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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

Thirty-seventh session
Geneva, 21–30 June 2010
Item 2 of the provisional agenda
Explosives and related matters

A proposed new DDT Test and Criteria for flash compositions

Transmitted by the expert from the United States of America[1]

I. Background

1. At its thirty-fourth session, the Sub-Committee considered several papers regarding the HSL Flash Composition Test transmitted by the expert from the United Kingdom (see ST/SG/AC.10/C.3/2008/105 and informal documents INF.34 and INF.34/Add.1). The proposed new test was adopted for incorporation within the Manual of Tests and Criteria with accompanying changes to Note 2 to 2.1.3.5.5 of the Model Regulations. The HSL Flash Composition Test is essentially a simplified version of the Test C.1: Time/Pressure test in section 23.4.1 of the Manual of Tests and Criteria in which a 0.5 gram sample of a candidate substance is tested in a pressure autoclave equipped with both a rupture disc set at 2070 psi and a rapid-response pressure gauge which measures the time-rise rate with a transient time capture apparatus.

2. There appeared to be no other methods of quantifying various pyrotechnic compositions in terms of their explosive hazard readily adoptable at the time that the existing HSL Flash Composition Test was adopted. However, it was observed by several other experts that the test itself has a fairly large standard of deviation and requires an investment of hardware, electronic equipment and training which could be beyond the capabilities of some regulatory authorities in developing countries. It also does not provide

[1] In accordance with the programme of work of the Sub-Committee for 2009-2010 approved by the Committee at its fourth session (refer to ST/SG/AC.10/C.3/68 para. 118(b) and ST/SG/AC.10/36, para. 14).

sufficient discrimination between compositions such as finely divided black powder, which has not been viewed as a typical flash composition by the pyrotechnics industry.

II. What are flash compositions?

3. The expert from the United States views that flash compositions represent a unique class of pyrotechnic compositions which:

(a) Are uniform powders which pass through a 40 mesh screen containing more than 40 percent by weight of certain finely divided oxidizing salts and more than 15 percent by weight of metallic particles, of which 100 percent are less than 53μ(microns);

(b) Will rapidly ignite and quickly transition to a detonation velocity of 1-3 Km/second depending on diameter; and

(c) Present a Division 1.1 explosive hazard in terms of their mass explosion and propagation either as substances or when incorporated into articles.

4. It is still not well understood how certain pyrotechnic mixtures fall into the category of flash compositions, i.e., exhibit Division 1.1 explosive behaviours, and others with similar chemical compositions can exhibit Division 1.3 explosive behaviours. Chemical balance of oxidizer to fuel plays an important role as does the intimacy of mixing of those two components. But the reduced particle size of the metallic fuels appears to exert a much greater effect on the ability of the mixture to behave as Division 1.1 substance than the reduced particle sizes of the oxidizing salts.

III. Proposal

5. There is a fundamental limitation inherent in the current methodology of categorizing flash compositions by their pressure-rise times at the very outset of their reactions. Specifically, their final reaction rates may be faster than other pyrotechnic mixtures that exhibit similar pressure-rise times in the beginning but which ultimately do not reach the supersonic velocities of true flash compositions. The expert for the United States, after considerable testing and evaluation, now believes that a modified DDT test may be more capable of definitively determining what constitutes a flash composition. The test method uses essentially the same pass-fail criteria as Test Series 5(a) Cap Sensitivity Test but with a modified initiation method and confining steel test fixture to convert it to a deflagration-to-detonation (DDT) test.

A. Modification of Test Series 5a to evaluate substances capable of DDT.

6. The following experimental changes to the Cap Sensitivity Test Series 5a were made to adapt it for evaluating potential flash composition mixtures:

(a) The standard electric detonator initiation source was replaced with an electric match inserted approx. 12 mm into the top-centre of the cardboard tube holder containing pyrotechnic mixture being evaluated;

(b) A much smaller diameter and length cardboard sample tube was employed. Instead of a sample tube of 80 mm in diameter by 160 mm in height, a sample tube of only 25 mm diameter and 150 mm in height filled approx. 1/3 to ½ full with only 25 grams of substance;

(c) The same witness plate – 1 mm in thickness and 160 mm x 160 mm square was employed supported by the same circular ring and base as shown in Figure 15.4.1.1 of the Manual of Tests and Criteria;

(d) A 38 mm thick mild steel confining cover or cap (sleeve) weighing approx. 2.87 Kg. and having an interior volume of the approximate height and diameter closely surrounded the cardboard sample tube was added to provide sample confinement similar to the French or USA DDT in Test Series 5(b).

7. Diagrams of the proposed alternative "Flash Composition Test" Apparatus are shown in Figure 1. The method is straightforward and inexpensive to conduct, and has a simple pass-fail criteria which has proven reproducible in preliminary testing. The required sample quantity per test is only 25 grams. While this is still fifty times greater than the sample size of the HSL Flash Composition Test, it is still well within the limits of most outdoor explosives testing facilities insofar as blast effects. Given that flash powders are dry mixtures of components which have different specific gravities, it is advantageous to have a large enough sample size to minimize errors due to stratification or sifting of these types of powder compositions.

B. Experimental results

8. After trial and error with various diameters and thicknesses of steel confining caps, it was found that powder test weights could be safely reduced to 25 grams using a 25 mm diameter, heavy cardboard convolute sample container surrounded by a cylindrical mild steel cap of the same height with an inner diameter and head thickness of 38 mm. an outer diameter of 102 mm., an interior depth of 152 mm and an overall exterior height of approx. 190 mm. The steel confinement fixture is rugged, cannot fragment, does not fly far when propelled upward by the force of the shock waves and withstands multiple testing cycles without any damage. Results from the test apparatus set up are shown in Figure 1. The proposed new DDT test prescription is provided in annex I. A list of examples of results for substances ranging from black powder to the most powerful perchlorate-metal compositions is provided in annex II.

IV. Future work

9. The expert from the United States invites other members of the Sub-Committee Working Group on Explosives to comment on this proposal and conduct their own evaluations to see if the test method may have merit as an alternative to the current HSL Flash Composition Method. If the results can be supported in other countries and by other experts, a new formal paper may be submitted for consideration.

Annex I

Modified DDT Test Prescription for flash compositions

Introduction

This modified DDT test may be used to determine the sensitivity of a solid substance containing a uniform mixture of finely divided oxidizing salts and organic or inorganic fuels to detonate upon ignition, under confinement and if positive results are obtained, to therefore be considered a “Flash Composition.”.

Apparatus and materials

The experimental set up for the Modified DDT Test consists of a heavy-wall cardboard convolute sample tube with an inside diameter of 25.4 mm and height 152 mm with a maximum wall thickness of 3.8 mm, closed at the base with a paper or thin cardboard cap membrane just sufficient to retain the sample. The ignition source is provided by an electric match-head inserted centrally in the top of the explosive sample in the tube to a depth approximately equal to its length. Surrounding the sample tube and also resting on the witness plate is placed a rugged mild steel confinement cover or “cap” with inner walls and head section approx. 32 mm thick with an inside diameter of 38 mm, an outside diameter of 102 mm and a height of 152 mm and weighs approx. 2.8 kg. Below the sample tube and surrounding steel confining cap is the square shaped steel witness plate, which is 1.0 mm thick and 152 mm on edge. The steel witness steel plate is then placed on a steel ring of approximately 51 mm height with an inner diameter of 90 mm and 3.5 mm wall thickness. The apparatus is placed onto a square shaped steel base plate of approx. 13 mm thickness and 152 mm on edge. (see Figures 1 and 2).

Procedure

The sample compositions are uniformly mixed and then twice passed through a Number 40 mesh screen immediately prior to testing to insure maximum uniformity and minimum segregation. Twenty-five (25) grams of the candidate substance tested is weighed into the cardboard sample tube. It should fill the sample tube somewhere between 1/3 and 2/3 full, depending on its density. For free-flowing granular substances, the sample is consolidated by allowing the tube to fall vertically through a height of 51 mm. In all cases, the final density of the explosive in the tube should be as close as possible to its density in a fireworks device. Those explosives whose sensitivity could be moisture dependent should be stored for at least 24 hours in desiccators at a temperature of 28 - 30 °C prior to testing. The sample tube is placed in the centre of a heavy steel confining sleeve fixture shown in the diagram in Figure 1. which rests on the witness plate, steel ring and steel base plate. The electric match-head is inserted centrally into the top of the explosive formulation. The electric match-head igniter is then initiated from a safe position. After initiation and a suitable interval to allow for falling debris, if any, the witness plate is recovered and examined. The test is conducted three times or until a detonation of the substance occurs and a positive result is achieved.

Test criteria and method of assessing results

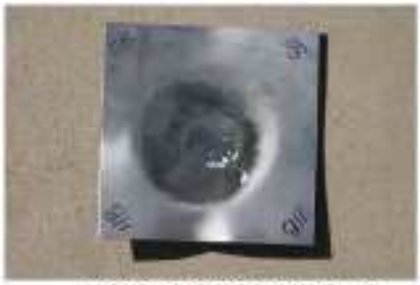
The result is considered "+" and the substance is considered to have “detonated” if in any trial the witness plate is torn, perforated, pierced or otherwise penetrated (i.e. light is visible through the plate). NOTE: Bulges or folds in the witness plate are not to be considered to be proof of “detonation”. Otherwise, the result is considered “—“.

Annex II

Examples of results

1	Goex Black powder -- 5Fa “Unglazed”	**(-)**
2	35% Potassium Nitrate (100% < 37 µ)/ 31% Potassium Perchlorate (100% < 37 µ) /13.5% Potassium Benzoate (fine powder)/ 10% Sulfur (fine powder)/10.5%Lampblack (nano-material).	**(-)**
3	**70% Potassium Perchlorate (100% < 37 µ) / 30% “Semi-coarse” Magnesium powder -- (297µ<25%>149µ; 148µ<58%>53µ; 52µ< 5%>44µ; 12%<43µ)**	(+)
4	**65% Potassium Perchlorate (100% < 44µ)/ 35% Magnesium (105µ 5%>74µ; 73µ <39%>44µ; 46%<43µ)**	(+)
5	**65% Potassium Perchlorate (100% < 44µ)/ 35% “Ground” Magnesium (100% <43µ)**	(+)
6	**70% Potassium Perchlorate (100% < 37 µ)/ 30% “Atomized” Aluminum powder (74µ<2.4%>53µ; 52µ<2.9%>44µ; 4.7%<44µ)**	(+)
7	**65% Potassium Perchlorate (100% < 44µ)/ 35% “Flake” Aluminum “A” (105µ <72%>53µ; 52µ <17%>44µ; 11.5%<43µ)**	(+)
8	**65% Potassium Perchlorate (100% < 44µ)/35% “Flake ” Aluminum “B” (74µ<39% >53µ; 52µ<22%>44µ; 40%<43µ)**	(+)
9	**70% Potassium Perchlorate (100% < 37 µ)/ 30% “Ground” Magnalium powder -- (74µ<37%>53µ; 52µ<11%>44µ; 52%<44µ)**	(+)
10	68% Barium Nitrate (105µ < 10% > 74 µ; 73 µ<12%>44 µ; 43 µ< 24%>37 µ; 53%<37 µ)/23% “Dark Flake” Aluminum (100%< 73 µ)/9% Sulfur(fine powder)	**(-)**

WITNESS PLATE IMAGES FROM ANNEX II



Sample Result No. 1

Sample Result No. 2

Sample Result No. 3

Sample Result No. 4

Sample Result No. 5

Sample Result No. 6

Sample Result No. 7

Sample Result No. 8

Sample Result No. 9

Sample Result No. 10

Figure 1 – Modified DDT Test Apparatus for flash compositions

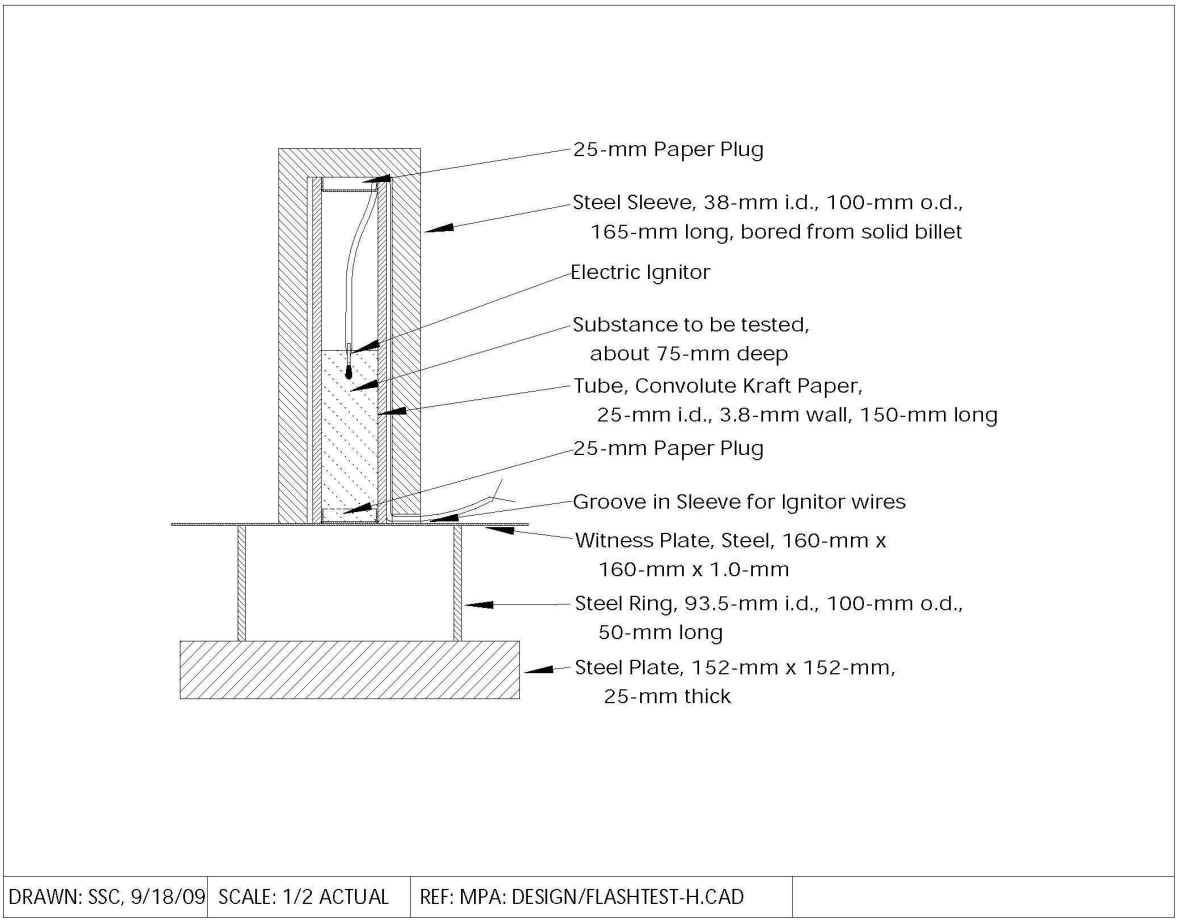


Figure 2 – DDT Test Apparatus for flash compositions photographs