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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

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Item 2 (a) of the provisional agenda
Explosives and related matters: tests and criteria for flash compositions

The effectiveness of US and HSL modified plugs for the HSL flash composition test

Transmitted by the expert from the United Kingdom[1]

Introduction

1. At the forty-third session of the Sub-Committee held in Geneva in June 2013, the expert from the United States of America presented a paper[2] which detailed the testing of a modified plug design to improve the performance of the HSL Flash Composition Test, which is described in the United Nations Recommendations on the Transport of Dangerous Goods - Manual of Tests and Criteria[3]. Work had also been undertaken at the Health and Safety Laboratory (HSL) in the United Kingdom to improve the plug design and usability. The Sub-Committee agreed that experts from other countries would perform tests on a range of compositions to corroborate the reproducibility claimed. The United Kingdom agreed to coordinate the testing between the participating countries.

[1] In accordance with the programme of work of the Sub-Committee for 2015–2016 approved by the Committee at its seventh session (see ST/SG/AC.10/C.3/92, paragraph 95 and ST/SG/AC.10/42, para. 15).

[2] ST/SG/AC.10/C.3/2013/23

[3] Recommendation on the Transport of Dangerous Goods - Manual of Tests and Criteria, 5th revised edition, Appendix 7, pp443 - 450

2. At the forty-fifth session the expert from the United Kingdom reported[4] on work undertaken by HSL in comparing the operation and performance of the two designs of modified plugs. The conclusions from this testing were that:

(a) Both the US and HSL modifications gave comparable results and produced a quicker rise time than respective results with the current plug design;

(b) Both plugs improved the operation and the time taken to conduct the tests; but

(c) The results failed to indicate any improvement in the variation in rise time recorded by using either of the modified plugs when compared to the existing design.

3. As part of the work programme, laboratories in the United States of America, Japan and the United Kingdom agreed to undertake tests on a range of compositions using the United States of America modified plug to demonstrate the reproducibility of results from different laboratories. The compositions used would be provided by the United Kingdom in an attempt to eliminate any variability due to raw materials or manufacturing process. Testing of these compositions had not been completed in time for the forty fifth session but these have now been concluded and the results from the various laboratories are provided in the annex to this paper.

Discussion

4. The list of compositions used and the preparation required prior to testing is provided in Table 1 in the annex. Preparation was required to replicate how compositions used in stars, whistles etc. would be used as a bursting charge. The intention was to provide each of the three laboratories with identical test material so as to remove one potential variable from the equation. However, constraints on the moving of loose substances meant that some preparation work would still be required. Laboratories were supplied with products from the same batch from a single manufacturer in the United Kingdom and a detailed procedure for selecting and preparing the test samples.

5. The minimum pressure rise times between the data sets of each of the participating laboratories are summarised in the table below; the data have been ranked in terms of the fastest to slowest rise times as determined by HSL.

[4] Informal document INF.20 (45th session)

Composition minimum pressure rise times

Sample Number	*Composition Name*	*HSL Current*[*]	*Rise time (ms)*		
			UK	JAPAN	US
1	Flash Report No. 2		0.34	1.18	1.15
11	Whistle,	1.04	0.52	1.64	0.97
4	15’ Sparkburst		0.58	2.04	5.21
2	Airburst Large Silver Glitter		0.64	0.72	4.93
6	25ft White +Tail comet		1.25	2.47	**Not tested
5	15’ Waterfall		1.33	7.11	2.7
9	1.5” 50-60’ Mine Silver	3.70	2.49	6.27	10.4
7	1.5” 50-60’ Mine Red		2.73	8.05	9.58
3	Super Gunshot Red		3.11	N/A	7.43
10	1.5” 50-60’ Mine Yellow	3.62	4.29	N/A	13.2
8	Theatrical Flash Large	8.51	12.73	N/A	54.4

N/A – upper threshold of 2070 kPa was not met – no data recorded

* From historical data (test samples not from same batches)

**Composition 6 was not tested by the US as insufficient material was available for their testing.

6. The thick bold lines indicate the demarcation between those results that exceed the 6 ms threshold and those that do not. A material would not be considered for classification as a flash composition if the rise time exceeded 6 ms. It can be seen that the number of compositions that would be classified as a flash composition would differ between test laboratories.

7. Assessment of the data in the table indicates that the United Kingdom laboratory consistently achieved faster pressure rise times than either the Japanese or US laboratories. The Japanese laboratory produced faster pressure rise times than the US laboratory for compositions 2, 7 and 9, whilst the United States laboratory produced faster pressure rise times than the Japanese results for compositions 1, 11 and 5

From the data sets received from the participating laboratories (Tables 2 to 4) it is evident that there is a level of variability in the results obtained. This variability is both between laboratories and within the data produced by a single laboratory. It is more noticeable where the compositions tested were assessed against the threshold of being classified as flash composition or not.

Out of the eleven compositions tested, only four (Compositions 1, 2, 4, and 11) would have been classified as a flash composition by all laboratories. In addition the United Kingdom would classify a further five compositions (Compositions 3, 6, 7, 9 and 10), whilst the Japanese would also additionally classify Composition 6 as a flash composition . From the data, this would lead to the United States and Japan not classifying compositions 3, 7, 9, and 10 as flash compositions, whereas the United Kingdom would.

All laboratories found the rise time for Composition 8 to be above 6 ms and would not classify it as a flash composition.

8. It is noted that all the gunpowder and gunpowder substitutes tested gave a rise time less than 6ms and would have been considered as flashpowders based on these results. The tests conducted with propellant powder did not give significantly consistent results to suggest that it would be suitable as a standard.

9. The differences between the data sets and the potential variation in classification of the formulations suggest that there may be some underlying differences affecting the data obtained. Laboratories have provided HSL with information on the pressure sensors used, bursting disc characteristics and the fusehead and these are summarised below:

Equipment	*Japan*	*US*	*UK*
Pressure Sensor make	PCB 112A05	PCB 102B06	Kulite ETS-1a-375-500SG
Sampling rate (microseconds)	1	50	20
Bursting Disc material	0.4 mm aluminium alloy tempered	0.18 mm aluminium H14	0.12 mm brass half hard tempered
Tensile Strength (MPa)	Not Known	105-145	330 - 500
Hardness Brinell (HB)	Not Known	34	65 -136
Fusehead	Davey Bickford	Daveyfire SA2001	Vulcan

10. The table demonstrates that there are a number of differences introduced by the selection of sensors, bursting discs and fuseheads used, which are potentially areas where variability in results could be introduced. The selection by HSL of brass as the material for the bursting discs highlights a discrepancy in the procedure provided in Appendix 7 of the Manual of Tests; paragraph 2.2 only refers to aluminium as the material of construction for the bursting disc but paragraph 3.1 offers the choice of aluminium or brass. HSL have selected brass bursting disc based on their experience in testing high burning temperature compositions; instances where the test fails to exceed the upper pressure limit (2070 kPa) are reduced, believed to be due to better tolerance of heat generated.

Conclusions

11. The inter-laboratory testing of the US modified plug within the HSL Flash Composition Test has shown that there appears to be variation in the results between laboratories. It has not been possible to confirm that the modification proposed by the US improved the consistency of results. However, as previously reported, the use of the US modified plug (and the United Kingdom version) improved handling and reduced the time taken conducting tests.

The data indicated that, in general, each laboratory ranked the compositions similarly based on rise time. However, rise times obtained by each laboratory for a particular composition varied significantly. The criteria for establishing whether a pyrotechnic composition should be considered to be a flash composition is based on the minimum rise time being less than or equal to 6 ms; consequently, the variations in rise time observed between laboratories would have led to inconsistencies in the application of the United Nations Default Fireworks Classification Table, with the potential for misclassification of articles for transport.

No single variable has been identified as the dominant influence on the overall results and differences between laboratories.

12. Each laboratory received samples from the same batch of composition and sample preparation was standardised in an attempt to eliminate variations in results due to differences in the substances under test. This included passing the substance through a 500 micron sieve where necessary to reduce variation in particle size. Whilst differences could not be eliminated completely, the continued spread in results suggests that they are not solely attributable to sample variation and differences in the choice of test equipment used may be contributory factors. Areas of particular interest are:

- The bursting disc,
- The fuse head type,
- Gas leakage from the apparatus.

Studies into the contribution of each of these variables are currently under consideration in order to identify ways that may improve the precision of the output from the test. Project work on the performance parameters of fuseheads is currently in hand.

Proposal

13. It is evident that improvements to the test procedure described in Appendix 7 of the Manual of Tests and Criteria can be made to improve handling, the time needed for the test and the consistency of materials used.

It is proposed that the procedure be revised and updated to:

i. Include brass as a material for bursting discs in paragraph 2.2 of Appendix 7 and specify the desired bursting pressure rather than thickness;

ii. Change the design of the firing plug to that proposed by the United States and United Kingdom as options.

Annex

Comparison of test results using U.S modified plugs in the HSL time/pressure test

Experimental

Sample selection and preparation

The laboratories from the United States of America, Japan and United Kingdom were supplied with samples from the same batch/lot numbers of finished articles from a Theatrical Pyrotechnic manufacturer based in the United Kingdom. Prior to testing, each sample was broken down to obtain the pyrotechnic composition. Some of these compositions required further preparation prior to testing; the location and pre-preparation of the samples (where applicable) are shown in Table 1 below.

Sample No.	*Pyrotechnic type*	*Quantity of selected composition in completed article (gms)*	*Location of selected composition within the completed article*	*Preparation*
1	Flash Report	5g	Loose contents of the device	Removed from article - no further preparation required.
2	Airburst	5g	Loose contents of the device	Removed from article - no further preparation required.
3	Super Gun Shot	12g	In cartridge at base of Tube	Cartridge removed from article and then pyrotechnic, removed from cartridge – no further preparation required.
4	Starburst	1.5g	Loose contents of the device	Removed from article - no further preparation required.
5	Waterfall	c. 25g	Contents of the device pressed into tube	Tube broken up and ground prior to sieving to < 500 µm.
6	White with tail comet	c. 1g	Contained in stars located under paper cap	Stars separated from other pyrotechnic in article. Stars crushed and sieved to < 500µm.
7	Red Mine	c. 10g	Stars located under	Stars separated

Sample No.	*Pyrotechnic type*	*Quantity of selected composition in completed article (gms)*	*Location of selected composition within the completed article*	*Preparation*
			paper cap	from other pyrotechnic in article Stars crushed and sieved to < 500µm.
8	Theatrical Flash	7g	Located under paper lid	Removed from article- no further preparation required
9	Silver Mines	c.10g	Stars located under paper cap	Stars separated from other pyrotechnic in article. Stars crushed and sieved to < 500µm.
10	Yellow Mine	c.10g	Contained in stars located under paper cap	Stars separated from other pyrotechnic in article. Stars crushed and sieved to < 500µm.
11	Whistle	c. 10g	Contents pressed into tube	Tube broken up and ground prior to sieving to < 500 µm.

Test Results

Tables 2 to 4 show the data sets from each of the laboratories. It can be observed that HSL (United Kingdom) completed nine test firings on each composition, as opposed to the three firings completed on each pyrotechnic composition by the United States and Japanese laboratories. HSL undertook these additional firings in an attempt to provide greater confidence in the variability of the tests. Both the United States and the United Kingdom test houses also completed tests on black powder and black powder substitutes to demonstrate that some formulations could achieve a minimum pressure rise time of less than or equal to 6 ms. Under the current sentencing criteria [(4)] this would classify them as a flash composition: data for these black powder and black powder substitutes are also shown within the tables where appropriate. The United Kingdom also tested a smokeless powder (Table 2), as it was envisaged that such a composition could have the potential to act as a standard between test laboratories. However, the Japanese laboratory was unable to undertake this testing due to the civilian restrictions on importation of these products into Japan.

The data set from the Japanese (Table 4) shows that for compositions 3, 8 and 10, no pressure rise time was obtained. This was due to the upper threshold of 2070 kPa not being met during the trials. This differs from the United States and United Kingdom testing where all compositions gave measurements. This failure to achieve the higher threshold was also seen in the Japanese testing of compositions 7 and 9, where one or two tests with

each individual test did not reach the upper threshold. Composition 5 of the Japanese data set also had an outlier within the initial data set and a further series of three tests were undertaken. The repeat test results can be seen at the bottom of Table 4 and demonstrate a variation in results when compared to the original data.

It was evident from the data that, often, two out of the three tests performed on a composition were similar in response, whereas the third seemed to deviate significantly in rise time. This appears to be a finding across all compositions tested, independent of laboratory and sample types. Interestingly, the position of the outlier within the three tests was not identified as always occurring on the first test of each composition undertaken but could be encountered anywhere within the three-test series.

The minimum pressure rise times between the data sets of each of the participating laboratories are summarised in the table in the main report; the data in the table have been ranked in terms of the fastest to slowest rise times determined by the HSL. Assessment of the data in the table indicates that the United Kingdom laboratory consistently achieved faster pressure rise times than either the Japanese or United States laboratories. The Japanese laboratory produced faster pressure rise times than the United States laboratory for compositions 2, 7 and 9, whilst the United States laboratory produced faster pressure rise times than the Japanese results for compositions 1, 11 and 5.

Table 2: UK data set for the US modified plug HSL Flash Composition Test data

Sample No.	Item Description	Rise time (ms)											
		Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8	Test 9	Min	Average	SD
1	Flash Report	0.98	0.77	0.34	0.40	0.65	0.79	0.75	0.85	0.72	0.34	0.69	0.21
2	Silver Glitter Airburst	2.71	1.67	0.64	3.08	1.71	1.19	1.73	2.44	1.66	0.64	1.87	0.76
3	LMA Super Gun Shot	3.79	3.19	4.74	5.05	4.77	3.37	5.17	3.11	3.16	3.11	4.04	0.88
4	15ft Starburst	0.63	0.58	0.99	2.03	1.85	2.49	1.33	0.82	1.17	0.58	1.32	0.67
5	15fr Waterfall	1.9	1.33	1.40	1.99	1.56	1.52	1.33	1.37	1.77	1.33	1.57	0.25
6	25ft White with Tail comet	2.3	1.25	2.63	1.47	1.34	1.54	1.51	2.06	1.26	1.25	1.71	0.5
7	Red 50-60ft mine	2.87	4.52	3.09	2.73	3.18	3.06	2.74	2.88	2.95	2.73	3.11	0.55
8	Silver 50-60ft mine	6.03	6.62	3.39	2.49	3.34	4.04	4.25	4.14	6.15	2.49	4.49	1.44
9	Yellow 50-60ft mine	5.17	4.77	4.29	4.53	4.58	4.55	5.69	5.09	4.83	4.29	4.83	0.43
10	Theatrical Flash	14.47	21.31	12.73	12.73	28.53	13.58	33.38	19.53	17.5	12.73	19.31	7.36
11	Whistle composition	0.80	0.52	0.64	0.86	1.12	0.66	0.60	0.65	0.6	0.52	0.72	0.18
12	Swiss No 1 black powder	2.70	1.67	2.79	2.09	2.16	2.46	2.23	1.36	1.97	1.36	2.16	0.46
13	FOA black powder	5.17	4.42	4.59	4.39	3.23	3.81	4.15	4.38		3.23	4.27	0.57
14	Hodgdon triple severn BP substitute	3.40	3.13	3.38	3.10	3.06	3.39	2.77	6.68	2.79	2.77	3.52	1.21
15	Pyrodex TW	9.35	5.03	7.46	5.15	4.76	7.90	6.96	7.98	3.95	3.95	6.51	1.84
16	Alliant “Bullseye”smokeless powder	4.36	3.82	3.14	2.41	4.49	3.18	4.19	4.18	3.57	2.41	3.71	0.69

Table 3: US data set from the US modified plug HSL Flash Composition Test data

Sample No.	Item Description	Rise time (ms)					
		Test 1	Test 2	Test 3	Min	Mean	SD
1	Flash Report No. 2	1.17	1.15	1.80	1.15	1.37	0.37
2	Airburst Large Silver Glitter	16.4	5.94	4.93	4.93	9.09	6.35
3	Super Gunshot Red	7.43	9.34	10.1	7.43	8.96	1.38
4	15’ Sparkburst	5.21	8.01	8.37	5.21	7.20	1.73
5	15’ Waterfall	5.30	2.70	2.90	2.70	3.63	1.45
7	1.5” 50-60’ Mine Red	9.58	19.00	10.3	9.58	12.96	5.24
8	1.5” 50-60’ Mine Silver	12.9	22.4	10.40	10.40	15.23	6.33
9	1.5” 50-60’ Mine Yellow	25.00	25.00	13.2	13.20	21.07	6.81
10	Theatrical Flash Large	128.9	54.4	63.89	54.40	82.40	40.55
11	Whistle,	1.38	1.23	0.97	0.97	1.19	0.21
12	GOEX Fg Black Powder	5.05	4.30	4.54	4.30	4.63	0.38
13	GOEX FFFg Black Powder	4.55	4.14	4.40	4.14	4.36	0.21
14	GOEX FFFFg Black Powder	3.93	3.01	3.50	3.01	3.48	0.46

Table 4: Japanese data set for the US modified plug HSL Flash Composition Test data

Sample No.	Item Description	Rise time (ms)					
		Test 1	Test 2	Test 3	Min	Mean	SD
1	Flash Report No. 2	3.09	1.18	1.55	1.18	1.94	1.01
2	Airburst Large Silver Glitter	2.44	1.97	0.72	0.72	1.71	0.89
3	Super Gunshot Red	N/A	N/A	N/A		0	
4	15’ Sparkburst	2.94	2.92	2.04	2.04	2.63	0.51
5	15’ Waterfall	*64.00**	7.11	9.70	7.11	26.94	32.12
6	25ft White with Tail comet	2.14	4.14	5.47	2.14	3.92	1.68
7	1.5” 50-60’ Mine Red	8.05	N/A	19.38	8.05	13.71	8.01
8	1.5” 50-60’ Mine Silver	N/A	N/A	6.27	6.27	6.27	
9	1.5” 50-60’ Mine Yellow	N/A	N/A	N/A		0	
10	Theatrical Flash Large	N/A	N/A	N/A		0	
11	Whistle	1.86	1.72	1.64	1.64	1.74	0.11
5**	15’ Waterfall	5.45	5.98	5.12	5.12	5.52	0.43

*** Perceived outlier**
**** Repeat test results 5.**
N/A Upper threshold of 2070 kPa not met