

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

Thirtieth session
Geneva, 4-12 (a.m.) December 2006
Item 2(a) of the provisional agenda

PROPOSALS OF AMENDMENTS TO THE RECOMMENDATIONS ON THE TRANSPORT OF DANGEROUS GOODS

Model Regulations on the Transport of Dangerous Goods

Comments on ST/SG/AC.10/C.3/2006/84 and INF.3 Note 2 to 2.1.3.5.5 Firework classification

Transmitted by the Expert from the Netherlands

Introduction

The Expert from the Netherlands welcomes the proposal from the United Kingdom to replace the current Note 2 to 2.1.3.5.5 with a performance based approach to define flash powders. The current definition, based on chemical composition and intended use of the composition, leaves too many loopholes. New, and sometimes dangerous compositions, are currently encountered in fireworks in an attempt to circumvent the flash powder definition and thus a more stringent default classification. Examples of these compositions are black powder where the potassium nitrate has been (sometimes: partly) replaced by potassium perchlorate; black powder enriched with antimony sulphide and nitrocellulose based compositions.

Using a performance based approach would screen out hazardous and too energetic compositions, based on test results.

The Time/pressure test is an existing test method from the UN Manual of Tests and Criteria and might be applied with minor changes.

It should be stressed that whether or not a composition is considered a flash powder may have serious consequences for the classification of the article in which the composition is contained. The test results should therefore be reliable and/ or err on the safe side.

Analysis of the data in INF.3

A careful study of the data supplied in INF.3 resulted in the following observations.

Standard deviation

The standard deviation of the data is very large, ranging from 8 to 60% for 0.5 g samples. For 1.0 g samples the situation is comparable (9 to 82%).

This is likely be due to the physical properties of the powders. When large particles are present in the mixtures the overall composition of a 0.5 g sample may differ considerably in either of the three tests. With these standard deviations it is not unlikely to get false positives or false negatives.

The standard deviation might be improved by using larger sample sizes. The results of the experiments with increasing amounts of gold sparkler powder show a decreasing tendency for the standard deviation. With larger samples (up to 5 g) the SD drops to acceptable values of about 5%.

However, using larger a sample size would lead to significantly shorter pressure rise times. This may give difficulties in setting a meaningful criterion. These shorter pressure rise times may also give conflicts with the accuracy of the measurement equipment currently in use all over the world.

The UN Manual states in the description of the TPT: *“Any pressure-measuring device may be used provided that it is not affected by the hot gases or decomposition products and is capable of responding to rates of pressure rise of 690-2070 kPa in not more than 5 ms.”* and one has to assume that a number of test laboratories might not be capable of measuring the rise times with an accuracy of , for instance, one tenth of a millisecond. It is concluded that using larger sample sizes may result in exchanging the large SD for a large uncertainty in pressure rise time.

The Expert from the Netherlands believes that the problem of the large standard deviation can be addressed by requiring more tests per substance. For instance six test runs instead of the current three. This will reduce the possibility for false results substantially.

Physical form of the sample

Another way of obtaining more homogeneous samples of 0.5 g is to grind the compositions to be tested. Changing the particle size often has a significant effect on the burning behaviour and much more compositions would fail any proposed criterion. When tested in this form, the performance as measured in the TPT has no relation anymore with the performance as obtained in the article and thus no relation anymore with the performance in classification tests.

The Expert from the Netherlands is of the opinion that the samples should be tested in the physical form as present in the article as much as possible. This could be achieved by prescribing that consolidated charges should be tested in the form of discs or chips.

The measured pressure rise time should be corrected for the actual mass used using a simple linear relation: measured rise time * (0.5/actual sample mass)

Comparison with Series 6 results

In a number of cases, the fireworks articles containing the compositions mentioned in INF.3 have been subjected to Test Series 6. This allows for a comparison of the proposed criterion (4 ms for 0.5 g samples) (rise times shorter than 4 ms would indicate amounts of flash powder in the articles of over 25% with a corresponding default classification) with the classification actually derived from Series 6.

- The potassium perchlorate based ‘black powders’ from the WP9 150 mm star burst shell (experiments C and E in INF.3) have a minimum rise time of 7.3 and 8.3 ms respectively. When corrected for the actual mass used in the test, these values are 7.0 and 7.9 ms. This means that the compositions are not considered flash powder, the amount of flash powder is

therefore less than 25% and a 1.3G default classification would result. However, the UN 6(b) test resulted in a mass explosion and thus a 1.1G classification.

- Furthermore it was noted that in some cases the Time/pressure tests were done with the pyrotechnic filling in the powdered form whilst in the article the filling is consolidated. Testing the sample in a consolidated form may have resulted in a much slower pressure rise time, the substance may have been judged as not a flash powder and the default classification would then match the experimentally derived classification.
- Only for the WP9 unsticked rocket (experiment AB in INF.3) the results of the Time/pressure test and Test Series 6 agree on a 1.1G classification.

It is concluded that the proposed criterion (and the physical form in which some samples were tested) should be adjusted to better match with the experimentally derived classification.

The proposals listed below are intended to match the classification based on the default list (in the cases where the amount of flash powder is the determining factor) with the experimentally derived classification.

The 4 ms criterion

The proposed criterion of 4 ms seems to be chosen rather randomly. Looking at the results provided in INF.3 and the actually known classification of a number of the articles involved a criterion of 8 ms may be more appropriate.

Conclusions

Using a performance based approach to decide whether a certain composition is considered a flash powder has many advantages over the current definition given in Note 2 to 2.1.3.5.5.

The Expert from the Netherlands has identified a number of issues in the proposal from the UK that can be modified by the following proposals.

Proposal

The Expert from the Netherlands proposes to accept the proposal listed in ST/SG/AC.10/C.3/2006/84 with the following amendments.

1. The criterion should be changed to 8 ms.

For the time pressure test:

1. A number of six tests should be performed with each composition.
2. The substances should be tested in the physical form as present in the article as much as possible. This can be achieved by prescribing that consolidated charges should be tested in the form of discs or chips.
3. The measured pressure rise time should be corrected for the actual mass used using a simple linear relation: measured rise time * (0.5/actual sample mass)

These amendments could be incorporated in the note itself or preferably in the Test Manual section 12.6 in the description of the Test Series 2(c)(i) “Time pressure test”. This could be discussed by the Sub-Committee.

Experts are encouraged to use the proposed test method and to share the data with the Sub-Committee to possibly further improve the test method.
