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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-second session
Geneva, 3 – 11 December 2012
Item 2 (a) of the provisional agenda
Recommendations made by the Sub-Committee at its thirty-ninth, fortieth and forty-first sessions and pending issues: explosives and related matters

Similarity of results of the HSL flash composition test and the US flash composition test

Transmitted by the expert from the Netherlands[1]

Introduction

1. At its forty-first session, the Sub-Committee, and the Working Group on Explosives, considered paper ST/SG/AC.10/C.3/2012/30, transmitted by the United Sates of America proposing the introduction of an alternative test for determining flash compositions. The issue has been discussed at three consecutive June/July sessions of the Sub-Committee. Many documents submitted by several experts provided experimental results and further improvements to the test method and description. At the forty-first session the Sub-Committee agreed to amend Note 2 of paragraph 2.1.3.5.5 of the Model Regulations and to add a new US Flash Composition Test as an Appendix 7 to the Manual. (see ST/SG/AC.10/C.3/82, paras 20-21 and ST/SG/AC.10/C.3/82/Add.1, (annexes I and II)).

2. It should be noted that during the three sessions the expert from the Netherlands had expressed reservations as reflected in the reports of the working group (see informal documents INF.73 (37th session), INF.58 (39th session) and INF.67 (41st session)). The reservations were on the fact that:

Only detonation phenomena would be addressed in the DDT test,

[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).

Traditional flash compositions (e.g. mixtures of barium nitrate and aluminium) showed negative results in the US test and

A comparison of TPT data and DDT results for black powders were requested.

3. During the forty-first session the expert from China queried whether both tests gave comparable results and which test would be the preferred test, so as to avoid problems of recognition of classification. The opinion of the working group was that both test methods led to the same results. After the meeting additional data was kindly provided by the expert from Japan giving comparative data for black powders.

Analysis

4. The Netherlands undertook a comparison of all available data. The detailed results are given in the annex to this document.

5. Of the 43 available comparisons:

24 (56%) gave agreement between the two methods.

19 samples (44%) showed no agreement; the HSL test being more strict in 18 cases.

6. With the new criterion of 6 ms in the HSL test, the result would change for two samples. Both would become not flash powder, for one of these two samples the US method gave a positive result. Therefore the numbers and percentages stay the same, but the HSL test is then more strict in 17 cases.

7. The conclusion of the analysis is that there is poor agreement between the two methods. Obviously, both tests address different characteristics. Where the HSL test covers both detonation and deflagration phenomena, de US test covers detonation only.

8. The importance of identifying flash composition for default classification is to classify fireworks with potential mass explosion hazards as 1.1G. It should be stressed that mass explosion does not only cover detonations but also (violent) deflagrations.

Discussion

9. In the 14th revised edition of the United Nations Recommendations on the Transport of Dangerous Goods, Model Regulations, flash composition was defined on chemical composition (oxidisers and metal fuel) and the intended use (report or burst). Several competent authorities noticed that metal fuel was frequently replaced by other energetic fuels such as benzoates, salicylates, phthalates, antimony trisulphide and nano materials. In that way the definition of flash composition was circumvented and a “lower” classification obtained. Such mixtures would behave differently from the ‘classical’ flash compositions, but they are equally energetic with comparable power and potential to mass explode. To address this issue a performance based definition and related test method was developed resulting in the inclusion of the HSL flash composition test in the Manual of Tests and Criteria.

10. The analysis given in the annex to this document was distributed to the members of the explosive working group. Several comments were received and the expert from Sweden added a column to the table giving a comparison with the definition of flash composition as given in the 14th revised edition of the Recommendations, see the last column of the table in the annex. For some of the 43 experimental results there was no composition given so the “old” definition could not be applied. Of the 36 remaining compositions 33 cases showed good agreement between US test results and the “old” definition. For the HSL test there was agreement in 17 of the 36 cases.

11. It is noteworthy that the results show that the HSL test gives positive results (i.e. the composition is to be considered as flash composition) for both mixtures of oxidisers and metals and of oxidisers with other fuels. The US test typically gives only positive results for the classical flash compositions containing metal.
This might be caused by the criterion used in the US test: perforation of the witness plate. This is a clear and easy to assess criterion but excludes the lower order reactions such as (violent) deflagrations with the potential to mass explode.

Consequences

12. The above analysis makes clear that in too many cases, both methods give a different result. This may cause problems for manufacturers and importers to arrive at the correct classification of their products. Furthermore, this can lead to difficulties in enforcement, for instance where a manufacturer has used the US test to screen for flash composition and an enforcing authority uses the HSL test (e.g. because less material is available). Usually an inspecting authority does not have the background information on how the classification displayed on the packaging has been established, by analogy or by test results. The (default) classification could differ depending on the method used. Unfortunately, the situation cannot easily be solved by changing, for instance, the criterion in the HSL test since the pressure rise times are relatively low. In the 19 cases where the results differ, 14 results are (well) below 4 ms. Changing the criterion of the US test might be more promising, but currently sufficient data to arrive at a new criterion is lacking.

Considerations

13. In his reaction the expert from the United Kingdom considered there were four different options to resolve the question:

(a) Withdraw (or postpone) the proposal, pending further work;

(b) Accept the proposal but continue the work to bring the criteria together;

(c) Introduce a different criterion in the US test (based on indentation depth of the witness plate), but currently there is little data to justify the value of the depth; or

(d) Include a note that in case of conflict the Competent Authority reserves the right to require series 6 testing for a definitive decision.

A number of working group members expressed support for option “d”.

In our view, introduction of an alternative flash composition test at this stage is not preferable, knowing that there will be significant changes in the near future. Therefore options “b’ and “d” are not preferable. Furthermore, there is no urgent need for an alternative test.

The preference of the Netherlands is a combination of option “c” and “a”. A certain degree of indentation of the witness plate represents a certain power of the test material. In that way, also deflagrations can be addressed with the US test.

Proposal

14. The Netherlands proposes that the introduction of the US Flash Composition Test and the amendment of Note 2 of paragraph 2.1.3.5.5 of the Model Regulations be postponed to the next biennium. The extra time obtained can be used to generate more data to arrive at a well-supported criterion for the indentation depth of the witness plate.

ANNEX

[English only]

Reference	*Sample description*	*Sample composition*	*HSL test result*	*US test result*	*Conclusion (HSL and US)*	*By old definition*
1	Red colour 1	not given	+ (7.1 ms)	+	agreement	*N/A*
1	Red colour 2	not given	- (10 ms)	-	agreement	*N/A*
2	Flash powder 1	Potassium Perchlorate (50%), Aluminium Dark Pyro (40%), Magnesium #6 - Active (10%)	+ (0.67 ms)	+	agreement	+
2	Flash powder 2	Potassium Perchlorate (40%), Magnesium #6 - Active (60%)	+ (1.41 ms)	+	agreement	+
2	Number 1 Black powder	not given	+ (2.14 ms)	+	agreement	*N/A*
2	Flash powder 3	Potassium Nitrate (60%), Magnesium #5 (40%)	+ (2.31 ms)	+	agreement	+
2	Black powder Substitute	not given (equivalent performance to FFFG black powder)	+ (3.08 ms)	-	no agreement	-
2	Flash powder 4	Potassium Perchlorate (64.2%), Aluminium – High Grade (20%), Magnesium # 5 (10%), Graphite (5.8%)	+ (3.11 ms)	+	agreement	+
2	Comet Composition	Potassium Perchlorate (64%), Barium Nitrate (2%), Magnesium #5 (10%), Acaroid Resin (18%)	+ (4.36 ms)	-	no agreement	-
2	FO/A Black powder	not given	+ (4.83 ms)	+	agreement	*N/A*
3	1	Goex Black powder -- 5FA “Unglazed”	+ (1.88 ms)	-	no agreement	*N/A*
3	2	35 wt. % Potassium Nitrate (100% < 37 μ)/ 31 wt. % Potassium Perchlorate (100% < 37 μ) /13.5 wt.% Potassium Benzoate (fine powder)/ 10% Sulphur (fine powder)/10.5%Lampblack (nano-material).	+ (0.88 ms)	-	no agreement	-
3	3	70% wt. Potassium Perchlorate (100% < 37 μ) / 30 wt. % “Semi-coarse” Magnesium powder -- (297μ<25%>149μ; 148μ<58%>53μ; 52μ< 5%>44μ; 12%<43μ)	+ (4.9 ms)	+	agreement	+
3	4	65 wt. % Potassium Perchlorate (100% < 44μ)/ 35 wt. % Magnesium (105μ 5%>74μ; 73μ <39%>44μ; 46%<43μ)	+ (0.96 ms)	+	agreement	+
3	5	65 wt. % Potassium Perchlorate (100% < 44μ)/ 35 wt. % Magnesium (105μ 5%>74μ; 73μ <39%>44μ; 46%<43μ)	+ (0.32 ms)	+	agreement	+
3	6	70 wt. % Potassium Perchlorate (100% < 37 μ)/ 30 wt. % “Atomized” Aluminium powder (74μ<2.4%>53μ; 52μ<2.9%>44μ; 94.7%<44μ)	+ (2.8 ms)	+	agreement	+

3	7	65 wt. % Potassium Perchlorate (100% < 44µ)/ 35 wt. % “Flake” Aluminium “A” (105µ <72%>53µ; 52µ <17%>44µ; 11.5%<43µ)	+ (0.40 ms)	+	agreement	+
3	8	65 wt. % Potassium Perchlorate (100% < 44µ)/35 wt. % “Flake ” Aluminium “B” (74µ<39% >53µ; 52µ<22%>44µ; 40%<43µ)	+ (0.44 ms)	+	agreement	+
3	9	70 wt. % Potassium Perchlorate (100% < 37 µ)/ 30 wt. % “Ground” Magnalium powder --(74µ<37%>53µ; 52µ<11%>44µ; 52%<44µ)	- (9.6 ms)	+	no agreement	+
3	10	68 wt. % Barium Nitrate (105µ < 10% > 74 µ; 73 µ<12%>44 µ; 43 µ< 24%>37 µ; 53%<37 µ)/23 wt. % “Dark Flake” Aluminium (100%< 73 µ)/9 wt. % Sulphur (fine powder)	+ (1.4 ms)	-	no agreement	+
3	11	85 wt. % Potassium Perchlorate (97% < 74µ & 30% < 37µ)/ 10 wt. % Sulphur (very fine ground flower)/ 5 wt. % powdered charcoal	- (8.3 ms)	-	agreement	-
3	12	80 wt. % Potassium Perchlorate (97% < 74µ & 30% < 37µ)/10 wt. % Sulphur (very fine ground flower)/10 wt. % powdered charcoal	- (8.2 ms)	-	agreement	-
3	13	75 wt. % Potassium Perchlorate (97% < 74µ & 30% < 37µ)/10 wt. % Sulphur (very fine ground flower)/15 wt. % powdered charcoal	+ (1.74 ms)	-	no agreement	-
3	14	70 wt. % Potassium Perchlorate (97% < 74µ & 30% < 37µ)/10 wt. % Sulphur (very fine ground flower)/20. wt % powdered charcoal	+ (2.64 ms)	-	no agreement	-
3	15	65 wt. % Potassium Perchlorate (97% < 74µ & 30% < 37µ)/10 wt. % Sulphur (very fine ground flower)/25 wt. % powdered charcoal	+ (2.12 ms)	-	no agreement	-
3	16	60 wt. % Potassium Perchlorate (97% < 74µ & 30% < 37µ)/10 wt. % Sulphur (very fine ground flower)/30 wt. % powdered charcoal	+ (2.96 ms)	-	no agreement	-
3	17	52 wt. % Potassium Perchlorate (97% < 74µ & 30% < 37µ)/17 wt. % Sulphur (very fine ground flower)/5 wt. % powdered charcoal/26 wt. % Antimony trisulphide	+ (2.08 ms)	-	no agreement	-
3	18	50 wt. % Potassium Perchlorate (97% < 74µ & 30% < 37µ)/30 wt. % Sulphur (very fine ground flower)/20 wt. % powdered charcoal	+ (3.68 ms)	-	no agreement	-
3	19	70 wt. % Potassium Perchlorate (97% < 74µ & 30% < 37µ)/20 wt. % Sulphur (very fine ground flower)/10 wt. % powdered charcoal	+ (2.32 ms)	-	no agreement	-
3	20	60 wt. % Potassium Perchlorate (97% < 74µ & 30% < 37µ)/30 wt. % Sulphur (very fine ground flower)/10 wt. % powdered charcoal	+ (4.32 ms)	-	no agreement	-
3	21	60 wt. % Potassium Perchlorate (97% < 74µ & 30% < 37µ)/20 wt. % Sulphur (very fine ground flower)/20 wt. % powdered charcoal	+ (2.16 ms)	-	no agreement	-
3	22	48 wt. % Potassium Perchlorate (100 < 37µ)/52 wt. % Iron Powder (100% <45µ and 94% < 37µ)	- (> 8 ms)	-	agreement	+
4	5FA Black powder	not given	- (10.31 ms)	-	agreement	*N/A*

4	Flash powder 5	Potassium Perchlorate (50%), Magnesium # 5 (30%), Magnesium #6 (20%)	+ (0.25 ms)	+	agreement	+
4	Flash powder 6	Potassium Perchlorate (50%), Aluminium (25%), Magnesium (25%)	+ (0.52 ms)	+	agreement	+
4	Flash powder 7	Potassium Perchlorate (40%), Magnesium #5 (40%), Magnesium/Aluminium (20%)	+ (1.89 ms)	+	agreement	+
4	Mortar 1	Sodium Nitrate (40%), Magnesium #6 (52%), Dextrin (8%)	- (8.03 ms)	-	agreement	+
4	Mortar 2	Ammonium Perchlorate (61%), Dextrin (4%), Strontium Nitrate (3%), Copper Benzoate (15%), Magnesium/Aluminium (17%)	+ (0.86 ms)	+	agreement	+
4	Rocket 1	CHAF - Stick-less rocket	+ (0.39 ms)	+	agreement	*N/A*
5	Kayaku Japan	Potassium nitrate (75%), charcoal (15%), sulphur (10%)	+ (3.55 ms)	-	no agreement	-
5	Wano 5FA	Potassium nitrate (75.5%), charcoal (15.2%), sulphur (9.3%)	+ (3.06 ms)	-	no agreement	-
5	Wano 4FA	Potassium nitrate (75.5%), charcoal (15.2%), sulphur (9.3%)	+ (5.61 ms)	-	no agreement	-
5	Wano 2FA	Potassium nitrate (75.5%), charcoal (15.2%), sulphur (9.3%)	+ (6.43 ms)	-	no agreement	-

References:

1. UN/SCETDG/39/INF.17 (Germany)

2. UN/SCETDG/39/INF.30 (UK)

3. ST/SG/AC.10/C.3/2012/30 (USA)

4. ST/SG/AC.10/C.3/2012/51 (UK)

5. UNSCETDG/41/INF.42 (Japan) with additional document

Old definition of flash composition (Rev 14 of UN Model Regulations): “Flash composition” refers to pyrotechnic compositions containing an oxidizing substance, or black powder, and a metal powder fuel that are used to produce an aural report effect or used as a bursting charge in fireworks devices.