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Classification of Chemicals According to UN-GHS and EU-CLP: A Review of Physical Hazard Classes and Their Intricate Interfaces to Transport and Former EU Legislation

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Abstract:

The Globally Harmonized System of Classification and Labelling of Chemicals (UN-GHS) is being implemented in more and more countries all over the world; the EU has done so with the CLP-Regulation (EU-CLP). Compared to the undeniably important questions on health and environmental hazards, the classification of physical hazards of chemicals often has not been in the focus, although their implementation can be challenging and there are traps and pitfalls to be avoided. The following overview of the classification systematics for physical hazards aims at a principle understanding without detailing all criteria or test methods. Similarities and differences between the classification systems of the UN-GHS and EU-CLP, the transport of dangerous goods and the former EU system are reviewed with regard to the physical hazard classes. Available physical hazard classifications for the transport of dangerous goods and according to the former EU system can be used as available information when classifying according to the GHS. However, the interfaces of these classification systems and their limitations have to be understood well when concluding on GHS/CLP classifications. This applies not only to industry when applying CLP but especially to legislators when adapting legislation that in one way or another refers to the classification of chemicals.

Keywords: GHS, CLP-Regulation, Classification of chemicals, Physical hazards

Introduction

The Globally Harmonized System of Classification and Labelling of Chemicals (UN-GHS) [1] is being implemented in more and more countries all over the world [2]. In Europe, it was implemented through the CLP-Regulation (EU-CLP) [3].

Physical hazards of chemicals are often not in the focus when it comes to chemicals legislation and European chemicals legislation is often driven by the - undeniably - important questions and issues regarding health and environmental hazards. However, the implementation and application of physical hazards can be quite challenging and there are some pitfalls to be avoided.

The classification of physical hazards of chemicals according to the UN-GHS – and thus EU-CLP – differs systematically from the former EU system (Substances Directive and Preparations Directive) [4]. Hence, a simple translation from the former EU classification of a chemical into the new system can often not be achieved easily. CLP requires in Article 8 (2) that tests for the classification of physical hazards be conducted, unless adequate and reliable information is available. Especially the classification of mixtures requires testing in most cases because there are only a few physical hazards for which concentration limits or calculation methods based on the ingredients are available. The physical hazards of the GHS are based on the classification criteria for dangerous goods according to the UN Recommendations on the Transport of Dangerous Goods (UN-TDG) [5] and many of the according test methods are contained in the UN Manual of Tests and Criteria [6]. Therefore, available transport classifications can provide useful information when classifying for GHS or CLP. However, the similarities, interfaces and differences between these classification systems must be well understood so that incorrect conclusions are avoided when making use of transport or former EU classifications.

The primary intention of this overview is to promote a principle understanding of the classification systematics for physical hazards and thereby to raise awareness for the complexity of the issue. On the hand, it aims to support stakeholders who – because of the intricacy of the subject – are faced with questions to that regard. On the other hand, expert knowledge of legislators in this area is just as important when adapting and amending legislation on chemicals and downstream-legislation.

Usability of transport and former EU classifications for GHS and CLP

As the system for the classification of physical hazards according to the UN-GHS - and thus the EU-CLP - differs in its systematics from the former EU system, a direct translation of an available classification of a chemical is possible only for a few hazard classes (see Table 1). For most physical hazard classes, further information and data are necessary in order to derive the correct classification. One important source of information is the transport classification of dangerous goods, because the UN-GHS and the UN-TDG make use of the same criteria for physical hazards. However, some different principles in both systems may result in different or additional classifications and therefore caution and expert judgement are necessary when translating transport classifications of dangerous goods into GHS or CLP classifications:

- The Dangerous Goods List for the UN-TDG contains many substances and mixtures classified by default. However, these classifications are not always based on the criteria but instead may be based on experience or certain circumstances specific to transport.
- In contrast to the GHS and CLP, the TDG applies a concept for the precedence of hazards. Some hazards are not reflected by the TDG classification or are considered only as subsidiary risks for transport. However, these hazards might be applicable for the purposes of GHS/CLP and in that case have to be classified in addition.
- Sometimes special provisions (SP) are linked to entries in the Dangerous Goods List and have to be observed. These special provisions might also impose conditions that are to be met in order to assign the respective class for transport (otherwise another classification might be applicable). One example is SP 306 which is assigned to ammonium nitrate: Classification of ammonium nitrate in accordance with UN No. 1942 or 2067 as oxidizing may only be used if it is too insensitive for acceptance into class 1 (explosives).
- A substance might also have different entries with different classifications in the Dangerous Goods List. One example is ammonium perchlorate which is classified as explosive according to UN No. 0402. Although rarely used, it might also be classified as an oxidizing solid according to UN No. 1442. Both entries have SP 152 assigned, according to which the classification depends on the particle size and the packaging.

Table 1: Comparison of hazard classes acc. to UN-GHS / EU-CLP and UN-TDG.

*	UN-GHS / EU-CLP		UN-TDG	
	Chapter	**Hazard class**	Class	**Division / Designation**
🟨	2.1	Explosives	1	Explosives
▨	2.2	Flammable gases	2	Division 2.1 Flammable gases
🟧	2.3	Aerosols	2	Division 2.1 or Division 2.2
🟦	2.4	Oxidizing gases	2	Division 2.2 Non-flammable, non-toxic gases
🟥	2.5	Gases under pressure	2	Gases - all divisions
🟦	2.6	Flammable liquids	3	Flammable liquids
▨	2.7	Flammable solids	4	Division 4.1 Flammable solids
🟧	2.8	Self-reactive substances and mixtures	4	Division 4.1 Self-reactive substances
🟩	2.9	Pyrophoric liquids	4	Division 4.2 Substances liable to spontaneous combustion
🟩	2.10	Pyrophoric solids	4	Division 4.2 Substances liable to spontaneous combustion
🟥	2.11	Self-heating substances and mixtures	4	Division 4.2 Substances liable to spontaneous combustion
▨	2.12	Substances and mixtures which in contact with water emit flammable	4	Division 4.3 Substances which in contact with water emit flammable gases
▨	2.13	Oxidizing liquids	5	Division 5.1 Oxidizing substances
▨	2.14	Oxidizing solids	5	Division 5.1 Oxidizing substances
🟨	2.15	Organic peroxides	5	Division 5.2 Organic peroxides
🟥	2.16	Corrosive to metals	8	Corrosive substances
🟧	2.17	Desensitized explosives	3 4	Liquid desensitized explosives or Division 4.1 Solid desensitized

* In addition, the relation to the former EU-system is illustrated by colours:

Green:	Hazard class has not changed
Turquois:	Hazard class has not changed but is newly subdivided
Blue:	Hazard class is familiar but has changed criteria
Yellow:	Hazard class has the same title but completely changed systematics
Orange:	Hazard class is new but most chemicals were also classified previously
Red:	Hazard class is new and the hazard has not been classified previously

As illustrated in Table 1, only two hazard classes of the GHS and CLP are actually identical to former EU classifications according to the Substances Directive (marked in green) whereas all other hazard classes differ to varying degrees from former EU classifications. In the following, each GHS physical hazard class is discussed with a special view to interfaces to the TDG and the former EU system. The chapters are ordered based on the similarity to the former EU-system, as indicated by the colours in Table 1:

- Unchanged hazard classes
- Unchanged hazard classes with new sub-categories
- Familiar hazard classes with changed criteria
- Hazard classes with completely changed systematics
- New hazard classes but the hazards have been covered previously
- New hazard classes and the hazards have not been covered previously.

Unchanged hazard classes

Pyrophoric liquids and pyrophoric solids

The UN-GHS and EU-CLP classification of pyrophoric liquids and pyrophoric solids corresponds to the former EU classification of liquids and solids classified as F; R17. Furthermore, it corresponds to the classification of liquids and solids of division 4.2 packing group I according to the TDG (see Figure 1).

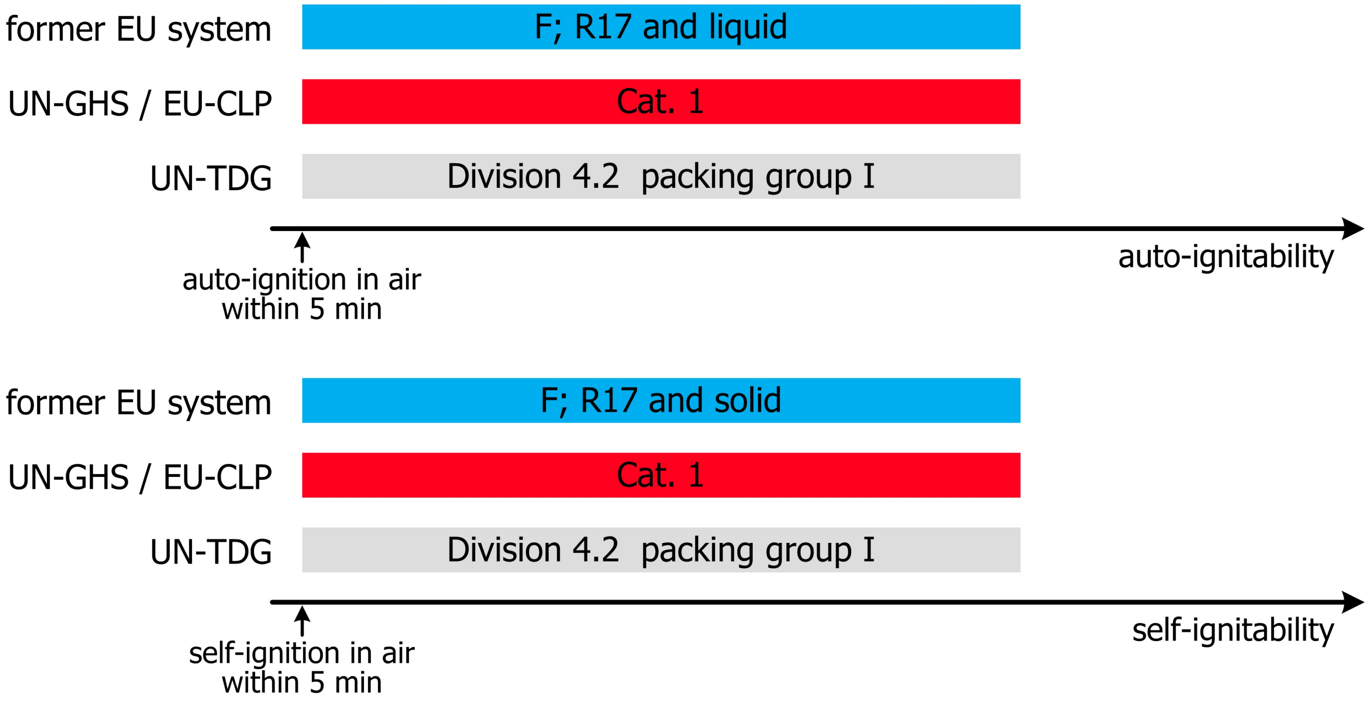

Figure 1: Comparison of classification systems for pyrophoric liquids and solids.

The UN tests N.3 for liquids and N.2 for solids according to the UN Manual of Tests and Criteria are referred to in the GHS and CLP. The classification criterion is the auto-ignition or self-ignition delay time in air of the liquid/solid, respectively. Both tests are easy to conduct so that the classification of substances and mixtures can be achieved easily. These tests are comparable to test method A.13 which was applicable for classifying liquids and solids as F; R17 according to the former EU system [7].

Unchanged hazard classes with new sub-categories

Flammable gases

The UN-GHS and EU-CLP classification of flammable gases corresponds to the former EU classification of gases classified as F+; R12. In addition, flammable gases are now divided into categories 1 and 2. Category 1 corresponds to the classification of gases of division 2.1 according to the TDG (see Figure 2).

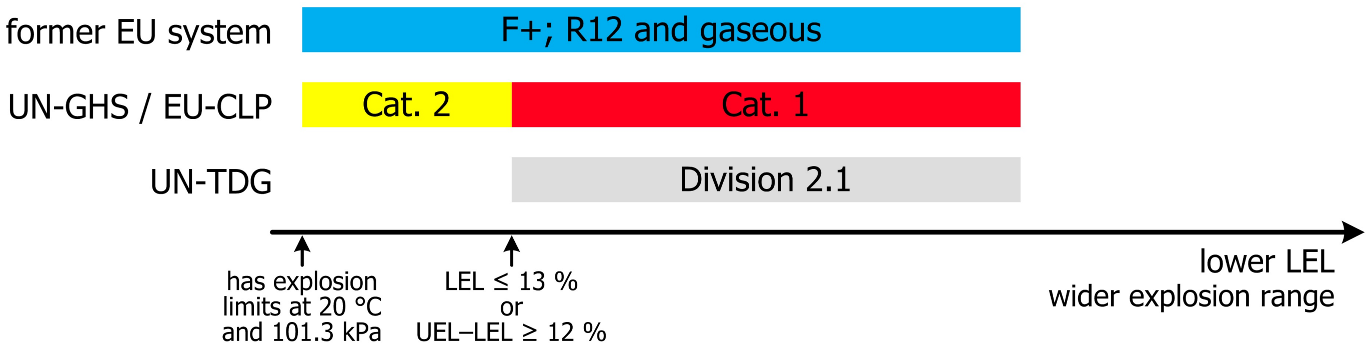

Figure 2: Comparison of classification systems for flammable gases.

For testing and calculation, the GHS and CLP refer to ISO 10156 [8]. The test method is similar to test method A.11 which was previously referenced in the EU. The classification criterion is the existence of an explosion range in air at atmospheric conditions. The principle is that mixtures of air and increasing test gas content are ignited in a glass cylinder and examined for flame propagation until the test gas content is such that the explosion limit is reached. Category 2 is identified based on the lower explosion limit (LEL) and the width of the explosion range (UEL−LEL).

The calculation method for the classification of mixtures is the same as formerly described in Annex VI No. 9 of the Substances Directive. It can be used instead of testing to determine whether a gas mixture containing flammable components has to be classified as flammable or not. According to the calculation method, a gas mixture does not have to be classified as flammable when the following inequality is satisfied:

$$\sum_{i=1}^{n} A_i \left(\frac{100}{T_{ci}} - 1\right) \leq \sum_{k=1}^{p} B_k K_k$$

where

n	number of flammable gases in the gas mixture
A_i	molar fraction of flammable component i, in %
T_{ci}	maximum content of flammable gas i, which, when mixed with nitrogen, is not flammable in air, in %
p	number of inert gases in the gas mixture
B_k	molar fraction of inert gas k, in %
K_k	coefficient of equivalency of inert gas k relative to nitrogen

The values for T_{ci} and K_k for the most commonly used gases are listed in ISO 10156, and thus it is easy to calculate whether a gas mixture has to be classified as flammable. If, based on the calculation, a gas mixture is classified as flammable, it has to be assigned to category 1. The calculation method is conservative, i.e. differences might be observed between classifications based on testing or calculation. It has to be noted, that the flammable properties of a mixture are not only determined by its flammable components but - through the K_k -value - also by its inert components (the same applies to oxidizing gas mixtures, for an example see Oxidizing gases below).

There are two additional sub-categories A and B for chemically unstable gases within the hazard class of flammable gases. These classifications were not part of the former EU system and they are also not part of the TDG. It must be noted, that gases are classified as chemically unstable only if they are classified as flammable. This is the case for most chemically unstable gases, but there are a few unstable gases which, therefore, are not classified as such (e.g. ozone or dinitrogen oxide). There is no calculation method for chemically unstable gases, however information on concentration limits for mixtures containing a chemically unstable gas is given in the UN Manual of Tests and Criteria, Section 35. This will facilitate the classification of mixtures.

The UN-GHS of 2015 introduces a further sub-category within the hazard class of flammable gases. Gases with an auto-ignition temperature ≤ 54 °C (this odd number results from the conversion of the corresponding Fahrenheit-value used in the US) are classified as pyrophoric gases [9]. This classification is not part of the TDG (although some requirements are linked to gases which are pyrophoric) and it was also not applied in the former EU system. The GHS refers to IEC 60079-20-1 and DIN 51794 for testing the pyrophoricity of gases. In addition, it contains a general concentration limit according to which gaseous mixtures containing more than 1 % pyrophoric components should be classified as pyrophoric if no data are available and thus (without stating it directly) classification of mixtures is not necessary if pyrophoric components are present below that concentration.

Flammable solids

The GHS and CLP classification criteria for flammable solids corresponds to the former EU classification of solids classified as F; R11. In addition, flammable solids are now divided into categories 1 and 2. These categories correspond to packing groups II and III of solids of division 4.1 according to the TDG (see Figure 3).

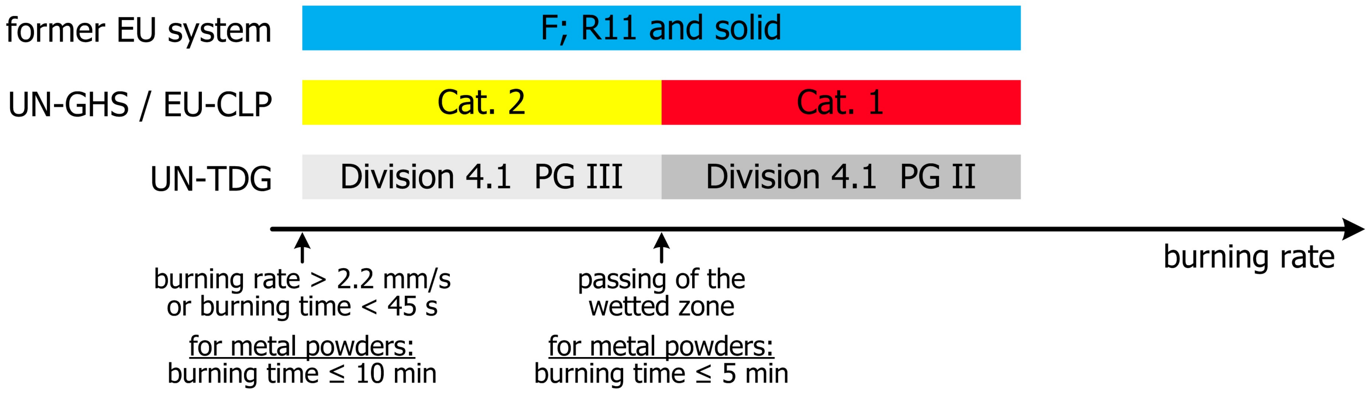

Figure 3: Comparison of classification systems for flammable solids.

The GHS and CLP refer to UN test N.1 of the UN Manual of Tests and Criteria. This test is similar to test method A.10 which was referenced in the EU by the Substances Directive. The classification criterion is the burning rate / time of the solid when ignited in the form of a defined strip or powder train. Distinction between categories 1 and 2 is achieved by a wetted zone close to the end of the strip. If the wetted zone is passed, category 1 has to be assigned. For metal powders, categories 1 and 2 are distinguished via the burning time.

Although the criteria for solids previously classified as F; R11 and for flammable solids according to the GHS and CLP are the same, the conversion is not biunique. Not all solids which were classified as F; R11 are now classified as flammable solids. According to GHS and CLP, they now may fulfil the criteria for self-reactive substances and mixtures (see 7.2 below). Furthermore, it has to be kept in mind that the classification of flammable solids is not predominant for transport and therefore might not be reflected in the transport classification – even though the criteria might be met.

Substances and mixtures which in contact with water emit flammable gases

The GHS and CLP classification of substances and mixtures which in contact with water emit flammable gases is similar to the former EU classification of liquids and solids classified as F; R15. In addition, they are now divided into 3 categories. These categories correspond to packing groups I, II and III of liquids and solids of division 4.3 according to the TDG (see Figure 4).

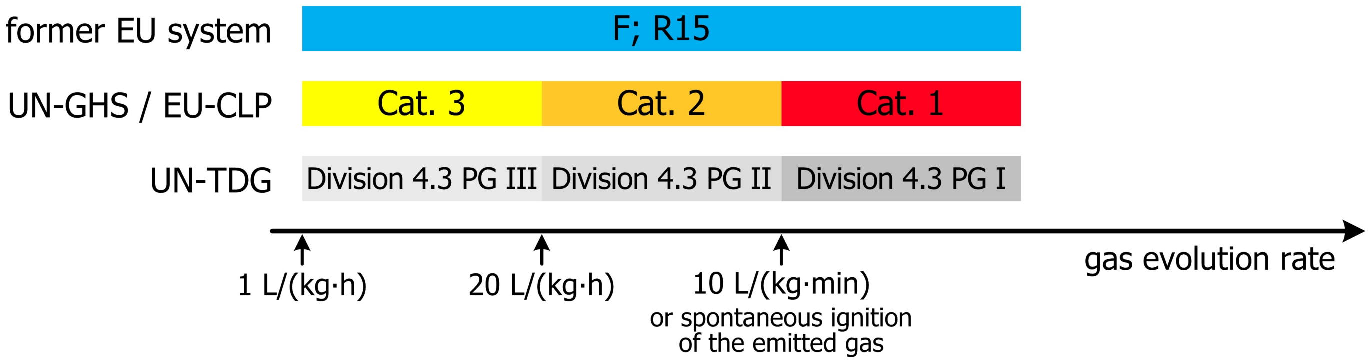

Figure 4: Comparison of classification systems for substances and mixtures which in contact with water emit flammable gases.

The GHS and CLP refer to UN test N.5 of the UN Manual of Tests and Criteria. This test is similar to test method A.12 which was applied in the former EU system. The principle is that the gas evolution rate of the test substance with water is determined. The limiting criterion for the gas evolution rate according to the former EU system was the same, however no further subdivision was foreseen. Furthermore, some aspects regarding the execution of the test methods are different, such as the amount of test sample and water, and the intervals in which the gas evolution rate has to be measured. Another difference is that pyrophoric substances did not have to be tested/classified according to the former EU system whereas this is required according to the UN Manual of Tests and Criteria. Therefore, expert judgement is necessary when assessing results of the former EU test method with respect to the GHS criteria. In addition, it must be kept in mind that transport division 4.3 is not predominant and thus might not be reflected in the transport classification.

Oxidizing liquids

The GHS and CLP classification of oxidizing liquids corresponds to the former EU classification of liquids classified as O; R9 or O; R8. In addition, oxidizing liquids are now divided into 3 categories. These categories correspond to packing groups I, II and III of liquids of division 5.1 according to the TDG (see Figure 5).

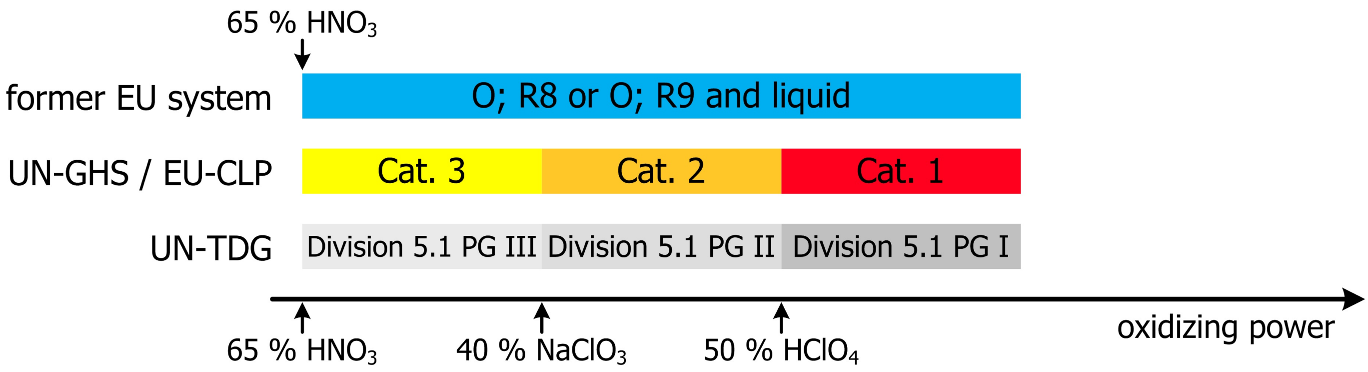

Figure 5: Comparison of classification systems for oxidizing liquids.

The GHS and CLP refer to UN test O.2 of the UN Manual of Tests and Criteria. The classification criterion is the oxidizing power as quantified by the pressure rise due to reaction of the liquid with cellulose. The pressure rise times are compared to those of mixtures of a reference substance with cellulose. The reference for test method A.21, which was applicable in the former EU system, and for category 3 according to the GHS and CLP are the same, namely 65 % nitric acid, i.e. exactly the same liquids are covered by the classification. However, further reference substances are used to assign categories 1 or 2.

Oxidizing solids

The GHS and CLP classification of oxidizing solids is similar to the former EU classification of solids previously classified as O; R9 or O; R8. In addition, oxidizing solids are now divided into 3 categories. These categories correspond to packing groups I, II and III of solids of division 5.1 according to the TDG (see Figure 6).

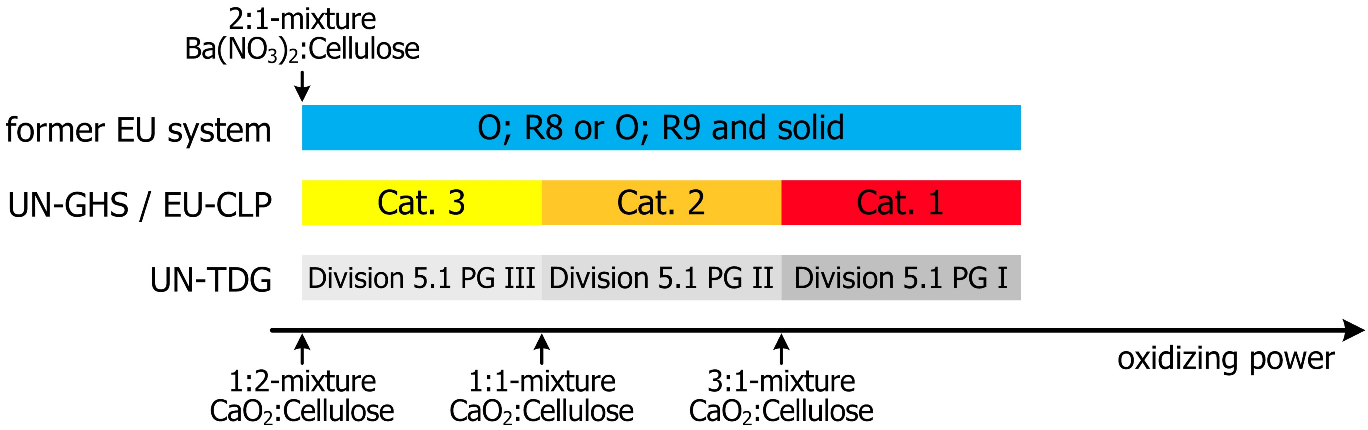

Figure 6: Comparison of classification systems for oxidizing solids

Calcium peroxide is the reference substance for the new UN test O.3.

The GHS - and thus CLP - and TDG refer to UN test O.1 of the UN Manual of Tests and Criteria. In addition, the GHS and the TDG refer to the newly introduced UN test O.3 [10]. The principle of this test and also of test method A.17 which was used in the former EU system, is that the burning rate of a defined strip (test method A.17) or pile (UN test O.1 and O.3) consisting of mixtures of the test substance with cellulose are compared to mixtures of reference substances with cellulose. However, the reference substances of the test methods and also some other aspects of the execution of the test have been changed. Therefore, expert judgement is necessary when assessing results according to the former EU test method with respect to the GHS criteria. As a consequence, there might be a few solids which are newly classified as oxidizing, and vice versa.

Familiar hazard classes with changed criteria

Oxidizing gases

Gases are classified as oxidizing based on their oxidizing power compared to air. The limiting criterion applicable for the GHS and CLP and for the TDG is identical. Such gases are classified as division 2.2 with subsidiary risk 5.1 for transport. The criterion is slightly different from the former EU system for the classification of gases as O; R8 (see Figure 7).

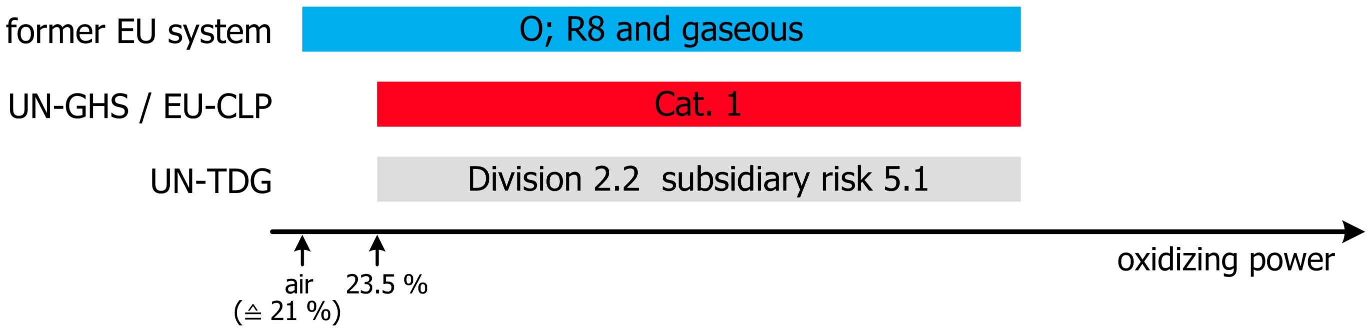

Figure 7: Comparison of classification systems for oxidizing gases.

The GHS, CLP and TDG refer to ISO 10156 for the test method and the calculation method which may be used for gas mixtures. Both correspond to the methods previously described in the Substances Directive. The principle of the test method is that the oxidizing power of the test gas is compared to that of air using a reference combustible. It must be noted that the limiting criterion according to the Substances Directive was the oxidizing potential of air, i.e. 21 %. However, the GHS and CLP explicitly refer to an oxidizing potential of 23.5 % as the limiting criterion. The higher value of 23.5 % is supposed to also cover artificial air which (in some cases) might have a slightly higher oxygen content.

Instead of testing, the calculation method can be applied to determine whether a gas mixture containing oxidizing components has to be classified as oxidizing or not. According to this calculation method, a gas mixture is classified as oxidizing when its oxidizing power OP is higher than 23.5 %:

$$OP = \frac{\sum_{i=1}^{n} x_i C_i}{\sum_{i=1}^{n} x_i + \sum_{k=1}^{p} K_k B_k} \cdot 100\ \%$$

where

n	number of oxidizing gases in the gas mixture
x_i	molar fraction of oxidizing component i, in %
C_i	coefficient of oxygen equivalency of oxidizing component i
p	number of inert gases in the gas mixture
B_k	molar fraction of inert gas k, in %
K_k	coefficient of equivalency of inert gas k relative to nitrogen

The values for C_i and K_k for the most commonly used gases are listed in ISO 10156 and, thus, the oxidizing power of mixtures with known composition can be easily calculated. The oxidizing power of a mixture is determined by the contained oxidizing components but, in addition (through the K_k -value) by its inert components. For example, a mixture in which nitrogen is replaced by argon - which has a lower K_k -value - has a higher oxidizing power and may well be classified as oxidizing, although the same mixture with nitrogen as the inert component is not.

Flammable liquids

Flammable liquids are classified based on their flash point and boiling point. The UN-GHS and EU-CLP limiting criteria correspond to those used for the TDG except that CLP and TDG have made use of the building block approach by not taking up category 4 of the GHS. The limiting criteria are similar but not identical to the former EU system for liquids classified as F+; R12, F; R11 or R10 (see Figure 8).

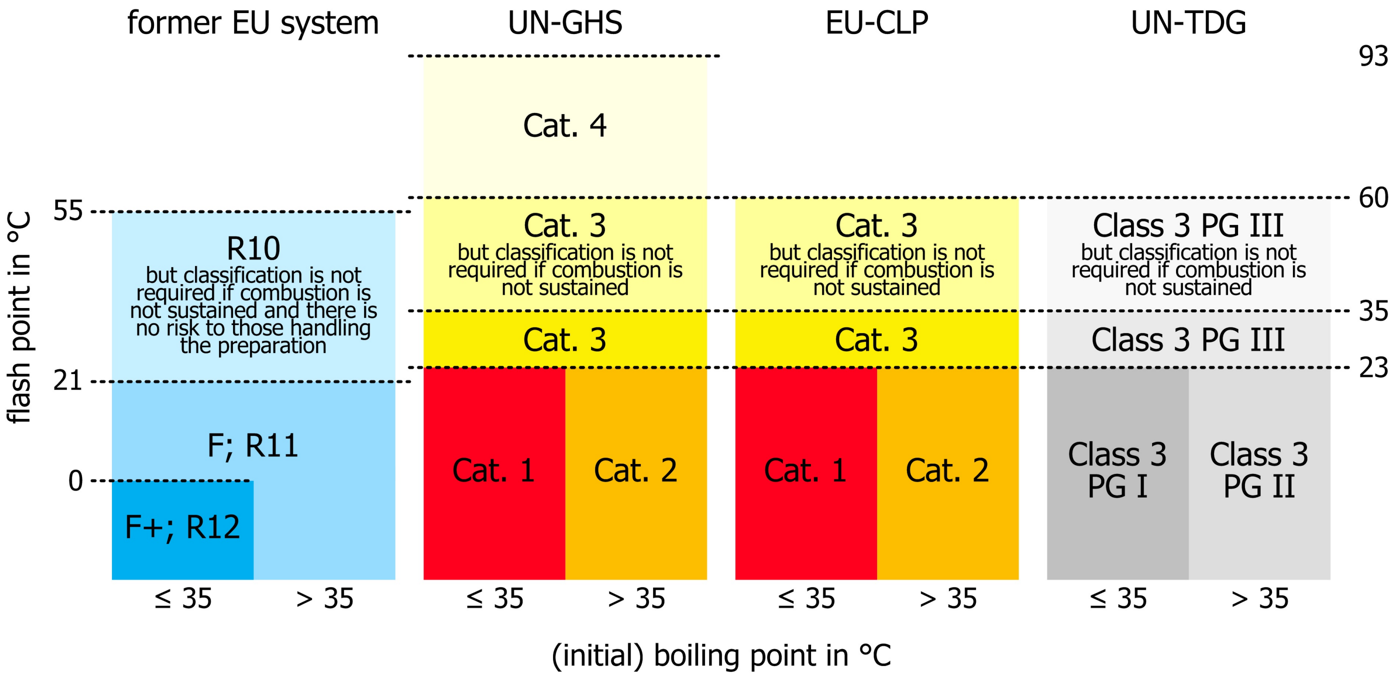

Figure 8: Comparison of classification systems for flammable liquids.

Compared to the former EU system, the limiting flash points have slightly increased. Consequently, some liquids previously classified as R10 will fall into category 2 (instead of category 3) and some liquids which previously were not classified now are classified as category 3. On the other hand, category 1 corresponds to F+; R12, even though the limiting flash point has changed. The reason is that liquids with a boiling point < 35 °C generally do not have a flash point > 0 °C (i.e. the area above F+; R12 in Figure 8 is 'empty'). Both, the CLP and the TDG have implemented categories 1 to 3 of the GHS, but have not taken up category 4 of the GHS.

The GHS and CLP refer to several standards for the determination of the flash point. Furthermore, they allow for using a calculation method for the flash point of mixtures if certain conditions are met [11]. The flash point is calculated as that temperature for which the vapour pressure of the mixture equals the lower explosion limit LEL of the mixture, see the following equation:

$$\sum_{i=1}^{n} \frac{P_i}{L_i} = 1$$

where

$L_i(t) = L_i(25) - 0{,}182 \cdot (t - 25)/\Delta H_{ci}$

$P_i = x_i \cdot \gamma_i \cdot P_i^s$

and

P_i	partial pressure of component i at temperature t
L_i	lower explosion limit of component i at temperature t
ΔH_{ci}	heat of combustion of component i
${P^s}_i$	vapor pressure of component i at temperature t
x_i	molar fraction of component i
γi	activity coefficient of component i at temperature t

It must be noted, that the calculation method is validated for mixtures with up to six components and that the components may contain only certain functional groups [12]. The data are needed for each component in the mixture and are not easily available. And if the calculated flash point is 5 °C or less above the limiting criterion, the flash point must be determined experimentally.

When assessing a former EU classification, it must be considered that not all liquids which were classified as flammable are now classified as flammable liquids. Instead, they may be classified as self-reactive (Self-reactive substances and mixtures below).

Hazard classes with completely changed systematics

Explosives

The classification of explosives according to the GHS and CLP corresponds to the TDG classification and consists of the same divisions. The GHS/CLP have one additional division covering explosives that are too dangerous to be transported and hence are not classified for TDG (see Figure 9).

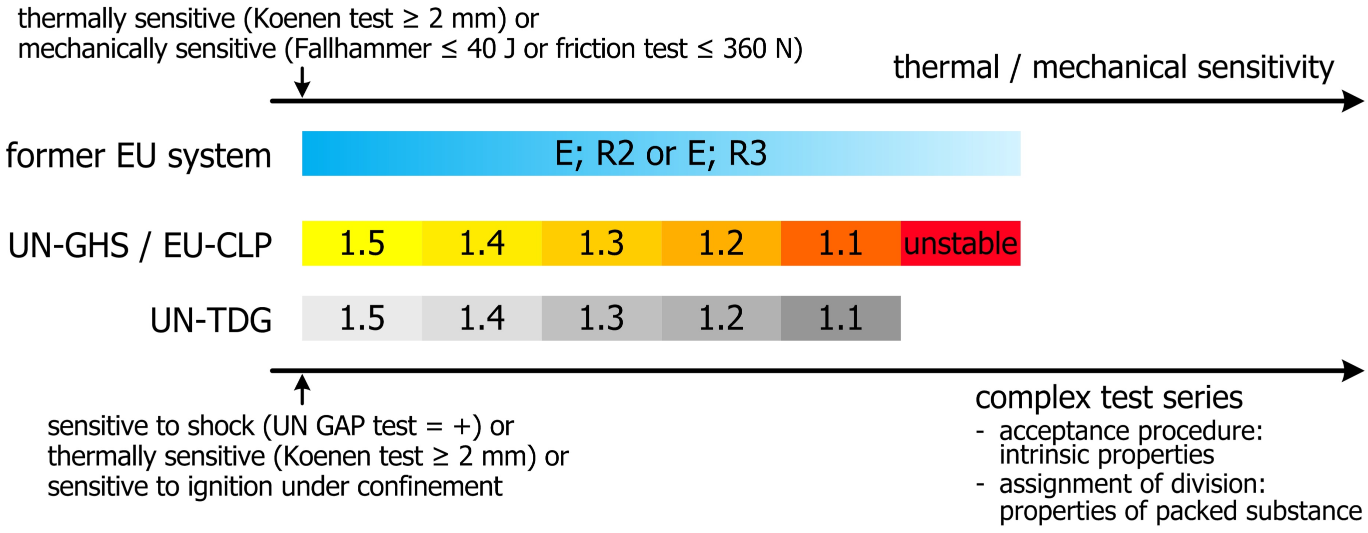

Figure 9: Comparison of classification systems for explosives.

Explosives of division 1.6 consist of extremely insensitive articles (generally for military purposes) and therefore are not considered in this context.

The classification system for explosives according to the GHS, CLP and TDG follows a very different approach than the former EU system according to test method A.14 and thus results in some different classifications, going in 'both directions':

Some substances and mixtures which were previously classified as E; R2 or E; R 3 are not necessarily classified as explosives according to the GHS. The reasons can be the following:

- Such substances or mixtures may be mechanically sensitive only. In the former EU system, test method A.14 identified substances that are mechanically sensitive (to impact and/or friction) under normal conditions of use and classified these as E; R2 or R3. Contrary to that, mechanical sensitivity is not relevant with regard to the acceptance procedure for explosives according to the GHS, CLP and TDG. For these, mechanical sensitivity is considered only to identify extremely sensitive substances which may not be transported at all.
- Testing for the assignment of a division according to GHS and TDG is carried out with the packed explosive. If no effects are observed outside the packaging during testing, no division is assigned, i.e. the explosive is 'de-classified'.

On the other hand, some further substances, mixtures or articles are classified according to the GHS but were not covered by the former EU system for the following reasons:

- Intentional explosives are classified as explosives by default for TDG, GHS and CLP, regardless of their intrinsic explosive properties. They do not need to be submitted to the acceptance procedure and may not be exempted based on the tests conducted for division assignment, i.e. a division is assigned even if no effects are found outside the package. If such explosives are very insensitive, they were not captured by the tests for thermal and mechanical sensitivity according to test method A.14 as applied for classification as E; R2 and R3.
- In contrast to other GHS hazard classes, this hazard class covers not only substances and mixtures but also articles. Articles were not within the scope of the Substances and Preparations Directive. Hence, explosive and pyrotechnic articles now fall within the scope of the classification system (it has to be noted though, that articles have always been covered by the TDG even though some articles are not classified in class 1 for transport but in class 9 instead, e.g. life-saving appliances such as air bag modules; however, these exemptions are specific for transport and do not apply for the GHS classification).

Organic peroxides

Organic peroxides are assigned to the hazard class of organic peroxides based on their content of available oxygen and hydrogen peroxide (see Figure 10). This is similar to the former EU system which classified organic peroxides as O; R7 based on slightly different limiting concentrations.

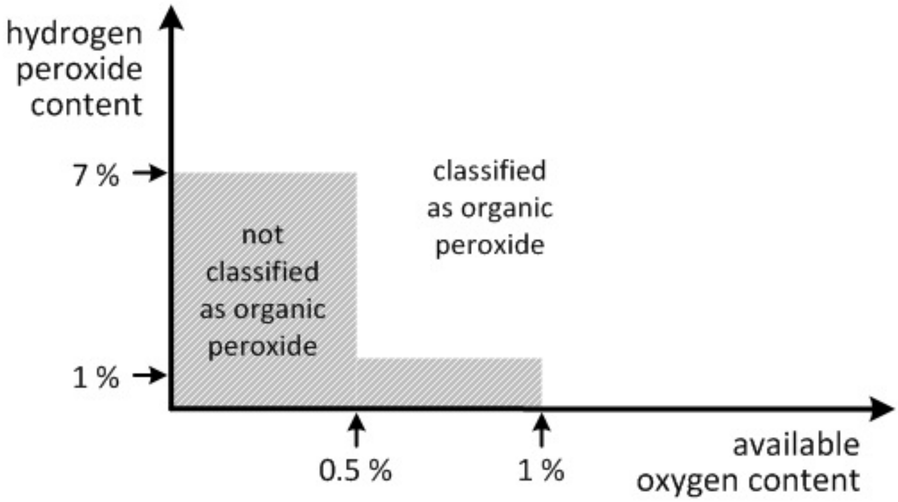

Figure 10: Assignment to the hazard class of organic peroxides according to the GHS/CLP and TDG based on the content of available oxygen and hydrogen peroxide.

Concentration limits acc. to the former EU system were as follows:

– organic peroxide > 5 % or
– available oxygen > 0.5 % and hydrogen peroxide > 5 %.

For mixtures containing one or more organic peroxide(s), the available oxygen content can be calculated according to the following equation:

$$\text{Available oxygen content in } \% = \sum_{i=1}^{n} \frac{n_i \cdot c_i}{m_i}$$

where

n_i number of peroxygen groups per molecule of organic peroxide i

c_i concentration of organic peroxide i, in mass%

m_i molecular mass of organic peroxide i

Organic peroxides are divided into categories which are called types A to G for this hazard class whereas the former EU system differentiated only between organic peroxides with explosive properties and those without (see Figure 11).

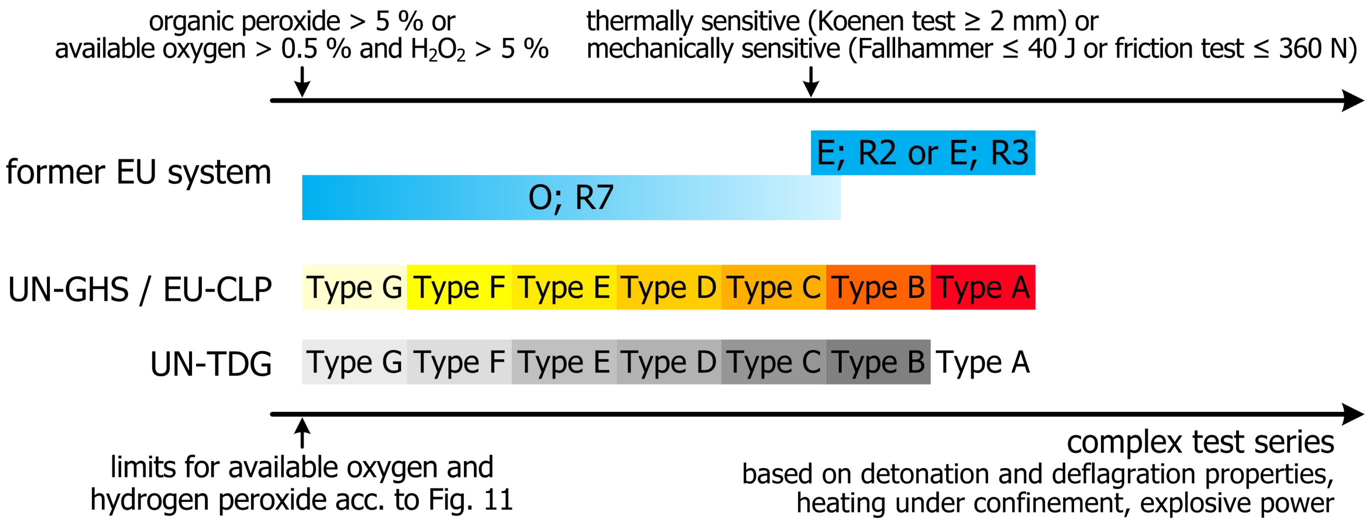

Figure 11: Comparison of classification systems for organic peroxides (type A may not be transported).

The assignment of the type is obtained on the basis of test series A to G for which the GHS, CLP and TDG refer to the UN Manual of Tests and Criteria. These complex test series achieve a fine differentiation based on the detonation and deflagration properties, the effects of heating under confinement and the explosive power. The former EU system did not foresee a division of organic peroxides but differentiated only insofar as organic peroxides with explosive properties according to test method A.14 were classified as E; R2 or E; R3. Such organic peroxides were often classified as both, O; R7 and E; R2 or R3 although these classifications were foreseen as exclusive according to the Substances Directive [13].

New hazard classes but the hazards have been covered previously

Aerosols

Aerosols are different from the other hazard classes insofar as (per definition) the aerosol dispenser is classified together with the contained chemicals. Aerosols of categories 1 and 2 are flammable. They correspond to aerosols of division 2.1 according to the TDG. Category 3 is assigned to aerosols not classified as flammable in the sense of category 1 or 2. Category 3 was introduced into the GHS in order to clarify the relation to gases under pressure. With its introduction, notes were added stating that aerosols do not have to be classified as gas under pressure in addition. Aerosols according to the GHS correspond to aerosols of division 2.2 according to the TDG. There was no equivalent classification in the former EU system which classified (only) the contained chemicals, i.e. an exact correlation is not possible (see Figure 12).

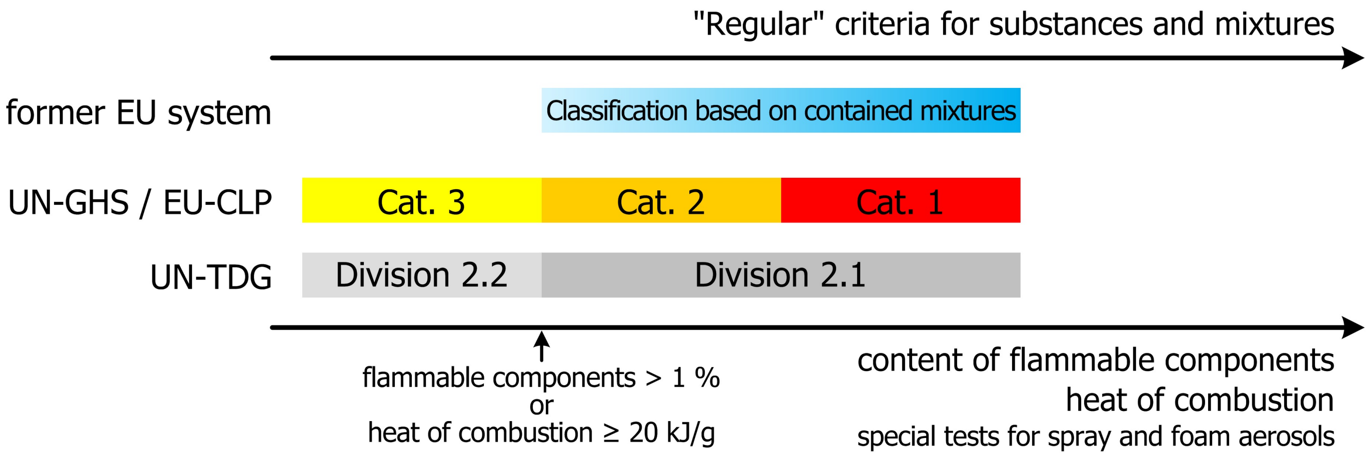

Figure 12: Comparison of classification systems for aerosols.

If the composition of the aerosol is known, no testing is necessary in order to decide whether an aerosol belongs to category 3 or whether it is flammable and therefore has to be assigned to category 1 or 2. It is classified as category 3 if both of the following conditions are fulfilled:

1. The content of flammable components is ≤ 1 %.
   Flammable components are flammable gases, liquids and solids. Flammable liquids of category 4 have to be considered as flammable components in this sense, even though they are not implemented as such in the EU-CLP.
2. The heat of combustion is < 20 kJ/g.
   For the heat of combustion all combustible components have to be taken into account, and not only those according to 1. (i.e. components classified as flammable as well as other combustible components).

The heat of combustion of a mixture can be calculated as follows:

$$\Delta H_c = \sum_{i}^{n} w_i \cdot \Delta H_{c_i}$$

where

ΔH_c	heat of combustion of the mixture, in kJ/g
w_i	mass fraction of the component i, in %
ΔH_{ci}	heat of combustion of component i, in kJ/g

If these conditions are not fulfilled, assignment of the category can be achieved based on specific tests for spray or foam aerosols. Depending on the test results, aerosols can even be 're-assigned' to category 3. Testing may be waived, and in that case the aerosol has to be assigned to category 1.

Self-reactive substances and mixtures

In the GHS and CLP, chemicals are assigned to the hazard class of self-reactive substances and mixtures based on their heat of decomposition and their self-accelerating decomposition temperature (SADT). The same classification criteria are applied for the purposes of TDG. These criteria were not part of the former EU system. Instead, the former EU system classified them as flammable or explosive (see Figure 13).

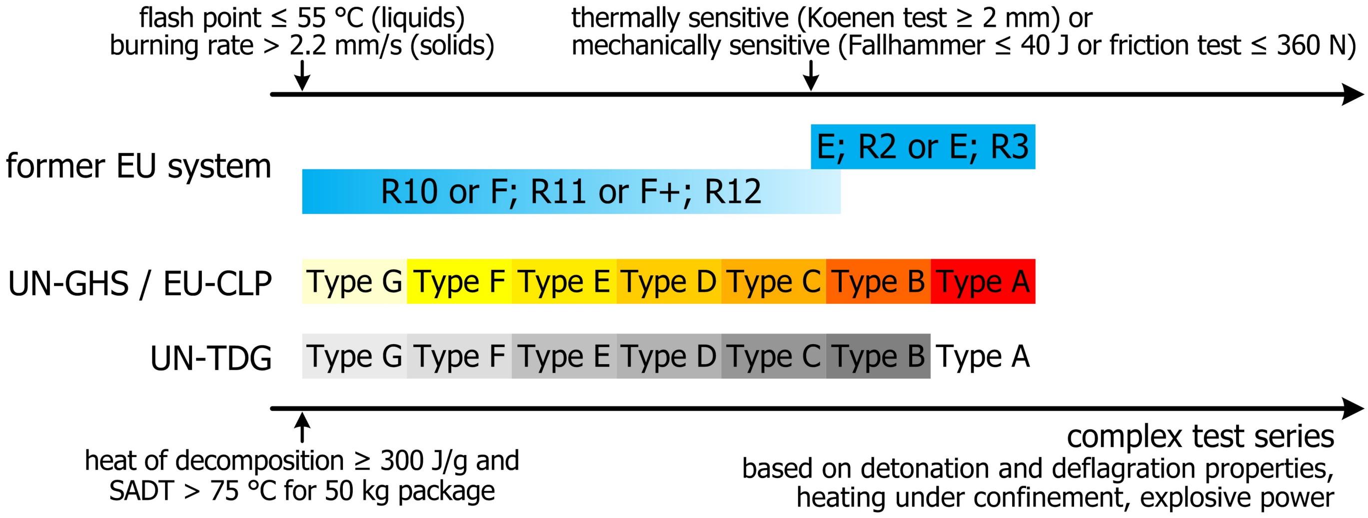

Figure 13: Comparison of classification systems for self-reactive substances and mixtures (type A may not be transported, hence it is not coloured for TDG).

The assignment of the category (called 'type' in this hazard class) is obtained based on test series A to G of the UN Manual of Tests and Criteria. These complex test series are referred to in the GHS - and thus CLP - and in the TDG. The result is a fine differentiation based on the detonation and deflagration properties, the effects of heating under confinement and the explosive power. The test series are the same as used for organic peroxides, and in fact, self-reactive substances and mixtures have comparable properties. In the former EU system, there was no specific classification of self-reactive substances and mixtures. Depending on their properties, they were mostly classified as explosive or as flammable.

Desensitized explosives

Desensitized explosives are classified in a separate hazard class which was newly introduced in the UN-GHS of 2015. Therefore it is not yet part of the EU-CLP. The TDG (currently) has no separate classification of desensitized explosives but classifies them as class 3 if they are liquid and as division 4.1 if they are solid. The former EU system did not foresee specific classification of desensitized explosives but had a so-called additional risk phrase R1 'explosive when dry'. However, R1 was not assigned systematically or consistently. If explosive properties according to test method A.14 were existent, regular classification as E; R2 (or R3) was required (see Figure 14).

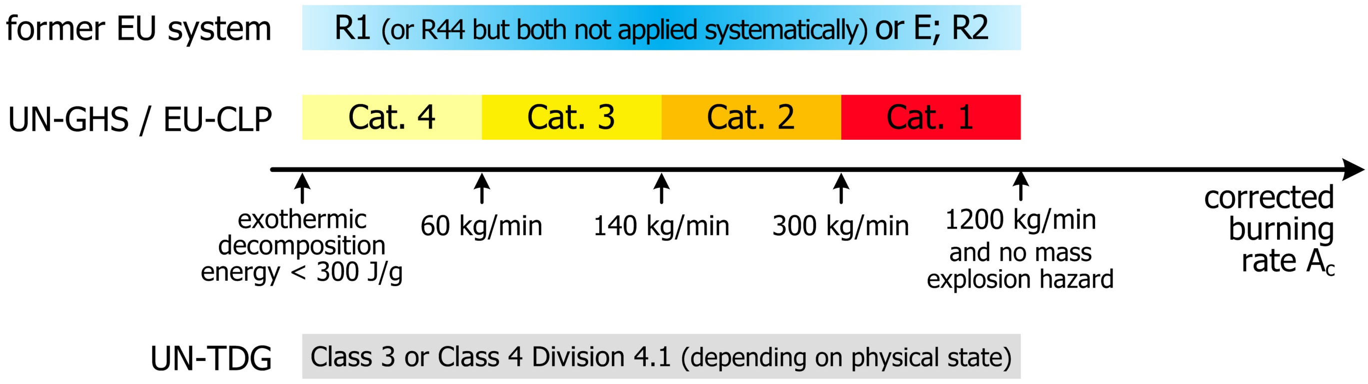

Figure 14: Comparison of classification systems for desensitized explosives.

The new hazard class for desensitized explosives is applicable to all explosives which are diluted in order to suppress or reduce their explosive properties, unless

- they are intentional explosives or have a mass explosion hazard or their corrected burning rate is $>$ 1200 kg/min; in that case they are classified as explosives or
- they have an exothermic decomposition energy $<$ 300 J/g; in that case they are neither classified as desensitized explosives nor as explosives (for these, waiving is possible based on the screening procedures as contained in Appendix 6 of the UN Manual of Tests and Criteria).

The assignment of the category is achieved based on the corrected burning rate in accordance with the UN Manual of Tests and Criteria (Part V subsection 51.4). Some data, which were used when developing this hazard class, are available on the UN website [14]. Further data can be found in the official publications of BAM on the German Explosives Act [15].

New hazard classes and the hazards have not been covered previously

Gases under pressure

For the purposes of GHS and CLP, gases are classified as such, based on the physical state, even if they have no other hazards (examples are compressed nitrogen or liquefied carbon dioxide). This is corresponding to TDG that classifies all gases and assigns them to class 2, independent of other hazards. In the EU, there was no such classification of gases under pressure. Gases were classified solely based on other hazards and the physical state was not considered (see Figure 15).

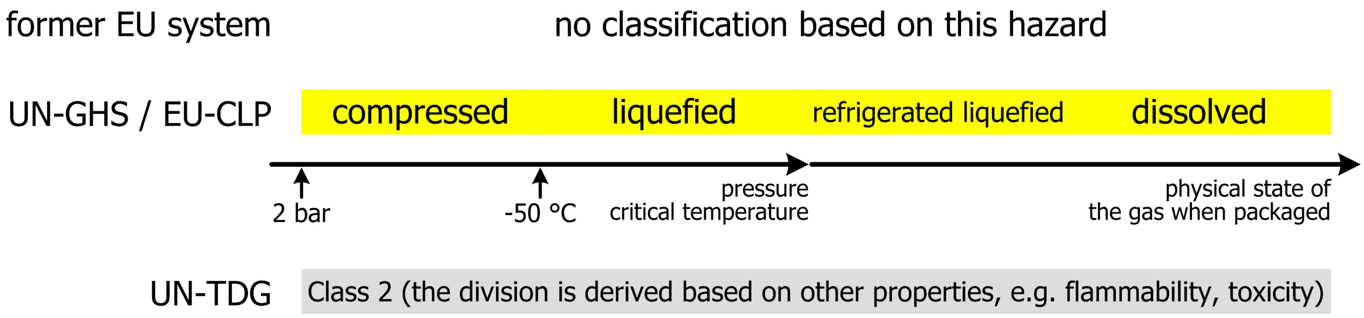

Figure 15: Comparison of classification systems for gases under pressure.

The category (called 'group' in this hazard class) is assigned based on the physical state of the packaged gas. Compressed and liquefied gases are distinguished based on the critical temperature. For mixtures, the pseudo-critical temperature of the mixture can be calculated using equation 6:

$$\text{Pseudo-critical temperature} = \sum_{i}^{n} x_i \cdot T_{crit_i}$$

where
x_i molar fraction of component i
T_{criti} critical temperature of component i, in °C or K

Self-heating substances and mixtures

Self-heating substances and mixtures can react with air without energy supply (i.e. without ignition source). Compared to pyrophoric solids, larger amounts are needed and ignition is not immediate but occurs only after an induction time of hours or days. This hazard may apply to combustible solids consisting of fine particles with large surface areas. The classification criteria for self-heating substances and mixtures according to the GHS, CLP and TDG are the same. In the former EU system, this hazard was not classified (see Figure 16). If self-heating substances and mixtures were classified according to the former EU system, this was based on other hazards which are considered independently (e.g. as F; R11).

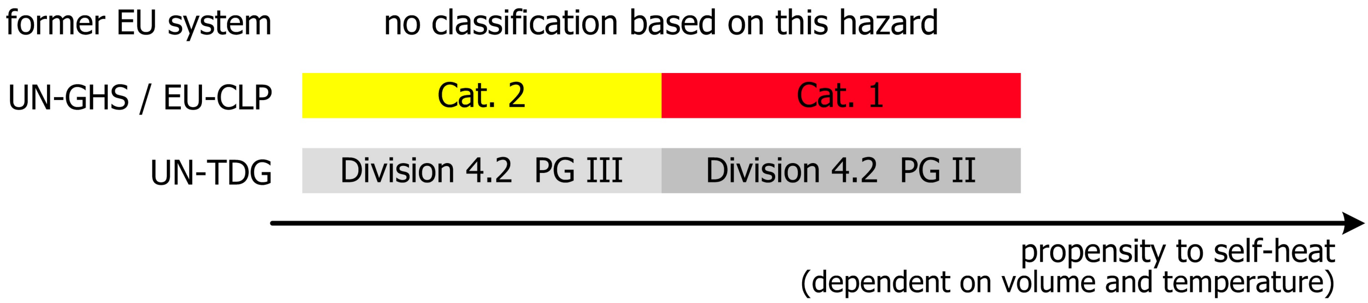

Figure 16: Comparison of classification systems for self-heating substances and mixtures.

The GHS - and thus CLP - and TDG refer to UN test N.4 of the UN Manual of Tests and Criteria. The principle of this test is that defined samples of the test substance are subjected to different temperatures for a certain time period in order to evaluate whether the sample either self-heats or ignites within that period.

When the transport classification is used, it must be kept in mind that transport division 4.2 is not predominant and thus might not be reflected in the transport classification.

Corrosive to metals

Chemicals are classified as corrosive to metals based on their corrosion rate on steel or aluminium. The GHS and TDG have the same criterion and both refer to test C.1 in Section 37.4 of the UN Manual of Tests and Criteria (see Figure 17).

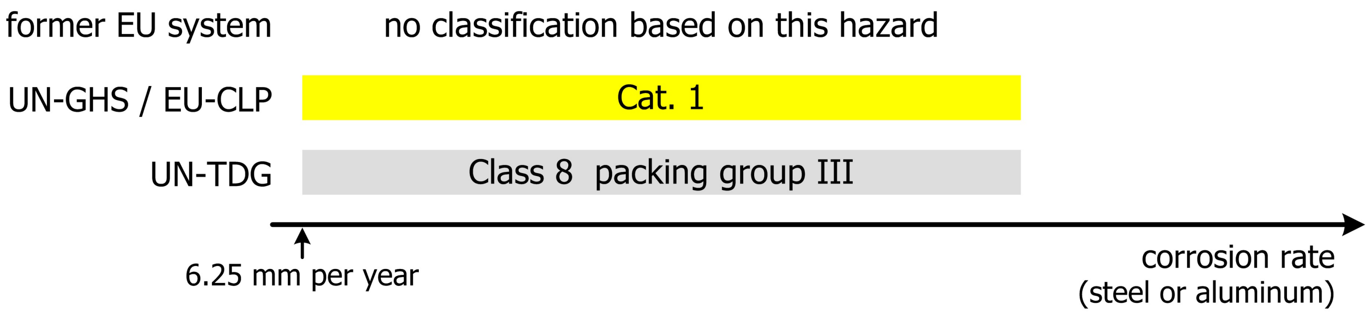

Figure 17: Comparison of classification systems for corrosive to metals.

Although the GHS and TDG criteria are the same, the transport classification cannot be used in order to deduce the GHS classification because it is not known whether the transport classification is due to skin or metal corrosive properties. Also the absence of a transport classification as class 8 cannot be used to preclude GHS classification as corrosive to metals, because all other classifications take precedence over class 8 packing group III.

Summary and conclusions

Compared to the – undeniably – important questions and issues on health and environmental hazards of chemicals, the classification of physical hazards is often not in the focus even though legislative implementation and actual application can be challenging and there are some traps and pitfalls to be avoided. Therefore, the principles of the UN-GHS and EU-CLP for the classification of physical hazards of chemicals are presented and compared to the former EU system and the transport of dangerous goods (UN-TDG). Similarities and differences between these systems are identified and discussed for each of the 17 physical hazard classes of the GHS.

The underlying systematics and criteria for the classification of physical hazards of chemicals according to the UN-GHS / EU-CLP and the former EU system are quite different and the following conclusions should be kept in mind when classifying chemicals:

- Simple translation of former classifications is possible for a few hazard classes only while the majority of chemicals have to be reassessed individually based on available data or testing.
- Useful information can be derived from classifications of dangerous goods because GHS and TDG are based on the same criteria and test methods. However, some principles in both systems differ and may result in different or additional classifications. Therefore, caution and expert judgement are necessary when translating transport classifications of dangerous goods into GHS / CLP classifications.
- As opposed to health hazards, concentration limits and calculation methods for the classification of mixtures based on their ingredients are available for a few physical hazard classes only. Such methods facilitate the classification of mixtures and thus help avoiding unnecessary testing. In all other cases, testing has to be conducted if no data or conclusive transport classification are available.

In the same way, expert knowledge on the classification of physical hazards of chemicals is necessary when adapting and amending legislation on chemicals and downstream-legislation to that regard, i.e. legislation that in one way or another refers to the classification of chemicals. Therefore, also legislators should be aware of the different classification principles with regard to physical hazards. Affected legislation ranges from chemicals legislation itself, such as REACH and CLP, to a great number of downstream-legislation such as for workers protection or market directives such as the pressure equipment directive. The following are a few examples of inconsistencies in current EU-legislation where these different principles have not been fully understood or overlooked:

- In some cases, references to physical hazard classifications are incomplete although they are supposed to be translations of the former classification system, e.g. in Art. 14, 40 and 119 of REACH. The references to physical hazard classes in these Articles exclude self-reactive substances and mixtures of Type C to F and oxidizing liquids and solids of category 3 even though these have been classified as dangerous under the Substances Directive.
- There are still (indirect) references to the Substances Directive in a number of legal provisions by using its no-longer defined terminology, e.g. in Annex VII to REACH.
- The Test Methods Regulation still contains a number of test methods which were necessary for the former EU-classification system only. Also REACH should be based on the current test methods which are also applied for the purposes of CLP, at least for those where scope and purpose are equivalent so that unnecessary duplication of tests can be avoided.

It is the hope, that future legislation or amendments affecting also physical hazard classification of chemicals are more carefully considered and that experts in these areas are consulted so that a consistent legal system also in this specific but complex area can be established and maintained.

References:

1. Globally Harmonized System of Classification and Labelling of Chemicals (GHS): <www.unece.org/trans/danger/publi/ghs/ghs_rev06/06files_e.html>.
2. Information about the world-wide GHS Implementation: <http://www.unece.org/trans/danger/publi/ghs/implementation_e.html>.
3. REGULATION (EC) No 1272/2008 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006.
4. Substances Directive (67/548/EEC) and Preparations Directive (1999/45/EC), both repealed on June 1st, 2015. In the following, these are referred to as the former EU system.
5. UN Recommendations on the Transport of Dangerous Goods – Model Regulations: <www.unece.org/trans/danger/publi/unrec/rev19/19files_e.html>.
6. UN Manual of Tests and Criteria: <www.unece.org/trans/danger/publi/manual/pubdet_manual.html>.
7. The test methods for physico-chemical properties as contained in the Test Methods Regulation (COUNCIL REGULATION (EC) No 440/2008) were referred to in the former EU system according to Substances and Preparations Directives. These are the so-called 'A-test methods'.
8. ISO 10156:2010 'Gases and gas mixtures -- Determination of fire potential and oxidizing ability for the selection of cylinder valve outlets'.
9. This new category for pyrophoric gases is foreseen to be introduced with the 12th ATP to CLP.
10. Test O.3 was introduced with the sixth revised edition of the GHS. Reference to Test O.3 is not yet implemented in CLP.
11. J. Gmehling, P. Rasmussen, 'Flash Points of Flammable Liquid Mixtures Using UNIFAC', 21:2 Industrial & Engineering Chemistry Fundamentals (1982), 186.
12. E. Brandes, M. Mitu, D. Pawel, 'The lower explosion point – A good measure for explosion prevention: Experiment and calculation for pure compounds and some mixtures', 20:4-6 Journal of Loss Prevention in the Process Industries (2007), 536.
13. Section 2.2.2.1 of Annex VI to the Substances Directive.
14. Informal document 12 of the 23rd session of the UN Sub-Committee of Experts on the GHS: <www.unece.org/trans/main/dgdb/dgsubc4/c4inf23.html>.
15. <www.tes.bam.de/de/mitteilungen/sprengstoffrecht/explosionsgefaehrlich.htm>.