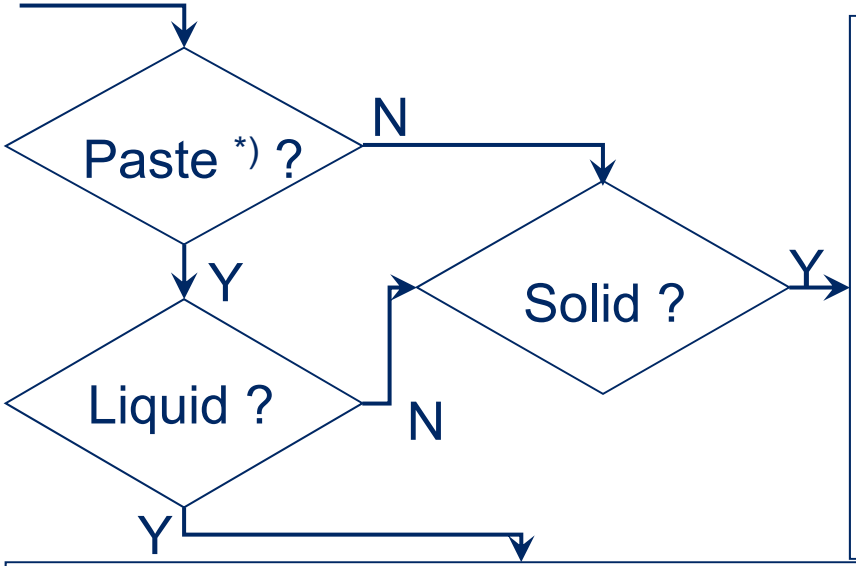
- no gas and no liquid.

General approach (1)



*) Definitions see Annex I, chapter 1.0

General approach (2)



2.1 Explosive ?
2.7 Flammable solid ?
2.8 Self-reactive subst. / mixture?
2.10 Pyrophoric solid?
2.11 Self-heating subst. / mixture?
2.12 Flamm. gas in cont. w\ water ?
2.14 Oxidizing solid?
2.15 Organic peroxide ?
2.16 Corrosive to metals ?

2.1 Explosive?
2.6 Flammable liquid?
2.8 Self-reactive subst. / mixture?
2.9 Pyrophoric liquid ?
2.12 Flamm. gas in contact with water?
2.13 Oxidizing liquid ?
2.15 Organic peroxide ?
2.16 Corrosive to metals ?

*) acc. to Penetrometer test
ADR, section 2.3.4

Aerosols (1)

Aerosols, … are any non-refillable receptacles … containing a gas compressed, liquefied or dissolved under pressure, with or without a liquid, paste or powder, and fitted with a release device allowing the contents to be ejected …

Classification	Category 1	Category 2	Category 3
GHS symbol			–
Signalwort	Danger	Warning	Warning
Hazard statement	H222: Extremely flammable aerosol H229: Pressurized container: May burst if heated	H223: Flammable aerosol H229: Pressurized container: May burst if heated	H229: Pressurized container: May burst if heated

Aerosols (2)

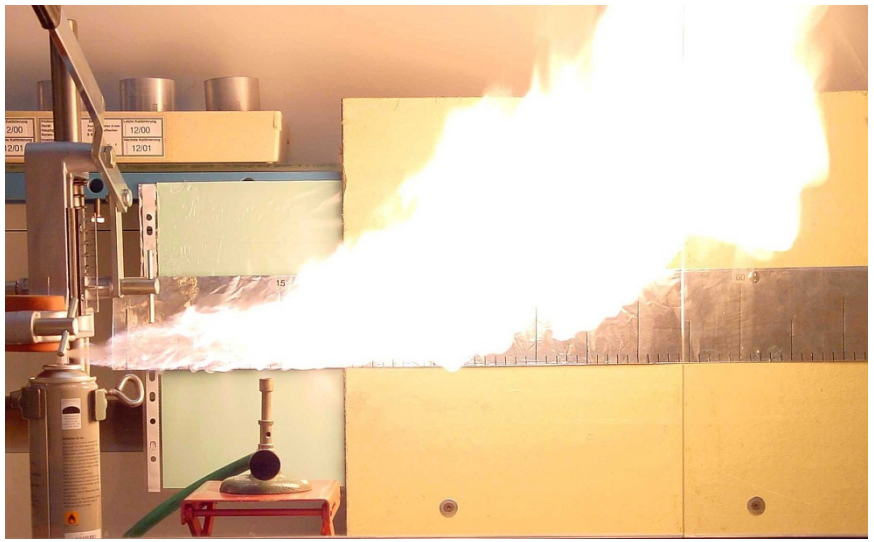
Ingredients relevant for classification:

- Liquids with a flashpoint ≤93 °C, including flammable liquids of chapter 2.6;
- Flammable gases (see chapter 2.2);
- Flammable solids (see chapter 2.7)

Aerosols (3)

Criteria for classification:

- Content of flammable components
- Heat of combustion
- Foam test for foam aerosols
- Ignition distance test and enclosed space ignition test for spray aerosols



Aerosols (4)

Aerosols do not fall additionally within the scope of chapters

- 2.2 (flammable gases),
- 2.5 (gases under pressure),
- 2.6 (flammable liquids) and
- 2.7 (flammable solids).

Depending on their contents, aerosols may however fall within the scope of other hazard classes, including their labelling elements (UN decision Dec. 2010).

Flammable gases (1)

Gas having a flammable range with air at 20 °C and a standard pressure of 101.3 kPa

Classification criteria: Lower flammability limit and range of flammability in air

Calculation method: ISO 10156:2010

Classification	Category 1	Category 2
GHS Pictogram		No pictogram
Signal Word	Danger	Warning
Hazard Statement	H220: Extremely flammable gas	H221: Flammable gas

Dang. Subst. Directive

F+, R12
Extremely flammable

CLP

Flammable gas
Cat. 1

Flammable gas
Cat. 2

Flammable gases (2)

The class of „flammable gases“ has been extended to include also chemically unstable gases (UN decision Dec. 2010):

	Category A	Category B
Criteria	Flammable gases which are chemically unstable at 20°C and a standard pressure of 101.3 kPa	Flammable gases which are chemically unstable at a temperature greater than 20°C and/or a pressure greater than 101.3 kPa
GHS Symbol	No additional symbol	No additional symbol
Signalwort	No additional signal word	No additional signal word
Hazard statement	May react explosively even in the absence of air	May react explosively even in the absence of air at elevated pressure and/or temperature

Oxidizing gases

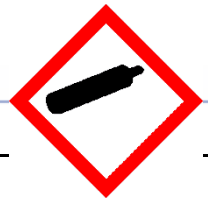
An oxidizing gas is any gas which may, generally by providing oxygen, cause or contribute to the combustion of other material more than air does.

Classification based on application of ISO 10156:2010

Classification	**Category 1**
GHS symbol	
Signal word	Danger
Hazard statement	H270: May cause or intensify fire; oxidizer

Dang. Subst. Directive	GHS
O, R8 Contact with combustible material may case fire	→ Oxidizing gas Cat. 1

Gases under pressure



Group	Criteria
Compressed gas	A gas which when packaged under pressure is entirely gaseous at -50 °C; including all gases with a critical temperature ≤ -50 °C.
Liquefied gas	A gas which when packaged under pressure, is partially liquid at temperatures above -50 °C. A distinction is made between: (a) High pressure liquefied gas: a gas with a critical temperature between -50°C and +65°C; and (b) Low pressure liquefied gas: a gas with a critical temperature above +65°C.
Refrigerated liquefied gas	A gas which when packaged is made partially liquid because of its low temperature.
Dissolved gas	A gas which when packaged under pressure is dissolved in a liquid phase solvent.

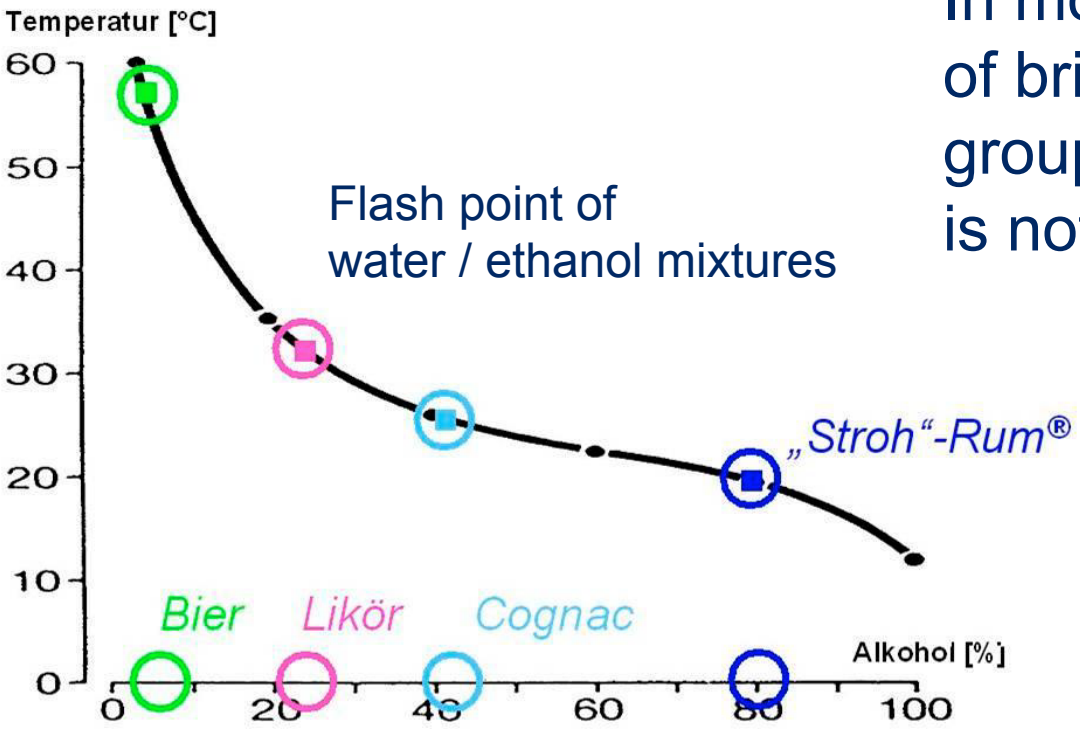
End of the good news

I was asked to give a presentation about physical hazards.

It is not my task to leave everybody in a good mood at the end of the presentation …

Mixtures of liquids and/or solids (1)

The physical properties of a mixture are generally not a linear combination of the properties of the individual compounds



In most cases, application of bridging principles, grouping and read across is not possible.

Mixtures of liquids and/or solids (2)

Beware:

- Particle size, surface treatment and physical form can strongly influence the physical behavior of a substance or mixture.
- The presence of impurities – especially (transition) metals – may have a strong influence on the chemical reactivity and the thermal stability of a mixture.
- The physical behavior and therefore the classification of a mixture may depend on the presence of a single substance whose properties become predominant (for flashpoint, sometimes even down to concentrations of 0,5 % or less!)
- Simple conclusions that appear to be straightforward are not always correct: a mixture of 2 non-flammable solids may be flammable after all!

Screening procedures[1)]

Required information: chemical structure, info about concentration

Range of application: most physical hazards

Main purpose:

- Determine which hazard classes do not apply (principle of elimination)
- Identify hazard potential, find out where testing may be necessary

Rigorous use of the screening procedures is highly recommended, but it cannot solve all problems!

[1)] UN Manual of Tests and Criteria, Appendix 6

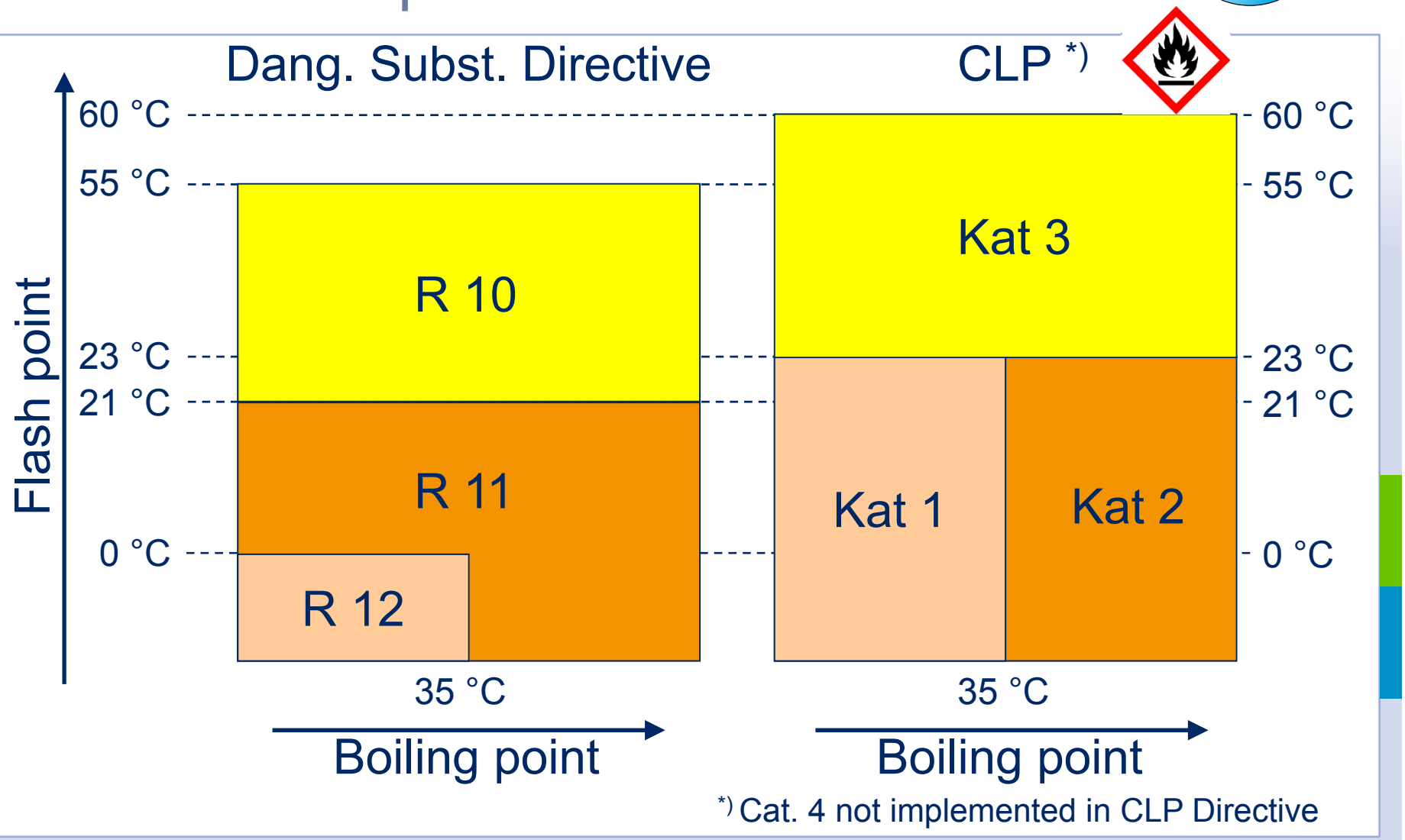
Corrosive to metals

Substances or mixtures with a corrosion rate on either steel or aluminium surfaces exceeding 6.25 mm per year at a test temperature of 55 °C when tested on both materials.

Scope of substances or mixtures to be tested:

- Liquids and solids having a melting point <= 56 °C and
  - having acidic or basic functional groups, or
  - containing halogen, or
  - having complexing or surface-active properties
- Hygroscopic solids which may become corrosive in the presence of moisture

Flammable liquids - overview



Flammable liquids – flashpoint calculation

Method as described by Gmehling and Rasmussen[1)]

Required information: For each component knowledge of

- Concentration
- Lower explosion limit
- Temperature dependence of saturated vapour pressure
- Activity coefficient for each component.

Applicability:

- Only homogeneous liquid phases
- Calculated flashpoint is at least 5 K above classification limit.

[1)] Ind. Eng. Chem. Fundament, 21, 186, (1982)

Flammable liquids – test methods

Test method:

- Flash point: Only closed cup tests may be used
- Selection of method has to take sample composition and properties into account

Guidance document:

- At least two test runs; one of them may be automated
- Special precedures for halogenated compounds

Flammable solids (1)

Dang. Subst. Directive Test method: EC A.10	GHS Test method: UN N.1 *)
R 11 Highly flammable Burning time < 45 s	Flammable solid Cat. 1 Burning time < 45 s Wetted zone does not stop propagation of flame
	Flammable solid Cat. 2 Burning time < 45 s Wetted zone stops propagation of flame

*) for metals special criteria

Flammable solids (2)

Screening test: Burning index acc. to VDI guideline 2263, part 1, 1990, *Test methods for the Determination of the Safety Characteristics of Dusts*

Observation	Burning index	Further testing
No ignition	1	Not required
Brief ignition and rapid extinction	2	
Localised combustion or glowing, practically no spreading	3	
Glowing or slow decomposition without flame	4	UN N.1 Required
Burning with open flame or generation of sparks	5	
Vary rapid combustion with or without flame	6	

Note: Behavior of the mixture is relevant; no conclusion from flammability of individual components!!!

Self-heating substances and mixtures (1)

Substances and mixtures which are liable to self-heat by reaction with air and without energy supply

This phenomenon is generally only relevant for large volumes and over extended periods of time (i.e. storage)

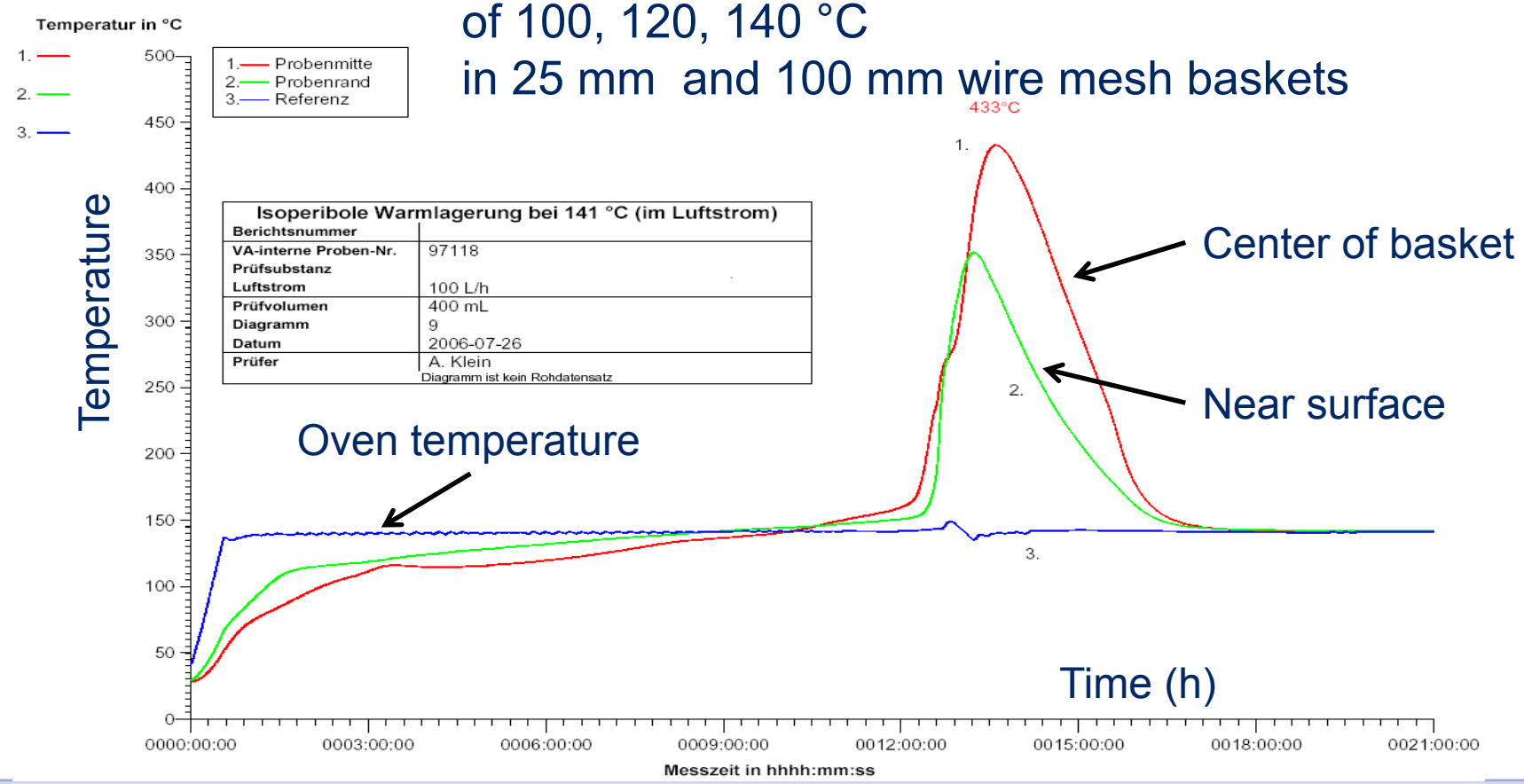
New hazard class without correspondence in the DSD

Classification	Category 1	Category 2
GHS symbol		
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)

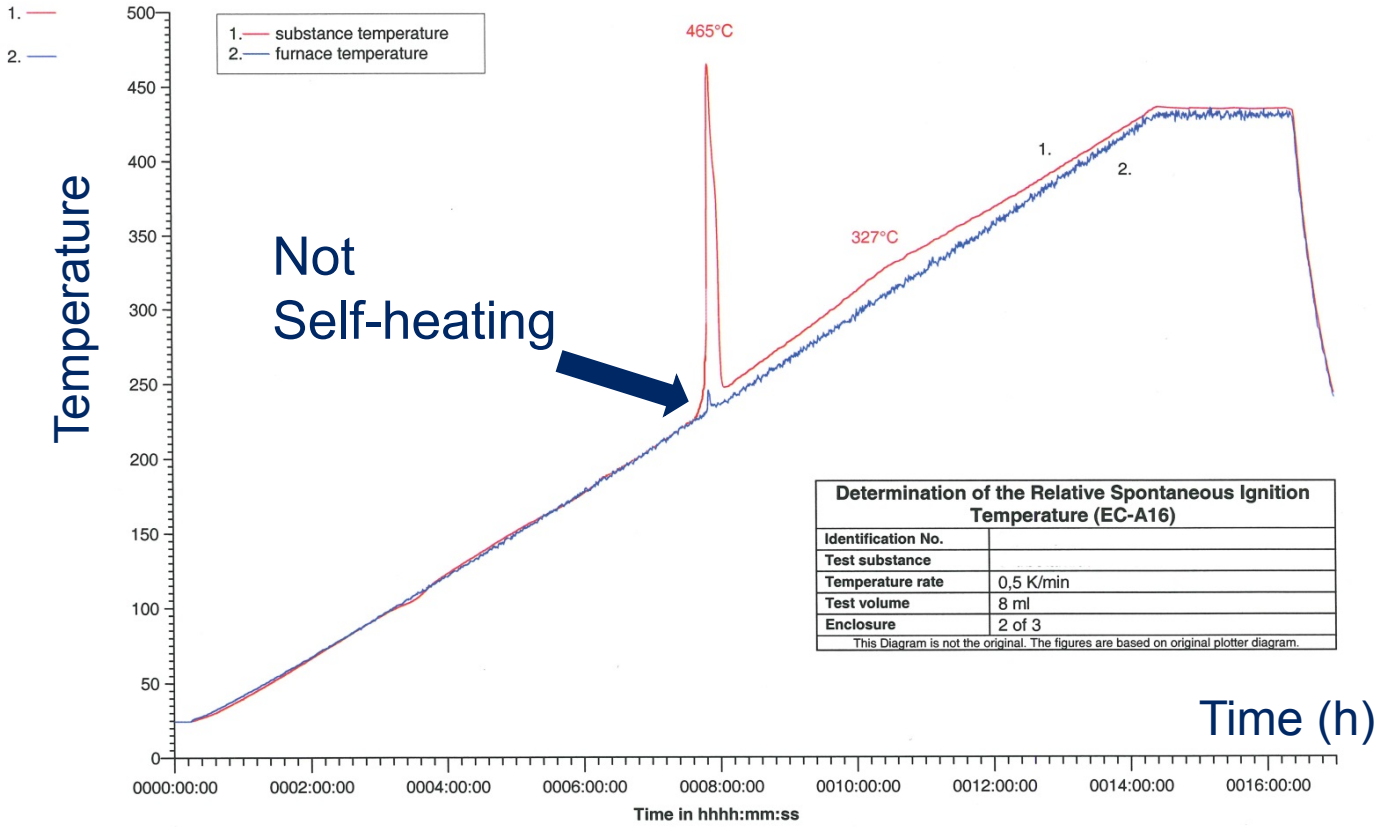
Test method: UN N.4 (Bowes-Cameron Cage Test)

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



Self-heating substances and mixtures (3)

NOTE: The „translation“ of data from test EC A.16 is only possible using the measurement plots. This is due to a ridiculous evaluation criterion in the EC method !



Self-heating substances and mixtures (4)

Note: The self-heating behavior of a mixture cannot be predicted by the properties of the individuals components.

Screening test: Grewer oven test (VDI guideline 2263, part 1, 1990, *Test methods for the Determination of the Safety Characteristics of Dusts)*

Liquids and solid mixtures which are **completely molten** up to a temperature of 160 °C should not be considered for this class (see Guidance on the Application of the CLP Criteria)

Contribution of individual substances

For the following classes, the properties of individual component(s) may have a direct influence on the classification of the mixture.

⟹ If individual substances of the following classes are not present, a corresponding classification of the mixture can be ruled out:

- Pyrophoric solids and liquids
- Substances which, in contact with water, emit flammable gases
- Oxidizing solids and liquids
- Organic peroxides.

Pyrophoric solids and liquids

Solids and liquids which ignite spontaneously in contact with air

Solids:	Hydrogenation catalysts (especially when saturated with hydrogen), n-hexyl lithium, trialkyl boranes, white phosphorus
Liquids:	Dimethylzinc, trichlorosilane, aluminium alkyls, magnesium alkyls, trialkyl boranes

Many of these substances also react vigorously with water!!

Note: When mixtures contain pyrophoric substances, also look for self-heating behavior!

Substances which, in contact with water, emit flammable gases (1)

TDG Packing group	GHS Category	Criterion
I	1	Spontaneous ignition or gas release rate ≥ 10 l /kg over any minute one minute.
II	2	Maximum gas release rate ≥ 20 l/kg of substance per hour
III	3	Maximum gas release rate ≥ 1 l/kg of substance per hour

Substances which, in contact with water, emit flammable gases (2)

Substance	Example	Gas evolved
Alkaline and alkaline earth metals	Li, Na, K, Ca, Mg	Hydrogen
Metal hydrides	$LiAlH_4$, NaH, CaH_2	Hydrogen
Metal alkyls	Al-Alkyls , Mg-Alkyls, Zn-Alkyls	Alkanes
Carbides, Phosphides, Sulphides	CaC_2, AlP, Ca_3P_2, Mg_3P_2, Zn_3P_2, P_2S_5	Acetylene, phosphine, hydrogen sulfide

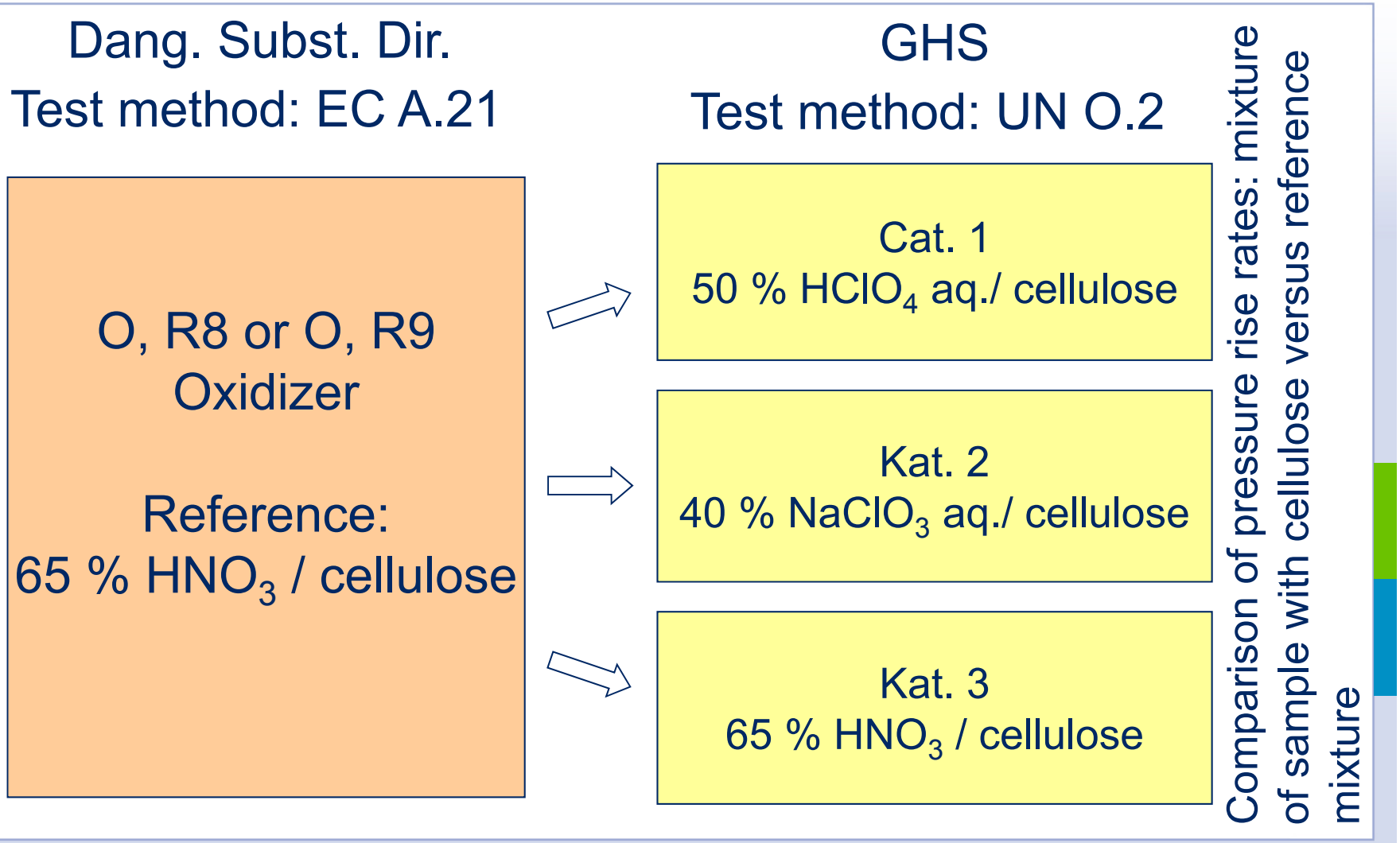
Oxidizing liquids and solids (1)

Substance or mixture which … may, generally by yielding oxygen, cause, or contribute to, the combustion of other material.

Features of the test method:

- Oxidation reaction of sample with cellulose
- Reference system: defined oxidizer and cellulose
- Comparison of reaction rates of reference system and mixture of sample with cellulose

Oxidizing liquids (2)



Oxidizing liquids and solids (3)

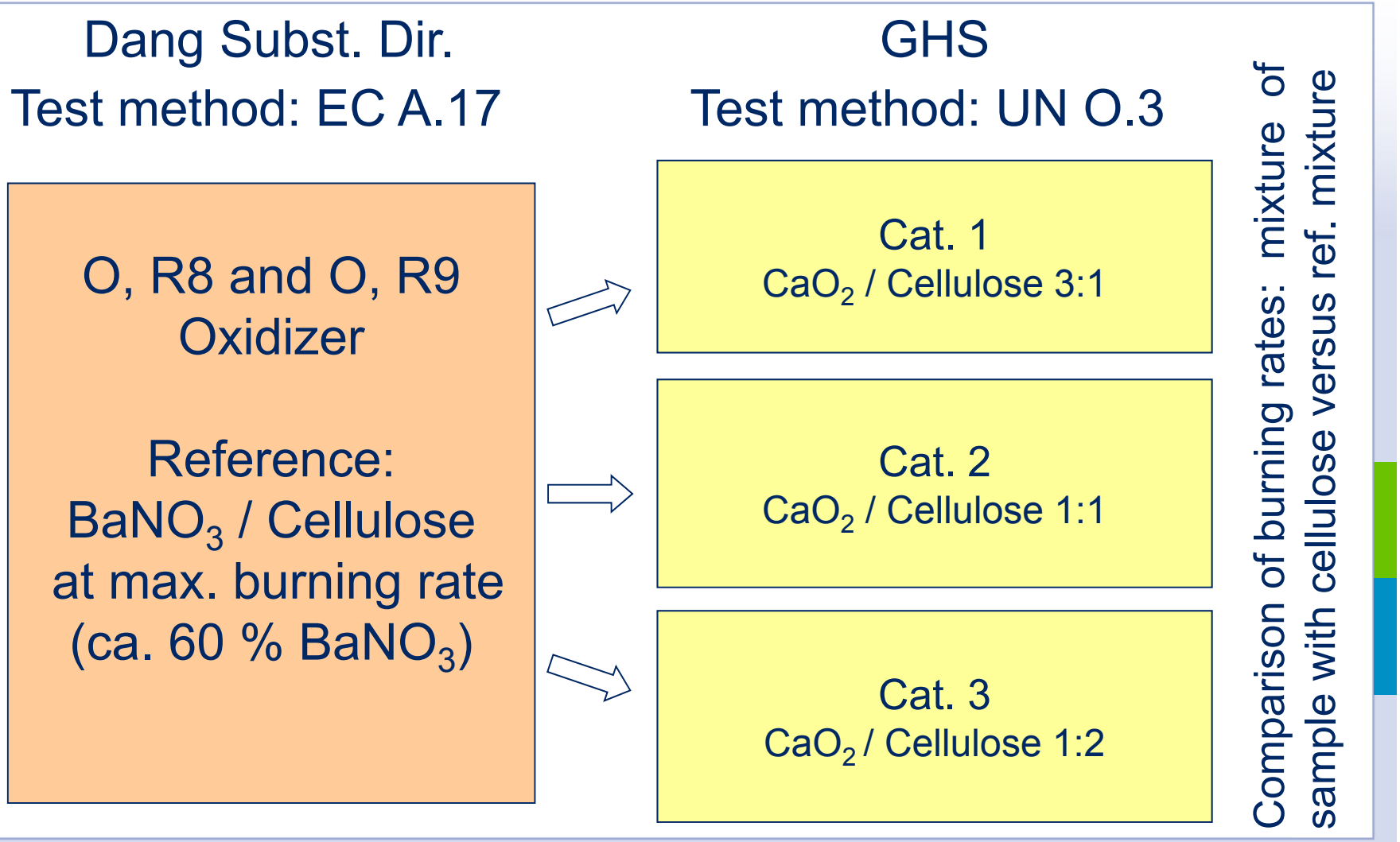
In test method UN O.1, small deviations in sample preparation and test setup may have severe impact on the results obtained. Therefore, the test method has been improved by a working group at UN level. Result: New test method UN O.3 is **preferred** method for solids (UN decision Dec. 2012)

False positive test results are obtained frequently. This may happen in the following cases:

- Exothermic decomposition (initiated under test conditions)
- Substances which may react exothermally with the hydroxy groups of cellulose (e.g. functional groups –NCO, $–SO_2Hal$, –COHal, $–CCl_3$)

⇒ High level of expertise of test lab required!!!

Oxidizing solids (4)



Oxidizing liquids and solids (5)

Notes:

- Use screening procedures to identify possible oxidizers!
- For substances carrying N-O, S-O and P-O bonds, seek expert advice!
- Mixtures of oxidizers with organic substances or other reducing agents may have explosive or self-reactive properties!
- Testing for the Class of Explosives is required for
  - Mixtures of ≥ 15 mass % of inorganic oxidizers, Cat. 1 or 2, with organic substances
  - Mixtures of ≥ 30 mass % of inorganic oxidizers, Cat. 3, with organic substances
- In low concentrations (< 5 %), in mixtures with only inert substances, the oxidizing properties will vanish.

Organic peroxides

Organic peroxide (OP): solid or liquid organic compound which contains bivalent -O-O structure

Properties:

- combination of high decomposition potential and low thermal stability
- Very sensitive to impurities!
- Seek expert advice if you have a new mixture not listed in the Transport Regulations!

Note: Special legal requirements may apply for these substances !

Self-reactive substances and mixtures (1)

- Self-reactive substance or mixture (SR): liquids or solid substance or mixture with a combination of increased decomposition potential and low thermalstability

Note: Special legal requirements may apply for these substances !

Temperature control (!) required when

- SRs: SADT*) <= 55 °C

*) SADT = Self-accelerating decomposition temperature acc. to UN test series H

Self-reactive substances and mixtures (2)

Classification criteria for SRs:

- Substances and mixtures with SADT ≤ 75 °C **and** decomposition energy ≥ 300 J/g, and
- No Explosive, no Oxidizer, no Organic Peroxide

No testing required when

- There are no chemical groups present in the molecule associated with explosive or self-reactive properties; examples of such groups are given in Tables A6.1 and A6.2 of the UN Test Manual

Note: A DSC measurement will help you in identifying the thermal stability of a substance or mixture. Statements in the SDS such as „stable under conditions of normal use“ or similar should be avoided!!!

Self-reactive substances and mixtures (3)

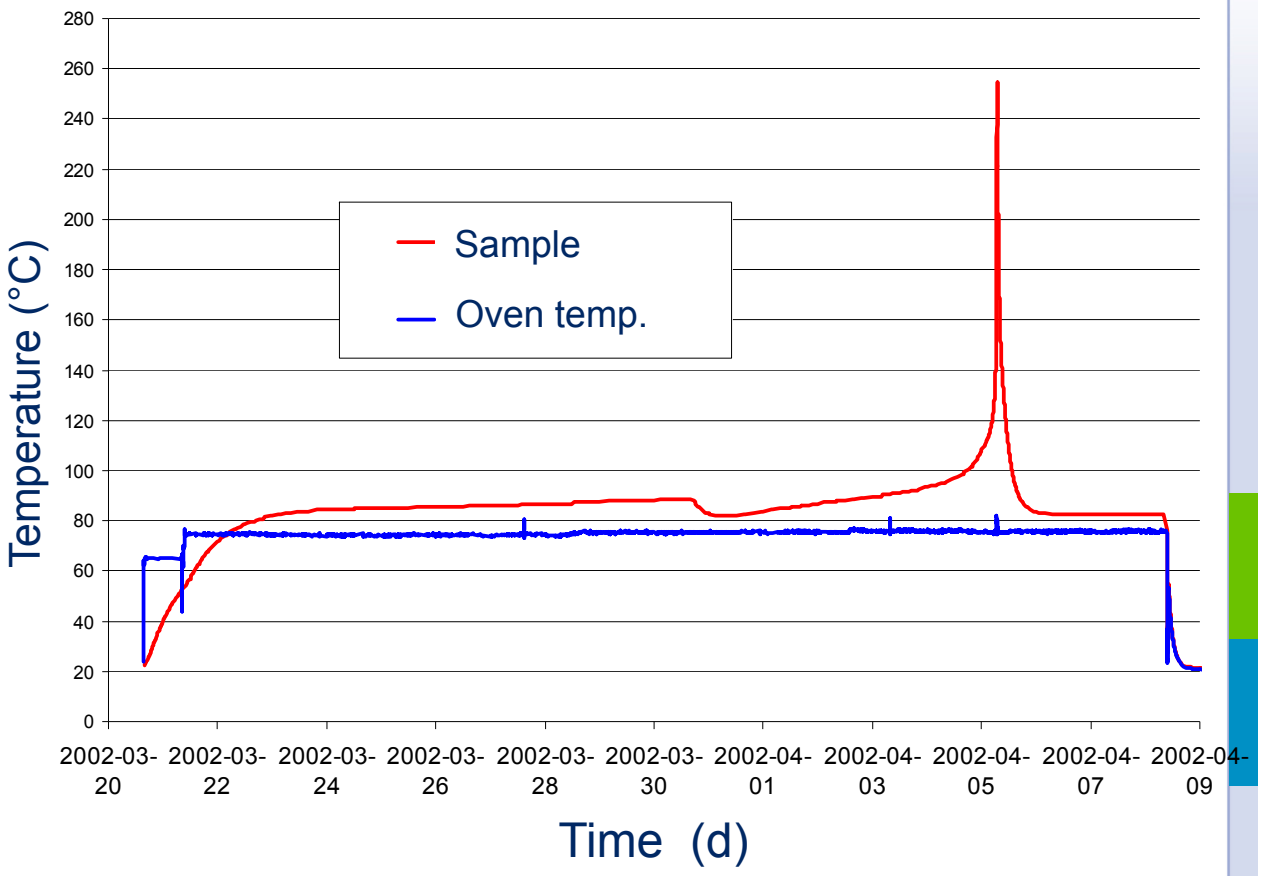
Table A6.1 EXAMPLES OF CHEMICAL GROUPS INDICATING EXPLOSIVE PROPERTIES IN ORGANIC MATERIALS

Structural feature	Examples
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

Structural feature	Examples
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

Dewar vessel for SADT determination



Self-reactive subst. and mixtures (4): Classification

Decomposition energy > 300 kJ/kg from DSC measurement

SADT < 75 °C

- Self-reactive substance acc. to CLP Directive
- Self-reactive substance acc. to Transport Regulations (Class 4.1)

- For further classification, comprehensive testing is necessary.
- Transport requires an approval by „Competent Authority“
- In most cases, transport is limited to small packages (<= 50 kg net mass)

Explosives (1): Screening procedure

Explosive properties are associated with the presence of certain chemical groups in a molecule …

The screening procedure is aimed at identifying the presence of such reactive groups and the potential for rapid energy release.

If the screening procedure identifies the substance or mixture to be a potential explosive, the acceptance procedure … **has** to be performed.

Explosives (2): Criteria for exclusion

No testing for class „Explosives“ necessary if

(a) there are no chemical groups associated with explosive properties present in the molecule. Examples of groups which may indicate explosive properties are given in Table A6.1 (Appendix 6, *UN Manual of Tests and Criteria)*; or

(b) The substance contains chemical groups associated with explosive properties which include oxygen and the calculated oxygen balance is less than - 200; or

(c) The exothermic decomposition energy is less than 500 J/g and the onset of exothermic decomposition is below 500 °C; …

Explosives (3): Need for action

Decomposition energy (J/g)	Decomposition onset (°C)	Testing for explosive properties required?
< 500	< 500	No
< 500	≥ 500	No
≥ 500	< 500	Yes
≥ 500	≥ 500	No

Explosives (4): Mixtures

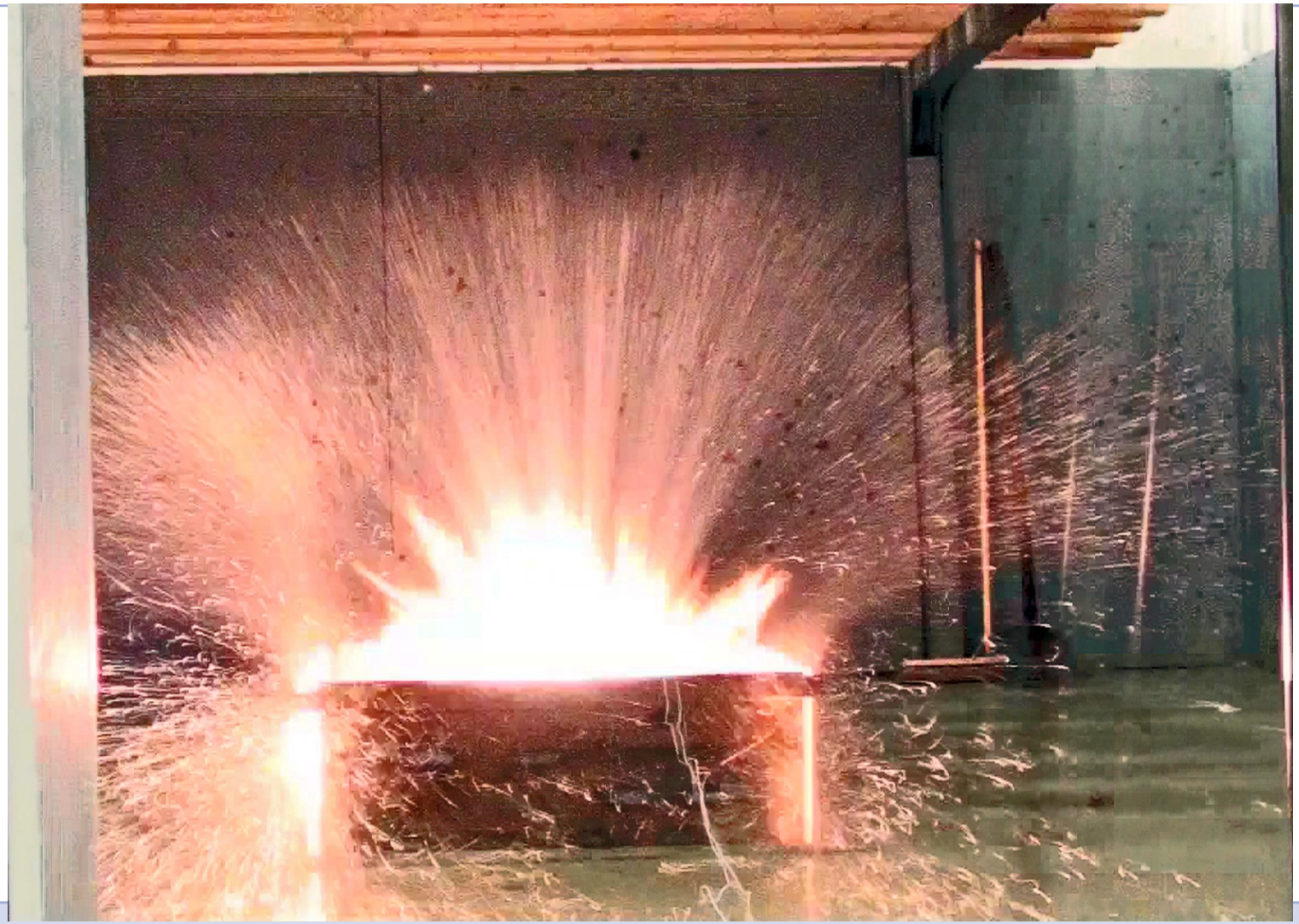
Testing is required for mixtures of organic substances with

- Oxidizers of Cat 1 or Cat in concentrations of ≥ 15 % (w/w%)
- Oxidizers of Cat 3 in concentrations of ≥ 30 % (w/w%)

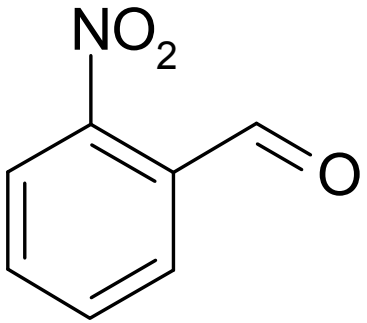
Explosives (5): DSD versus CLP/GHS

Dang. Subst. Dir. Test method: EC A.14	CLP / GHS Test method: UN test series 2
Impact sensitivity 50 mg sample	Sensitivity to detonative shock 2 kg sample !
Friction sensitivity about 500 mg	Ignition under confinement about 15 g
Heating under confinement (Koenen test) about 30 g	Heating under confinement (Koenen test) about 30 g
	… followed by further extensive testing

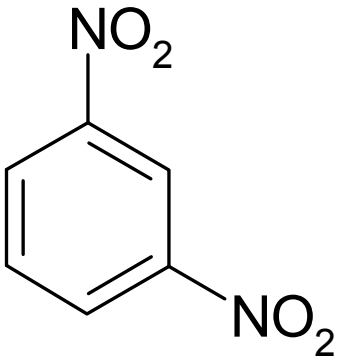
Explosives (6): Propagation of detonation



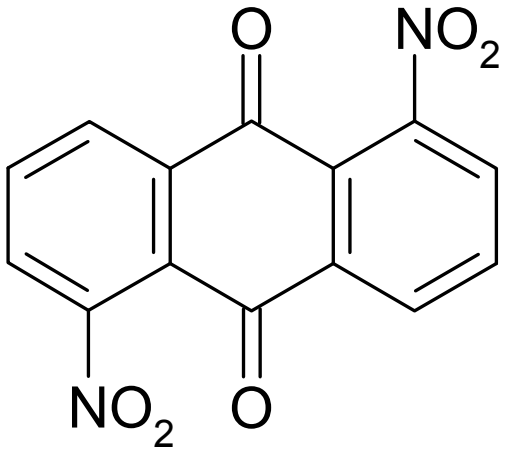
Explosives (7): Prediction of properties



Not explosive



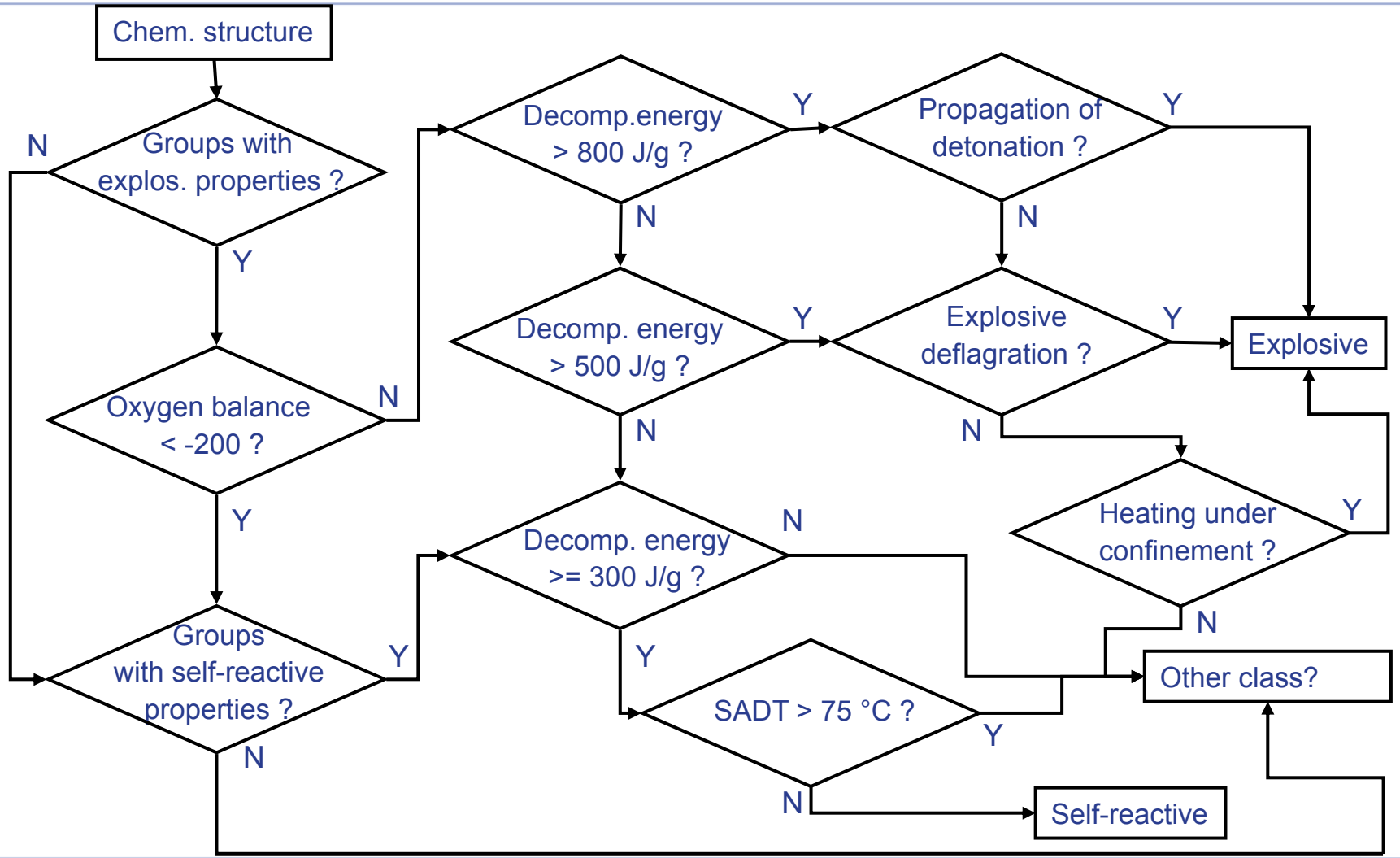
Not explosive



Explosive

German SprengG:
Group C

Testing of energetic substances (simplified)



Explosion protection

Dangerous explosive atmospheres as well as fire and explosion protection are covered by ATEX
and are not subject to CLP and REACH

Dust explosion hazard (1)

UN decision of Dec. 2012: Amend Annex 4 (SDS) as follows:

(a) For Section 2 of the SDS (Hazard Identification), sub-section A4.3.2.3:

"**A4.3.2.3 *Other hazards which do not result in classification***

Provide information on other hazards which do not result in classification but may contribute to the overall hazards of the material, for example, formation of air contaminants during hardening or processing, dust explosion hazards, suffocation, freezing or environmental effects such as hazards to soil-dwelling organisms. The statement "May form explosible dust/air mixture if dispersed" is appropriate in the case of a dust explosion hazard."

(b) For Section 5 of the SDS (Fire-fighting measures), sub-section A4.3.5.1:

"**A4.3.5.1 *Suitable extinguishing media***

Provide information on the appropriate extinguishing media. In addition, indicate whether any extinguishing media are inappropriate for a particular situation involving the substance or mixture (e.g., high pressure media which could cause the formation of a potentially explosible dust/air mixture)."

Dust explosion hazard (2)

(c) For Section 7 of the SDS (Handling and Storage), paragraph A4.3.7.1.1:

"A4.3.7.1.1 Provide advice that:

(a) allows safe handling of the substance or mixture;

(b) prevents handling of incompatible substances or mixtures;

(c) draws attention to operations and conditions which create new risks by altering the properties of the substance or mixture, and to appropriate countermeasures; and

(~~c~~ d) minimizes the release of the substance or mixture to the environment."

Current UN program of work (selection)

- Desensitized explosives
- Corrosivity
- Water activated toxicity / water reactive material
- Substances capable of polymerization
- Pyrophoric gases
- Dust explosibility
- Revision of Annexes 1, 2 and 3: Precautionary statements
- Labelling of small packagings
- Development of a list of chemicals classified in accordance with the GHS
- Revision of Section 9 of Annex 4 of the GHS

Conclusions

Apply UN test methods for new substances and mixtures.

Verify carefully the applicability of the translation tables in case of intended use.

Get advice from competent expert.

Consider possible consequences in downstream legislation.

Take minimum data requirements of REACH into account.

Check whether a classification into one of the new classes is relevant for your products.

Apply special care for energetic substances / mixtures; a DSC measurement will help you to identify the need for action.

Requirements for DSC measurements*)

- Representative sample
- Closed crucible
- Sample preparation under inert conditions if necessary
- Heating rate: 3 – 5 K/min
- Inert material of crucible

*) UN Manual of Tests and Criteria, Section 20.3.3.3

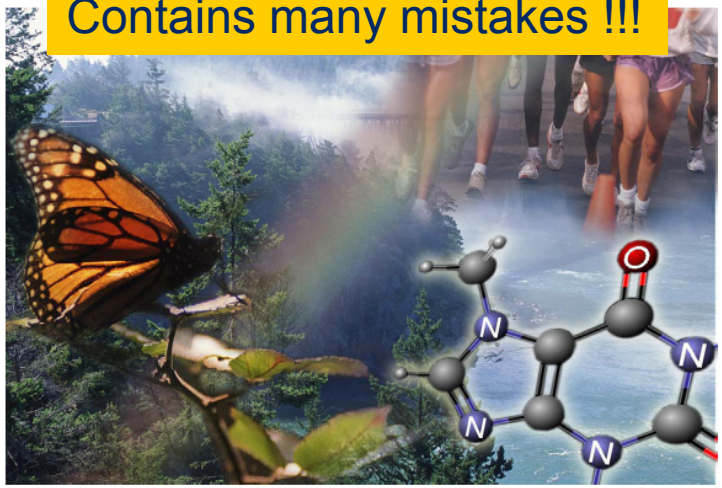
Guidance (1)

ECHA

Guidance on information requirements and chemical safety assessment

Chapter R.7a: Endpoint specific guidance

Contains many mistakes !!!



May 2008

Guidance for the implementation of REACH

ECHA
http://echa.europa.eu

Guidance on the Application of the CLP Criteria

Guidance to Regulation (EC) No 1272/2008 on classification, labelling and packaging (CLP) of substances and mixtures

Very detailed, expert level

Guidance (2) Current status:

- R.7a was revised in a fast-track procedure (no detailed expert discussions), alignment of CLP and REACH was performed as far as possible.
  -> Consultation concluded, new edition 2013

http://echa.europa.eu/web/guest/guidance-documents/guidance-on-information-requirements-and-chemical-safety-assessment

Guidance (3) Current status

- Part E: Risk characterisation: extensive discussions with ECHA: ECHA tries to introduce risk assessment for physical hazards -> not accepted by experts

➡ Copy only statements from eSDS to CSR, DO NOT discuss exposure scenarios for physical hazards!

Exposure scenarios …

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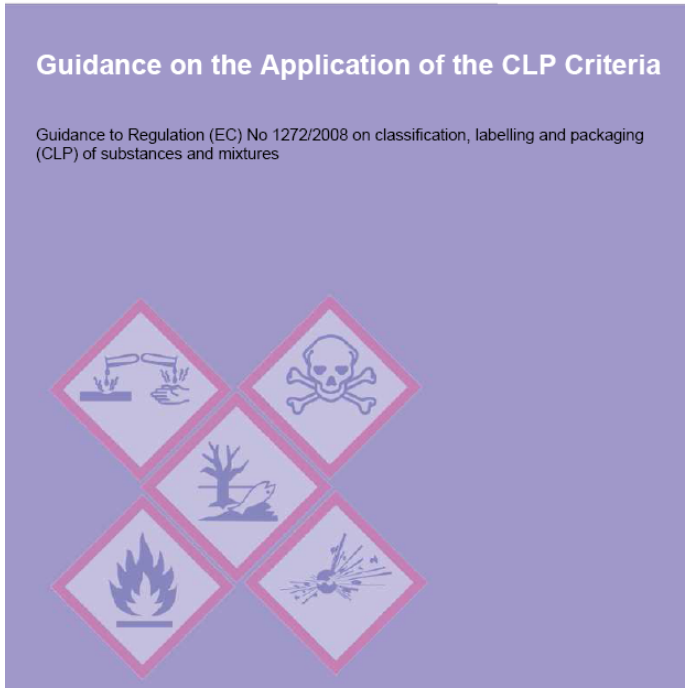
Guidance (4) Current status

- Guidance on the Application of the CLP Criteria
- Update for second and 4th ATP: PEG discussions completed; published in Nov. 2013



About the use of computerized translation tools (CLP-VO, Annex VII)

Computers allow you to produce errors more quickly and more reliably.

See http://www.dohrendorf.de/pages/startseite/berufsleben/vom-teen-ager-zum-man-ager.php

Science For A Better Life

Thank you for your attention!

Dr. Dieter Heitkamp

Bayer Technology Services GmbH

OSS-PPS CHP, 51368 Leverkusen

Telefon +49 214-30 61938

E-Mail: dieter.heitkamp@bayer.com