# Defining Flash Compositions: Modifications to UN Time/ Pressure Test

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**Abstract:** *The Time/Pressure Test from the UN Manual of Tests and Criteria has been modified to define flash compositions in the default classification lists for fireworks in the UN Model Regulations. This modified test is known as the HSL flash composition test. This paper summarises the history of this change from a composition-based to a performance-based definition and describes more recent work to improve the method when testing pyrotechnic compositions. A modified test method has been developed with a new firing plug that has been designed to improve reliability and reproducibility by changing the sample geometry and removing the primed cambric. The system has been manufactured and tested and was presented as a proposal to the UN Subcommittee of Experts on the Transport of Dangerous Goods as an additional test method for the Manual of Test and Criteria specifically for defining hazardous compositions with flash-like properties. The method and apparatus is now incorporated into the UN scheme for the classification of dangerous goods, specifically for fireworks.*

**Keywords**: *Flash Composition, UN Default List, Time/Pressure Test.*

## Introduction

There are numerous instances of fireworks being involved in major incidents that have resulted in damage to storage premises, homes, ships and manufacturing sites. Probably the worst such incident was that at Enschede in the Netherlands which occurred in May 2000.[1] This incident was one of the main driving forces for a European Project entitled "Quantification and Control of the Hazards Associated with the transport and storage of Fireworks" with the acronym 'CHAF' for short.[2] The project provided a number of results, ranging from small-scale (single and multiple fireworks),[3,4] medium-scale (transport package(s))[5–7] and large-scale (ISO container).[8,9] The project culminated in an international conference[10] organised by the International Symposium on Fireworks, attended by world pyrotechnic experts. Discussion during the conference suggested that one major omission was work at the composition level and that this could lead to a more cost effective means of testing potentially hazardous fireworks.[11]

Traditionally, explosives undergo a series of tests from the UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria[12] to classify them as UN hazard division 1 substances and articles, and to assess their hazard in transport. This transport classification is often used as a guide to assess hazard in storage without additional experimentation. For pyrotechnic items, the defining tests are series 6, which comprises tests under confinement and in a fire. One of the firework types tested in the CHAF project was subjected to the standard UN series 6 tests, giving results typical of a UN hazard division 1.3 material; that is a major fireball was produced in the UN series 6(c) test and it did not give a mass explosion in the 6(a) or (b) test. However, when the fireworks were tested in large-scale trials undertaken by the CHAF project, a large mass explosion took place in an ISO container full with these fireworks.[13] The CHAF project undertook testing on transport packages of fireworks in a medium sized pressure vessel. This approach differentiated between the fireworks that mass exploded in the large-scale trials and those that did not.[7]

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The UN Recommendations on the Transport of Dangerous Goods – Model Regulations has developed a default classification scheme for the classification of fireworks.[14] This "default list" uses the amount (either absolute amount or percentage) of flash composition within fireworks or components of the firework. Flash composition was defined in the Model Regulations, Editions 13 and 14 as a mixture of oxidiser and powdered metal. However, this definition did not capture all mixtures being employed to function as a flash composition and a performance-based test was thought to offer a more objective means of assessing the potential hazard. The UN Manual of Tests and Criteria does contain a test that can offer an objective means of determining differences between flash, flash-like and other pyrotechnic compositions, the Time/Pressure Test. This paper outlines the main features of the existing test and describes the work undertaken to develop and improve the test into a practical means of quantitatively testing fireworks compositions to be able to differentiate between highly hazardous and those less so.

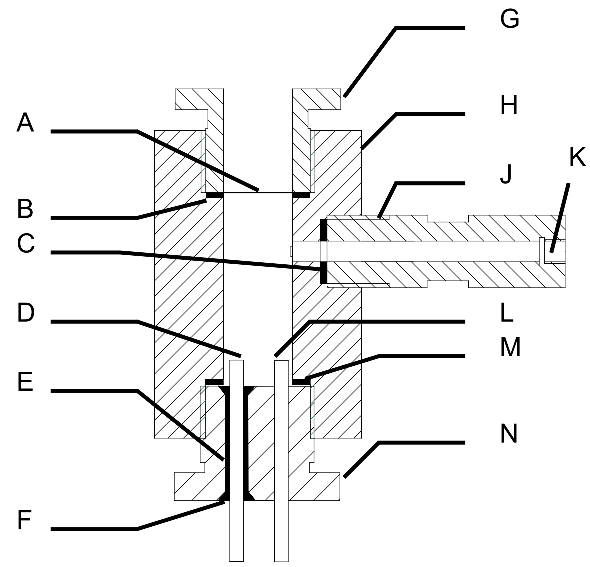


**Figure 1.** *Time/pressure test equipment. A: bursting disc; B: soft lead washer; C: copper washer; D: insulated electrode; E: insulation; F: steel cone; G: bursting disc retaining plug; H: pressure vessel body; J: side arm; K: pressure transducer; L: earthed electrode; M: soft lead washer; N: firing plug.*

## The UN test method

The Time/Pressure Test is part of the United Nations scheme for the assessment of the hazard during transport of dangerous goods and is found within the United Nations Transport of Dangerous Goods, Manual of Tests and Criteria.[12] The test method is used in Test Series 1 to determine if a substance has explosive properties, and Test Series 2 to determine how explosive a substance is. The test methods are Test 1(c)(i) and Test 2(c)(i) respectively.

The method as described in the UN test normally uses 5 g of substance, unless the material is suspected of being particularly energetic, when the sample size may be reduced to as little as 0.5 g. The ignition system in use at HSL employs an electric fuse head attached to a firing plug, with a 13 × 13 mm piece of primed cambric tied around the fuse head. A diagram of the original apparatus is shown in Figure 1.

A 5 g sample of substance is subjected to an incendive flame from the ignition source in a pressure vessel fitted with a pressure recording device and a bursting disc. The vessel has a volume of 20 ml and the bursting disc is designed to burst at approximately 2200 kPa. The test substance is regarded as capable of presenting a risk of an explosive deflagration if the time taken for the pressure to rise from 690 to 2070 kPa is less than 30 milliseconds. The procedure is performed three times using the same mass of sample, and due to the variability, the result is the fastest time taken for the pressure inside the vessel to rise from 690 kPa to 2070 kPa. The UN Manual of Tests and Criteria does not state any limits of repeatability or reproducibility. In the standard test, HSL uses a slightly modified version of the UN firing plug, with threaded bars with small nuts to secure the fuse head rather than soldering the fuse head on to points located on the firing plug. This system was developed after a number of accidental ignitions of the fuse head during soldering. The bar and nuts also eliminate the need for removing all of the insulation on the Testex fuse head.

**Summary of reported data on pyrotechnic samples in the unmodified Time/Pressure Test**

Pyrotechnic compositions from fireworks have been tested in the Time/Pressure Test, following the original method with primed cambric/Testex fuse as the initiating system and 0.5–5.0 g of sample. These results have been reported in a paper to the UN[15] and in a report for HSE.[16] These tests showed that different types of pyrotechnic composition have markedly different rise times in the existing test, and showed promise as a test method to distinguish between the sample types. A summary of the results carried out on 1 g samples is provided in Table 1.

Tests to show reproducibility of result using the existing primed cambric/fuse head initiation were conducted and these proved to be disappointing with some large variation in results. This is illustrated in the cluster analysis, Figure 2. The issue of the variation in rise time was raised and discussed at the UN committee on the transport of dangerous goods.[19–23] It was decided that a modification to the initiation system was desirable to reduce this variation, the rationale being that with a small sample, the pyrotechnic material may not be in contact with the primed cambric. A large proportion of the rise time was thought to be due to the variation in time taken for the burning cambric to fall onto the sample and initiate sufficient of the pyrotechnic surface to achieve the upper pressure (2070 kPa). Thus, a more consistent method of initiation was required.

## Modification of the test apparatus

Primed cambric is used as a secondary source of ignition for substances that may be difficult to ignite in the original UN Time/Pressure Test method (1(c)(i) & 2(c)(i)). With a 5 g sample this will be in good contact with the test sample, however with the smaller sample used for pyrotechnic materials this is not necessarily the case. In simple laboratory tests with pyrotechnic compositions at HSL it was shown that the compositions would ignite from a single electric fuse head without the primed cambric. In removing the primed cambric, it is necessary to ensure that the composition to be tested is close to the fuse head and directly in the path of a spark. Additionally, the sample must not be "blown out" and dispersed by the small explosion of the initiating electric fuse head. Thus, the fuse head needed to be above the sample but not in direct contact.

Several efforts were made to retrofit the UN test equipment with sample holders to hold the small sample mass in contact with the fuse head, or increasing the size of the chamber to allow larger samples to be tested. However, none of these

**Table 1.** *Time/pressure rise times for 1 g pyrotechnic mixtures taken from fireworks.*

| Composition | Physical form | Source[a] | Minimum rise time (ms) | Mean rise time (ms) | Standard deviation |
|---|---|---|---|---|---|
| Black powder lift charge | Granular | WP9, 150 mm star burst shell | 6.1 | 6.7 | 0.9 |
| Black powder burst charge | Granular | WP9, 150 mm star burst shell | 5.1 | 6.0 | 0.9 |
| Black powder from rocket motor | Powder | WP9, unsticked rocket | 8.6 | 12.2 | 3.1 |
| Flash composition | Powder | WP9, unsticked rocket | <1 | <1 | — |
| Waterfall composition | Powder | WP9 waterfall | <1 | <1 | — |
| Waterfall composition | Powder | WP6 waterfall | 4.8 | 6.4 | 1.7 |
| Star fragments | Chips | WP9, 150 mm star burst shell | 8.2 | 9.2 | 1.5 |
| Whistle composition[b] | Powder | Wheel driver unit | 1.7 | 1.9 | 0.3 |

[a] WP6 and WP9 are work packages in the CHAF project. Details of the materials can be found in the work package reports.[17,18] [b] Potassium perchlorate/sodium benzoate.

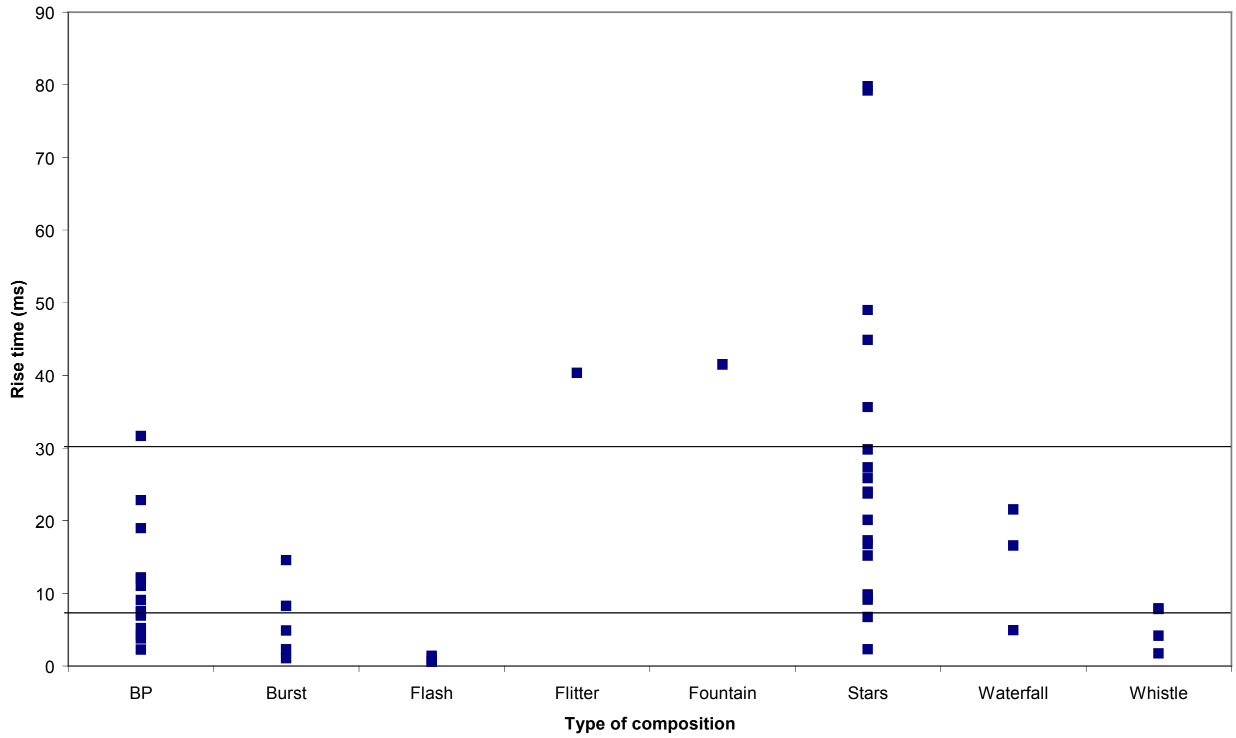


**Figure 2.** *Cluster analysis of rise time results***.**

proved successful, either due to repeatability, time or cost issues and a revised "cone in plug" design was adopted.

The new firing plug with a central recess to hold the sample, as shown in Figure 3, was manufactured using mild steel, with Tufnol™ as the insulating material. This new "cone in plug" firing system accommodated an inverted Vulcan™ fuse head with a length of insulated wire in the chamber as shown in Figure 4. Other suitable electric fuse heads could be used if they had similar igniting power. The cone was 1 mm narrower than the internal diameter of the time/pressure vessel to allow the plug to fit into the vessel.

The non-insulated section of each lead wire from the fuse head had to be accurately measured on the 'insulated' terminal to prevent short circuits. The leads from the fuse head are twisted just below the foils to strengthen the fuse head, and to avoid breaking the soldered connection on the foils.

## Results

The 'cone in plug' firing plug was validated by comparing results obtained from the original test

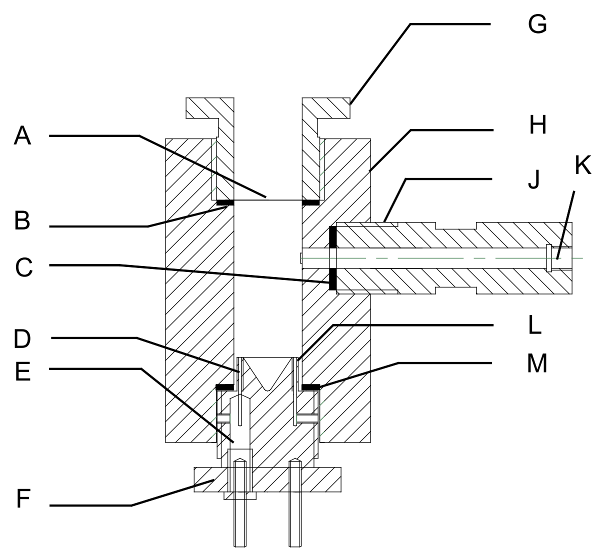


**Figure 3.** *"Cone in plug" time/pressure apparatus***.**
*A: bursting disc; B: soft lead washer; C: copper washer; D: insulated electrode; E: insulation; F: firing plug; G: bursting disc retaining plug; H: pressure vessel body; J: side arm; K: pressure transducer; L: earthed electrode; M: soft lead washer.*

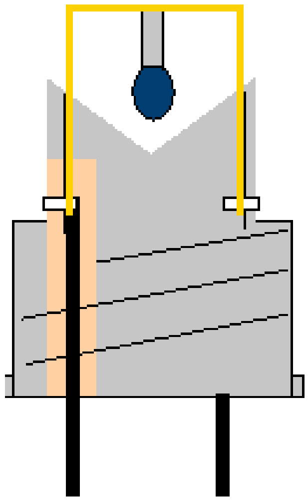

**Figure 4.** *Location of Vulcan fuse head in the "cone in plug".*

equipment using the original test method (0.5 g of sample with 3 repeats (unless stated otherwise) with those from the "cone in plug" apparatus. Two types of commercial flash powder were tested along with a commercial black powder. The results obtained are detailed in Table 2. Composition data are given in Table 3.

Additional validation data has been obtained from the black powder sample used. The results are tabulated in Table 4. Since validating the modified apparatus additional samples have been tested. Specimen results are presented in Table 5.

## Discussion

### Original UN series 1 and 2 apparatus

The initial attempts to investigate pyrotechnic compositions in the UN Series 1(c) and 2(c) apparatus using primed cambric and an electric fuse, were designed to investigate material that may have energetic properties. That is, it is intended to be part of the preliminary tests to ascertain properties below the severity of explosives but none the less posing hazard in transport. It is intended that a 5 g sample will normally be used for the test but does allow for lower sample size down to 0.5 g. With many pyrotechnic material (which do have explosive properties) the 5 g sample was found to be excessive for the test to differentiate between samples, the upper burst pressure being achieved rapidly for many different samples. Thus lesser amounts of pyrotechnic were tried. Within the existing UN series 1 and 2 apparatus 1 g samples were the lowest practical amount to ensure reliable ignition. These results (Table 1) showed differentiation between different pyrotechnic types but with a relatively high variation as measured in the standard deviation. Typically this ranged from 10 to 25% of the mean. There were additional difficulties in ignition with some materials that may be caused by the lack of direct contact of the pyrotechnic with the primed cambric in the ignition system. This variation in result and problems with initiation led to the development of a different plug body, the main aims being to provide reliable initiation and better reproducibility.

### Cone in plug development

The cone in plug assembly has developed through a number of modifications; initially, placing a cone within the existing base plug, through to redesign and production of an integral cone. All designs require that there be an insulated path to allow a circuit to the electric fuse to be formed. This has presented a number of technical challenges. The corrosive nature of pyrotechnic compositions and their products has caused difficulties with the grub screws used to form the circuit. Ceramic grub screws were sourced for test to ascertain if they overcome this difficulty. While they would be resistant to corrosion they were found to be too brittle and broke too readily when being inserted or removed. Currently a plastic insert attached to the end of the metal grub screw is being trialled to see if it reduces corrosion of the metal grub screw. This has been found to be successful and is now standard on the apparatus used at HSL.

The use of an inverted conical cup to hold the pyrotechnic has ensured that there is a large pyrotechnic surface close to the initiating fuse. This has given more reliable initiation of the pyrotechnic compared with the original UN series 1 and 2 plug.

Reproducibility of result has also been improved. Table 2 shows all samples having a lesser standard deviation, both in absolute value and as a percentage of the of the mean value. Typically this has reduced from greater than 20% to less than 15% of mean.

**Table 2.** *Comparison of original test method and new firing plug – 0.5 g samples.*

| Composition | Original method | | Cone in plug method | |
|---|---|---|---|---|
| | Mean rise time (ms) | Standard deviation | Mean rise time (ms) | Standard deviation |
| Flash powder 1 (5 repeats) | 0.78 | 0.14 | 0.70 | 0.10 |
| Flash powder 1 (second set) | 0.74 | 0.17 | 0.84 | 0.08 |
| Flash powder 2 | 3.11 | 3.31 | 1.51 | 0.47 |
| Black powder (10 repeats) | 5.10 | 1.18 | 4.98 | 0.65 |

**Table 3.** *Composition data.*

| Composition | Composition (% mass) | | | | | | |
|---|---|---|---|---|---|---|---|
| | Potassium perchlorate | Magnalium | Sulphur | Aluminium | Carbon | Potassium nitrate | Titanium |
| Flash powder 1 | 45 | 22 | 11 | 22 | — | — | — |
| Flash powder 2 | 60 | — | — | 25 | — | — | 15 |
| Henry Crank fine black powder | — | — | 10.4 | — | 15.6 | 74.0 | |

## Validation testing

The validation results for 0.5 g samples in Table 2 show reduced standard deviation compared with the original apparatus utilising primed cambric. The original large variation in results was a major criticism of the test at the UN[19–23] and was the major driver for the development of the current test apparatus. “Flash powder 2” appears to have had initiation difficulties when using the original plug system. This may be due to a higher ignition temperature of the material caused by the lack of sulphur (see Table 3 for composition data). Certainly, with the plug in cone system more reliable ignition of this sample was achieved. With all the materials tested in this comparative investigation of the two plugs (original vs. modified) the cone in plug reduced the measured standard deviation in rise time.

## Reproducibility testing

The UN Default table permits the use of black powder in some fireworks, e.g. rocket burst charges for a UN HD 1.4G classification. HSE/HSL had originally proposed a ≥4 ms rise time in the modified cone in plug apparatus as the differentiation point between materials that were considered to be as hazardous as flash and those that were considered less hazardous than flash. A commercial black powder (Henry Crank fine black powder) was used as the “standard” material for investigating this aspect. A series of trials over a 6–7 week period (Table 4) was used to ascertain reproducibility. In general, results for this black powder were in the range 4–6 ms with the occasional outlier. Standard deviation was, as expected, found to be less for sets of 10 than for sets of 3, however, sets of 3 are more practical and

**Table 4.** *Black powder study.*

| Date | Minimum rise time(ms) | Average rise time (ms) | Standard deviation | No. of tests |
|---|---|---|---|---|
| 08/07/2009 | 4.57 | 5.46 | 0.63 | 10 |
| 23/07/09–28/07/09 | 4.38 | 6.18 | 0.81 | 10 |
| 31/07/2009 | 4.22 | 5.62 | 1.26 | 3 |
| 25/08/2009 | 3.63 | 4.98 | 1.23 | 3 |

**Table 5.** *Sample testing results.*

| Sample/description | Min rise time (ms) | Average rise time (ms) |
|---|---|---|
| Potassium perchlorate fireworks report flash composition | <1.0 | <1.0 |
| Potassium perchlorate theatrical flash composition | 2.7–4.2 | 2.8–5.3 |
| Potassium nitrate theatrical flash composition | 3.2 | 4.6 |
| Strontium nitrate theatrical flash composition | 2.7 | 3.0 |
| Meal powder theatrical gerb composition | 2.8–12.1 | 6.7–16.4 |
| Rocket motor black powder[a] | 8.6 | 12.2 |
| Black powder[a] burst charge | 5.1–6.1 | 6.0–6.7 |
| Potassium perchlorate enhanced black powder | 2.44–3.46 | 2.69–3.35 |
| Fireworks whistle composition | 1.7 | 1.9 |

[a] Black powder as defined: "a mixture of potassium nitrate and carbon with or without sulphur".

give sufficient reproducibility to be a practical test method.

**Day to day testing**

Numerous different pyrotechnic compositions have now been tested and the results summarised in Table 5. Some of this work has been undertaken as part of an HSE programme for compliance with the UN default classification scheme[24] and some in an ongoing programme on the HSL flash composition test. True black powders (potassium nitrate, carbon and sulphur) from fireworks have generated rise times greater than 4 ms and are generally well differentiated from true flash (metal/oxidiser) which have generated rise times. Whistle and potassium perchlorate enhanced black powders have been found to consistently have a rise time less than 4 ms. Theatrical gerb compositions based on meal powders have shown the largest variation in rise time. This is most likely due to the wide range of size in the metal powders depending on the effect desired in the devices. It could be argued that 4 ms is the best rise time to differentiate between the more hazardous pyrotechnic compositions and those deemed to pose a lesser hazard.

## Conclusions

The cone in plug apparatus has achieved the aims of the project and a modified test has been developed. Certainly, the modification has produced a reduction in the variability of rise time compared to the original UN apparatus. While the UN default scheme for firework classification uses a cut-off of 8 ms rise time to differentiate between acceptable compositions for a UN HD 1.4G and those deemed to be too hazardous for this classification without UN series 6 data, this programme has found that true black powders generally lay in the rise time range 4–8 ms. Thus where black powder burst charges are not allowed for a UN HD 1.4G classification (e.g. shells) the test results is likely to result in a default classification of UN HD 1.3G, which may not have been the original intent of this work.

## Disclaimer

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