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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****Forty-first session**

Geneva, 25 June – 4 July 2012

Item 2 (d) of the provisional agenda

Explosives and related matters: DDT Test and Criteria for flash composition**A follow on report on the comparison of the results obtained
for a set of pyrotechnic compositions subjected to the HSL
Flash Composition Test and the proposed US Modified DDT
Test****Transmitted by the expert from the United Kingdom¹****I. Background**

1. At its 37th and 39th sessions the Sub-Committee considered papers regarding the proposed new US modified DDT Test and Criteria for flash compositions (see informal documents SCETDG/37/INF.34 UN/SCETDG/39/INF.16; UN/SCETDG/39/INF.22; UN/SCETDG/39/INF.30 and UN/SCETDG/39/INF.44 and document ST/SG/AC.10/C.3/2010/31 transmitted by the experts from the Germany; Japan; United States of America and the United Kingdom).

2. In its reports to both the 37th and 39th sessions (informal document SCETDG/37/INF.73 and SCETDG/39/INF.58) the Working Group on Explosives noted that it would be desirable to have both the HSL Flash Composition Test (T-P test) and the US Modified DDT Test (DDT test) test performed on samples so that the results could be evaluated as to whether the tests provide comparable results.

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).

3. The experts from the United Kingdom and Japan also observed that their work indicated that further work on granular compositions might identify whether or not the United States of America modified DDT Test is a suitable method for discriminating “Flash composition” as defined in the notes to 2.1.3.5.5 of the Model Regulations from “non-flash compositions” used as a bursting charge etc. in fireworks.

4. The expert from the United Kingdom reports here on further results from a second round of work that was commissioned from the Health and Safety Laboratory (HSL) to compare the performance of samples of pyrotechnic compositions in both the HSL Flash Composition Test and the US Modified DDT Test.

II. Follow on testing

5. The second round of work conducted by HSL used compositions from the same set of samples that were reported in informal document SCETDG/39/INF.30 with the addition of six further compositions comprising a range of types of pyrotechnic mixtures. These additional samples were selected using the same criteria as detailed in informal document SCETDG/37/INF.34. i.e.:-

- Presenting a range of actual or expected performances in the T-P test;
- Representing a range of compositions with the potential to be encountered as burst charges in fireworks;
- Representing a range of particle sizes;
- Representing a mixture of granular and finely divided compositions.

6. The sample selection also took account of the comments of the expert from the Netherlands in the report of the Working Group on Explosives to the 37th session and the comments of the expert from the United Kingdom in the informal paper SCETDG/37/INF.34 in relation to:-

- The broader types of composition that can be regarded as flash according to the description in Note 2 to 2.1.3.5.5 of the Model Regulations;
- The potential for the proportion of flash contained within a firework to be used to determine its likely hazard division.

7. Details of all the compositions are summarized in annex 1.

III. Comments on the second round of testing undertaken by HSL

8. The expert from the United Kingdom previously reported that the US modified DDT Test procedure contained a number of discrepancies (informal document SCETDG/39/INF.30).

9. During the follow-on testing a further discrepancy was identified between the description and the actual assembly of the cap/cover and what could be physically manufactured. This related to the weight of the confining cover or cap (sleeve), stated as approx. 2.87 kg whereas the confining cap produced by HSL which was made in accordance with ST/SG/AC.10/C.3/2010/31, was 102 mm in diameter and weighed 10.87 kg.

10. It is noted that the cap had been reduced in diameter to 63 mm in informal document SCETDG/39/INF.44, which would give a weight of approx. 2.87 kg.

11. The second round of comparison testing carried out by HSL was conducted using the same equipment used to generate the data reported in informal document SCETDG/39/INF.30 and is detailed below:

- Cardboard tubes for the sample were 152 mm long, 25 mm internal diameter, 3.5 mm wall thickness, and closed off with 1 mm thick card;
- Spiral wound sample tubes were used instead of convoluted tubes to ensure consistency with the previous round of testing;
- A mild steel tube of 38 mm internal diameter, 102 mm outside diameter, 190 mm long with an internal pocket 152 mm deep was used, approx. weight 10.87 kg;
- A Nobel's Vulcan fusehead was used to fire the sample,
- All samples were screened through a 425 micron sieve unless the sample was too coarse (indicated in the results table in annex 1).

12. As was noted in informal document SCETDG/39/INF.30 the 190 mm long mild steel tube was used because there were concerns that a shorter tube, would result in the limited end thickness of the sleeve presenting potential safety issues.

IV. Consideration of the Results

13. A tabulated comparison of the test results can be found at annex I. The tabulated comparison includes the data from the previous round of testing.

14. It is noted that the cap (cover) used by HSL was heavier than the updated test proposed by the expert from the United States (informal document SCETDG/39/INF.44) but that similar results were nevertheless obtained.

15. In samples which are close to the cross over threshold as designated "Flash"/"Not Flash", the weight of the cap may have implications, in that a lighter a cap would enable a sample to be considered "-" whereas a heavier a cap could result in a "+". It is postulated that the degree of confinement produced by the heavier cap may result in the test sample developing such a performance as to make it more likely that the witness plate is punctured before the cap can lift, reduce the pressure or its rate of increase and thereby reduce the burning rate of the substance under test.

16. Within the tests conducted by HSL, three samples did not give uniform responses. Sample 3 gave a "-" result in four out of six shots; Sample 4 gave a "+" result in three out of four shots and Sample 8 gave "-" result in five out of six shots. These results indicate that there can be a variable response at or around the "DDT" threshold.

17. It is observed that Samples 3 and 8 are conventional blackpowders and both gave a "+" response in the DDT test.

18. Similarly there was some variability in the damage to the witness plate between different runs for several of the samples. These responses are described in detail in the footnotes to annex I.

19. The table below comprises a comparative risk ranking between the two techniques. It is observed that there is generally good correlation between the performance rankings obtained from the two techniques.

20. There was however a discrepancy between the rankings obtained from the blackpowder substitute in the DDT test (“-“) and T-P Test (average Rise time 3.62ms).

Table (English only)

<i>Sample</i>	<i>Description</i>	<i>DDT Test</i>	<i>DDT Test</i>	<i>T-P Test Result</i>	<i>T-P Test Result</i>	<i>T-P Test Result</i>
		<i>% “+”</i>	<i>Ranking</i>	<i>Min. Rise Time (ms)</i>	<i>Ranking (Min Values)</i>	<i>Ranking (Average Values)</i>
1	Flashpowder 1	100%	1=	0.67	4	3
2	Flashpowder 2	100%	1=	1.41	6	6
3	Number 1					
	Blackpowder	33%	10	2.14	8	9
4	Flashpowder 3	75%	9	2.31	9	8
5	Blackpowder					
	Substitute	0%	12=	3.08	10	10
6	Flashpowder 4	100%	1=	3.11	11	12
7	Comet					
	Composition	0%	12=	4.36	12	11
8	FO/A					
	Blackpowder	16.5%	11	4.83	13	13
9	5FA					
	Blackpowder	0%	12=	10.31	15	15
10	Flashpowder 5	100%	1=	0.25	1	4
11	Flashpowder 6	100%	1=	0.52	3	2
12	Flashpowder 7	100%	1=	1.89	7	7
13	Mortar 1	0%	12=	8.03	14	14
14	Mortar 2	100%	1=	0.86	5	5
15	Rocket 1	100%	1=	0.39	2	1

V. Conclusions

21. The objective of the requirements of Note to 2.1.3.5.5 of the Model Regulations appears to be to ensure that fireworks classified according to the use of the default table do not include compositions that would present an enhanced hazard, different to that which would be expected purely from the fireworks’ size and construction.

22. Both the US DDT test and the HSL T-P test provide methods to identify compositions, both powdery and granular, that could, if they were included in fireworks, present an enhanced hazard i.e. comprise “flash compositions”.

23. The degree of variability of response in both the US DDT test and the HSL T-P test are such as to indicate that threshold effects could, in some circumstances, be significant and that there is therefore value in taking a precautionary approach towards using an individual technique as the sole mechanism for identifying a composition as **not** comprising “flash”.

VI. Proposals

24. The expert from the United Kingdom asks that the Working Group on Explosives considers introducing the Modified US DDT Flash composition test described at annex II as a new Appendix 8 to the Manual of Tests and Criteria.

25. The expert from the United Kingdom asks that the Working Group on Explosives considers whether the results of these further comparative tests indicate that the adoption of criteria in the Model Regulations combining the results from both the HSL Flash Composition Test and the US Modified DDT Test would have value by reducing the uncertainty around threshold effects and whether the Note to 2.1.3.5.5 can be revised to:

“Flash composition” in this table refers to pyrotechnic substances in powder form or as pyrotechnic units as presented in the firework that are used to produce an aural effect or used as a bursting charge, or lifting charge unless:-

(a) The time taken for the pressure rise is demonstrated to be more than [6]ms for 0.5g of pyrotechnic substance in the HSL Flash Composition Test in Appendix 7 of the Manual of Tests and Criteria;

(b) The pyrotechnic substance gives a negative result in the Modified US DDT test in Appendix 8 of the Manual of Tests and Criteria; or

(c) The time taken for the pressure rise is demonstrated to be more than [4]ms for 0.5g of pyrotechnic substance in the HSL Flash Composition Test and the pyrotechnic substance gives a result in the Modified US DDT test that is no more severe than [a simple tear in the witness plate which is no more than 10mm in length in each of 3 “+” runs and which is, in each case, aligned with the circumference of the supporting steel ring].

Annex I

English only

Results of Comparative Tests including follow-on tests

Sample	Description	Chemical Composition	Grain Size	T-P Test Result (ms)			DDT Test Result		
				Min	Average	SD	Run 1	Run 2	Run 3
Sample 1	Flashpowder 1	Potassium Perchlorate (50%), Aluminium Dark Pyro (40%), Magnesium #6 - Active (10%)	<425 micron	0.67	0.72	0.06	+ ²	Not Run	Not Run
		Second set of firings					+ ³	+	+
		Third set of firings					+ ⁴	+	+
Sample 2	Flashpowder 2	Potassium Perchlorate (40%), Magnesium #6 - Active (60%)	<425 micron	1.41	1.57	0.23	+	Not Run	Not Run
		Second set of firings					+ ⁵	+	+
Sample 3	Number 1 Blackpowder	N/A	0.25 – 0.50mm	2.14	2.84	0.47	- ⁶	+	+
		Second set of firings					- ⁷	-	-
Sample 4	Flashpowder 3	Potassium Nitrate (60%), Magnesium #5 (40%)	<425 micron	2.31	2.40	0.14	+ ⁸	Not Run	Not Run
		Second set of firings					+ ⁹	-	+
Sample 5	Blackpowder Substitute ¹⁰	Proprietary product marketed as providing an equivalent	<425 micron	3.08	3.62	0.38	- ¹¹	-	-

² Plate punched through³ Plate shattered in 1st shot and punched through in 2nd and 3rd shots⁴ Plate torn in all three shots⁵ Plate punched through centre in all three shots⁶ Plate domed in 1st shot, small tear which may have resulted from the cap falling back onto the plate after the 2nd shot and plate spilt around edge of stand on 3rd shot⁷ Plate domed in all three shots⁸ Plate punched through⁹ Plate torn and centre holed in 1st shot, domed in 2nd shot and torn in 3rd shot¹⁰ This sample was run using a 1.5 mm thick sample tube as part of the setting up of the equipment.¹¹ Plate domed in all three shots

Sample	Description	Chemical Composition	Grain Size	T-P Test Result (ms)			DDT Test Result		
				Min	Average	SD	Run 1	Run 2	Run 3
		performance to FFFG blackpowder							
		Second set of firings ¹²					- ¹³	-	-
Sample 6	Flashpowder 4	Potassium Perchlorate (64.2%), Aluminium – High Grade (20%), Magnesium # 5 (10%), Graphite (5.8%)	<425 micron	3.11	5.40	1.50	+ ¹⁴	Not Run	Not Run
		Second set of firings					+ ¹⁵	+	+
Sample 7	Comet Composition	Potassium Perchlorate (64%), Barium Nitrate (2%), Magnesium #5 (10%), Acaroid Resin (18%)	<425 micron	4.36	5.37	0.97	- ¹⁶	-	-
		Second set of firings					- ¹⁷	-	-
Sample 8	FO/A Blackpowder	N/A	0.25 – 0.8mm	4.83	5.83	0.84	- ¹⁸	+	-
		Second set of firings					- ¹⁹	-	-
Sample 9	5FA Blackpowder	N/A	0.425 – 1mm	10.3	11.16	0.98	- ²⁰	-	-
		Second set of firings					-	-	-
New additional sample details									
Sample 10	Flashpowder 5	Potassium Perchlorate (50%), Magnesium # 5 (30%), Magnesium #6 (20%)	<425 micron	0.25	0.81	0.32	+ ²¹	+	+
Sample	Flashpowder 6	Potassium	<425	0.52	0.56	0.0	+ ²²	+	+

¹² Second set of shots used 3.5 mm thick sample tubes

¹³ Plate domed in all three shots

¹⁴ Plate holed and punched through

¹⁵ Plate torn in 1st shot, holed in 2nd and destroyed in 3rd

¹⁶ Plate domed in all three shots

¹⁷ Plate dented but not punctured

¹⁸ Plate domed in 1st and 3rd shots, Split along the stand edge in 2nd shot

¹⁹ Plate dished but not broken in all three shots

²⁰ Plate slightly domed in all three shots

²¹ Plate destroyed in 1st and 3rd shots and holed in 2nd shot

²² Plate destroyed in all three shots

				T-P Test Result (ms)			DDT Test Result		
				Min	Average	SD	Run 1	Run 2	Run 3
Sample 11		Perchlorate (50%), Aluminium (25%), Magnesium (25%)	Grain Size micron			8			
Sample 12	Flashpowder 7	Potassium Perchlorate (40%), Magnesium #5 (40%), Magnesium/Aluminium (20%)	0.425 - 1 mm	1.89	2.27	0.34	+ ²³	+	+
Sample 13	Mortar 1	Sodium Nitrate (40%), Magnesium #6 (52%), Dextrin (8%)	<425 micron	8.03	9.81	2.54	- ²⁴	-	-
Sample 14	Mortar 2	Ammonium Perchlorate (61%), Dextrin (4%), Strontium Nitrate (3%), Copper Benzoate (15%), Magnesium/Aluminium (17%)	<425 micron	0.86	1.49	0.57	+ ²⁵	+	+
Sample 15	Rocket 1	CHAF - Stick-less rocket	<425 micron	0.39	0.43	0.03	+ ²⁶	+	+

²³ Plate destroyed in all three shots²⁴ Plate domed in all three shots²⁵ Plate torn in all three shots²⁶ Plate torn in all three shots

Annex II

DDT Flash Composition Test

1. Introduction

This test is used to determine whether pyrotechnic substances in powder form or as pyrotechnic units as presented in fireworks, that are used to produce an aural effect, or used as a bursting charge or lifting charge are considered to be flash composition for the purposes of determining the classification of fireworks using the UN default fireworks classification table in 2.1.3.5.5 of the Model Regulations.

2. Apparatus and materials

- 2.1 The experimental set up for the DDT Flash Composition Test is shown in Figure 1.
- 2.2 A twenty-five (25) gram sample of a loose powder confined in either:
 - a) A heavy-wall cardboard convolute sample tube with an inside diameter of 25.4mm and height 152 mm with a maximum wall thickness of 3.8 mm,
 - or
 - b) A spiral wound cardboard sample tube with an inside diameter of 25.4mm and height of 152mm with a maximum wall thickness of 3.5mm, closed at the base with a paper or thin cardboard cap or membrane just sufficient to retain the sample.
- 2.3 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.
- 2.4 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 between 63 mm and 102mm and a height of between 185 mm and 190 mm and weighs between approx. 2.9 kg and approx. 10.9 kg. Below the sample tube and surrounding steel confining cap is the square shaped steel witness plate, which is 1.0 mm thick and at least 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.

3. Procedure

- 3.1 The sample compositions are uniformly mixed and then twice passed through either
 - (a) A Number 40 mesh screen; or
 - (b) A 425 micron sieve

except where the nature is clearly granular in nature and is too coarse for the mesh or sieve.

3.2 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.

3.3 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.

3.4 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.

3.5 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.

3.6 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 positive result is achieved.

4. Test criteria and method of assessing results

4.1 The result is considered "+" and the substance is considered to be a "flash" composition if in any trial the witness plate is torn, perforated, pierced or otherwise penetrated (i.e. light is visible through the plate). Bulges or folds in the witness plate are not to be considered to be "+" results.

4.2 Otherwise, the result is considered "-".

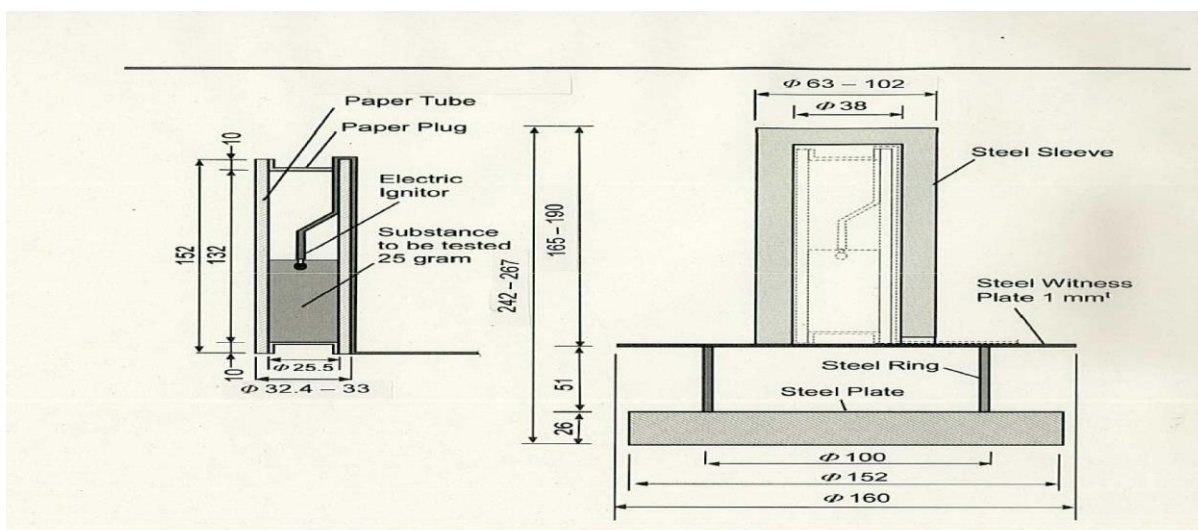


Figure A8.1: DDT Flash Composition Test Apparatus Drawing