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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

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Classification criteria and related hazard communication:

work of the Sub-Committee of Experts on the Transport of Dangerous Goods (TDG) on matters of interest to the GHS Sub-Committee

Classification of desensitized explosives for the purposes of supply and use according to UN GHS chapter 2.17: Test results on industrial nitrocellulose

Transmitted by the European Chemical Industry Council (CEFIC) on behalf of the World Nitrocellulose Producers Association WONIPA

Introduction

- 1. During its twenty-eighth meeting the Sub-Committee of Experts on the Globally Harmonized System of Classification and Labelling of Chemicals held in Geneva from 10 to 12 December 2014 adopted the introduction of a new chapter on desensitized explosives in the GHS as well as the relevant test method as contained in document ST/SG/AC.10/C.4/2014/2 considered at the 27th session. The proposal for the new chapter and consequential amendments to the GHS in document ST/SG/AC.10/C.4/2014/16 were adopted with a minor amendment to the decision logic 2.17.1.
- 2. At its forty-first session (June 2012), the Sub-Committee of experts on the Transport of Dangerous Goods (TDG Sub-Committee) had endorsed the conclusions of the Working Group on Desensitized Explosives concerning desensitized explosives (see ST/SG/AC.10/C.3/82, paras. 3 and 45) as follows:
 - (a) The conclusions of the Working Group on Explosives as reflected in informal document INF.67 (TDG Sub-Committee, 41st session), para. 6 were confirmed;
 - (b) A new chapter on desensitized explosives in the GHS is needed;
 - (c) The German methodology is a good starting point to develop a comprehensive approach;
- 3. In the following meetings in the years 2012 to 2014 of the Expert group on explosives test methods and criteria for the classification of desensitized explosives were developed based on the "Directive for the assignment of storage classes for substances having explosive properties (SprengLR011)" of Germany. The test procedure and the classification limits of the new test method described in Section 51 "Classification Procedures, Test Methods and Criteria relating to the Hazard Class Desensitized Explosives" of the UN Manual of Tests and Criteria are exactly the same as those described

in the German regulation "SprengLR011", only the nomenclature of the categories is different. This allows to use the test results of the tests done in the past according to "SprengLR011" for the classification of desensitized explosives according to the UN GHS chapter 2.17. By doing this, a lot of work and material can be saved.

- 4. CEFIC, on behalf of the Worldwide Nitrocellulose Producers Association (WONIPA), which represents manufacturers of industrial nitrocellulose and accounts for 80% of the worldwide production (approximately 200.000 tpa), presented test results from tests of the German competent authority (Federal Institute for Material Research and Testing (BAM)) according to "SprengLR011" in the nomenclature of Section 51 "Classification Procedures, Test Methods and Criteria relating to the Hazard Class Desensitized Explosives" of the UN Manual of Tests and Criteria in an informal documents INF.10 (51st session) and INF.4 (33rd session) in the July 2017 meetings.
- 5. The GHS Sub-Committee was informed in the July 2017 meeting that the TDG Sub-Committee had endorsed the conclusion of the Working Group on Explosives on using the results of the SprengLR011 test for classification of industrial nitrocellulose products according to Chapter 2.17 of the GHS. The GHS Sub-Committee noted that an intersessional informal group led by CEFIC at the TDG Sub-Committee would consider how to include the results in the GHS, the United Nations Recommendations on the Transport of Dangerous Goods, Model Regulations or the Manual of Tests and Criteria to make them available worldwide.
- 6. The GHS Sub-Committee expressed support for this work and invited the representative of CEFIC to take account of the comments made, in particular as regards acknowledging the possibility of performing self-classifications.
- 7. This informal document presents the proposal of the intersessional informal group led by CEFIC for the inclusion of the test results as Annex 10 in the Manual of Tests and Criteria.

Background

- 8. WONIPA members deliver since more than 30 years industrial nitrocellulose products to the German market (currently approximately 10.000 tpa, as UN 2555, 2556 and 2557¹) and have ample experience with the German test method and the assignment to storage groups.
- 9. The German test methods appropriately identify the burning rate and heat radiation hazards for the different nitrocellulose grades. All tests of products produced by WONIPA members have been performed by BAM with the industrial nitrocellulose packed in UN approved fibre board boxes (4G) or fibre drums (1G) according to packing instruction P406. The test results in the table can therefore only be used for the classification of industrial nitrocellulose products packed in UN approved fibre board boxes (4G) or fibre drums (1G) according to packing instruction P406.
- 10. All these industrial nitrocellulose products tested by BAM in the last 30 years had an ignition temperature above 180 $^{\circ}$ C for UN 25551 and UN 2556 and above 170 $^{\circ}$ C for

UN 2555 NITROCELLULOSE WITH WATER (not less than 25 % water by mass) UN 2556 NITROCELLULOSE WITH ALCOHOL, not less than 25 % alcohol by mass, and not more than 12,6 % nitrogen by dry mass) UN 2557 NITROCELLULOSE, with not more than 12,6 % nitrogen by dry mass, MIXTURE WITH or WITHOUT PLASTICIZER, WITH or WITHOUT PIGMENT

- UN 2557. Tests of ignition temperature were done according to section 2.3.2 of ADR². All these industrial nitrocellulose products fulfilled the test requirements of the Bergmann Junk test for the thermal stability demonstrated by the fact that the quantity of nitrous vapours given off was not more than 2.5 ml NO during the test at 132 °C. The test is described in Annex 2 of the UN Working paper ST/SG/AC.10/C.3/2017/3.
- 11. Annex 1 provides the results for more than 200 industrial nitrocellulose products, classified by BAM. The results according to "SprengLR011" were transformed to the category classification of UN GHS chapter 2.17 and can now be used for the classification of Industrial Nitrocellulose products worldwide, without the necessity to perform new tests, if the requirements for the packaging and the thermal stability are fulfilled. The range of product composition, norm viscosities and nitrogen content are representative for nearly all grades of industrial nitrocellulose products produced worldwide. Annex 2 provides a "Comparison of the Categories according to UN GHS chapter 2.17 desensitized explosives and the storage groups according to "SprengLR11" of Germany".
- 12. Without any exception all the industrial nitrocellulose products tested over the last 30 years were classified by BAM as flammable solids, desensitized explosives of Division 4.1 (see Annex 1), none were classified as explosive. For each product BAM has issued a certificate stating the storage group and the burning speed of the tested nitrocellulose product. BAM publishes the results of the assignment to storage groups for industrial nitrocellulose products in the information "Amtliche Bekanntmachungen" of the BAM.

Proposal

- 13. WONIPA proposes to use the test results already achieved by the German competent authority BAM for the classification of industrial nitrocellulose products according to the tests and criteria of "SprengLR011" in the last 30 years for the classification of industrial Nitrocellulose products according to the new UN GHS chapter 2.17 desensitized explosives as the test methods and the criteria are exactly the same. By doing this, a lot of test work can be saved.
- 14. The information collected in the tables may be used by competent authorities worldwide for the classification of Industrial NC products according to the test description for the CLASSIFICATION PROCEDURES, TEST METHODS AND CRITERIA RELATING TO THE HAZARD CLASS DESENSITIZED EXPLOSIVES in SECTION 51 of the UN Manual of Test and Criteria, paragraph 51.4.1.2 (a):
 - 51.4.1.2 A substance or mixture, as packed for supply and use , may be unambiguously assigned to a burning rate and category by a competent authority on the basis of results from other tests or available information; or .

Justification

- 15. The German test method and criteria of "SprengLR011" were used for the development of the new test method and criteria described in Section 51 "Classification Procedures, Test Methods and Criteria relating to the Hazard Class Desensitized Explosives" in the UN Manual of test and criteria.
- 16. As the whole range of industrial nitrocellulose products produced worldwide was already tested by BAM in the last 30 years, there are no additional tests necessary, which would save costs for industry worldwide.

European Agreement concerning the International Carriage of Dangerous Goods by Road

Annex 1

Amendments to the UN Manual of Tests and Criteria

Insert a new appendix 10

Appendix 10

Compilation of classification results on industrial nitrocellulose for the purposes of supply and use according to UN GHS chapter 2.17, which can be used for the classification of Industrial NC products.

Requirements for the use of the test results for the classification of industrial nitrocellulose products:

- 1. The test results in this appendix can only be used for the classification of industrial nitrocellulose products packed in UN approved fibre board boxes (4G) or fibre drums (1G) according to packing instruction P406. They cannot be used for nitrocellulose products in other pressure resistant packaging like steel drums.
- 2. The test results in this appendix can only be used for industrial nitrocellulose products which fulfill the test requirements of the Bergmann Junk test for the thermal stability demonstrated by the fact that the quantity of nitrous vapours given off is not more than 2.5 ml NO during the test at 132 °C. The test is described in Annex 2 of the UN Working paper ST/SG/AC.10/C.3/2017/3.

Test results

- 3. All industrial nitrocellulose products worldwide can be made comparable based upon their nitrogen content and their Norm-viscosities (according to DIN EN ISO 14446). WONIPA has therefore used this method for presenting the results of the BAM tests in the following table. It should be noted that BAM also uses the Norm-viscosities in the publications of the storage group classifications, whereby the storage group classification refers to the storage of industrial nitrocellulose in warehouses.
- 4. According to their Nitrogen content three types of industrial nitrocellulose products have been defined:
 - (a) E grades as ester soluble products with nitrogen content from 11.8 to 12.3 %;
 - (b) **M**-grades as medium soluble grades with nitrogen content of 11.3 to 11.8 %;
 - (c) A-grades as alcohol soluble grades with a nitrogen content of 10.7 to 11.3 %.

The testing results have been grouped accordingly into 3 separate tables.

- 5. The first column of the tables provides the types of the industrial nitrocellulose, which are identified according to ISO 14446 by a combination of two elements:
 - (a) A 1- or 2-digit number, which indicates the concentration of the NC solution that is required for a viscosity of 400 + -25 mPa.s; and
 - (b) A letter which identifies the solvent in which the NC-product is soluble.
 - E stands for ester soluble
 - M stands for medium soluble

• A stands for alcohol soluble

For example for the NC-type 4E in the first table, with a concentration of 4 %, a viscosity of 400 + 25 mPa.s.is achieved.

The viscosities are measured in a solvent mixture of 95 % acetone/5 % water with a Höppler viscometer. Historically industrial nitrocellulose types have been developed for a number of Norm-viscosities only and not for all Norm-viscosities. As it is technically possible to produce products with all Norm-viscosities, all relevant Norm-viscosities were entered in the tables, but some cells in the tables therefore remain empty.

6. The results of the tests are presented per phlegmatizer content for the phlegmatizers Isopropanol (IPA), Ethanol (ETH), Butanol (BUT) and Water.

Compilation of category classifications for NC-Norm grades according to UN GHS chapter 2.17 desensitized explosives (Tests made by BAM in the years from 1981 to 2011

IPA = Isopropanol, ETH = Ethanol, BUT = Butanol

(a) Part Ester soluble E-grades with a Nitrogen Content of 11.8 to 12.3 %

NC-	urt Ester solds							NC-Chips
type	IPA 35 %	IPA 30%	ETH	ETH	BUT	BUT	Water	with
type	II A 33 70	II A 3070	LIII	LIII	DOT	DOI	vv atci	20 %
			35 %	30 %	35 %	30%	35 %	Plasticizer
3E								
4E	1 (330)	1 (760)	3	3	1 (530)	1 (540)		1 (1115)
5E								
6E	2		3		1 (390)			1 (1115)
7E	2	1 (430)	3	3	1 (320)	1 (420)		1 (1115)
8E	2		3		2	1 (420)		1 (1115)
9E	2	1 (330)	3	3	2	1 (420)		1 (1115)
10E	2		3		2			1 (1115)
11E								
12E	3	2	4	3	2	1 (330)	4	1 (1115)
13E	3		4		2			1 (1115)
14E								
15E	3	2	4	3	2	2		1 (1115)
16E								
17E								
18E	3		4		3			1 (1115)
19E								
20E	3	3	4	3	3			1 (1115)
21E					3	3		1 (1115)
22E	3	3	4	3	3	3	4	1 (1115)
23E	3	3	4		3		4	1 (1115)
24E	3	3	4	3	3	3		1 (1115)
25E	3	3	4	3	3	3	4	1 (1115)
26E								
27E	3	3	4	3	3	3		1 (1115)
28E	3	3	4		3			
29E								
30E					3	3		
31E	3		4					1 (1115)
32E	3	3	4	3	3	3		1 (1115)
33E								
34E	4	3	4	3	3			1 (1115)
35E								
36E								
37E								
38E								

Compilation of category classifications for NC-Norm grades according to UN GHS chapter 2.17 desensitized explosives (Tests made by BAM in the years from 1981 to 2011 (continued)

IPA = Isopropanol, ETH = Ethanol, BUT = Butanol

(b) Part Medium soluble M-grades with a Nitrogen content of 11.3 to 11.8 %

NC-								NC-Chips
Type	IPA 35 %	IPA 30%	ETH	ETH	BUT	BUT	Water	with
			25.0/	20.0/	25.0/	200/	25.0/	20 %
			35 %	30 %	35 %	30%	35 %	Plasticizer
12M					3			
13M								
14M	3	3	4	3				1 (1115)
15M					3	2		
16M								
17M	3	3	4	3	3			1 (1115)
18M	3	3	4	3	3			1 (1115)
19M								
20M								
21M	3	3	4	4	3			1 (1115)
22M								
23M								
24M					3	3		
25M					3	3		
26M								
27M	4	3	4	4	3	3	4	1 (1115)
28M								
29M								
30M					3	3		
31M								
32M					3	3		
33M								
34M	4	3	4	4	4			1 (1115)

Compilation of category classifications for NC-Norm grades according to UN GHS chapter 2.17 desensitized explosives (Tests made by BAM in the years from 1981 to 2011 (continued)

IPA = Isopropanol, ETH = Ethanol, BUT = Butanol

(c) Part Alcohol-soluble A-grades with a Nitrogen content of 10.7 to 11.3 %

NC-	art Arconor-so							NC China
type	IPA 35 %	IPA 30%	ETH	ETH	BUT	BUT	Water	NC-Chips with
type	11 11 33 70	11 11 30 70	LIII	LIII	DOI	DOI	,, arci	20 %
			35 %	30 %	35 %	30%	35 %	Plasticizer
7A								
8A								
9A	4	3	4	3	3			1 (1115)
10A								
11A								
12A								
13A								
14A								
15A	4	3	4	3	4	2		1 (1115)
16A								
17A								
18A								
19A								
20A								
21A								
22A								
23A	4	3	4	4	4			1 (1115)
24A					4	3		
25A					4	3		
26A								
27A	4	3	4	4	4	3		1 (1115)
28A								
29A								
30A	4	3	4	4	4	3	4	1 (1115)
31A	4	3	4	4				1 (1115)
32A	4	3	4	4	4	3		
33A		3	4					1 (1115)
34A								
35A								

Annex 2

Comparison of the Categories according to UN GHS chapter 2.17 desensitized explosives and the storage groups according to "SprengLR11" of Germany

Category according to UN GHS chapter 2.17	Storage group according to "SprengLR011"	Test criteria for determining the burning behavior of substances or mixtures are:
1	Ia	Any substance or mixture with a corrected burning rate AC equal to or greater than 300 kg/min but not more than 1200 kg/min.
2	Ib	Any substance or mixture with a corrected burning rate AC equal to or greater than 140 kg/min but less than 300 kg/min
3	II	Any substance or mixture with a corrected burning rate AC equal to or greater than 60 kg/min but less than 140 kg/min
4	III	Any substance or mixture with a corrected burning rate AC less than 60 kg/min