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**COMMITTEE OF EXPERTS ON THE TRANSPORT OF
DANGEROUS GOODS AND ON THE GLOBALLY
HARMONIZED SYSTEM OF CLASSIFICATION
AND LABELLING OF CHEMICALS**

Sub-Committee of Experts on the
Transport of Dangerous Goods

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

Thirteenth session
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Item 2 (a) of the provisional agenda

**UPDATING OF THE GLOBALLY HARMONIZED SYSTEM OF CLASSIFICATION AND
LABELLING OF CHEMICALS (GHS)**

Physical hazards

Clarification and updating of some issues regarding flammable liquids addressed in the GHS

Transmitted by the expert from Germany

Introduction

1. The issues addressed in this document have been introduced during the December 2005 sessions of both Sub-Committees (ST/SG/AC.10/C.3/2005/36 and ST/SG/AC.10/C.4/2005/5). Both Sub-Committees agreed that they should be considered by the Sub-Committee of Experts on the Transport of Dangerous Goods as the focal point for physical hazards. Moreover, it was agreed that a new document with some more detailed proposals should be provided. As a first step, this more detailed proposal aims at introducing the respective changes to the GHS. Once the proposals have been accepted by both Sub-Committees, proposals to amend the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria* will be presented accordingly.

I2. In this document, only the following issues regarding flammable liquids are addressed:

- (a) Sustained combustion;
- (b) Calculation of the flash point of mixtures;
- (c) Standards cited for the determination of the flash point; and
- (d) Determination of the boiling point / initial boiling point.

Sustained combustion

3. Currently NOTE 2 of section 2.6.2 of the GHS refers to the *sustained combustibility test L.2, Part III, section 32 of the UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria*.

4. However, the test temperatures (60.5 °C and 75 °C) given in the sustained combustibility test L.2, Part III, Section 32 of the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria* are not suitable for testing liquids of category 4. The test temperatures of 60.5 °C and 75 °C give reliable results only for category 3 liquids. Therefore, NOTE 2 should be restricted accordingly to category 3.

5. In the future it should be checked whether sustained combustion may also be a suitable criterion for category 4 for some regulatory purposes (e.g. storage); this means that a similar exception may be reasonable for this category as well, and if so, appropriate test temperatures should be fixed.

Proposal No. 1:

6. Amend NOTE 2 of the GHS, section 2.6.2 to read as follows:

“NOTE 2: *Liquids with a flash point of more than or equal to 35 °C and less than or equal to 60 °C may be regarded as non-flammable liquids for some regulatory purposes (e.g. transport) if negative results have been obtained in the sustained combustibility test L.2, Part III, Section 32 of the UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria.”.*

Calculation of the flash point of mixtures

7. The GHS offers in sub-section 2.6.4.2.2 the possibility to calculate the flash point of mixtures. This calculation method is not part of the classification procedure of the *UN Recommendations on the Transport of Dangerous Goods* for Class 3 flammable liquids (chapter 2.3). The *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria* contain in Appendix 6, paragraph 4 a calculation method for flash points as a screening procedure for flammable liquids. Both, GHS and *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria* refer to the same method (Gmehling and Rasmussen: Ind. Eng. Chem. Fundament 21, 86, (1982)). However, neither the GHS nor the

Manual of Tests and Criteria clearly state the necessary boundary conditions for applying the calculation method according to Gmehling and Rasmussen.

8. The intention of this proposal is to state clearly the conditions necessary for applying the calculation method according to Gmehling and Rasmussen. It is not the intention of this proposal to amend the UN Recommendations on the Transport of Dangerous Goods, chapter 2.3 on Class 3 flammable liquids.

9. One of the conditions under which the flash point need not be determined experimentally is that the calculated flash point is at least 5 °C greater than the relevant criterion. In order to avoid possible misunderstandings this condition could be phrased in an unambiguous way by adding a footnote explaining under which conditions it is not acceptable to apply the calculation method to sub-section 2.6.4.2.2 of the GHS.

10. In 2.6.4.2.2 (b) of the GHS and in Appendix 6, paragraph 4 of the Manual of Tests and Criteria it is stated that the flash point of the components shall be known. However, the method referred to in 2.6.4.2.3 and in Appendix 6, paragraph 4 does not use the flash points but it uses the lower explosion limit of the components for calculating the flash point of the mixtures.

11. In 2.6.4.2.2 (c) it is stated that the activity coefficients including temperature dependence of the components shall be known. However, knowledge of the activity coefficients is not sufficient and the saturated vapour pressure and its temperature dependence must be known as well according to the method cited in 2.6.4.2.3 and in Appendix 6, paragraph 4. Both should be indicated correctly in 2.6.4.2.2 and in Appendix 6, paragraph 4.

12. Up to now, the cited method is validated for mixtures containing up to six volatile components. These components may be flammable liquids like hydrocarbons, ethers, alcohols, esters (except acrylate), and water. It is however not yet validated for mixtures containing e.g. halogenated, sulfurous and/or phosphoric substances as well as reactive acrylates. Therefore, such mixtures should be excluded until the applicability of the method is validated e.g. by literature data by changing the existing footnote.

Proposal No. 2:

13. Amend 2.6.4.2.2 to read as follows:

“2.6.4.2.2 In the case of mixtures³ containing known flammable liquids in defined concentrations, although they may contain non-volatile components e.g. polymers, additives, the flash point need not be determined experimentally if the calculated flash point of the mixture, using the method given in 2.6.4.2.3 below, is at least 5°C⁴ greater than the relevant classification criterion (23 °C and 60 °C, respectively) and provided that:

- (a) The composition of the mixture is accurately known (if the material has a specified range of composition, the composition with the lowest calculated flash point shall be selected for assessment);

- (b) The lower explosion limit flash point (closed cup as given in 2.6.4.2.5 below) of each component is known (an appropriate correlation has to be applied when these data are extrapolated to other temperatures than test conditions) as well as a method for calculating the lower explosion limit of the mixture;
- (c) The temperature dependence of the saturated vapour pressure and of the activity coefficient is known for each component as present in the mixture including its temperature dependence;
- (d) The liquid phase is homogeneous.

³ Screening procedures are well established for ideal mixtures of solvents, i.e. mainly hydrocarbons. Up to now, the calculation method is validated for mixtures containing up to 6 volatile components. These components may be flammable liquids like hydrocarbons, ethers, alcohols, ester (except acrylates) and water. It is however not yet validated for mixtures containing halogenated, sulfurous, and/or phosphoric compounds as well as reactive acrylates.

⁴ If the calculated flash point is less than 5 °C greater than the relevant classification criterion, the calculation method may not be used and the flash point shall be determined experimentally.”.

Standards cited for the determining the flash point

14. In sub-section 2.6.4.2.5 of the GHS standards for determining the flash point of flammable liquids are listed. Many of the cited standards are withdrawn and replaced by new versions. And most of the former international, European and national standards are harmonized (as requested by the experts of dangerous goods). This means that the international standard - e.g. ISO 3679 - and the European standard - e.g. EN ISO 3769 - are identical. The European version EN ISO is adopted as a national version in the European countries (this may easily be checked by visiting the websites of the respective national standardization bodies). Therefore, it is no longer necessary to refer to national standards except for those national standards which do not have a harmonized international equivalent.

15. As a result of the international harmonisation of standards most of the French and British standards are also covered by the named ISO standards. The experts from France and the United Kingdom therefore might consider agreeing to the deletion of references of the respective British and French standards in this chapter as well. Therefore, the expert from Germany would like to invite the experts from France and the United Kingdom to prepare an informal document.

16. Standards which are referred to in the *UN Recommendations on the Transport of Dangerous Goods* are dated by indicating the year of publication. The Sub-Committee may wish to consider adding the year of publication when referring to standards in the GHS in general as well.

Proposal No. 3:

17. Amend 2.4.6.2.5 to read as follows:

“2.4.6.2.5 The following ~~is a list of documents describing~~ methods for determining the flash point of flammable liquids shall be used:

International standards:

ISO 2719

ISO 13736

ISO 3679

ISO 3680

ISO 1516

ISO 1523

National standards:

American Society for Testing Materials International, 100Barr Harbor Drive, PO Box C 700, West Conshohocken, Pennsylvania, USA 19428-2959:

ASTM D 3828-93, Standard test methods for flash point by small scale closed tester

ASTM D 56-93, Standard test method for flash point by tag closed tester

ASTM D 3278-96, Standard test methods for flash point of liquids by setaflash closed-cup apparatus

ASTM D 0093-96, Standard test methods for flash point by Pensky-Martens closed cup tester

Association française de normalisation, AFNOR, Tour Europe, 92049 Paris La Défense:

French Standard NF M 07 – 019

French Standard NF M 07 - 011 / NF T 30 - 050 / NF T 66 – 009

French Standard NF M 07 – 036

British Standards Institute, Customer Services, 389 Chiswick High Road, London, N7 8LB:

British Standard BS EN 22719

British Standard BS 2000 Part 170

Deutsches Institut für Normung, ~~Burggrafenst. 6, Burggrafenstr. 6, D-10787 Berlin:~~

Standard DIN 51755 (flash points below 65 °C)

~~Standard DIN 51758 (flash points 65 °C to 165 °C)~~

~~Standard DIN 53213 (for varnishes, lacquers and similar viscous liquids with flash points below 65 °C)~~

State Committee of the Council of Ministers for Standardization, 113813, GSP, Moscow, M-49 Leninsky Prospekt, 9:

GOST 12.1.044-84”.

Determination of the boiling point

8. In order to classify a flammable liquid, data on its flash point and initial boiling point are needed (see 2.6.4.2.1). The GHS offers several methods for determining the flash point (see 2.6.4.2.5), but does not provide a suitable method for determining the initial boiling point of flammable liquids. Appropriate methods should be referred to in the GHS because the initial boiling point is **the** criterion which distinguishes between Category 1 and Category 2. This could be done in the same way as for the flash point.

Proposal:

Add a paragraph 2.6.4.2.6 to read as follows:

“2.6.4.2.6 The following methods for determining the initial boiling point of flammable liquids shall be used:

International standards:

ISO 3924

ISO 4626

ISO 3405

National standards:

American Society for Testing Materials International, 100Barr Harbor Drive, PO Box C 700, West Conshohocken, Pennsylvania, USA 19428-2959:

ASTM D 86 (current edition)

ASTM D 1078 (current edition)

Further acceptable methods:

Method A.2 as described in Directive 67/548/EEC, Annex V, A.2, 1.4.2

Method A.2 as described in Directive 67/548/EEC, Annex V, A.2, 1.4.3”.
