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

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Issues relating to the Globally Harmonized System of Classification and Labelling of Chemicals: Classification criteria for flammable gases

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

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Joint work with the Sub-Committee of Experts on the Transport of Dangerous Goods (TDG Sub-Committee)

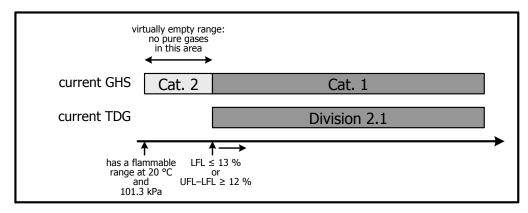
Classification criteria for flammable gases – comments on informal document INF.15 (TDG, 48th session) – INF.4 (GHS, 30th session)

Transmitted by the expert from Germany, the European Industrial Gases Association (EIGA) and the European Chemical Industry Council (CEFIC)

- 1. The Joint TDG-GHS Informal Working Group (IWG) worked out new classification criteria for flammable gases aiming at sub-dividing GHS category 1. The status of its work is presented in informal document INF.15 (TDG, 48th session) INF.4 (GHS, 30th session). Experts from Germany, CEFIC and EIGA participated in the discussions of the IWG and support their conclusion to suggest option 3 as the preferred solution for dividing flammable gases.
- 2. The proposals of the IWG are based on the mandate as agreed by the TDG Sub-Committees. Thus, the proposals do not refer to GHS category 2. This document proposes to use the criteria as proposed by the IWG, but to include also GHS category 2 in the new categorization, as the discussions on this issue revealed that, in practice, such an approach would not lead to different classifications for transport. On the other hand, the proposed approach would lead to a simplification of the hazard class flammable gases as the creation of additional sub-categories can be avoided. The goal is maximum stringency of the hazard class and more consistency with the way in which other physical hazard classes are organized and divided into categories within the GHS.

Current classification criteria for flammable gases

3. Currently, flammable gases are sub-divided into category 1 and 2 according to the GHS. Category 1 contains all gases having a lower flammability limit, LFL \leq 13 % by volume or a flammable range (upper flammability limit, UFL minus lower flammability limit, LFL) of at least 12 percentage points. All other gases having a flammable range are assigned to category 2. The gases corresponding to GHS category 1 are assigned to division 2.1 according to the UN Model Regulations. The following figure is a schematic diagram illustrating these classification systems for flammable gases:



- 4. The limiting criteria for TDG division 2.1 were established (more than 3 decades ago) in order to keep ammonia (and methyl bromide) out of division 2.1. In the meantime, the determination methods for flammability have changed, so that ammonia (and methyl bromide) actually would fulfil the criteria for classification in TDG division 2.1 (and GHS category 1). However, they are not classified as TDG division 2.1 based on their entries in the Dangerous Goods List as UN Nos. 1005 and 1062. The GHS acknowledges that by a note referring to ammonia and methyl bromide stating that they are special cases for some regulatory purposes. There are no pure gases that fulfil the criteria of category 2 as currently defined in the GHS
- 5. When the GHS was established, it was based on the criteria as applied for transport with regard to physical hazards. Consequently, GHS category 1 of the hazard class flammable gases was based on the criteria for TDG division 2.1. GHS category 2 was introduced in order to cover also all other gas (mixtures) having a flammable range (even if not classified for transport). This is based on the principles for explosion protection worldwide because any gas mixture having a flammable range in air might cause problems in case of a leakage or an accident.

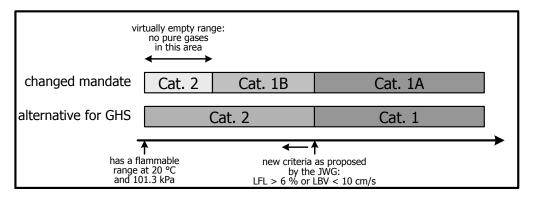
Task and mandate of the IWG

6. As currently there is no graduation of the flammable properties of flammable gases in the GHS (category 2 is virtually empty and thus gases are clustered in category 1), the IWG was established in order to define criteria which would allow such a graduation. However, in order not to provoke changes to the TDG classification system, the originally proposed mandate was changed by the TDG Sub-Committee so that only sub-dividing of GHS category 1 into 1A and 1B should be looked into by the IWG (see para. 88 of ST/SG/AC.10/C.3/92).

Alternative categorization of flammable gases

7. When considering the options discussed in the IWG, several experts felt that a reasonable graduation of flammable gases should take into account the GHS hazard class as a whole (and not only category 1). Furthermore, (as pointed out in informal document INF.58 (TDG, 47th session) – INF.16 (GHS, 29th session)) the hazard class flammable gases in the GHS is already quite complicated and interaction with the other criteria (e.g., pyrophoric gases and chemically unstable gases) of the chapter should be looked into to ensure that the classification criteria, hazard communication, and decision logics and guidance of the flammable gases addressed by this chapter are not compromised and are presented in a clear, concise manner.

- 8. Thus some effort was put into a solution which would allow for the same graduation as proposed by the IWG but which would also simplify the hazard class as whole and get rid of unclear interfaces between categories and supplemental categories. Such an alternative was identified by taking the virtually empty category 2 into account.
- 9. The alternative proposal in principle is the same as contained in informal document INF.15 (TDG, 48th session) INF.4 (GHS, 30th session) of the IWG except that the old (and virtually empty) category 2 is used instead of creating a new sub-category 1B. It is based on the same criteria as proposed by the IWG. The principle is that all flammable gases are assigned to the new GHS category 1, but they may be moved to category 2 if they have a LFL > 6 % by volume or a laminar burning velocity, LBV < 10 cm/s as shown in the following figure:

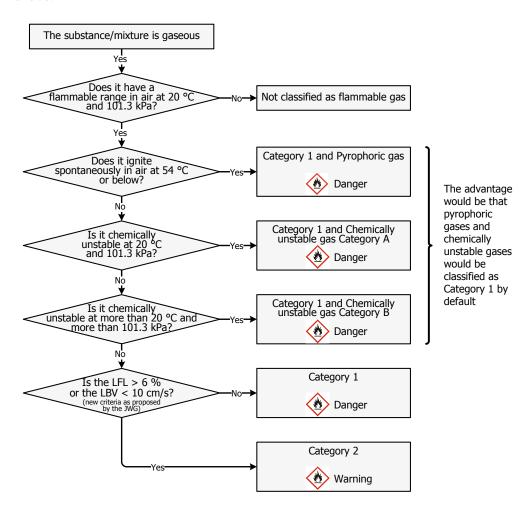


- 10. This would allow to make good use of category 2:
 - (a) instead of further sub-dividing category 1,
 - (b) while keeping an old, virtually empty category 2 at the same time, which once was created based on data which are outdated nowadays,
 - (c) thus avoiding further complication of the hazard class flammable gases which is already rather complicated because it contains supplemental categories for pyrophoric gases and chemically unstable gases.
- 11. In addition, appropriate hazard communication for the new GHS category 2 could be considered and a pictogram (symbol flame) could be assigned also to this new category 2.

Implementation of the alternative classification in a flowchart

- 12. Furthermore, the authors of this document considered whether the above proposal could be reflected in the GHS flow-charts for the categorization of flammable gases appropriately.
- 13. Currently, there are three different flow-charts contained in chapter 2.2 of the GHS, one for flammability, and two further flow-charts for the supplemental categories of pyrophoric gas and chemically unstable gases. The simplification as proposed above could also be used in order to simplify the flow-charts. Merging the three flow-charts would allow to clearly communicate the interfaces between the categories of flammable gases and the supplemental categories for pyrophoric and chemically unstable gases.

- 14. Based on the hazards associated with pyrophoric gases (self-ignition in air, i.e. no external ignition source is needed) and chemically unstable gases (explosion can occur without air, i.e. also within a containment), such gases should always be classified as GHS category 1 by default. This was also discussed and agreed in the IWG.
- 15. As a result the new flow-chart combining the old three flow-charts would look as follows:

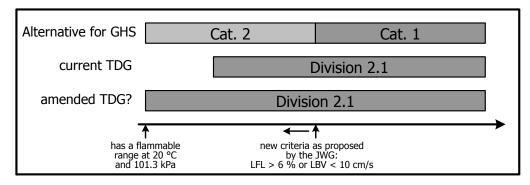


Consequences for TDG

- 16. The proposed alternative categorization would result in changes in TDG in order to be harmonized with the GHS. The building block approach would allow to adopt:
 - · category 1 only or;
 - category 1 and 2 (together).

It does not foresee taking up only part of a category.

17. In order not to lower the level of protection, TDG division 2.1 could be extended. Division 2.1 then would cover all gases having a flammable range (i.e. all flammable gases as defined in the GHS) as shown in the following figure:



- 18. This would be in line with the principles for explosion protection world-wide: Any gas mixture having a flammable range in air might cause problems in case of a leakage or an accident, not only in supply and use but also during transport. Drivers and rescue personnel etc. should be aware about flammable properties in order to take appropriate measures, avoid ignition sources etc. GHS and TDG then would be harmonized for flammable gases.
- 19. The formal consequences in the UN Recommendations on the Transport of Dangerous Goods would be limited to the deletion of a few words in section 2.2.2.1 (a) as follows:
- (a) Division 2.1 Flammable gases

Gases which at 20 °C and a standard pressure of 101.3 kPa:

- (i) are ignitable when in a mixture of 13 per cent or less by volume with air; or
- (ii) have a flammable range with air-of at least 12 percentage points regardless of the lower flammable limit.

Flammability shall be determined by tests or by calculation in accordance with methods adopted by ISO (see ISO 10156:2010). Where insufficient data are available to use these methods, tests by a comparable method recognized by a national competent authority may be used;

- 20. No further amendments would be necessary in the UN Recommendations on the Transport of Dangerous Goods. There would be no need for any changes in the Dangerous Goods List itself. Ammonia and methyl bromide could remain in Division 2.3 according to UN Nos. 1005 and 1062 as currently given in the Dangerous Goods List. No pure gases would be classified differently.
- 21. A few mixtures might be in the new range and these then would be classified as division 2.1 (unless they have a named entry in the Dangerous Goods List). However, as mentioned above, any mixture having a flammable range in air might cause problems in case of a leakage or an accident also during transport and drivers and rescue personnel etc. should be aware about flammable properties. This is also reflected in some Safety Data Sheets where companies assign gas mixtures to transport division 2.1 for safety reasons (even though they would not meet the criteria) because they have a flammable range in air.
- 22. Moreover, current practice assigns most mixtures having a flammable range to division 2.1 for transport anyway because of the calculation method as contained in ISO 10156 (referred to in chapter 2.2 of the GHS and also in the UN Recommendations on the Transport of Dangerous Goods, see the box in paragraph 19 above). This calculation method allows to determine whether a gas mixture is flammable or not, but it does not allow to determine the flammable range. However, the flammable range is needed in order to classify in the current GHS category 2 and also to exclude it from the current TDG

- division 2.1. As a consequence, gas mixtures for which the flammability is calculated, are assigned to GHS category 1 and TDG division 2.1 (even though they might be outside of TDG division 2.1, should they actually be tested).
- 23. For a more detailed assessment of the impact on TDG classifications of gases, please refer also to the Annex to this document.

Proposal

24. The TDG and GHS sub-committees are invited to discuss the approach of this proposal. If the principle is supported, a formal document with proposals for amendments to the text of the UN Model Regulations and the GHS will be submitted to the next sessions of both Sub-Committees.

Annex

Impact assessment on TDG classifications of gases

1. The formal changes in section 2.2.2.1 (a) of the UN Recommendations on the Transport of Dangerous Goods are comparatively minor:

- (a) Division 2.1 Flammable gases
 - Gases which at 20 °C and a standard pressure of 101.3 kPa:
 - (i) are ignitable when in a mixture of 13 per cent or less by volume with air; or
 - (ii) have a flammable range with air of at least 12 percentage points regardless of the lower flammable limit.

Flammability shall be determined by tests or by calculation in accordance with methods adopted by ISO (see ISO 10156:2010). Where insufficient data are available to use these methods, tests by a comparable method recognized by a national competent authority may be used;

2. As a consequence of the proposal, gases that have a flammable range in air but where the LFL is >13 % by volume and the flammable range is <12 percentage points would be covered in addition by the criteria for TDG division 2.1, see also the last line in the following table:

LFL	Flammable range	TDG Divison 2.1?	
in %	in percentage points	currently	proposed
≤ 13	≥ 12	yes	yes
≤ 13	< 12	yes	yes
> 13	≥ 12	yes	yes
> 13	< 12	no	<u>yes</u>

- 3. <u>However, when applying ISO 10156:2010 (referred to in section 2.2.2.1 (a) of TDG and in chapter 2.2 of the GHS), no gases at all would be assigned to the last line (i.e. to the current category 2 of the GHS or out of division 2.1).</u>
- 4. Originally, ISO 10156 was worked out for the selection of cylinder valve outlets and used for TDG. In clause 3.2.4 it is explicitly stated that the test substance shall be classified as flammable if the test is positive (i.e. if the gas has a flammable range at all). Later, when ISO 10156:2010 was also used for the purposes of GHS, a new clause 3.5 was added, stating that "this International Standard does not include methods to classify flammable gas mixtures into either category 1 or category 2 according to the GHS (see Annex A). Consequently, all mixtures containing flammable gases or flammable liquids as components and meeting the criteria of the testing method or the calculation method should be classified as category 1". The calculation method determines only whether a gas mixtures is flammable (has a flammable range in air) or not. Therefore gas mixtures, for which the calculation method determines that they are flammable, are assigned to GHS category 1 and TDG division 2.1 (regardless of whether they might be one of the rare cases actually belonging to the last line in the above table).
- 5. But what about actual changes to real TDG classifications of pure gases and gas mixtures?

Pure gases classified in the Dangerous Goods List

6. The Dangerous Goods List does not contain any pure gas that fulfils the criteria of the last line in the above table. That means all gases that are currently assigned to division 2.2 or 2.3 would still be classified correctly and in accordance with the criteria as "non-flammable" even if the criteria for division 2.1 were changed as proposed.

Gas mixtures

- 7. There might be some gas mixtures (N.O.S. entries) fulfilling the criteria of the last line according to the above table. Theoretically, these would be newly covered by TDG division 2.1 (if ISO 10156 is not applied and if they do not have a named entry in the Dangerous Goods List).
- 8. However, in practice such gas mixtures are already assigned to TDG division 2.1. The reason is that gas mixtures in most cases are classified based on the calculation method as given in ISO 10156:2010. And as explained above, in that case also any gas mixture that would fall into the last line of the above table is assigned to TDG division 2.1 and GHS category 1.

Special cases ammonia and methyl bromide

- 9. Ammonia and methyl bromide could remain in Division 2.3 according to UN Nos. 1005 and 1062 as currently given in the Dangerous Goods List.
- 10. Ammonia has a flammable range well above 12 percentage points (see for example IEC 60079-20-1:2010 according to which ammonia has an LFL of 15.0 % and an UFL of 33.6 %, i.e. a flammable range of 18.6 %. Even when considering slight differences to different test methods, it is clear that the flammable range of ammonia would never be below 12 percentage points.
- 11. Methyl bromide has an LFL of 8.6 % (according to ISO 10156:2010.
- 12. Therefore it is clear that both, ammonia and methyl bromide already now are classified outside of TDG division 2.1 based on other considerations and not based on criteria. And this situation could remain as is, even if TDG division 2.1 was changed as proposed.

8