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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

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Item 2 (a) of the provisional agenda
Explosives and related matters: Tests and criteria for flash compositions

Behaviour of waterfalls in large quantities; results of a research project

Transmitted by the expert from the Netherlands

1. In document ST/SG/AC.10/C.3/2014/59 the expert from the Netherlands proposes changes to the classification of fountains and to the default table with regards to 1.1G classification of fountains, with consequential amendments in paragraph 2.1.3.5.1, note 2 of 2.1.3.5.5 and Appendix 7.

2. The proposals are based upon the results of a research project on the behaviour of waterfalls in large quantities performed in 2012 and 2013 in the Netherlands. The results are given in the Annex to this informal document.

ANNEX: RESULTS OF THE RESEARCH PROJECT

There have long been questions regarding the applicability of the transport classification of pyrotechnic articles, including fireworks, for the transport and storage of large amounts of these articles. The tests to arrive at the proper transport classification are typically performed with a volume of 150 litres or 3 transport packages, whichever is the greater. It is suspected that fireworks could react more violently in larger quantities.

In 2003 an EU funded research program, named: "Quantification and Control of the Hazards Associated with the transport and storage of Fireworks" better known by its acronym CHAF, was started. The program was performed by a consortium consisting of HSL (UK), BAM (Germany) and TNO (the Netherlands). The main conclusions of the project were presented at the 9th International Symposium on Fireworks, Berlin, Germany, 2006. In short it was concluded that in almost all cases the transport classification accurately predicts the behaviour of large quantities of materials in question. However, there was one exception with a firework type called 'waterfall'. In a partially filled container the fireworks burned with intense heat, corresponding to their confirmed 1.3G classification. Though, a full container burned for approximately 3 seconds before a very violent mass explosion occurred. The reasons for this behaviour could not be found within the framework of the CHAF project.

In a follow-up project funded by the Netherlands TNO further studied the behaviour of waterfalls, using the same articles left over from the CHAF project. The properties of the pyrotechnic composition were included in the program as this had not been the case in the CHAF project.

METHODS

The experimental program included both the determination of the properties of the pyrotechnic composition and the properties of the articles.

Description

One waterfall article consists of 10 cylindrical fountains connected through a quick fuse and supported by rope and metal wire. Each fountain has a nominal length of 250 mm and an inner diameter of 20 mm and contains approximately 100 g of pyrotechnic composition.

For experimental reasons single fountains were used in the research programme. Therefore, in this paper the word article means one single fountain. The pyrotechnic composition is listed in Table 1.

Table 1 Details of the waterfall composition

Component	Percentage (%)
Potassium perchlorate	44
Aluminium (flakes)	36
Aluminium (powder)	8
Sulfur	6
Magnalium	4
Phenolic resin	2

The particle size distribution is given in Table 2, a picture of a representative sample of waterfall composition taken with a Scanning Electron Microscope (SEM) is given in Figure 1.

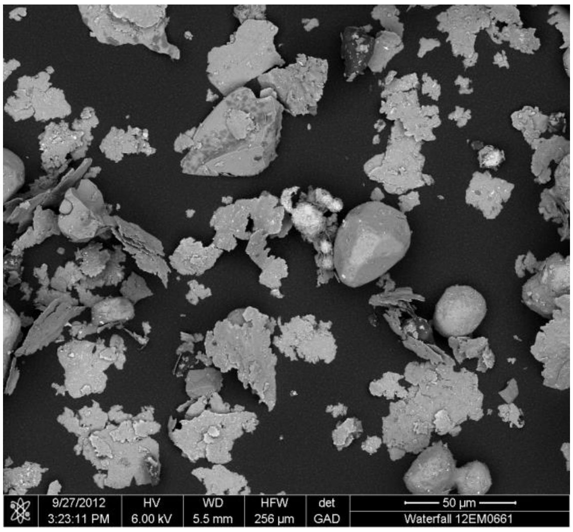


Figure 1 SEM photo of the waterfall composition, the flake shaped particles are aluminium, the rounder particles are potassium perchlorate crystals, the dark particles are resin.

Table 2 Particle size distribution of the waterfall composition

Mass (g)	Fraction (µm)	(%)
5.96	> 250	85,6
1.69	106 – 250	59,3
5.70	53 – 106	63,6
6.64	< 53	59,3
316		267,8

Characteristic properties of the components as determined with SEM-EDX are listed in Table 3.

Table 3 Overview of components characterised with SEM-EDX

Component	Particle size	Shape	Surface composition (atom-%)
Aluminium, flake	400 nm – 30 µm	thickness 300 nm	Al(88), O(9), C(1.5), Zn(1)
Aluminium, irregular	300 nm – 10 µm	fissures in surface	Al(80, Fe(1), Zn(1), O(12), C(2), Si (1)
Aluminium, elongated	0.5 – 3 mm	elongated	Al(80), Mg(5), O(10), C(2), Zn(1)
Magnalium	10 – 90 µm	irregular, angular	Mg(45), Al(35), O(20), C(1)
Phenolic resin	variable	smeared over particles, spherical	C(80), O(20)
Potassium perchlorate	up to 70 µm	rounded, oval	K, Cl, O, always some Al
Sulfur	300 µm	irregular, porous	S

It is confirmed that the components given by the manufacturer are present in the composition. No quantitative analysis has been performed, in earlier work this was already done by HSL. Contamination, most likely originating from the clay plugs at both ends of the tubes, has been found.

The morphology of the aluminium flakes show large similarities with the so-called “dark” aluminium frequently used in report compositions.

Sensitivity of the composition

The *sensitivity to impact* is determined using the BAM fallhammer apparatus as described in the UNMTC, test 3(a)(ii). The limiting impact energy, i.e. the lowest impact energy at which the result “explosion” is obtained in at least one out of six trials, is found to be 4 J. For comparison: the limiting impact energy below which a substance is believed to be too dangerous for transport is 2 J.

Since there were indications in literature that the impact sensitiveness might increase at higher temperatures, impact tests at 20, 100, 180 and 225 °C were performed using a Bruceton up-and-down method. It was found that the variations in 50%-points were all within the standard deviation which means that the sensitiveness remains constant in this temperature region.

The *sensitivity to friction* is determined with the BAM friction apparatus UNMTC test 3(b)(i). The limiting load, i.e. the lowest load at which the result “explosion” is obtained in at least one out of six trials, is found to be 72 N. For comparison: the limiting load below which a substance is believed to be too dangerous for transport is 80 N.

The *sensitivity to electrostatic discharge (ESD)* is determined with an apparatus capable of generating sparks with a voltage in the range of 3.3 to 10 kV. The spark energy can be varied by choosing the corresponding voltage and capacitance (between 5.1 and 199 nF). The spark energy can further be influenced by a variable resistance in the range of 16.9 to 10,000Ω.

The 50% ignition point is determined in duplicate trials and is found to be 887 mJ and 958 mJ respectively. For comparison: as determined with this apparatus, PETN has the 50% ignition point at 30 mJ, RDX at 55 mJ and TNT at 116 mJ.

To quantify the *sensitivity to flame* the maximum distance over which the burning flashed over to an adjacent conical pile of composition was determined. Both the donor and acceptor pile are of predetermined shape and size and contained 115 g of composition. The maximum flash over distance was found to be 75 cm.

The method described in STANAG 4488, Annex A was used to determine the *sensitivity to shock*. The method is a water gap test and is also known as the BICT gap test. In this test the length of the water column between the donor charge and the acceptor (and thus the incident pressure on the acceptor) is varied in the test series using a Bruceton up-and-down method. From the results the 50% point (M_{50}) and the standard deviation (SD) can be calculated. The tests were performed with and without additional confinement, a steel ring with 2.2 mm wall thickness was placed around the acceptor. The results are summarized in Table 4. The apparent density in the fountains is approximately 1.26 g/cm^3. However, most experiments were performed at a lower density to obtain the maximum reproducibility in filling the acceptor rings.

Table 4 – Summary of shock sensitivity determination

Condition	**Density (g/cm^3)**	**M_{50} (mm)**	**SD (mm)**	**M_{50} (MPa)**
unconfined	0.87	40.4	0.92	430
confined	0.87	43.3	0.63	340
confined	1.24	44.5	*	320

*: limited number of tests, SD could not be calculated

The fountain composition was found to be very sensitive to shock. Standards for designing fuses for (military) ammunition require that explosives to be situated “in-line” with the main charge should have a shock sensitivity of at least 1070 MPa. In this regard the sensitiveness of the waterfall composition is comparable with primary explosives.

Another relevant sensitivity property is the propensity to undergo a *deflagration-to-detonation transition (DDT)*. The method known as the USA Flash Composition test (formerly known as USA DDT test) is described in ST/SG/AC.10/C.3/2013/24 and UN/SCETDG/43/INF.31 both from the USA. In this test, 25 g of the test sample is contained in a convolute kraft paper tube with an inner diameter of approximately 25 mm, a wall thickness of 4 mm, and length of 150 mm, closed at the bottom with a paper plug. An electric igniter was fitted just in the top layer of the sample and the top of tube was closed with a paper plug. The tube was placed on a 1-mm thick steel witness plate and covered with a steel sleeve having an outer diameter of 63 mm, an inner diameter 38 mm, and a mass of approximately 2.7 kg. Perforation of the witness plate is indicative of the occurrence of a DDT. The waterfall composition gave a very clear indication of a DDT.

The test was also performed without the confining sleeve. The paper plug on the top of the kraft paper tube was replaced by a PVC plug, glued tightly to prevent venting of the reaction products. In this case a DDT took place as well. Also, with a reduced wall thickness of the kraft paper tube (2.5 mm) a DDT occurred. It was concluded that little confinement is needed for a DDT to occur.

The waterfall composition was not tested in the *HSL Flash composition test* in the project. However, the composition was previously tested by HSL, the pressure rise time was found to be 2 ms, well below the criterion of 6 ms.

The *detonation velocity* was determined in the UN Detonation test, test A.6. The test sample was confined in a steel tube (length: 500 mm, inner diameter: 50 mm, wall thickness 5 mm) and was initiated with a 200-g RDX/ wax donor in contact with the tube. The velocity was measured with a continuous velocity probe. Two tests were performed;, one with a density of 1.05 g/cm3 and the other with a density of 1.14 g/cm3. The measured velocities were 1485 and 1655 m/s, respectively.

The *dust explosion properties* of the waterfall composition were determined as well, the results and a comparison with other powders are given in Table 5.

Table 5 – Characteristic dust explosion properties of waterfall composition and a comparison with other powders

Sample	KST (m.bar/s)	Maximum pressure (bar)	Minimum ignition energy (mJ)	Minimum ignition temperature (°C)
waterfall	17	4.4	>1000	> 1000
lycopodium	119	8.5	5 – 10	410
cork dust	170	8.1	3 – 10	430
aluminium	620	12.4	10	560
fructose	102	9.0	1	430
wheat gluten	105	8.7	10 – 30	540
epoxy resin	136	7.6	3 – 10	520
potato starch	69	9.1		480

It is concluded that the powdery form of the waterfall composition has low power and a very high minimum ignition energy and temperature. A dust explosion during the large-scale trial in CHAF is therefore very unlikely.

The *ignition temperature* was determined using a method consisting of a stainless steel sphere with a diameter of 20 mm preheated at a given temperature. The sphere is dropped (remotely) in a container with the test substance. The temperature of the sphere at which ignition of the sample occurs is a good indication of the ignition temperature. With the sphere preheated at 300°C no ignition occurs in 3 out of 3 tests. At 350°C ignition occurs in all 3 tests. No attempt was made to determine the temperature more accurately.

The *burning velocity* under atmospheric conditions were found to be 0.31 m/s for a composition with a density of 0.84 g/cm^3. With a density of 1.02 g/cm^3 the burning rate was 0.18 m/s. This is considerably higher than usually reported in literature on comparable compositions.

The effect of *heating under confinement* was determined using the Small-scale Cook-off Bomb (SCB) as described in the second edition of the UNMTC, Test Series 1(b)(iii).

The volume of the vessel is 400 cm^3 and the wall thickness is 3 mm. The vessel (and the sample) is heated with two electrical element with a power rating of 400 W each. By varying the power, the heating rate can be adjusted. The violence of the reaction is assessed by tearing or fragmenting of the vessel and deformation or perforation of the witness plates. Three tests were performed with different heating rates. With a heating rate of 48°C/min the temperature at which explosion took place was 328°C. For heating rates of 3°C/min and 0.5°C/min the temperatures were 337 and 329°C, respectively.

For conventional explosives, the explosion temperature and violence of the reaction increases with decreasing heating rates. Since the vessel was hermetically sealed and there was only very little head space, the gaseous oxygen in the vessel will be consumed rather quickly. (Because of the different expansion of aluminium and aluminium oxide, heating will cause cracks in the oxide layer. The exposed elemental aluminium will instantaneously react with oxygen to form new aluminium oxide until as gaseous oxygen is consumed.) It seems that the waterfall composition 'just' ignited in all three tests. The ignition temperature of approximately 330°C corresponds to what was reported above.

Properties of the articles

The *sensitivity to flame* was also determined for articles in two orientations. When the donor and acceptor are placed parallel to one another, ignition of the acceptor takes place with a distance of 60 mm between the articles in three out of three tests. With a separation distance of 70 mm no ignition occurs in three out of three tests. Because of the directional effects of the fountain, ignition occurs at a larger distance when the donor is pointed towards the acceptor. Flashover takes place at a distance of 250 mm, but not at 300 mm.

The results indicate that the articles can be easily ignited, even when not connected with a fuse and even when not in contact with each other. In the transport packaging, all articles are in close contact, and in practice in a container the boxes are all touching each other. Flame propagation is therefore very likely and quick.

The *burning time* as a function of the number of articles was also determined. In the original CHAF project is was found that the total burning time decreases with an increasing number of waterfalls. However, these tests were performed with different waterfalls then used in the full-scale tests. The tests were repeated with the same waterfalls as involved in the full-scale tests.

One article burned for the nominal time of 60 seconds. A bundle of 7 articles, the central article ignited, burned in total for 35 s and a bundle of 19 articles for 10 s. Increasing the amount further to 37 articles resulted in a burning time of 15 – 20 s. Video recordings showed that there was a tendency of pushing the articles outwards of the bundle, especially in the case of 37 articles.

To investigate the behaviour of when the articles cannot be pushed outwards, a bundle of 19 articles was placed in a thin-walled steel tube with open front and end. In both tests the burning accelerated to an explosion fragmenting the tube into large pieces.

When the bundle is kept together with wire gauze an explosion did not occur. It is not yet known whether this behaviour is caused by a slightly increased pressure or by more favourable thermal conditions (less heat loss and/ or expanding reaction products).

Burning in a partially closed vessel

To simulate the situation as that which took place in the full-scale tests, experiments have been performed where several amounts of the waterfall composition and different numbers of articles were burned in a partially closed vessel.

In the full-scale test one of the two doors of the container opened as result of the internal pressure caused by the internal ignition of the waterfalls. In vent size experiments and calculations, the ratio of the area of the vent and the total volume is used as the main parameter. For a 20 foot container with one open door this ratio is 0.085 m^{-1}.

The vessel used for these experiments was the USA DDT tube as described in the UNMTC, Test 5(b)(ii) which has a volume of nearly 2 litres. The vent opening to obtain the same ratio therefore needs to have a diameter of 14.5 mm. A hole of that size was drilled in the steel screw cap.

The tube is fitted with a steel tube with an inner diameter of 5 mm. At the other end of this tube a connection is made with another tube filled with hydraulic oil. This oil transmits the pressure to a pressure transducer to measure the pressure inside the tube where the burning takes place. This set-up introduces a short delay time in measuring the pressure, but protects the transducers from the harsh environment (high temperature, abrasive particles, etc.) in the tube. See Figure 2 for an impression of the set-up of the test.

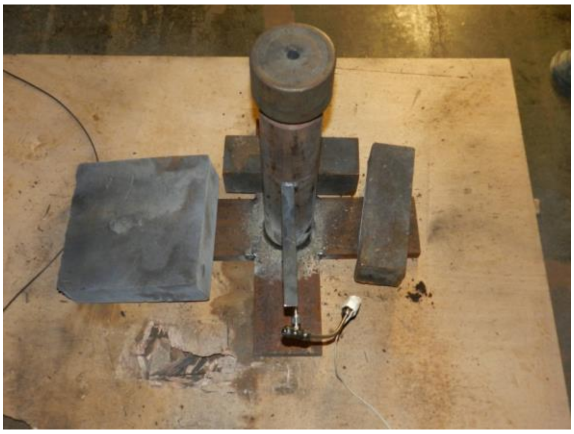


Figure 2 – Impression of the test set-up with pressure transducer visible just below the steel blocks

The waterfall composition is placed in a plastics holder as illustrated in Figure 3. Figure 3 also shows the igniter used to initiate the composition. The igniter is placed centrally in the cup with the fuse head pointing upwards. The test sample is poured over the igniter, so that initiation takes places from within the sample. Amounts of 50, 100 and 200 g of waterfall composition were used in the tests. A number of tests were performed with a much larger vent opening, without the steel screw cap. One experiment was performed where the igniter was placed on top of the pyrotechnic composition. The pressure profiles for the tests with 50, 100 and 200 g are shown in Figure 4.

Figure 3 – Plastics sample holder and electrical igniter for use in steel tube

In all three pressure profiles, time ‘zero’ is actually the time of ignition of the fuse head.

For amounts of 50 and 100 g a ‘gradual’ increase in pressure is observed before a transition to a very fast pressure rise takes place. The ‘spikes’ on the pressure signal are believed to be caused by reflecting shock waves through the tubes leading to the pressure transducer.

From Figure 4 it can be seen that the events take place earlier with increasing mass. The first indication of pressure rise in the test with 50 g of composition occurs after 17 or 18 ms, the transition takes place after approximately 37 ms. In the test with 100 g of composition a slight rise in pressure can be seen from time ‘zero’ onward and the transition occurs after 31 ms.

In the test with 200 g of composition, the first change in pressure is observed after 7.5 ms followed by a transition to detonation within 1 ms.

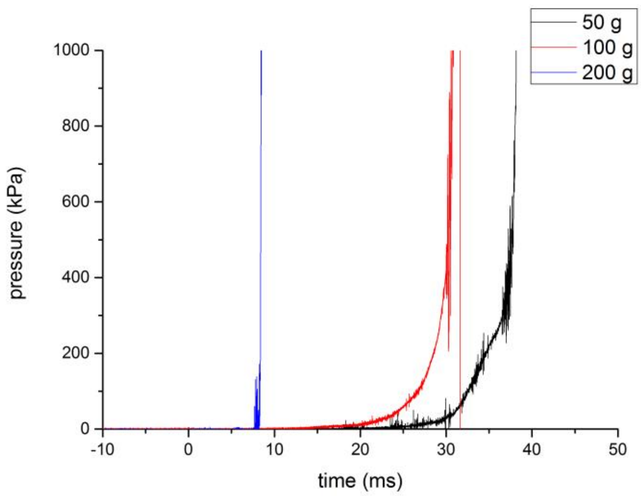


Figure 4 – Time – pressure profile for burning of three amounts of waterfall composition.

To investigate whether there would be a different behaviour with a larger vent size, the test with 200 g was repeated without the screw cap on the tube. The vent area is here 26 times larger and, if of influence, the event should occur later than in the test with the cap attached. The result is shown in Figure 5 together with a duplicate test with the screw cap present on the tube.

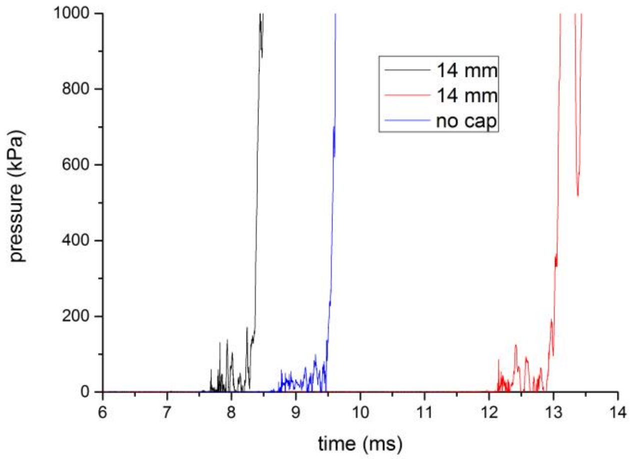


Figure 5 – Time – pressure signal for burning 200 g waterfall composition with (black (same as in Figure 5) and red signal) and without the screw cap (blue signal).

Figure 5 shows that there is no influence of the screw cap with amounts of 200 g. The experiment without cap is in between the duplicate tests with the cap on. The differences in reaction times are believed to be caused by the different response times of the electrical igniters. It is concluded that in the case of the 200 g, self-confinement is sufficient to cause ‘immediate’ DDT after ignition.

A test performed with the 100-g sample without cap indicated that the same events occur as in the test with cap, but only after a longer period of time. The transition occurs here after 52 ms (versus 30 ms with cap) indicating that the cap had some influence on the phenomena.

To investigate the situation when ignition is initiated on the surface of an amount of waterfall composition an experiment was performed with the igniter resting on top of the pile of composition. Normal burning occurred with sparks and reaction products streaming out of the vent hole for approximately 3 s followed by an explosion. The pressure gradient before (200 kPa/ms) and after (5600 kPa/ms) the transition are comparable with the test with the 100-g sample where ignition occurred from within the pile (Figure 6).

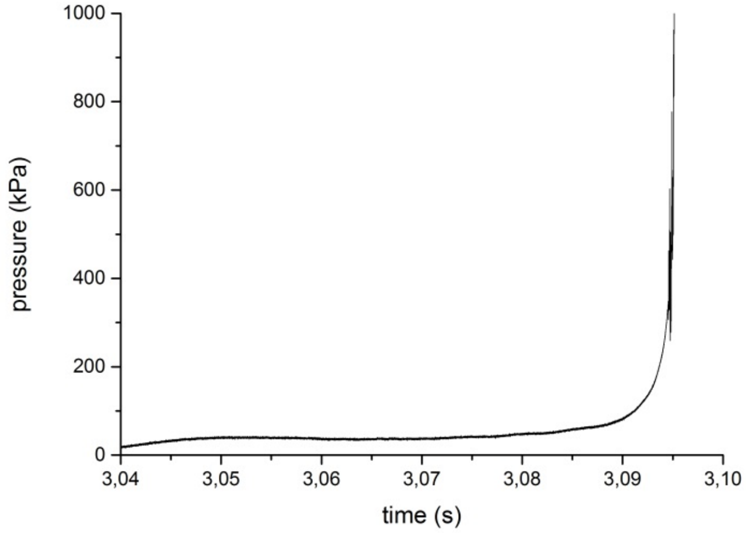


Figure 6 – Time – pressure profile for burning of 100 g waterfall composition where ignition occurs on top of the pile

The only difference is the time before transition occurs. Apparently, it takes some time before the conditions are favourable enough for the pressure to increase. An increased pressure results in an increased burning rate thus further increasing the pressure resulting eventually in a DDT.

As stated above, experiments were also performed with articles in the partially closed tube. Part of the fuse connecting the individual fountains was used to ignite the articles. The fuse was initiated with an electric fuse head. Where more than one article was tested all fused were ignited simultaneously by taping them together around the fuse head see Figure 7.

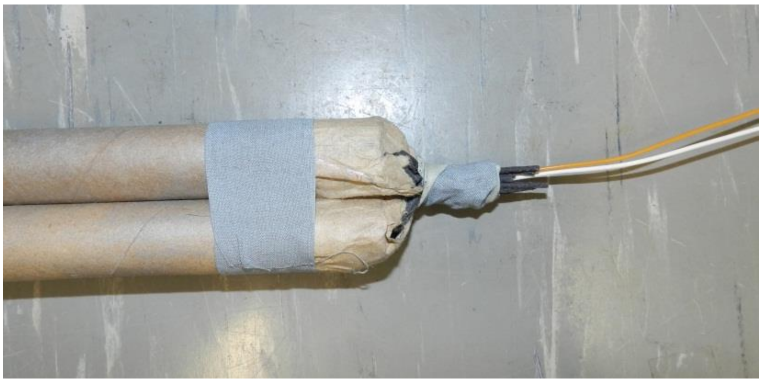


Figure 7 – Method of igniting multiple articles, in this example two fountains

In both tests with one article in the tube equipped with a screw cap a nominal burning time of approximately 60 s was observed with no significant pressure effects. With two articles in the tube the burning time was reduced, although not reproducible. In one test the articles burned for 22 s, in the duplicate test for 40 s, with some pressure effects. With three articles ignited in the tube, nearly instantaneous explosion occurred in two of the three tests. In the third test the articles burned for approximately 20 s before transition to detonation occurred. In Figure 8 the signal of all three tests with three articles are given. The time scale for the test where normal burning occurred before an explosion took place is shifted to obtain the three signals in one picture.

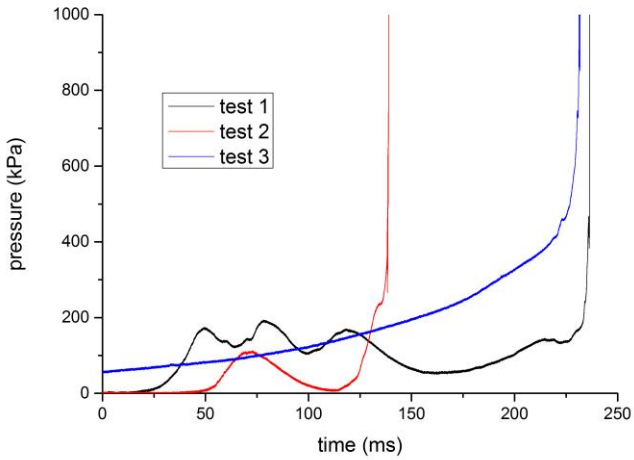


Figure 8 – Pressure profile of three tests with three burning waterfall articles, showing an 'instantaneous' detonation (black and red signal) and regular burning before detonation occurred (blue signal, time shifted to fit).

The main difference between the three tests with the three articles is the time frame at which the phenomena occur. In test 1 the transition occurs at 280 ms, in the duplicate test (2), it occurs after 140 ms. In the third test the transition only occurs after 21 s. As can be seen in Figure 11 the base level of the pressure in the tube is at a much higher level before explosion than in the other tests, indicating that the phenomena are not driven by pressure (alone).

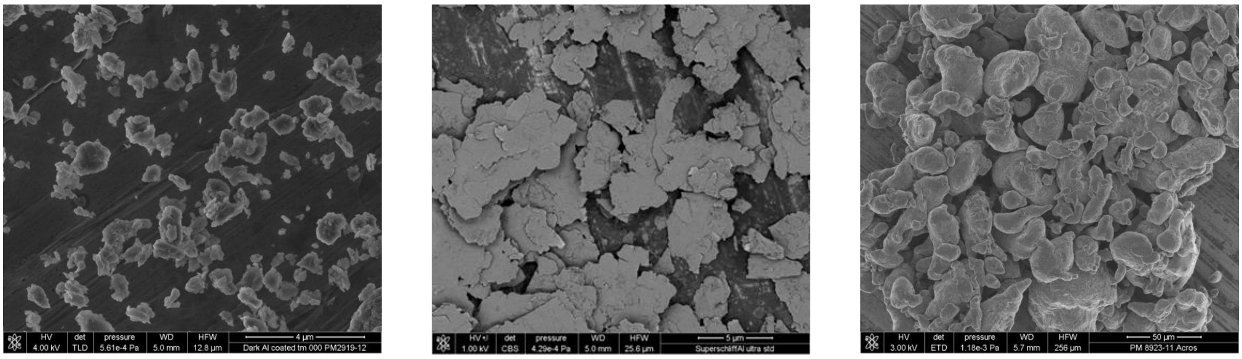
The results with three articles largely agree with those found for loose composition, although the time scale is larger for the articles. This is likely caused by the powder being in the separate compartments (i.e. the articles) and not in a 'continuous' mass . The circumstances are less favourable (with regards to self-confinement) in this case.

To investigate whether the observed behaviour was specific to this waterfall composition mixtures were made with raw materials available at TNO. The mixture was somewhat simplified compared to Table 1 to contain only four components (no sulfur and no phenolic resin) and the percentages were altered as well. Three different composition were made in which three of the four components were kept constant. The fourth component, aluminium, was the variable. The details of the three compositions are given in Table 6.

Table 6 Details of the three reference compositions

Component	Percentage	A	B	C
$KClO_4$	50	X	X	X
Magnalium	12.5	X	X	X
Aluminium flakes	12.5	X	X	X
Aluminium, type "0000", dark coated	25	X		
Aluminium, Superschliff Ultra	25		X	
Aluminium, atomised, 74 µm	25			X

SEM photos of the three different types of aluminium are given in Figure 9.



Aluminium in composition A Aluminium in composition B Aluminium in composition C

Figure 9 – SEM photos of the 3 different types of aluminium, note the different scaling (4, 5 and 50 µm respectively)

Tests were performed with the set-up given in Figures 2 and 3 with an amount of 50 g. The first test was performed without the screw cap on the tube, if no explosion was observed the test would be repeated with the screw cap and the smaller vent area.

Compositions A and B gave a clear explosion with the large vent area. Composition C could not be ignited with the electrical igniter and burned only partially when ignited with 5 g of black powder both with the large and smaller vent area.

From these tests it can be concluded that the behaviour (small degree of self-confinement results in a DDT) is not specific to the waterfall composition and that a similar behaviour can be obtain with other raw materials, different composition and other ratios of the components.

The most important parameter is the type of aluminium, the spherical particles obtained by atomisation appear to be much less reactive than the flake shape particles obtained by ball-milling or hammering. This could possibly be explained by a larger specific surface area but this is not experimentally confirmed.

CONCLUSION

The substance can be characterized as rather sensitive for impact, sensitive for friction and flame and very sensitive for DDT and shock. Furthermore, the substance is detonable. It is established that the burning velocity increases with increasing amount of articles resulting in an explosion. The tests performed in partially closed vessels show a very clear transition from deflagration to detonation. Self-confinement of a relatively small amount is sufficient to achieve a DDT. It has been experimentally confirmed that this behaviour is not specific for this particular waterfall composition. Other compositions made with other raw materials, different composition and other ratios of the components show, under the same conditions, the same behaviour as the waterfalls. There are strong indications that the main parameters for this behaviour are the physical properties and morphology of the fine aluminium.

The experiments have also demonstrated that explosion in the full-scale test was not a scale effect. When ignited in a partially closed volume small amounts of ‘loose’ composition (50 g) or three articles already give a DDT. The time to transition might vary somewhat with different amounts but the DTT always occurs under these conditions.

The waterfalls have been subjected to the full test series 6. No mass explosion was observed in the 6(a) and 6(b) test. Even in an up scaled version of the 6(b) test, performed with 27 boxes, no mass explosion was found. In the 6(c) the heat radiation was just above 4 kW/m^2 at 15 metres resulting in a 1.3G classification.

In the default table the waterfall would be classified as 1.3G as well (fountains, ≥ 1 kg composition).

The research project demonstrated that:

- The observed differences in behaviour in the classification tests and the mass explosion in a 20 foot container was not a scale effect. This means that the conclusion of the CHAF project, namely that the small-scale tests of series 6 are representative and predictive for the behaviour on a large-scale, remains valid.
- The existing tests (of series 6) are not in all cases adequate to predict the behaviour in practical conditions.

The chemical composition of the waterfall is largely comparable to the 'classic' flash composition based on perchlorate and aluminium, although the ratio of oxidiser and fuel differs somewhat.

The conditions when the flash composition test needs to be performed for default classification are defined in the UN Model Regulations, paragraph 2.1.3.5.5, note 2: *"Flash composition" in this table refers to pyrotechnic substances in powder form or as pyrotechnic units as presented in the firework that are used to produce an aural effect or used as a bursting charge, or propellant charge unless the time taken for the pressure rise is demonstrated to be more than 6 ms for 0.5 g of pyrotechnic substance in the HSL Flash Composition Test in Appendix 7 of the Manual of Tests and Criteria.*

The waterfall composition is not used to produce an aural effect or as bursting charge or as propellant charge and is therefore not eligible to be subjected to the flash composition test.

However, if the tests are performed the waterfall composition gave a clear positive result, both in the HSL and in the USA Flash Composition Test as reported above.

This might be the solution to address the classification of fountains. Changes to note 2 of 2.1.3.5.5 are necessary to include fountains and an entry in the default table providing for a 1.1G default classification in case the pyrotechnic substance in the fountain is flash composition needs to be created.

Contrary to other firework types, the results of test series 6 cannot take precedence over the default classification since test series 6 results in a 1.3G classification and a mass explosion was found when ignited in a container.