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 **20 June 2012**

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

Comments on the proposed US modified DDT Test and Criteria to classify the flash compositions

Transmitted by the expert from Japan

Background

1. A modified DDT Test and Criteria for flash compositions being proposed by United State of America (see ST/SG/AC.10/C.3/2010/31, 2012/30 and UN/SCETDG/39/INF.44) has been evaluated experimentally by United Kingdom, Germany and Japan because of its potential to be a complementary method with the HSL Flash Composition Test in Appendix 7 of the Manual of Tests and Criteria.

2. At the thirty-ninth session of TDG Sub-Committee, the experts from United Kingdom reported the test results of the modified DDT test using granular black powders and pointed out the possible influence of grain size on the result. The experts from Germany suggested that the mass of the steel sleeve might affect the classification result (see informal documents SCETDG/39/INF.16 and INF.44).

3. The experts from Japan discussed the definition of the sample by showing the case where firework products used a bursting charge that consisted of core material such as rice chaff, cottonseed and cork coated with pyrotechnical substances. In such case, in order to examine actual explosive behaviour of the bursting charge, it seemed reasonable to test 25 g coated core material as presented in the fireworks instead of testing 25 g fine powder of the same pyrotechnical substances without the core material (see SCETDG/39/INF.22).

4. Thus, further study has been anticipated to specify the proper mass of the steel sleeve and definition of the sample of the modified DDT test.

5. This paper expressed some views on abovementioned issues based on the results of recent experiments conducted by the Japan Pyrotechnics Association (JPA).

Discussion

6. The outline and results of the experiments were shown in the Annex of this document. The experimental apparatus shown in Fig. 1 and Fig. 2 were the same as that used in the previous paper (SCETDG/39/INF.22). In this work, however, the mass of the steel sleeve was adjusted to be three different values, 2.7, 10.8 and 18.9 kg, by adding steel weights to the steel sleeve as shown in Fig. 3.

7. The tested firework substances and results were summarized in Table 1. Four types of granular black powders having different grain sizes were tested to study the effect of grain size on the witness plate deformation. Two of four the black powders (WANO 5FA

and Kayaku Japan) were tested under three different sleeve mass conditions to study the effect of the steel sleeve mass on the witness plate deformation. Furthermore, four types of pyrotechnical substances that are typically used for producing flash report, whistle, red coloring and waterfall effects were also tested.

8. All black powders showed (-) regardless of grain size and steel sleeve mass. However, as shown later, remarkable effects of grain size and steel sleeve mass on the deformation of the witness plate were observed. As for other pyrotechnic substances, flash report composition showed (-), while whistle, red colouring and waterfall compositions showed (+). Although the classification of the red colouring composition was critical as shown in Fig. 5, these results were consistent with the JPA's assessment.

9. In order to evaluate numerically the effects of grain size and steel sleeve mass on the deformation of the witness plate, a dent depth: d was measured in the experiments using black powders. As shown in Fig. 4, the dent depth: d was defined as a height of the dome shaped expanded part of the witness plate measured from the virtual bottom surface of the dome.

10. The dependencies of the dent depth on the steel sleeve mass and the grain size were summarized in Fig. 6. In Fig. 6(a), average values of the measured dent depth were plotted as a function of steel sleeve mass with error bars such as $d_{ave} \pm 3 \times \sigma$, where d_{ave} is average value and σ was standard deviation of the measured dent depth. It was found that dent depth increased with steel sleeve mass on average, but the standard deviations also showed tendency to increase with mass. In case of 18.9 kg mass condition, the error bars for both samples from WANO 5FA and Kayaku Japan become significantly large. Although the data number was limited and reason was not clear for such increase of the standard deviation as sleeve mass increased, this result suggested that the steel sleeve mass within the range of 2.7 to 10.8 kg was adequate in terms of reproducibility of the measurement.

11. In Fig. 6(b), it was clearly shown that the dent depth significantly increased as the grain size decreased. This indicated that the classification results particularly for the granular pyrotechnical substances on the border of the classification may be strongly influenced by their grain size.

12. Figure 7 showed again the results already reported in the previous informal document (SCETDG/39/INF.22) at 39th session of TDG. The 25 g of fine powder ($KClO_4$/C) showed (-), while 25 g of rice chaff coated with the same powder showed (+) despite the mass of the fine powder was 20.5 g in the 25 g of coated rice chaff. This result demonstrated that the intensity of explosion could be enhanced by core materials even if the amount of the pyrotechnic substance was reduced to be less than 25 g.

13. From the experimental results and discussions mentioned in 11 and 12, it was considered that the sample should be tested in the form as presented in the fireworks. In other words, any type of form, such as powdered, granulated or coated on a core material, should be maintained in the sample being tested if the sample was used in fireworks in such form. Furthermore, in case that the pyrotechnical substance was coated on core material, the definition of sample mass 25 g should include the mass of core material because such definition would be practical if the sample was extracted from actual firework products.

Proposal

14. The expert from Japan supports the modified DDT test as a complementary method with the HSL Flash Composition Test. However the Sub-Committee is invited to discuss following views from the experts from Japan,

- the mass of the steel sleeve should be within the range of 2.7 to 10.8 kg ,

- any type of form, such as powdered, granulated or coated on a core material should be maintained in the sample being tested if the sample was used in fireworks in such form, and,.

- in case that the pyrotechnical substance is coated on core material, the definition of sample mass 25 g should include the mass of core material.

Annex

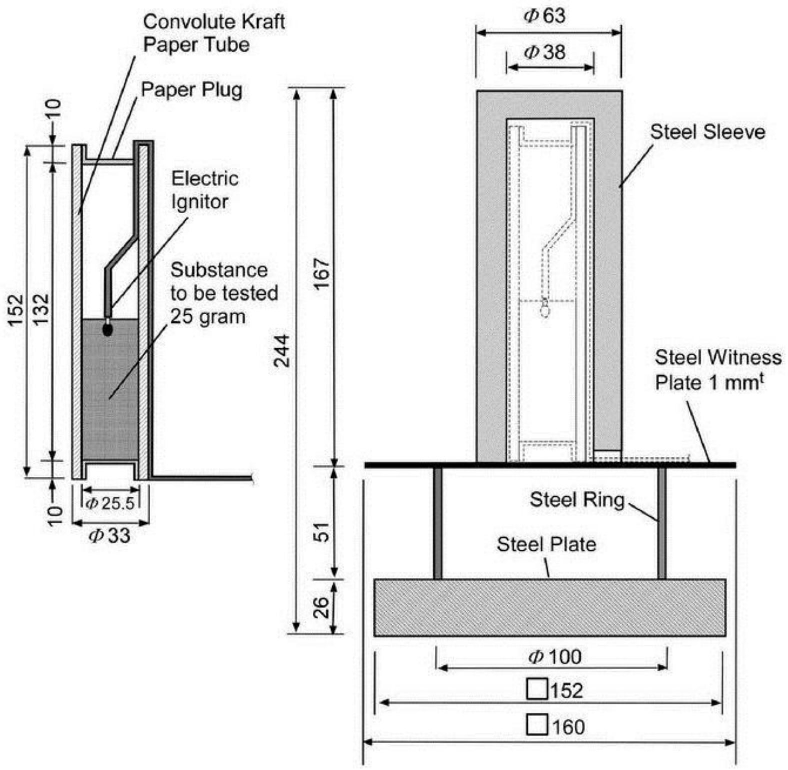


Fig. 1 Test apparatus in this work.

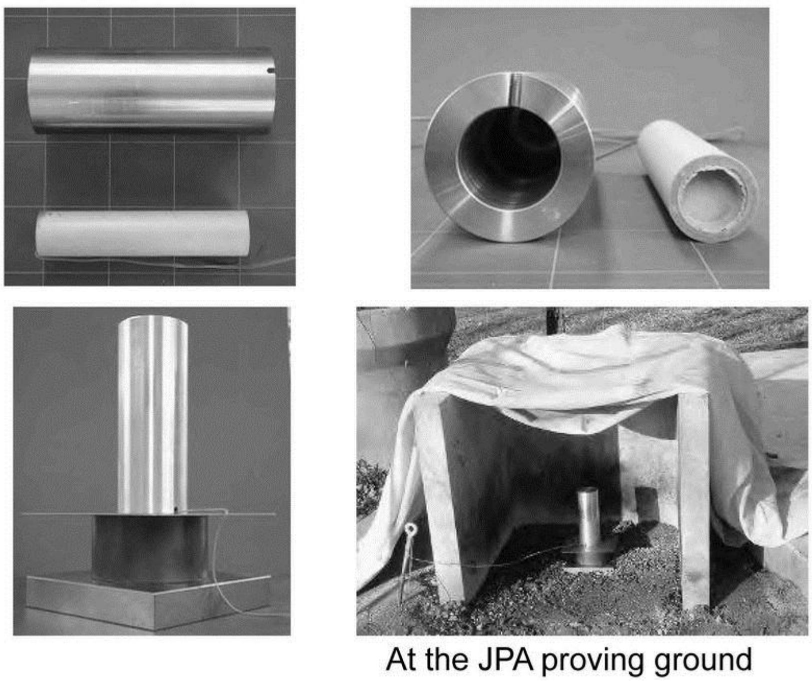


Fig. 2 Test apparatus in this work (cont'd).

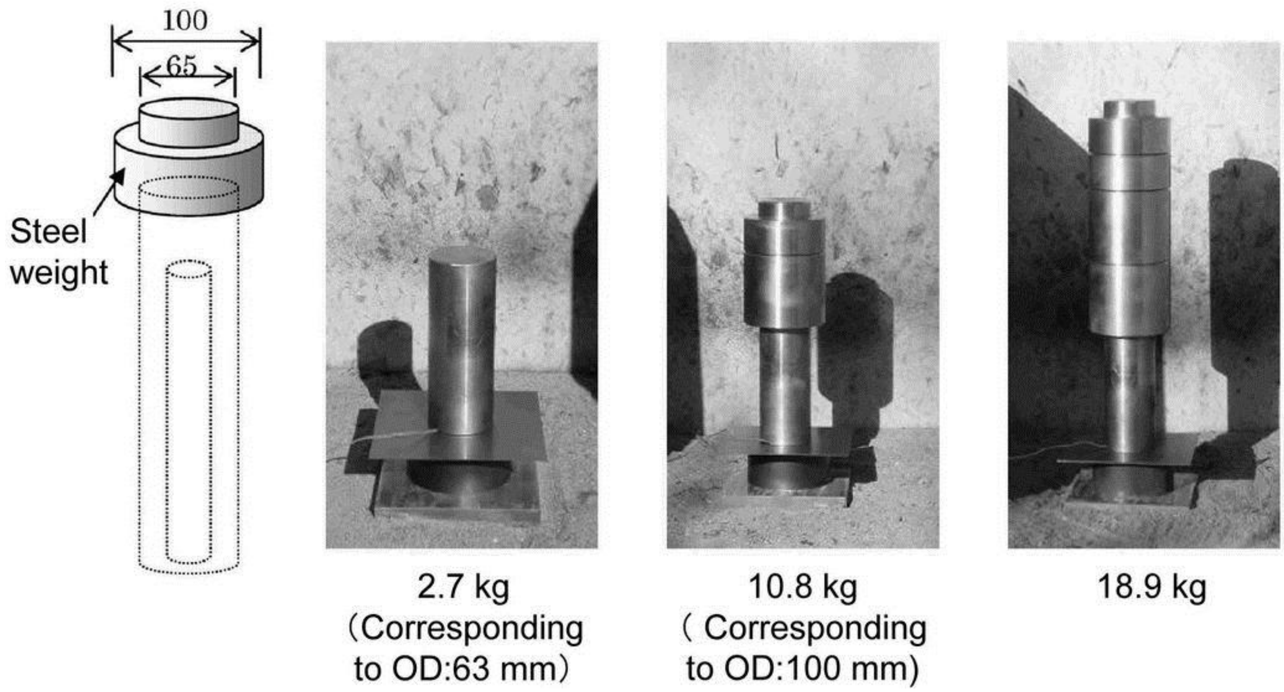


Fig. 3 Adjustment of the steel sleeve mass

Powder (mass = 25 g for all)				Sleeve mass & result					
No.	Type or purpose	Composition (wt. %)	Avg grain Size (mm)	2.7 kg		10.8 kg		18.9 kg	
				Number of tests	result	Number of tests	result	Number of tests	result
1	Black powder (WANO 5FA)	KNO_3 / C / S = 75.5 / 15.2 / 9.3	0.7	3	-	3	-	3	-
2	Black powder (WANO 4FA)	"	1.5	3	-				
3	Black powder (WANO 2FA)	"	3.8	3	-				
4	Black powder (Kayaku Japan.)	KNO_3 / Charcoal / S =75 / 15 / 10	1.1	3	-	3	-	3	-
5	Flash report	$Ba(NO_3)_2$ / MgAl / Al (FF) = 52 / 43 / 5	--	3	-				
6	Whistle	$KClO_4$ / Potassium Terebiphthalate = 71 / 29	--	1	+				
7	Red coloring	$KClO_4$ / Vinsole resin / Chlorinated rubber / C / $SrCO_3$ = 58 / 12 / 6 / 6 / 18	--	3	+				
8	Waterfall	$KClO_4$ / Al (FF) / Al (CF) = 53 / 16 / 31	--	1	+				

Al (FF):fine flake aluminum, Al (CF):coarse flake aluminum

Table 1 Tested firework compositions and results.

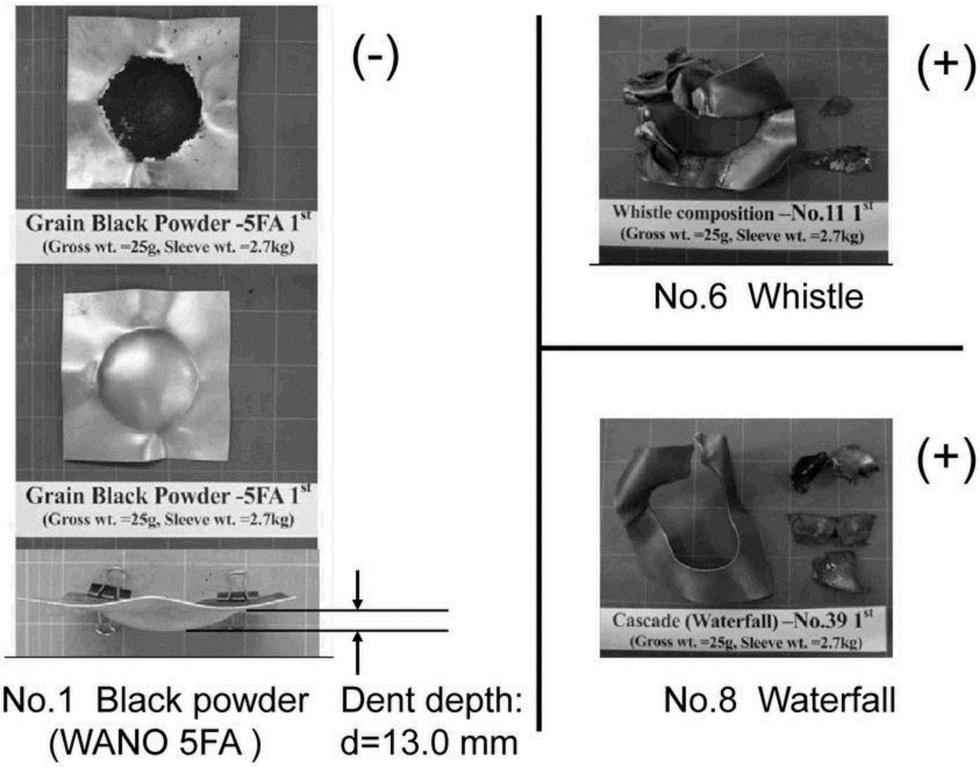


Fig. 4 Examples of witness plates after tests.

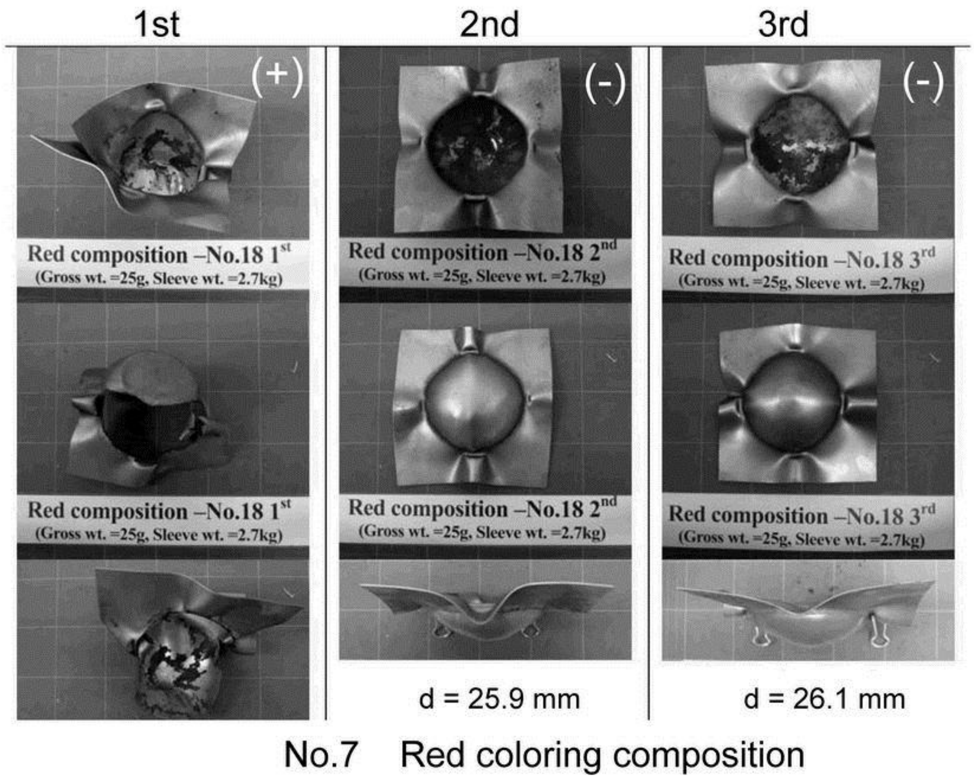


Fig. 5 Critical determination of red coloring composition.

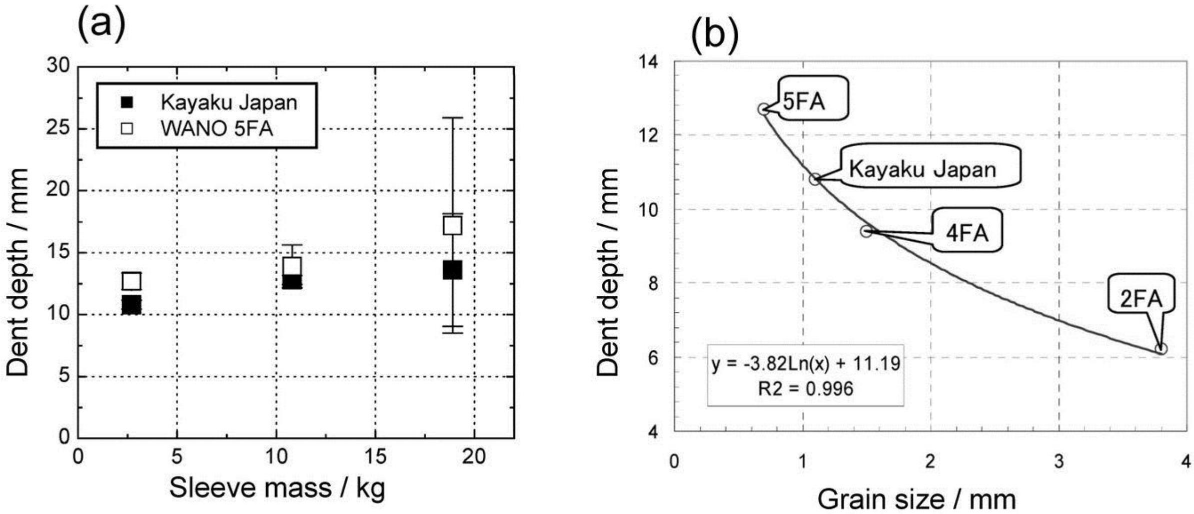
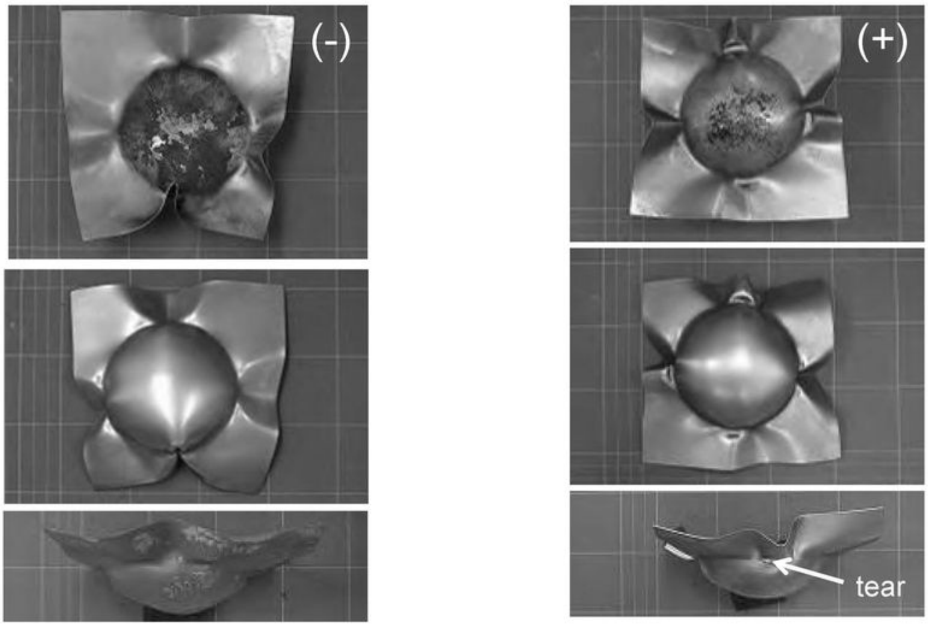


Fig.6 Dependencies of the dent depth on steel sleeve mass and grain size.



No.3 ($KClO_4$ / C)
Fine Powder
Powder mass 25 g

No.3 ($KClO_4$ / C)
Rice chaff core
Net explosive mass 25 g
(Powder mass 20.5 g)

Fig. 7 Result from previous experiment showing hazard enhancement by core material (see SCETDG/39/INF.22).