UN/SCETDG/33/INF.33

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-third session
Geneva, 30 June-9 July (a.m) 2008
Item 2 of the provisional agenda

EXPLOSIVES AND RELATED MATTERS

Definition of flash composition as part of the default fireworks classification table (2.1.3.5.5)

Transmitted by the expert from Germany

Proposal

The expert from Germany suggests reconsidering the decision taken during the thirtieth session of the sub-committee concerning the inclusion of a reference to the UN 2(c)(i)-test in Note 2 of section 2.1.3.5.5 (default fireworks classification table) and to abstain from including such a reference. (Decision recorded in document ST/SG/AC.10/C.3/60, item no. 50).

Reason

In Germany's view, the background for including such a test is not sufficiently developed at this moment. Test data has been produced since the time when the decision was taken on the basis of a first input (see ref. [1]). A number of details need clarification before any benefit can be expected from including a reference to this test.

Among the issues to be clarified are the questions, how to apply the referenced test in practice (by dismantling fireworks or by consulting a data base), how to handle the spread in data (see Annex, esp. comp-d and comp-e) due to combustion variations, and how to proceed in cases where the proposed 0.5 g of substance seem insufficient to achieve pressure values needed for the set analysis interval.

Detailed arguments

The following issues should be considered and resolved before including the changes as written in document ST/SG/AC.10/C.3/60, item no. 50 (report of the SCE-TDG):

1) General considerations

The UN model regulation represent a general fundament for the transport of dangerous goods and the classification of such goods. The scope of application is very comprehensive and provisions should be set out in an unambiguous way and should be straight-forward to implement.

It may occur that some effort is undertaken by interested parties to get around restrictive regulations. Especially in the sector of fireworks transport this became evident, when the default fireworks classification table was introduced with the aim to make dangerous goods classification easier. However, by establishing threshold values for certain characteristics, exactly these were used to adjust manufacture and/or documents to comply with required limits, or were used to escape unwished restrictions.

It should not be forgotten, that the default fireworks classification table was introduced to provisionally solve an urgent problem, but not to be the better approach to dangerous goods classification. It is felt by the experts of Germany, that with the amendment of Note 2 and the reference to the UN 2(c)(i)-test, (1) problems of enforcement and not of the code are tackled, (2) regulations are unnecessarily further complicated, and (3) problems of an improper approach are trying to be solved by patch-working the present situation.

The process of classifying fireworks by default and by paper work is a very rough tool. All experts should probably agree, that the prediction of the behaviour of packaged fireworks articles from knowledge about the contained substances is extremely difficult and only very coarsely possible.

2) Application conflict: default classification, by technical data or through further testing

The default fireworks classification table was introduced to provide a simpler tool than the full testing programme for the very busy field of fireworks transport. Since this table cannot take into account every detail of packaged fireworks, the classification result would often be more restrictive than what would have been obtained through testing.

A crucial aspect in this context, and in order to correctly identify potentially mass-explosive fireworks is the definition (and identification) of very energetic pyrotechnic compositions, which have been named "flash composition" for simplicity. A prominent example is the mixture of 70% $KClO_4$ with 30% Aluminium powder. If a certain proportion of flash composition is exceeded, the classification 1.1 shall be given. According to the proposed change to the model regulations reference to a test shall be made in order to identify compositions with comparable behaviour as the $KClO_4$/Al-mixture.

The reference to a test within the default fireworks classification table brings the question about, whether then a further test will be required or not, whether dismantelling of fireworks articles is necessary or not, or whether a table with known compositions will be easily accessible for consultation, or who shall be maintaining, updating, and amending such a source of information.

The proposed wording "... *unless [...] demonstrated to be more than 8 ms* ..." leaves it open, who has to attend to this duty.

3) Modification of 2(c)(i)-test, which then no more is a 2(c)(i)-test

The modification of the original UN 2(c)(i)-test to using only 0.5 g instead of 5 g has lead to the problem of reliable ignition of the test substance. This problem was recently tackled by research done in UK[2]. A firing plug with an altered design seems to improve reliable ignition considerably.

Data gained at the Federal Institute for Materials Research and Testing (BAM, Germany) included in the Annex to this paper show, that with the firing plug as defined for the UN 2(c)(i)-test and for 0.5 g of substance a notable variation in combustion behaviour is found (the primed cambric was omitted, just as in the work done in UK). In several cases the amount of 0.5 g of composition would not be sufficient to reach a pressure of 2070 kPa or to rupture the bursting disc. Varying the amount may be necessary depending on the situation.

Furthermore it should be noted, that "*Any pressure measuring device [...] capable of responding to rates of pressure rise of 690-2070 kPa in not more than 5 ms.*" is not sufficient anymore for the application of this test. BAM has replaced the device as described in the test manual by a piezo-electric pressure transducer (Kistler model 6215). According to personal communication, tests in UK employed a Kulite transducer instead of the normal one.

To the opinion of the experts of Germany it is problematic to still refer to the modified test as "the UN 2(c)(i)-test" when so many changes have been made or have become necessary.

4) More confidence-giving data needed

Data for pyrotechnic compositions gained with the (partly modified) UN 2(c)(i) test were presented for the first time during the thirtieth session of the SCETDG[1] and later during the 2007 Fireworks Symposium in Montreal[2].

In the above mentioned investigations only the resulting rise times for the pressure interval 690 -2070 kPa have been reported and unfortunately no traces were shown. In the Annex traces of data recorded recently at BAM are shown. Having the traces accessible together with the resulting figures is very revealing and leads to the following observations (compare with Annex):

- The pressure generated from the combustion of 0.5 g of pyrotechnic composition lay in the range of 1-4 MPa, in the case of black-powders also below 1 MPa.
- While some traces are cut off at the moment where the bursting disc broke, in some other cases the disc was not removed or the pressure even did not rise to the value of 2.07 MPa,

- The fixed pressure interval of 690 -2070 kPa probes different phases of the combustion process for different substances, i. e. the given interval could correspond to the initial phase, the middle phase, or the combustion could not encompass the entire interval.

- Influence of grain size is expected to be significant. No detailed investigation is available at present relating results of the UN 2(c)(i)-test to grain-size.

A consolidated variant of the UN 2(c)(i)-test seems to be very promising for a scientific study of different pyrotechnic compositions. A great advantage of such a test is its simplicity and the fact that during a short period of time many tests can be performed. However, there are still some technical issues to be resolved, and for each test series done the experimental conditions have to be described in detail, to make data comparable to other investigations.

The Federal Institute for Materials Research and Testing (BAM) of Germany is keen to continue the work already started.

References

[1] K A Nash and M Marriott, *Time/pressure Test for Pyrotechnic Compositions*, Proceedings of the Tenth International Symposium on Fireworks, 2007, Montreal Canada, pp. 137-154

[2] K Nash and M Davies, *Results of time/pressure test carried out at Health and Safety Laboratory (HSL)*, Annex to document ST/SG/AC.10/C.3/2006/84

Annex

Test results with a modified UN 2(c)(i)-test on various pyrotechnic compositions

1) Description of the experimental set-up

The tests were performed with a standard UN 2(c)(i)-test apparatus, however with a more rapidly responding pressure transducer (Kistler model 6215). For the ignition the primed cambric was omitted. An electric igniter was used and mounted in such a way, that the cables were bent back with the fusehead pointing to the base of the volume. Only 0.5 g (- 0g, +0.05 g) of substance were used. The substance covered the base of the volume and the fusehead would be not more than 1 mm away from the pyrotechnic composition.

A thicker bursting disc (0.5 mm) was used in order to be able to study pressures to slightly higher values. It turned out, however, that the maximum pressure achieved before the bursting disc ruptured was not notably higher than with the standard bursting disc of 0.2 mm. The igniter by itself would produce a peak pressure of around 5 kPa, where the bursting disc would not break.

2) Pyrotechnic compositions investigated

Traces of six pyrotechnic compositions are shown here. In the following their composition and origin are explained:

comp-a) CHAF waterfall composition, where the container trial led to a mass explosion not found in other tests; 50% $KClO_4$, 43% Al and Magnalium, 7% S; sample taken from dismantled fireworks.

comp-b) simplified waterfall composition; 50% $KClO_4$, 50% Al powder; sample produced by mixing of chemicals as used in fireworks manufacture.

comp-c) modified black-powder as found in some of the CHAF fireworks; 72% $KClO_4$, 22% S, 6% C; sample mixed from powdered chemicals as used in fireworks manufacture.

comp-d) red star composition; 50% $KClO_4$, 20% Magnalium, 15% $Sr(NO_3)_2$, 15% Accaroides; sample mixed from powdered chemicals as used in fireworks manufacture.

comp-e) black-powder + Titanium mixture from a fire-cracker prototype (manufacturer and composition information undisclosed).

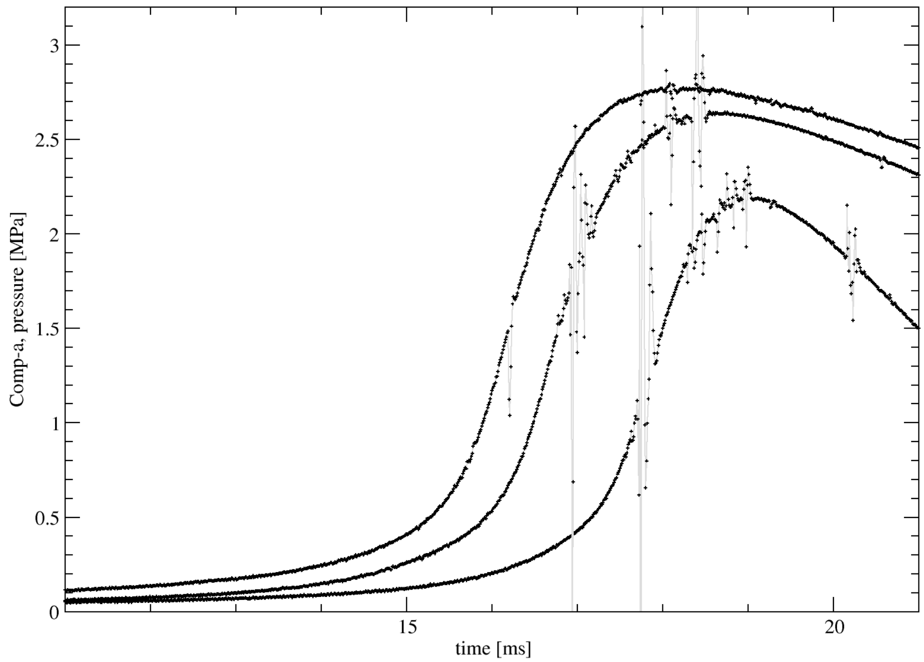
comp-f) black-powder from a commercial fire-cracker (manufacturer undisclosed); 63% KNO_3, 20% S, 17% C; sample taken from dismantelling the item, traces of clay in the sample could not be avoided.

3) Results and traces

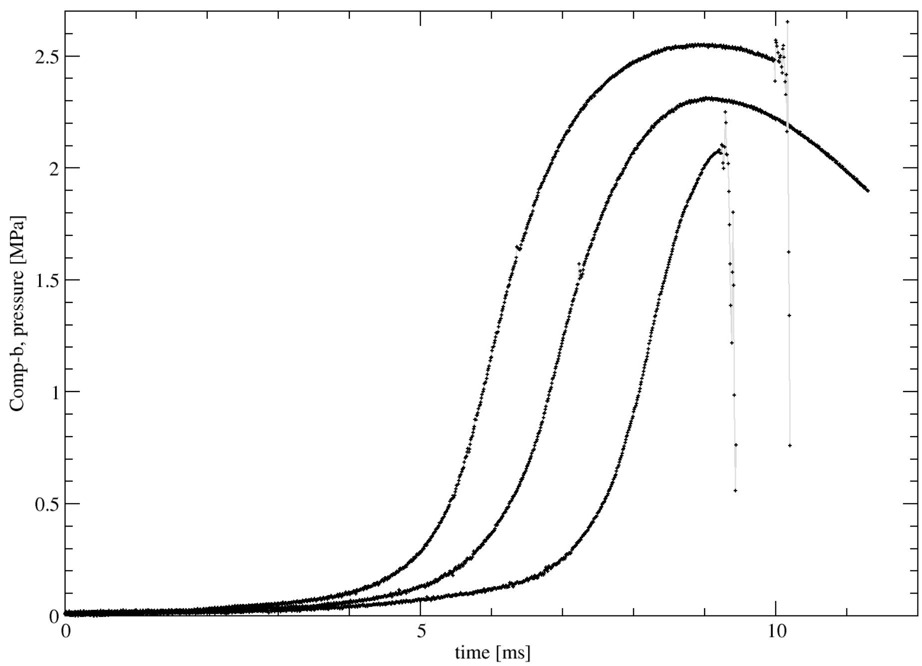
It was found that ignition even without the primed cambric was always fully reliable. Except for the last composition, three traces have been recorded each and are shown in the following diagrams. The variations between traces have no obvious cause and represent the statistical spread. There was no systematic development recognisable and the sequence of traces was any random combination of highest, middle and lower trace. For the purpose of generating graphs the traces have been moved along the time-axis in such a way, that they do not intersect.

The time interval between 690 kPa and 2070 kPa is referenced through t_{UN2c}.

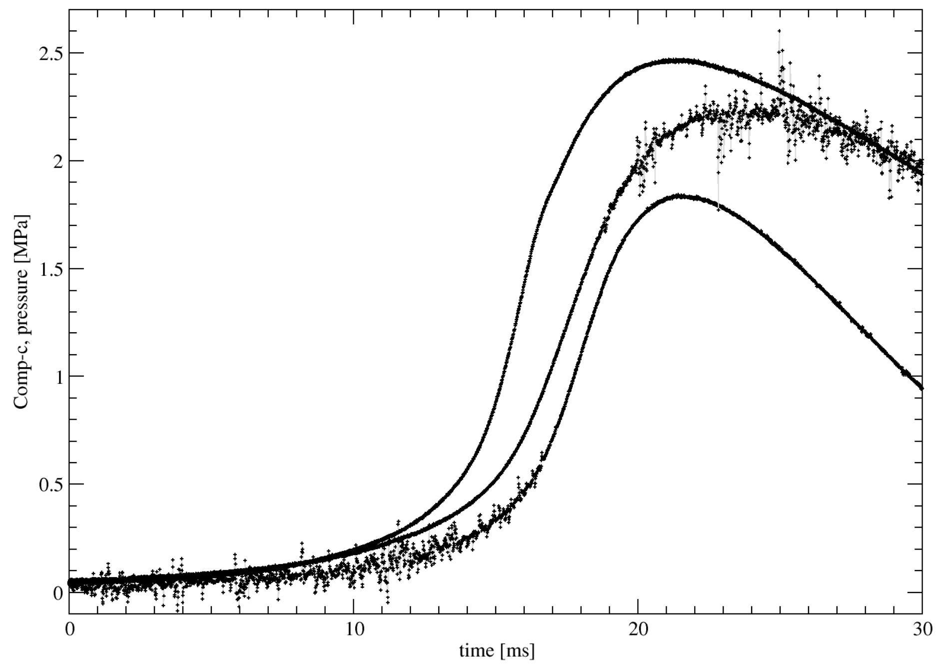
In the case of comp-d (red star composition) and comp-e (black-powder with Titanium) the difficult case occurs, where values above and below the set 8 ms appear to be both valid results. The combustion behaviour plays an important role.



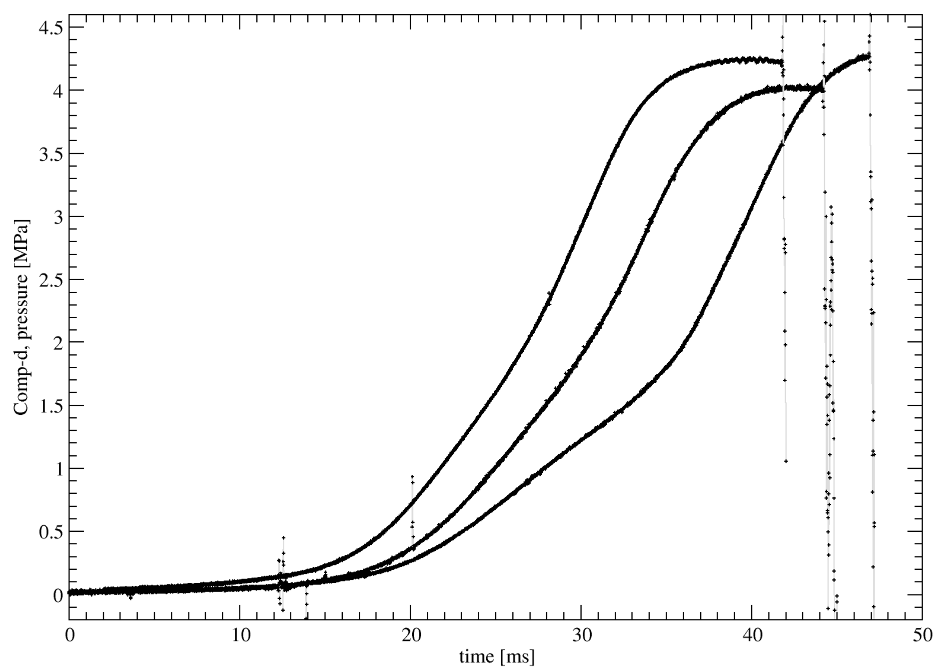
comp-a: Values for t_{UN2c} are 0.95 ms, 0.95 ms, 1.15 ms



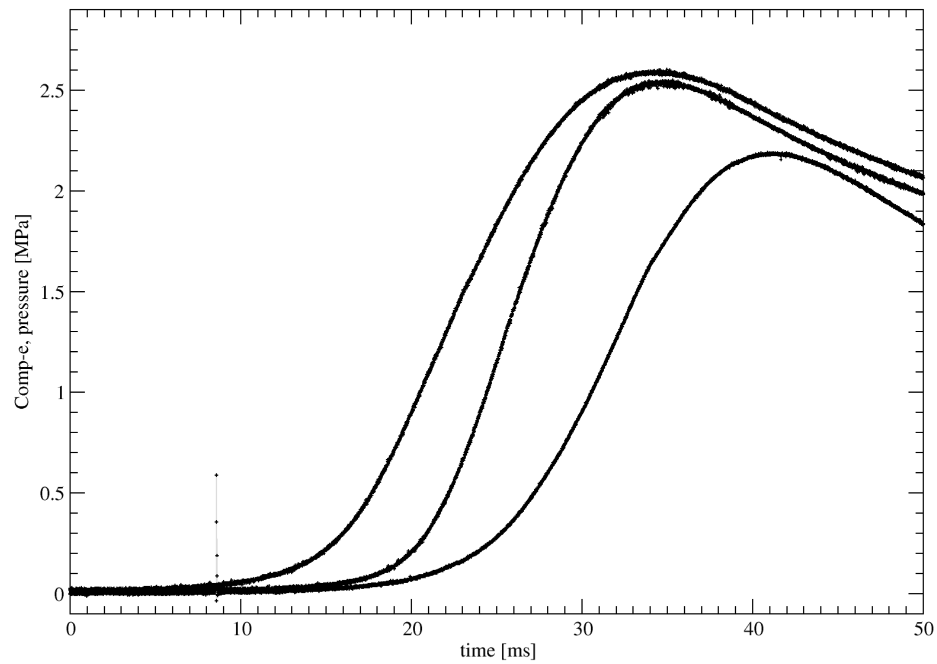
comp-b: Values for t_{UN2c} are 1.29 ms, 1.47 ms, 1.38 ms



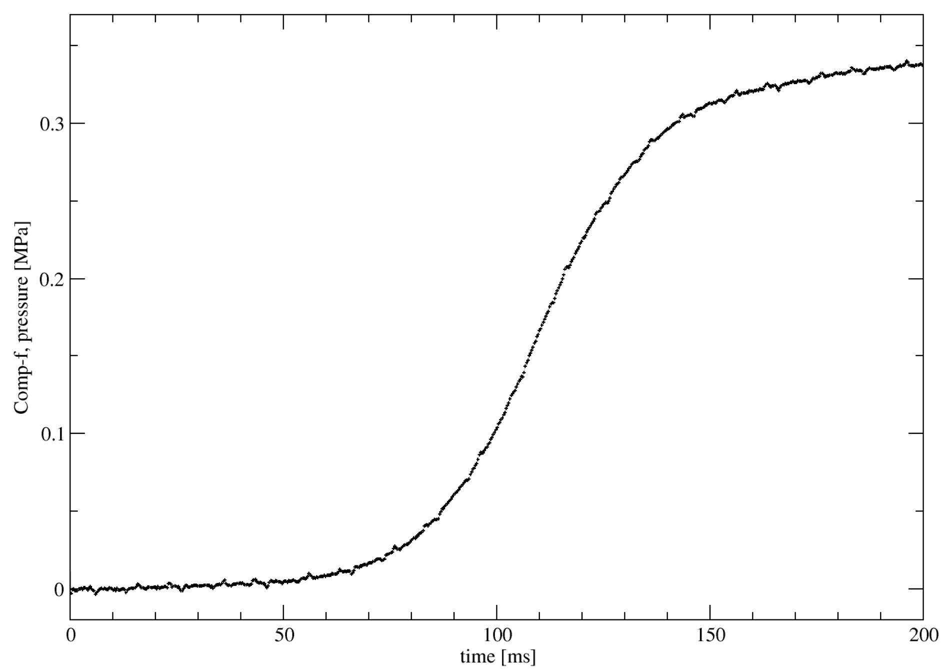
comp-c: Values for t_{UN2c} are 3.2 ms, 4.7 ms, n/a



comp-d: Values for t_{UN2c} are 7.2 ms, 7.9 ms, 11.5 ms



comp-e: Values for t_{UN2c} are 7.6 ms, 5.8 ms, 9.1 ms



comp-f: Analysis of rise-time t_{UN2c} is not possible since pressures were not achieved. More substance may be required in the test volume.