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Explosives and related matters: desensitized explosives

Sub-Committee of Experts on the Globally Harmonized System of Classification and Labelling of Chemicals
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Item 2 (a) of the provisional agenda
Updating the Globally Harmonized System of Classification and Labelling of Chemicals: physical hazards

Classification of desensitized explosives for the purposes of supply and use: Test results on industrial nitrocellulose

Transmitted by the International Council of Chemical Associations (ICCA)[1]

Introduction

1. During the last meetings of the Sub-Committee of Experts of the Transport of Dangerous Goods and the Sub-Committee of Experts on the Globally Harmonized System of Classification and Labelling of Chemicals both sub-committees supported the continuation of the work on the development of criteria for the classification of desensitized explosives for supply and use (reports ST/SG/AC.10/C.3/80 and ST/SG/AC.10/C.4/44). The experts were also asked to provide test results about typical desensitized explosives to the Working Group on Explosives.

2. The Working Group on Desensitized Explosives examined the list of desensitized explosives currently assigned to Class 3 and Division 4.1 and tentatively categorised them with regard to the dominant hazard (ST/SG/AC.10/C.3/2009/11). The experts found that the hazard of desensitized explosives varies considerably.

3. In Germany substances having explosive properties are classified according to their hazard ("Directive for the assignment of storage classes for substances having explosive properties (SprengLR011)"). This covers mainly substances considered to be non-

[1] In accordance with the programme of work of the Sub-Committee for 2011-2012 approved by the Committee at its fifth session (refer to ST/SG/AC.10/C.3/76, para. 116 and ST/SG/AC.10/38, para. 16).

intentional explosives, i.e. substances which have not been manufactured with the intention of producing an explosive or pyrotechnic effect in practice.

4. ICCA, 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), herewith presents test results and the test method used in Germany by the competent authority (Federal Institute for Material Research and Testing (BAM)). Provided that there is no mass explosion or projection hazard, substances which may show explosive properties (e.g. desensitized explosives as industrial nitrocellulose) are classified into four types ("storage groups") according to their burning rate in a bonfire test. For reasons of comparability this burning rate is given in relation to a quantity of 10.000 kg.

I. Background

5. 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 25572) and have ample experience with the German test method and the assignment to storage groups.

6. 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.

7. All these industrial nitrocellulose products tested by BAM in the last 30 years had an ignition temperature above 180 °C for UN 2555 and UN 2556 and above 170 °C for UN 2557. Tests of ignition temperature were done according to section 2.3.2 of ADR[3].

8. Annex 1 provides the results for more than 200 industrial nitrocellulose products, classified by BAM. The range of product composition, norm viscosities and nitrogen content are representative for nearly all grades of industrial nitrocellulose products produced worldwide.

9. 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.

10. The users of industrial nitrocellulose in Germany are informed about the storage group and the fire hazard for each nitrocellulose product delivered to them, as the storage group is printed on the label of every nitrocellulose package.

11. Annex 2 describes the test method for determining the 10.000 kg burning rate and the assignment of substances, having explosive properties, into storage groups.

[2] 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

[3] European Agreement concerning the International Carriage of Dangerous Goods by Road

II. Proposal

12. WONIPA proposes to introduce the German classification system of storage groups for industrial nitrocellulose products worldwide, by adding the test method for the determination of the burning rate as a test method for desensitized explosives in the UN Manual of Tests and Criteria, maybe as test 6(e), and by introducing a special provision for industrial nitrocellulose in the new chapter which has to be created in the GHS.

13. The information about the storage group could be included in the safety data sheets. Comparable test methods are also used in other countries e.g. the Netherlands and the United Kingdom.

III. Justification

14. The German system has proven to achieve a high safety level.

15. 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.

Annex 1

Test results

1. 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.

2. 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 %; and

(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.

3. 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.

4. The results of the tests are presented per phlegmatizer content.

Compilation of storage group classifications for NC-Norm grades according to SprengLR011 made by BAM in the years from 1981 to 2011

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

NC-type	IPA 35 %	IPA 30%	ETH 35 %	ETH 30 %	BUT 35 %	BUT 30%	Water 35 %	NC-Chips with 20 % Plasticizer
3E								
4E	Ia (330)	Ia (760)	II	II	Ia (530)	Ia (540)		Ia (1115)
5E								
6E	Ib		II		Ia (390)			Ia (1115)
7E	Ib	Ia (430)	II	II	Ia (320)	Ia (420)		Ia (1115)
8E	Ib		II		Ib	Ia (420)		Ia (1115)
9E	Ib	Ia (330)	II	II	Ib	Ia (420)		Ia (1115)
10E	Ib		II		Ib			Ia (1115)
11E								
12E	II	Ib	III	II	Ib	Ia (330)	III	Ia (1115)
13E	II		III		Ib			Ia (1115)
14E								
15E	II	Ib	III	II	Ib	Ib		Ia (1115)
16E								
17E								
18E	II		III		II			Ia (1115)
19E								
20E	II	II	III	II	II			Ia (1115)
21E					II	II		Ia (1115)
22E	II	II	III	II	II	II	III	Ia (1115)
23E	II	II	III		II		III	Ia (1115)
24E	II	II	III	II	II	II		Ia (1115)
25E	II	II	III	II	II	II	III	Ia (1115)
26E								
27E	II	II	III	II	II	II		Ia (1115)
28E	II	II	III		II			
29E								
30E					II	II		
31E	II		III					Ia (1115)
32E	II	II	III	II	II	II		Ia (1115)
33E								
34E	III	II	III	II	II			Ia (1115)
35E								
36E								
37E								
38E								

Compilation of storage group classifications for NC-Norm grades according to SprengLR011 made by BAM in the years from 1981 to 2011 *(continued)*

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

NC-Type	*IPA 35 %*	*IPA 30%*	*ETH 35 %*	*ETH 30 %*	*BUT 35 %*	*BUT 30%*	*Water 35 %*	*NC-Chips with 20 % Plasticizer*
12M					II			
13M								
14M	II	II	III	II				Ia (1115)
15M					II	Ib		
16M								
17M	II	II	III	II	II			Ia (1115)
18M	II	II	III	II	II			Ia (1115)
19M								
20M								
21M	II	II	III	III	II			Ia (1115)
22M								
23M								
24M					II	II		
25M					II	II		
26M								
27M	III	II	III	III	II	II	III	Ia (1115)
28M								
29M								
30M					II	II		
31M								
32M					II	II		
33M								
34M	III	II	III	III	III			Ia (1115)

Compilation of storage group classifications for NC-Norm grades according to SprengLR011 made by BAM in the years from 1981 to 2011 ***(continued)***

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

NC-type	*IPA 35 %*	*IPA 30%*	*ETH 35 %*	*ETH 30 %*	*BUT 35 %*	*BUT 30%*	*Water 35 %*	*NC-Chips with 20 % Plasticizer*
7A								
8A								
9A	III	II	III	II	II			Ia (1115)
10A								
11A								
12A								
13A								
14A								
15A	III	II	III	II	III	Ib		Ia (1115)
16A								
17A								
18A								
19A								
20A								
21A								
22A								
23A	III	II	III	III	III			Ia (1115)
24A					III	II		
25A					III	II		
26A								
27A	III	II	III	III	III	II		Ia (1115)
28A								
29A								
30A	III	II	III	III	III	II	III	Ia (1115)
31A	III	II	III	III				Ia (1115)
32A	III	II	III	III	III	II		
33A		II	III					Ia (1115)
34A								
35A								

Annex 2

Determination of the 10.000 kg scale burning rate

1. Introduction

1.1. The test series for the determination of the burning rate at 10.000 kg scale are used to determine the behavior of desensitized explosives in packages, involved in a fire resulting from external or internal sources. The 10.000 kg-scale burning rate can be used for classification into different types.

1.2 The series 6 types 6 (a) and 6 (b) are performed with the desensitized explosives in package in alphabetical order before the test series for determination of burning rate by large-scale testing are performed.

1.3 However, it is not always necessary to conduct tests of all types. Test type 6 (b) may be waived if in each type 6 (a) test:

(a) The exterior of the package is undamaged by internal detonation and/or ignition; or

(b) The contents of the package fail to explode, or explode as feebly as would exclude propagation of the explosive effect from one package to another in test type 6(b).

1.4 Test for determination of the burning rate by large-scale test can be waived if in test type 6 (b) there is an instantaneous explosion of the nearly total contents of the stack. In this case the product is assigned to Division 1.1.

1.5 If a substance gives a "—" result (no propagation of detonation) in the Series 1 type 1(a) test, the 6(a) test with a detonator may be waived. If a substance gives a "—" result (no or slow deflagration) in a Series 2 type 2(c) test, the 6 (a) test with an igniter may be waived.

The burning rate is defined as the burning rate of a mass of 10.000 kg. In practice, this burning is determined using a stack of packages with a total mass approximately 500 kg.

The tests are performed with the substances in the packages as prepared for storage.

All types of packages are subjected to the tests unless:

(a) The desensitized explosive, including any package, can be unambiguously assigned to a burning rate and type by a competent authority on the basis of results from other tests or of available information; or

(b) The desensitized explosive, including any package is assigned to Division 1.1.

2. Apparatus and materials

2.1 The test performance is arranged in such a way that the most unfavorable results will be obtained.

2.2 The following items are needed:

Tests are performed in singular (i.e. without a replicate) with:

(a) 1, 6 and 10 packages, up to a maximum total weight of 500 kg with packages up to weight 25 kg;

(b) 1, 3 and 6 packages, up to a maximum weight of 500 kg with packages with a weight between 25 kg and 50 kg;

(c) 1 or more packages, up to a maximum of total weight of 500 g with packages with a weight over 50 kg;

(d) Suitable catch-trays;

(e) Wooden pallets (DIN 15146), wood-wool and fuel;

(f) Suitable ignition means of ignition to ignite the wooden pallets/ wood-wool;

(g) Cine or video cameras, thermo columns or infrared sensors.

The number of tests and/or the total mass (whereas necessary) are increased if the test results and the corresponding hazards cannot be adequately evaluated.

3. Procedure

3.1 The packages are placed on wooden and leveled pallets. The pallets are placed in one (or two, if necessary) catch-trays. A catch-tray must comprise at least one complete pallet including 10 cm open space all around the pallet. Flammable material is placed under and around the packages in such a way that an optimum ignition of the desensitized explosive is guaranteed.

NOTE: *A quantity of about 10 kg dry wood-wool is usually sufficient. The wooden pallets and the dry wood-wool shall be soaked with a liquid mixture of fuel (light heating oil 90 % and light petrol 10 %).*

3.2 The heat of radiation is measured during the test by suitable equipment at, at least three locations with three different distances from the seat of fire.

The distances are:

(a) sufficiently large, on the one hand

(b) so as to enable detection of sufficient large signals with respect to the resolution of the equipment, on the other hand.

3.3 Suitable equipment to measure e.g. the radiation, are calibrated thermo columns or infrared sensors.

3.4 The signals are continuously recorded. The starting-point of the fire outbreak is defined as the moment when a reaction of the test substance is detected. The end of the fire is determined from registered radiation curves.

4. Method of assessing results

4.1 Evaluation of the test and calculation of the burning rate of 10.000 kg of desensitized explosives

If a mass explosion or individual explosions or metallic projections (fragments) occur, the desensitized explosives are classified in Class 1.

(a) The end of the fire is characterized by a decrease in radiation level I, as caused by the fire, to less than 5 % of the maximum level I*max*;

(b) The effect of either remainders or burning materials, if present, shall be taken into account in the evaluation;

(c) The burning time *t* is the time span between the starting point and the end of the fire;

(d) The burning rate *A* [kg/min] can be calculated for each tested quantity *m* [kg] and its corresponding burning time *t* [min] from the equation:

$$A = \frac{m}{t}$$

(e) The percent average radiation efficiency *ŋ* at a distance from the seat of fire is determined from the measured radiation levels and the theoretical maximum energy;

(f) The theoretical maximum energy is calculated by multiplying the individual mass of tested substance [kg] with the heat of combustion [kJ/kg]. The amount of energy that in practice appears to be transferred by radiation is determined by integrating the area below the measured radiation curve;

(g) To this end a graph is made showing the radiation level *I* [kW/m2] as a function of time. The complete radiation dose is calculated by integration of the smoothed and corrected curve down to 1 % to 5 % of I*max*;

(h) I*relevant* is obtained from the maximum of the curve of heat radiation calculated as average value of the radiation by converting the integrated area in a rectangle of equal size during the same time span;

(i) The form factor *f* that must be taken into account during the maximum fire intensity, can be determined from the formula:

$$f = \frac{I_{relevant}}{\quad}$$

The criteria for classification is the burning rate A_C for a quantity of 10.000 kg of desensitized explosives.

The burning rate A_C is determined as follows:

(a) Log A is plotted against log m, where A is the measured burning rate A, and m is the mass of desensitized explosive used for the test. The observed test results are extrapolated by means of this graph to an uncorrected burning rate A for a mass of 10000 kg by applying of the formula:

$$A \sim m^{\frac{2}{3}}$$

(b) The extrapolation is, in general best performed on the basis of the largest test quantities. The value A10t shall be corrected to the genuine burning rate for a 10000 kg mass of desensitized explosives Ac by the formula:

$$A_c = A_{10t} \times \frac{H_v}{33500} \times \frac{ŋ}{0{,}25} \times \frac{f}{2{,}78}$$

in which H_v is the heat of burning of the substance [kJ/kg] (i.e. reaction enthalpy of the burning reaction). A_C is the corrected burning rate [kg/min] for a quantity of 10000 kg.

Determination of (storage) types:

Type Ia: The A_C is equal or more than 300 kg/min

Type Ib: The A_C is equal or more than 140 kg/min but less than 300 kg/min

Type II: The A_C is equal or more than 60 kg/min but less than 140 kg/min

Type III: The A_C is less 60 kg/min

5. Examples of results of typical desensitized explosives

The nitrocellulose formulations are packed in fibre drums (1G) with maximum mass of 100 kg and fibre board boxes (4G) with maximum mass of 25 kg.

5.1 Ester soluble E-grades nitrocellulose formulations with different phlegmatizer and a nitrogen content of 11.8 % to 12.3 %

NC-type	IPA 35 %	IPA 30 %	ETH 35 %	ETH 30 %	BUT 35 %	BUT 30 %	Water	Chips[a)]
12E	II	Ib	III	II	Ib	Ia (330 kg/min)	III	Ia (1115 kg/min)
22E	II	II	III	II	II	II	III	Ia (1115 kg/min)
25E	II	II	III	II	II	II	II	Ia (1115 kg/min)

IPA (Isopropanol), ETH (Ethanol), BUT (Butanol)

a) NC-Chips with 20 % plasticizer

5.2 Medium soluble M-grades nitrocellulose formulations with different phlegmatizer and a nitrogen content of 11.3 % to 11.8 %

NC-type	IPA 35 %	IPA 30 %	ETH 35 %	ETH 30 %	BUT 35 %	BUT 30 %	Water	Chips[a)]
15M					II	Ib		
27M	II	II	III	III	II	II	III	Ia (1115 kg/min)
34M	II	II	III	III	IIII			Ia (1115 kg/min)

IPA (Isopropanol), ETH (Ethanol), BUT (Butanol)

a) NC-Chips with 20 % plasticizer

5.3 Alcohol soluble A-grades nitrocellulose formulations with different phlegmatizer and a nitrogen content of 10.7 % to 11.3 %

NC-type	IPA 35 %	IPA 30 %	ETH 35 %	ETH 30 %	BUT 35 %	BUT 30 %	Water	Chips[a)]
15A	III	II	III	II	II	Ib		Ia (1115 kg/min)
30A	III	II	III	III	II	II	III	Ia (1115 kg/min)
32 A	III	II	III	III	IIII	II		

IPA (Isopropanol), ETH (Ethanol), BUT (Butanol)

a) NC-Chips with 20 % plasticizer

Literature

[1] German "Guideline for the assignment of substances which may show explosive properties to Storage Groups (SprengLR011)"

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