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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

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

Physical hazards due to explosive properties

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

Transmitted by the expert from Germany

**1. Introduction**

The issues addressed in this document have been introduced during the last 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 (TDG Sub-Committee) as the focal point for physical hazards. Moreover, it was agreed that a new document with some more detailed proposals should be provided.

In this document, only those issues which are associated with physical hazards due to explosive properties are addressed because these shall also be dealt with by the Working Group on Explosives of the TDG Sub-Committee.

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## 2. Background

### (a) Ammonium nitrate<sup>1</sup>

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

The problem regarding the dangerous properties of ammonium nitrate is a complex issue, because they are normally not detected by the classical test methods for explosive properties or oxidizing properties. However, due to its dangerous properties, it is currently classified for transport on the basis of defined compositions (these classifications are based on a “grandfather clause” by listing in the UN Model Regulations and they are not necessarily based on test results):

Transport: Ammonium nitrate is classified according to its composition by entry in the Dangerous Goods List of the UN Recommendations on the Transport of Dangerous Goods under the UN Nos. 0222, 1942, 2067, 2071 and 3375. Provisions for the transport are linked to these entries.

Storage and use: In the current GHS system, ammonium nitrate is not specifically regulated and is not covered except in preparations which are specifically listed in the UN Model Regulations. Therefore there is need for action for the GHS. At present only one adequate system concerning the storage and use of ammonium nitrate is known, which is based on compositions and on experience as well<sup>2</sup>

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

There are some types of substances (e.g. organic peroxides, self-reactive substances and some other substances classified in other hazard classes such as corrosives, e.g. hydroxylammonium salts, but also substances which are not classified under any other GHS hazard class) which have explosive properties although they are not specifically classified as explosives due to the criteria in the respective decision logic. 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 are not classified or labeled completely adequately. Test series 1 and 2 which are described in the UN Manual of Tests and Criteria for the acceptance procedure for classification of substances into Class 1 require testing for the thermal sensitivity by the Koenen test but they do not require testing of the mechanical sensitivity to impact and friction. This is also the case for organic peroxides and self-reactive substances.

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<sup>1</sup> In this context ammonium nitrate means technical pure ammonium nitrate and ammonium nitrate based formulations (e.g. fertilizers, emulsions, suspensions).

<sup>2</sup> This has been introduced in the so-called EU Seveso Directive based on the transport system.

However, if explosive properties according to tests for the mechanical sensitivity are existent, these hazards have to be communicated in order to ensure safe handling, storage and use.

The explosive properties of substances which are mechanically sensitive become evident in impact tests (such as the Fallhammer test) and the friction tests as described in Test Series 3 of the UN Manual of Tests and Criteria. These tests have to be carried out after a substance is considered for Class 1<sup>3</sup> in the context of Test Series 3. However, these properties should be tested irrespective of considering a substance for Class 1 so that all substances (and therefore also those which are not considered for Class 1) are tested for their explosive properties.

(c) Explosives and explosive articles which are not packed for transport

Currently explosive properties of unpacked substances<sup>4</sup> are not communicated at all, not even as a subsidiary risk (if they differ from the packed substance). Once a substance or article is provisionally accepted as an explosive or explosive article according to the acceptance procedure in the UN Manual of Tests and Criteria and the GHS, subsequent testing for the assignment to a division of Class 1<sup>5</sup> (by test series 6) is carried out together with the packaging of the substance or article.

The assignment of a symbol, signal word and hazard statement is done solely based on this assignment. This approach is sufficiently safe for transport and storage dealing only with packed substances and articles. However, this approach is not appropriate to point out the hazards of unpacked<sup>4</sup> explosive substances and articles to ensure their safe handling and use.

The packaging can have a significant influence on the explosive effects of substances and articles. The type of packaging can change the response of packed explosives or explosive articles in Test Series 6. One and the same explosive substance or article can therefore be assigned to different hazard groups or even be rejected from Class 1 for transport depending on the packaging used (see the example for the blasting caps given in ST/SG/AC.10/C.3/2005/36 and ST/SG/AC.10/C.4/2005/5).

As a result, the explosive hazard of unpacked substances or articles can be different from the labeled hazard of the packed substances or articles (and most likely it will be more severe). It is therefore necessary to communicate these possible differences so that whoever handles a substance or article (independent from being a skilled or unskilled worker) would know whether removing of the (outer) packaging would result in a substance or article with a higher explosive hazard.

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<sup>3</sup> Class 1 in TDG corresponds to hazard class "explosives" in GHS.

<sup>4</sup> In this context unpacked substance means a substance not yet packed or removed from its package.

<sup>5</sup> A division in class 1 in TDG corresponds to a category in hazard class "explosives" in GHS.

(d) Desensitized explosives

Desensitized explosives are solid or liquid explosive substances which are wetted, diluted, dissolved or suspended with a phlegmatizer in order to suppress or at least reduce their explosive properties.

For transport some desensitized explosives are specifically listed and special provisions which are to be met are assigned to them. Depending on their physical state and the substances used to achieve desensitization they are then classified as flammable solids or flammable liquids. Desensitized explosives are currently not classified in a separate hazard class according to the GHS and therefore are not covered appropriately.

However, desensitized explosives may become again explosive under certain circumstances – especially after long term storage and during handling and use, e.g. when the phlegmatizing substance is removed or its concentration is decreased for example due to evaporation – and some desensitized explosives may have explosive properties even in the desensitized state.

Therefore, correct classification and communication of the special hazards associated with handling of desensitized explosives are especially important.

### **3. Proposals**

(a) Ammonium nitrate

Correct classification of ammonium nitrate could be achieved by establishing a new sub-category for ammonium nitrate within the GHS. Since the UN Recommendations for the Transport of Dangerous Goods already classify ammonium nitrate within the Dangerous Goods List no change is necessary for transport. The new GHS sub-category could be established based on these entries and should include the hazardous properties of ammonium nitrate (e.g. detonability, self-sustaining decomposition). These issues should be discussed in the Working Group on Explosives e.g. with regard to inclusion by listing in the GHS, and or based on criteria (to be developed as appropriate).

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

Correct knowledge of the sensitivity of substances with explosive properties could be achieved by adapting the respective tests for thermal sensitivity and for mechanical sensitivity to impact and friction according to test series 2 and 3 of the UN Manual of Tests and Criteria as preliminary tests with partially modified criteria. These preliminary tests would have to be carried out irrespective of the normal classification procedure for all substances which are suspected of having explosive properties (see also Appendix 6 of the UN Manual of Tests and Criteria). Therefore, these tests should not be a part of the classification procedure of explosives alone but they should be part of a preliminary procedure instead (which is not yet described by the GHS). An appropriate solution of this problem should be discussed in the Working Group on

Explosives to find a practical way to determine and communicate the explosive properties of such substances.

(c) Explosives and explosive articles which are not packed for transport

The issues mentioned in section 2 (c) of this document should be discussed in the Working Group on Explosives to find a practicable way to determine and communicate the explosive hazard of unpacked substances and articles if the hazard differs from that of the packed material.

(d) Desensitized explosives

In order to meet the special hazards associated with desensitized explosives a separate hazard class or category should be incorporated into the GHS. This could be divided into categories for solid and liquid desensitized explosives and also differentiate between those desensitized explosives which do not have explosive properties (as long as care is taken, that they are not concentrated for some reason and that the phlegmatiser remains efficient) and those that may have (reduced) explosive properties (these would have positive results in the above proposed preliminary test for explosive properties).

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