

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 Globally Harmonized System of Classification and Labelling of Chemicals

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

Physical Hazards

Identification of some open issues not yet properly addressed in the GHS

Transmitted by the expert from Germany

1. Introduction

Currently some hazardous properties of certain types of substances which are partly covered by the UN Recommendations on the Transport of Dangerous Goods and also partly by European Directives are not yet completely addressed in the GHS. However, due to the hazardous physical properties of these substances, their incorporation into the GHS should be considered in order to ensure safe handling, storage and transportation.

These types of substances are:

- *Ammonium nitrate;*
- *Substances having explosive properties although not classified as explosives;*
- *Explosives which are not packed for transport;*
- *Desensitized explosives;*
- *Certain properties of flammable liquids;*
- *Chemically unstable gases.*

2. Background

(a) Ammonium nitrate:

A correct classification of ammonium nitrate is indispensable for its safe handling and transportation. The consequences of disregarding its dangerous properties became last apparent in the major accident at a fertilizer plant in Toulouse.

The problem regarding the dangerous properties of ammonium nitrate is a bit complicated, because they are normally not detected by the classical test methods for explosive properties or resistance to detonation or oxidizing properties. However, due to its dangerous properties it is currently classified for transport, storage and use on a listing principle as follows (these classifications

are based on a “grandfather clause” and not on test results, meaning that the named ammonium nitrates are assigned to the respective class irrespective of the test results):

Transport: Ammonium nitrate is classified in the UN Recommendations on the transport of dangerous goods:

- UN No. 0222 AMMONIUM NITRATE with more than 0.2% combustible substances, including any organic substance calculated as carbon, to the exclusion of any other added substance†
Class 1.1 D
- UN No. 1942 AMMONIUM NITRATE, with not more than 0.2% total combustible material, including any organic substance, calculated as carbon to the exclusion of any other added substance.
Class 5.1 (corresponding GHS hazard class: oxidizing solid)
(assigned due to listing and not due to test results)
- UN No. 2067 AMMONIUM NITRATE BASED FERTILIZER
Class 5.1 (corresponding GHS hazard class: oxidizing solid)
(assigned due to listing and not due to test results)
- UN No. 2071 AMMONIUM NITRATE BASED FERTILIZER
Class 9 (no corresponding hazard class in the GHS)
- UN No. 3375 AMMONIUM NITRATE EMULSION or SUSPENSION or GEL , intermediate for blasting explosives
Class 5.1 (corresponding GHS hazard class: oxidizing liquid or solid)
(assigned due to listing and not due to test results)

Storage and use: Ammonium nitrate is specifically named in Directive 96/82/EC (Seveso-II-Directive) and its amendment Directive 2003/105/EC, which is harmonized in principle with the transport regulations for Europe (ADR/RID) with regard to its composition but not with regard to its hazardous characteristics.
The amendment requires that all ammonium nitrate fertilizers have to be tested for the capability of self-sustaining decomposition (ammonium nitrate > 45%) and for their resistance to detonation (ammonium nitrate > 70%). If they do not pass the detonation test, the threshold according to the Seveso-II-Directive is so low that these preparations are virtually not used as fertilizer.

(b) Substances having explosive properties although not classified as explosives:

There are some types of substances (examples are organic peroxides, self-reactive substances and substances of other classes such as hydroxylammonium salts but also substances which are not classified in any other class) which have explosive properties although not classified as explosives. In this context explosive properties mean thermal sensitivity (Koenen test) and mechanical sensitivity (to drop weight impact and friction).

Currently, according to the classification system of the GHS these substances are only partially tested for explosive properties and as a result not classified or labelled completely adequate. This is also the case for test series 1 which is described in the UN Test Manual of Tests and Criteria for the acceptance procedure for classification of explosives into class 1. All these substances are tested for their thermal sensitivity by the Koenen test but they are not tested for mechanical sensitivity by shock (impact) and friction. However, if explosive properties according to these tests are existent they must be communicated in order to ensure safe handling.

The explosive properties of these substances become evident in the A.14 method as described in the annex of Directive 67/548/EEC (Dangerous Substances Directive). In this test series the intrinsic material properties of potentially explosive substances are determined by the thermal sensitivity test, the mechanical sensitivity test for shock and the mechanical test for friction.

If substances show explosive properties either in the thermal sensitivity test or in a mechanical sensitivity test by shock (impact) or friction, two possibilities exist:

1. The substances also have other hazardous properties and are classified accordingly (e.g. as organic peroxide, self-reactive substance or substances currently assigned to classes 4, 5.1 or 8). These substances then need additional labeling of the explosive properties (for organic peroxides and self-reactive substances this is already regulated in Annex A.2.8 and A.2.15 of the GHS, but for the other substances this needs to be regulated as well).
2. The substances do not have other hazardous properties and as a result are currently not classified by the normal classification procedure. These substances are currently classified by a “grandfather clause” or they are not classified at all. This should be avoided and possible non-classification of such substances should not be risked.

(c) Explosives which are not packed for transport:

Once a substance is classified as an explosive either according to test series 2 or because it is intended to be used as an explosive further testing according to TDG, GHS and the UN Test Manual is carried out. These tests consist of:

1. Test series 3 in order to determine the sensitivity of a new substance (mechanical sensitivity amongst others).
2. Tests for the assignment to a division of class 1 which are carried out together with the packaging of the substance or article.

As the test results for the assignment to a division depend on the packaging they do not reflect the intrinsic material properties and might even contradict the results of the mechanical impact test in test series 3.

(d) Desensitized explosives:

Solid desensitized explosives are explosive substances which are wetted with water or alcohols or are diluted with other substances, to form a homogeneous solid mixture to suppress or at least reduce their explosive properties.

Liquid desensitized explosives are explosive substances which are dissolved or suspended in water or other flammable or non-flammable liquid substances, to form an homogeneous liquid mixture to suppress or at least reduce their explosives properties.

Desensitized explosives are currently not classified as a separate hazard class according to the GHS. Some desensitized explosives for TDG are classified by listing depending on their physical state and the agents used to achieve desensitization as flammable solid or flammable liquid. However, even such desensitized explosives may become explosive under certain circumstances – especially after long term storage and during handling and use – and some desensitized explosives may even show explosive properties in the desensitized state.

Due to their specific dangerous properties desensitized explosives are currently classified for transport, storage and use as follows:

Transport: Solid desensitized explosives are classified in the UN Model Regulation on the transport of dangerous goods (all class 4.1 – flammable solids):

Entries in the Dangerous Goods List for solid desensitized explosives are UN 1310, UN 1320, UN 1321, UN 1322, UN 1336, UN 1337, UN 1344, UN 1347, UN 1348, UN 1349, UN 1354, UN 1355, UN 1356, UN 1357, UN 1517, UN 1571, UN 2555, UN 2556, UN 2557, UN 2852, UN 2907, UN 3317, UN 3319, UN 3344, UN 3364, UN 3365, UN 3366, UN 3367, UN 3368, UN 3369, UN 3370, UN 3376 and UN 3380.

Liquid desensitized explosives are classified in the UN Recommendations on the transport of dangerous goods (all class 3 – flammable liquids):

Entries in the Dangerous Goods List for liquid desensitized explosives are: UN 1204, UN 2059, UN 3064, UN 3343, UN 3357 and UN 3379.

Storage and use: Regulations regarding storage and use of desensitized explosives are issued at national level.

(e) Certain properties of flammable liquids:

Boiling point:

The GHS offers several methods for determining the flash point, but does not provide a suitable method for determining the initial boiling point of flammable liquids. An appropriate method should be referred to.

Calculation of flashpoint:

In chapter 2.6.4.2.2 (b) of the GHS there is a reference to the flashpoint of the individual components of a mixture which must be known as necessary requirement for the calculation of the flashpoint of the mixture. This reference is not correct since actually the lower explosion limit is required. Furthermore an additional restriction should be mentioned. The cited method is reliably applicable only for binary and ternary mixtures the components of which do not interact and have a well known combustion stoichiometry. The same is valid for Appendix 6, section 4.1 (b) of the UN Test Manual of Test and Criteria.

Methods for determining the flashpoint:

The list of methods for determining the flashpoint needs to be updated thus considering harmonization which in the meantime took place.

(f) Chemically unstable gases:

Among the gases classified according to the GHS there are gases which are chemically unstable. However, these gases are not classified as such but based on other hazardous properties. In the UN Test Manual of Test and Criteria there is also no test method for the classification of chemical instability. The classification of chemically unstable gases is achieved on the basis of other dangerous properties and these gases are classified together with stable gases e.g. as flammable, oxidizing or toxic.

However, when handling, storing or transporting a chemically unstable gas, specific precautions are necessary. Their necessity becomes apparent during occasional accidents especially in connection with acetylene, ethylene oxide and vinyl chloride.

3. *Proposals*

The named types of substances and the problems mentioned should be discussed with regard to amendments to the GHS and, if necessary, to the UN Model Regulation on TDG - and with regard to their classification procedure and appropriate hazard communication:

- (a) Ammonium nitrate: For ammonium nitrate a separate sub-category in the GHS might be useful since the general test criteria not really meet its dangerous properties. Furthermore test series 8 should be reviewed with regard to its suitability for the determination of the specific hazardous properties of ammonium nitrate emulsions, suspensions and gels leading to appropriate additions or amendments, including appropriate hazard communication.

- (b) Substances having explosive properties: A test series for explosive properties should be required by the GHS for all substances with some kind of indication for explosive properties. It should be checked whether the method A 14 according to Directive 67/548/EEC and if available other suitable methods from other existing systems should be included in the UN Manual of Tests and Criteria and should be referenced in the GHS.
- (c) Explosives which are not packed for transport: The further assignment of explosives to divisions should be reconsidered with regard to handling and manufacturing of explosives which are not packed for transport, including appropriate hazard communication.
- (d) Desensitized explosives: Desensitized explosives should be incorporated as a new category into the GHS. As these products are transported and used world-wide, a harmonized classification scheme including appropriate hazard communication should be discussed for inclusion in the GHS.
- (e) Certain properties of flammable liquids: The methods for determining characteristics of flammable liquids should be corrected and updated with regard to a method for determining the boiling point, calculation of the flashpoint of mixtures and the list of cited methods for determining the flashpoint.
- (f) Chemically unstable gases: Currently a method for the assignment of chemically unstable gases based on general criteria is not available but the subject "chemical instability" should be considered for future work. The establishment of general criteria for the assignment of chemically unstable gases should be considered in order to allow their adequate classification and hazard communication in the future.

The Sub-Committee is invited to discuss the issues and to decide on appropriate ways to tackle them. As some of the issues may also concern the transport of dangerous goods, close co-operation with the Sub-Committee on Transport should be ensured.
