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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

13 November 2017

Sub-Committee of Experts on the Transport of Dangerous Goods

Fifty-second session

Geneva, 26 November - 6 December 2017

Item 2 (e) of the provisional agenda

Explosives and related matters: stability tests for industrial nitrocellulose

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

Thirty-fourth session

Geneva, 6-8 December 2017

Item 2 (a) of the provisional agenda

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 GHS chapter 2.17

Transmitted by the Sporting Arms & Ammunition Manufacturers' Institute (SAAMI)

Introduction

1. This proposal augments the proposal UN/SCETDG/52/INF.7 - UN/SCEGHS/34/INF.4 from CEFIC and their member WONIPA to add test results as examples in the UN Manual of Tests & Criteria (the Manual) to avoid redundant non-transport classification testing of various configurations of wetted nitrocellulose (NC). SAAMI presents test results on "energetic" nitrocellulose wetted with water for inclusion in the Manual, in addition to the WONIPA data, and proposes to include the ability for water-wet material (UN2555) to be packed in metal drums, in accordance with the packing instruction. This paper also suggests changing the abbreviation for Packing Instruction 406 from "P406" to PI406" to avoid confusion with GHS precautionary statements.

2. From 2007 – 2014 an initiative on desensitized explosives was led by Germany, including some meetings in Berlin, and this provided the basis for the creation of GHS Chapter 2.17. Representatives of the nitrocellulose manufacturing industry were active participants on behalf of industry, including WONIPA and SAAMI. A new 500 kg bonfire test method was adopted based on German test protocols for desensitized explosives and other energetic dangerous goods, and it was placed in a new Part V of the Manual relating to sectors other than transport. It was understood that new testing using this method should be avoided for products which were already well-characterized. BAM and WONIPA have a long history of testing, and there is a large amount of data on WONIPA products. Testing related to SAAMI was done over 40 years ago and data is not readily available. This experience likely resulted in the UN entries 2555 and 2556, which are both as opposed to many other desensitized explosives which may require a competent authority approval. As part of the initiative, SAAMI conducted new Test Series 1, 3 and 6 tests in 2008, and presented them to the informal correspondence group working on GHS 2.17. A report on a incident happening at that time was also presented.

3. The current CEFIC proposal seeks to complete the original intention of the working group and insert test results in the Manual for the purpose of avoiding further testing, but only for "industrial" nitrocellulose, and it would forbid the use of metal drums. While some of the configurations presented by CEFIC are used in the energetics industry, no 500-kg-bonfire data is presented for "energetic" higher-nitrogen content nitrocellulose, i.e. exceeding 12.6% nitrogen. SAAMI proposes to include our 2008 results in the Manual. While the test method is not the same as Part V, in our opinion SAAMI's data on water-wet NC in a metal drum shows such a low level of reactivity that the 500 kg quantity of Part V is not relevant, so the explosives test methods of Part I may be presented as conclusive.

Discussion

4. SAAMI wishes to clarify that the difference between "industrial" and "energetic" nitrocellulose for safety and security purposes is subjective:

(a) The difference in available nitrogen levels is small. The nitrocellulose specifications in the BAM data range from 10.7% - 12.3% nitrogen. SAAMI's test data is on 13.2% nitrogen. The maximum nitrogen content generally attainable is around 13.45%. The nominal value for this type of NC is 13.4% with a minimum of 13.35%.

(b) "industrial" nitrocellulose is regularly blended into energetic mixtures to attain desired percentages of nitrogen. This material may be detonable.

(c) the use of water instead of alcohol is the most important factor for safety, much more than the nitrogen percentage. Based on SAAMI's testing, the choice of water instead of alcohol as a desensitizer at percentages over 25% (UN2555) conclusively mitigates safety concerns for "energetic" nitrocellulose. Water-wetted results always achieve the lowest classification in CEFIC's data on "industrial" nitrocellulose. There is no visible flame with water-wet material in a bonfire, whereas alcohol-wet NC is extremely flammable and constitutes the 3 higher classification categories in the Part V test.

(d) A steel drum is an option in the packing instruction for UN2555. While we do not present an opinion or test results for alchol-wetted nitrocellulose (e.g. UN2556, limited to 12.6% nitrogen), we can see no reason that a metal drum would not be safe and appropriate for UN2555 according to our test results. Steel drums are used routinely by a major and historical US producer of NC.

5. SAAMI attaches a test report as an annex providing data on UN 2555 "Nitrocellulose With Water (not less than 25% water, by mass)", with a nitrogen content of 13.2%. This includes results from Test Series 1(a), 1(b), 1(c)(i), 6(a) and 6(c). We will also show a PowerPoint presentation with pictures of the testing and of a truck-tire-fire incident, the same presentation as was presented in 2008 to the explosives working group. Highlights of the testing are:

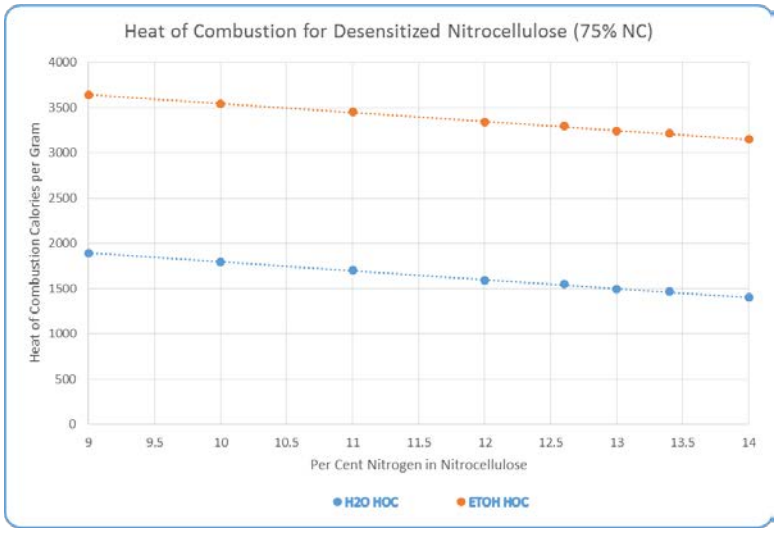
(a) Since nitrocellulose is already classified as a desensitized explosive, positive results in Test Series 2 may be assumed. For the purposes of familiarization, the more severe Test Series 1 was performed which resulted in positive results in Test Series 1(a) (Gap) and 1(b) (Koenen). These results are not directly related to the current discussion. At the time the explosives tests of Part I of the Manual were being considered for adaptation into new protocols for desensitized explosives, which SAAMI thought might be too severe. We were looking for false positives, e.g. in the Koenen test, and we demonstrated a false positive by testing water alone in Test Series 6(c), when steam sent the metal lid over 15 meters.

(b) Series 6(a) results were as follows. The test was conducted with a detonator on a 5-gallon bucket sample of the material, buried in sand for confinement. This was intentionally more severe than the requirement for this product to ignite with an electric match. There was no reaction. In line with discretion allowed in the Manual, we believe this result is scalable to any amount. For an additional degree of surety, the test was repeated with a match and 20 grams of black powder. There was no initiation. This last test with black powder is not in the report but we have the picture that was presented to the explosives working group in 2008.

(c) Series 6(c) results were as follows. One full metal drum, containing 231 pounds net of nitrocellulose wetted with water at 29% was placed in the bonfire. No flames or energetic reaction were seen. A pressure reaction occurred where the lid was propelled 17 meters. The drum had a bulged bottom and fell over. Vented NC remained unburnt on the ground, adjacent to the fire. SAAMI also performed a control test on water alone, and demonstrated that steam can also project the metal lid to a distance over 15 meters.

(d) The SAAMI PowerPoint presentation also has pictures of a tire-fire impacting a truckload of this material. No energetic reaction occurred.

6. As appropriate desensitization by either water or alcohol reduces its deflagration-to-detonation possibility to nearly zero, as shown for water based on the above testing, the primary concern with desensitized NC is its heat output in a fire. It is well known with energetic materials that decreasing the amount of oxidizer increases the available combustion energy. This is very apparent for NC where the degree of nitration is a direct measure of internal oxidizer. The downward trend illustrated in the chart below that shows heat of combustion becomes smaller as the percent nitrogen rises, for both 25% water wet and 25% ethanol wet NC. There is also a significantly greater amount of combustion energy available with alcohol wet NC versus water wet NC, shown by the two lines; the amount of heat released in a fire by alcohol wet NC is double that of water wet material.



In summary, this data substantiates the classification of water wet NC as a flammable solid material regardless of the nitrogen content, if it is sufficiently wetted to prevent detonation. Water-wet NC has a much lower heat of combustion than alcohol wet

NC, and higher “energetic” nitrogen percentages produce less heat than lower-nitrogen “industrial” grades.

7. Separately, we suggest a stylistic change to the CEFIC proposal as follows. “P406” should be changed to “PI406” or “packing instruction 406”, since it references a TDG packing instruction, rather than a GHS precautionary statement. In our experience the use of the letter “P” to reference a packing instruction causes confusion with GHS, and this is essentially a GHS proposal.

Proposal

8. Amend the following statement in the CEFIC proposal:

“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~~ PI406. They cannot be used for nitrocellulose products in other pressure resistant packaging like steel drums, with the exception of water-wet nitrocellulose classified as UN 2555.

9. Enter a test result for water-wet nitrocellulose in the proposed Appendix 10 to the Manual, as follows:

Additional Test Results

It has been demonstrated by Part 1 testing that water-wet nitrocellose of 13.2% nitrogen and 29% water, classified for transport as UN2555 and packed in specification 1A2 metal drums, has no significant reaction to fire or detonator. This result may be used in lieu of testing according to Part V, and applies to nitrogen percentages not exceeding 14.0%.

Annex

10. The test report described in paragraph 5 is attached.

INDIVIDUAL COMPANY DATA PROPRIETARY

SAFETY CONSULTING ENGINEERS, INC.
2131 Hammond Drive
Schaumburg, Illinois 60173

Project Name: DG Advisor
Project No. 2008-68-D-C
Date: 30 June 2008
Report No. 300608)

REPORT OF TESTING RESULTS FOR DESENSITIZED NITROCELLULOSE

This report covers testing on the following
Water-wetted 13.2% Densensitized Nitrocellulose, 29% water wet,
of ATK, Radford, Virginia. USA.

1.0 Item Description and Packaging Configuration:

DESCRIPTION	SHIPPING DRUM/AMOUNT OF PRODUCTS
Nitrocellulose, containing 13.2% nitrogen, 29% water	Metal open-head drum: 33" height x 22.5" diameter; 164 pounds dry weight, 231# wetted weight, 279 pounds gross weight.

2.0 Testing Performed at the SCE Test Site Facility on the Wetted Nitrocellulose:

2.1 Test 1(a) UN Gap Test

The density of the nitrocellulose (NC) in the drums was measured at 32.9 lbs/ft^3. In the first test, the NC was filled into the pipe while tapping the side of the pipe. This resulted in 8 ounces of material at a density of 26.5 lbs/ft^3. The pipe was fragmented and the plate was pierced. The plate did not have a neat hole and the metal fragments appeared to be torn rather than sheared.

The second test was identical in set up but the plate was not pierced. In the third test, 10 ounces of material were used to match the density of the NC in the drum. A clean hole was made in the witness plate and the pipe fragments exhibited adiabatic shearing. The nitrocellulose failed this test.

2.2 Test 1(b) Koenen Tests

The test is used to determine the sensitiveness of the substance to the effect of intense heat under high confinement.

The apparatus consisted of a steel tube (25-mm OD, 24 mm ID and 75 mm long) with one end closed with a closing device, installed in a heating and protective device. The open end of the tube is flanged. The closing plate with an orifice, through which the gases from the decomposition of the test substance escape has diameter holes: 1.0, through 20.0-mm. The heating is provided by propane

gas and distributed by the manifold to the four burners. Heating is undertaken in a protective welded box.

The NC with density of 26.5 lbs/ft^3 was tested and the fragments of the tube are collected and analyzed for any of the following effects:

"O": Tube unchanged
"A": Bottom of tube bulged out.
"B": Bottom and wall of the tube bulged out.
"C": Bottom of the tube split.
"D": Wall of the tube split.
"E": Tube split into two fragments.
"F": Tube fragmented into three */ or more mainly large pieces which in some cases may be connected with each other by a narrow strip.
"G": Tube fragmented into many mainly small pieces, closing device undamaged; and
"H": Tube fragmented into many very small pieces, closing device bulged out or fragmented.

The test criteria are as follows:

"Violent" - the limiting diameter is greater than or equal to 2.0 mm.
"Medium" - the limiting diameter is equal to 1.5 mm.
"Low" - the limiting diameter is less than 1.0 mm and the effect in all tests is of type "O".

The results of the Koenen tests for the NC (density = 26.5 lbs/ft^3 are summarized in Table 1.

Table 1

Trial #	Net Sample Weight (60 mm Height) (gm)	Orifice diameter (mm)	Observations	Tube Condition (Effect type "O" through "H")	Explosion per criteria YES/NO
1	13.8	10.0	No smoke, no fire. Burned out clean.	"O"	NO
2	15.5	2.0	21 seconds – time-to-reaction	"F"	YES
3	14.9	5.0	Flash of fire in 30 seconds. Popped in 1 minute.	"O"	NO
4	14.9	3.0	24 seconds – time-to-reaction	"F"	YES
5	14.7	5.0	Pop of noise at 43 sec., no smoke or fire.	"O"	NO
6	15.6	5.0	Pop of noise at 45 sec., no smoke or fire.	"O"	NO

2.3 Test 1(c)(i) Time/Pressure Test

The test is used to determine the effects of igniting the substance under confinement in order to determine if ignition leads to a deflagration with explosive violence at pressures which can be attained with substances in normal commercial packages.

The apparatus consisted of a cylindrical steel pressure vessel 89 mm in length and 60 mm in external diameter. Five-gram sample size of the nitrocellulose is loaded in the pressure vessel so as to be in contact with the ignition system. The charged vessel is transferred to the firing support stand, bursting disk uppermost, which should be contained in a suitable, armoured fume cupboard or firing cell. The ignitor is connected to the external terminals of the firing plug and the charged is fired.

The test is carried out three times. The time taken for the pressure to rise from 690 kPa to 2070 kPa above atmospheric is noted. The shortest time interval should be used for classification.

Test Criteria

The test results are interpreted in terms of whether a gauge pressure of 2070 kPa is reached and, if so, the time taken for the pressure to rise from 690 kPa to 2070 kPa. gauge.

Results

The results of the Pressure Vessel tests for the nitrocellulose are summarized in Table 2.

Table 2

Material Tested	Trial	Amount Of Sample (gm)	Maximum Pressure (kPa)	Time for Pressure Rise from 190 to 2070 kPA (min:sec)	Results
Nitrocellulose, containing 13.2% nitrogen, 29% water	1	5.0	352	--	"Negative" pressure equal or greater than 2070 kPa not achieved.
	2	5.0	331	--	Same as trial 1
	3	5.0	241	--	Same as trial 1
	4	5.0	241	--	Same as trial 1
	5	5.0	345	--	Same as trial 1
Reference Water Wet Nitrocellulose	1	5.0	565	--	"Negative" pressure equal or greater than 2070 kPa not achieved
	2	5.0	372	--	Same as trial 1
	3	5.0	524	--	Same as trial 1

2.4 Test 6(a) UN Single Package Test (with detonator)

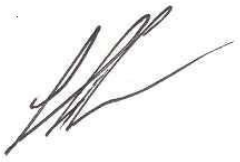
As a preliminary test, a 5-gallon metal bucket having an internal diameter of 0.96 feet was filled to 1.0-ft height with 24 pounds of wetted nitrocellulose. This achieved a density roughly equal to that in the drum, i.e. 32.9 lbs/ft^3. A #8 blasting cap was placed in the center of the material. A metal lid was crimped on the bucket. The bucket was placed in a hole and covered in all directions by a minimum of 20" of sand. The blasting cap did not ignite the material or affect the bucket, other than some traces of nitrocellulose escaped around the lid and some of the crimps were loosened.

Because no ignition occurred, it was judged unnecessary to proceed with a full-scale test of the drum. The nitrocellulose passed this test.

2.5 Test 6(c) UN External Fire (Bonfire) Test

One drum containing 231 pounds of nitrocellulose (29% water) was used for this test. The drum was placed onto a steel stand 2 feet above the ground with 45 gallons of diesel (and gasoline) fuel. The fuel was ignited and observations were made. None of the following events were noted:

- Explosion of total contents of the test package;
- Any perforation of any of the three vertical witness screens;
- More than 10 metallic projections, each with mass exceeding 25 grams thrown more than 50 meters from the stack edge;
- A fireball extending beyond any of three witness screens;
- Fiery projections from the product thrown more than 15 meters from the stack edge;
- Any indentation of any one of three screens;
- Any thermal effect or blast effect that would significantly hinder fire fighting or other emergency response efforts in the immediate vicinity (i.e. 5 meters) of the package.



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C. James Dahn
Registered Professional Engineer

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