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COOKOFF BEHAVIOUR OF PYROTECHNICS

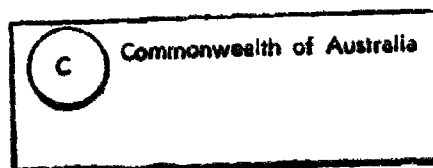
L. V. de YONG AND L.D. REDMAN

MRL-TR-91-44

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Cookoff Behaviour of Pyrotechnics

L.V. de Yong and L.D. Redman

MRL Technical Report
MRL-TR-91-44

Abstract

The US Navy has officially adopted a policy of Insensitive Munitions (IM) and the Australian Defence Forces are currently considering adoption of a similar IM policy. One major area of uncertainty is whether pyrotechnic stores respond in an unacceptably violent manner to IM threat scenarios, and whether they should be subjected to rigorous IM testing. At present there is only a limited amount of information available on the response of pyrotechnics to IM threat scenarios. The study reported in this paper generates some much needed data on the cookoff behaviour of pyrotechnics.

The results of the response of several pyrotechnic compositions to both fast and slow cookoff using the Super Small Scale Cookoff Bomb (SSCB) and the Royal Armament Research and Development Establishment (RARDE) Small Scale Booster Cookoff Test (SSBCT), supported by Differential Scanning Calorimetry/Differential Thermal Analysis (DSC/DTA) data, are presented. The results suggest that most pyrotechnic compositions do not present a serious threat in terms of the level of response to these test stimuli.

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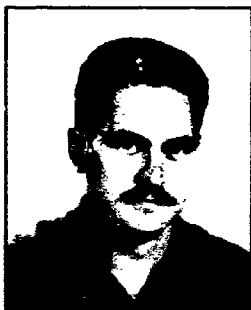
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Cookoff Behaviour of Pyrotechnics

1. Introduction

A modern arsenal consists of high performance munitions and related ordnance stores. Many of these systems can react in an extremely violent manner, up to detonation, when subjected to unplanned hazardous stimuli at any time over their life cycle during production, transport, storage and operational use. This has led to the concept of Insensitive Munitions (IM) which "reliably fulfill their performance readiness and operational requirements on demand, but which reduce to an acceptable level the violence of their response and subsequent collateral damage when subjected to unplanned hazardous stimuli" [1].

The realization that platform vulnerability and other logistic considerations could be substantially improved by the adoption of IM has resulted in all the Western countries considering their operational policies. Foremost in this regard is the US Navy (USN) which has a firm policy for transition of the fleet to IM [2]. The Australian Defence Force (ADF), and in particular the RAN, with its relatively small number of high value delivery platforms, is considering adoption of an official policy. This initiative has been undertaken by the Australian Ordnance Council (AOC) [1, 3]; adoption of a policy or policies should occur in the near future.

A credible Australian IM policy must first and foremost be relevant to Australia's needs. The seven hazardous stimuli covered by the USN IM policy for IM qualification testing are as follows [4]:

1. Fast cookoff (fuel fire),
2. Slow cookoff,
3. Bullet impact,
4. Fragment impact,
5. Sympathetic detonation,
6. Shaped charge jet impact, and
7. Spall impact.

Only 1 to 4 are mandatory for IM qualification; 5 to 7 may additionally be required on the basis of a threat analysis. The policy covers all explosive

ordnance including bombs, missiles, torpedoes, mines, pyrotechnics, demolition charges and special purpose devices [2].

As part of the process of developing an Australian IM policy, credible threat stimuli need to be identified and criteria for an acceptable response defined. For example, the USN requirement for slow cookoff is that the store be heated at 6°F (3.3°C) per hour, with burning as the maximum response. A heating rate this slow can only occur on a ship with a steam leak in a magazine [5], and no RAN ships have steam lines in magazines. If a more realistic higher heating rate were chosen, munition response is likely to be milder and restrictions on the ordnance to pass the test less severe.

Another aspect of USN IM policy of relevance to Australia's considerations is inclusion of pyrotechnic stores. There is only limited information available on response of pyrotechnics to IM threat scenarios, but it is currently an area of considerable R & D activity in the US. As the first part of generating an IM technology base on pyrotechnics, an investigation was undertaken to measure the response of a range of pyrotechnics to both fast and slow cookoff. This report details the results of investigations using differential scanning calorimetry/differential thermal analysis (DSC/DTA) and cookoff bombs to evaluate the response of several pyrotechnic compositions.

2. Test Methodology

There are several tests which may be used with relatively small amounts of energetic material to yield information on thermal stability, self-heating and cookoff behaviour under various conditions.

The thermal decomposition of materials is conveniently studied using thermochemical techniques such as DSC, DTA, and thermal gravimetric analysis (TGA). These techniques yield information on the reaction mechanism and kinetic parameters of interest (activation energy, enthalpy, ignition temperature). Whilst these tests provide information on the response of the material to the particular stimuli, they do not give any indication of the severity of the response, i.e. the "explosiveness" of the sample.

Several methods have been developed to assess the response of confined explosives to thermal initiation. Early tests developed ranged from small scale fuel fires to hot wire ignition tests, but in most of these tests the heating rate is difficult to control. It has been found that by using confined samples and an external heat source, reliability and reproducibility of results increases. One such test, the Small scale Cookoff Bomb (SCB) test, has been adopted by the UN as a suitable test for classifying energetic materials in regard to their thermal response [6]; a scaled down version of the SCB test, the Super Small scale Cookoff Bomb (SSCB) is also in use [7, 8]. Another such test, the RARDE Small Scale Booster Cookoff Test (SSBCT), uses similar hardware but the sample is more confined [9].

Our work used the SSCB and the RARDE SSBC test as its basis.

3. Experimental

3.1 SSCB Test

The design of the SSCB test assembly was taken directly from that used at Naval Weapons Center (NWC), China Lake [7] and subsequently adopted at MRL for evaluation of plastic bonded explosives (PBXs) [8].

The SSCB test uses a sample of about 20 g of energetic material of cylindrical geometry with a diameter of 15.9 mm and a length of 63.6 mm. The SSCB test vehicle is shown diagrammatically in Figure 1 and a photograph of the assembled hardware is shown in Figure 2. It consists of an outer steel cylinder which is spot welded to a 9.6 mm thick steel baseplate. Two band heaters, each rated at 250 W/240 V, are clamped around this cylinder with hose clamps, and are connected to a variable voltage supply (Variac) to provide heating at the desired rate. The Variac is set to supply 240 V for the fast heating rate or either 150 V or 120 V for the slow heating rate. An aluminium inner liner with a slot for a thermocouple for monitoring the temperature-time history during the test is placed inside the outer cylinder. This liner assists in evening out the heating delivered to the sample from the heaters. The pyrotechnic sample is pressed directly into the two inner cylinders at 1000 kg dead load, which are then inserted into the aluminium liner. A thin standoff washer is placed below the inner cylinders and the pyrotechnic and provides an air gap between the pyrotechnic and the baseplate. A steel top plate, also 9.5 mm thick, closes the top of the test assembly, and is secured to the baseplate with four bolts. The top plate incorporates a hole for the thermocouple, and also has a central hole which is closed with a steel plug. The 120 V setting was used for all the smoke compositions whilst the 150 V setting was used for the remaining compositions. The 150 V setting was required to achieve the temperatures needed for initiation at the slow heating rate; the standard setting of 120 V was inadequate due to large heat losses from the system. In an attempt to reduce the heat losses, the SSCB was insulated with fibreglass foam for all the tests except those for the smoke compositions.

The SSCB tests were conducted in a firing chamber with the power supply for the heaters and the thermocouple amplifier/chart recorder located in a remote control and instrumentation room, isolated with safety interlocks. The SSCB was suspended vertically in the centre of a large steel cylinder approximately 30 cm diameter and 45 cm high. Power was applied to the heaters from the control room and the time to the event was measured with a timer watch. The thermocouple temperature was also monitored in the control room and provided an indication that the test was proceeding normally.

The temperature on the outside of the sample was monitored with a Type K thermocouple connected to an amplifier which provided an output of 10 mV per °C.

After the test, the SSCB was examined for any signs of damage. Any deformation of the hardware was recorded and photographed. The thermocouple temperature was obtained from the chart recorder and the temperature at the surface of the sample was derived from the calibration graph.

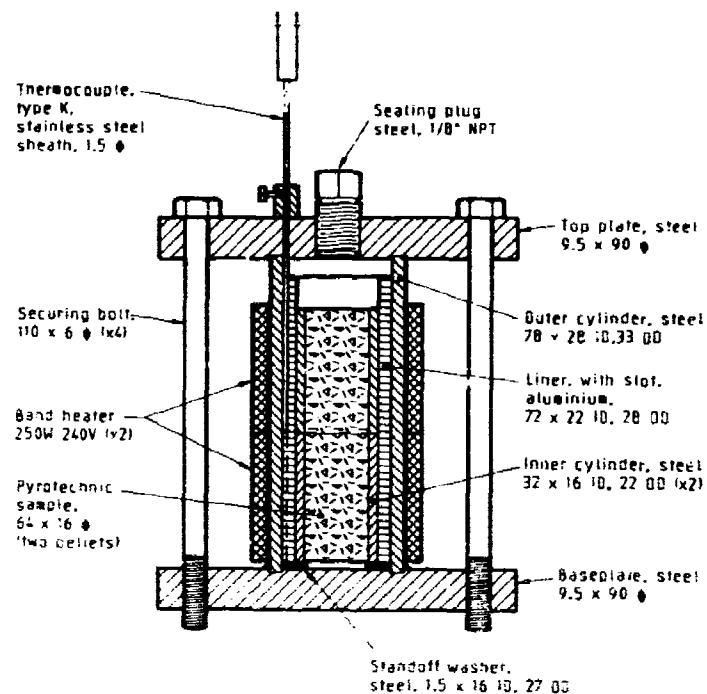


Figure 1: SSCB Test Vehicle.

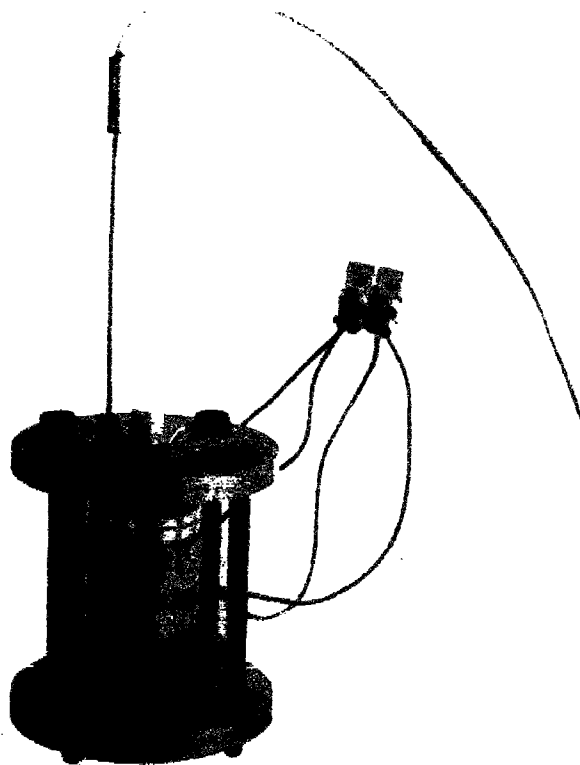


Figure 2: SSCB Test Vehicle after assembly.

3.2 SSCB With Electrical Initiation

Several compositions were tested in the normal SSCB hardware but were initiated with an electrical initiator (fusehead). The thermocouple probe was removed and replaced by the fusehead. The electric band heaters were in place but were not connected to the Variac. To ensure that the pyrotechnic composition ignited from the fusehead, 1.0 g of SR252 (Silicon/Potassium Nitrate/Sulphurless Mealed Powder, 40:40:20) [10] priming composition was pressed on top of the main composition.

3.3 RARDE SSBC Test (SSBCT)

The RARDE SSBC test is shown in Figure 3. The design was taken directly from that used at Royal Armament Research and Development Establishment (RARDE), Fort Halstead, UK [9]. The test geometry has been slightly modified to ensure that it matches the SSCB geometry as closely as possible. The outer container and the threaded end caps were mild steel with a wall thickness of 6 mm. An aluminium sleeve was placed inside the outer tube and the pyrotechnic composition was pressed into two outer steel cylinders at 1000 kg dead load. A single SSCB band heater was clamped around the outer steel cylinder with a hose clamp and was connected to a variable voltage power supply (Variac). The SSBC tests were conducted in a firing chamber in exactly the same manner described above for the SSCB tests.

3.4 Thermal Characterization

Differential Scanning Calorimetry (DSC) was conducted using a Perkin Elmer DSC operating in the non isothermal mode controlled by a Perkin Elmer Model 3600 data station. All samples were accurately weighed (5 to 50 mg) on a Mettler ME30 analytical balance directly into aluminium pans and the lids placed over the samples. The purge gas was nitrogen and the scan rate was set according to the type of test being conducted.

The Differential Thermal Analysis/Thermal Gravimetric Analysis (DTA/TGA) measurements were conducted with approximately 1.5 mg in open platinum pans on a Stanton Redcroft STA 1500 Thermal Analyser. A nitrogen atmosphere was used at a flow rate of 25 mL per minute. The heating rate was 10° per minute. The mass losses were not corrected for changes in buoyancy effects on heating.

3.5 Pyrotechnic Compositions

The pyrotechnic compositions selected for evaluation represent a wide range of pyrotechnic output including flares (visual and infrared), colored smokes, flash composition and several novel fuel/oxidant mixtures. Details of the compositions tested are presented in Table 1.

Table 1: Pyrotechnic Compositions for Testing

Chemical Ingredient	Composition (% w/w)								
	OS	OSR	MSN	MSNE	MTV	APP	APB	ACU	AAN
Potassium Chlorate	21.5	20.4							
Lactose	21.5	20.4							
Kaolin	12.0	11.4							
Dye	45.0	42.8							
Flame Retardant ¹		5.0							
Sodium Nitrate			50.0	50.0					
Magnesium ²			50.0	39.0	61.1				
Teflon					33.9				
Viton					5.0				
Aluminium						60	15	20	40
Lead Chromate							85		
Copper Oxide								80	
Ammonium Nitrate									60
Binder ³				11.0					
Potassium Perchlorate						40			

1. Hexabromocyclododecane (Saytex HBOD)

2. Grades O, V and Type E.

3. Ethylene vinyl acetate (Elvax 210)

The majority of the pyrotechnic compositions were made using the standard repetitive dry mixing/sieving procedure to produce a homogeneous blend of the ingredients. The magnesium/Teflon/Viton (MTV) composition was prepared using the shock gel process - the Viton was dissolved in acetone and the magnesium and Teflon added with stirring. Excess hexane was added which precipitates the Viton out onto the magnesium. The magnesium/sodium nitrate/binder composition (MSNE) was prepared by dry mixing/sieving magnesium powder coated in binder with the sodium nitrate. The magnesium powder was mixed with the binder in a suitable solvent and the solvent allowed to evaporate. The coated magnesium was allowed to air dry then passed through a BSS 14 sieve to breakup any agglomerates and produce a uniform particle size.

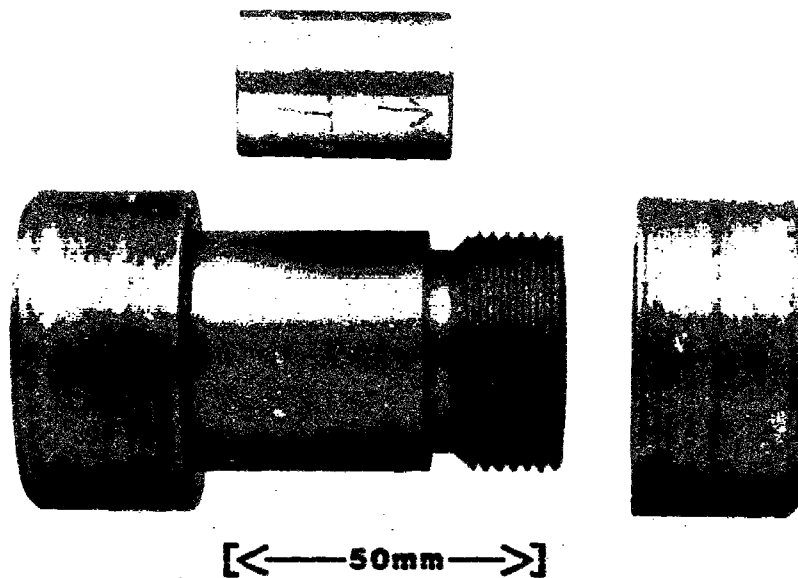
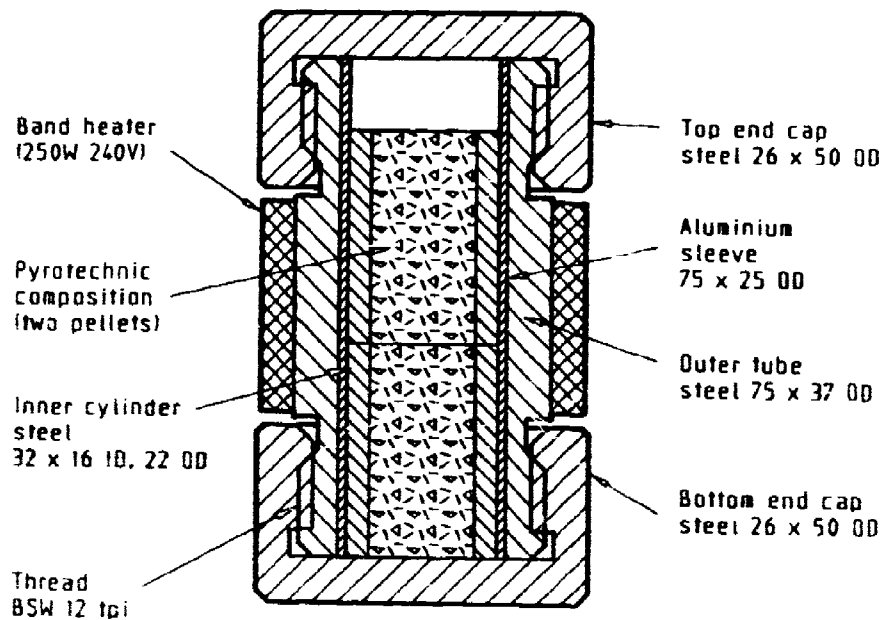


Figure 3: RARDE SSBC Test Vehicle.

3.6 Temperature Calibration

The temperature recorded during an SSCB test was that sensed by the thermocouple in the aluminium liner (Fig. 1). The temperature reached by the outer surface of the pyrotechnic composition during the test was obtained from a calibration chart produced by heating an inert (sand) filled SSCB which had a second thermocouple welded to the inner surface of the inner steel cylinder. From these two temperature/time curves, the temperature reached by the outer surface of the pyrotechnic composition was estimated.

The temperature of the sample during the RA RDE SSBC test was estimated from a calibration conducted using an inert filling in the cylinder (sand). A hole was incorporated in the top threaded cap and a thermocouple (Type K, output 10 mV per degree C) inserted into the centre of the sand. The temperature/time curve was recorded for several Variac settings. From these curves, it was possible to estimate the temperature reached in the centre of the pyrotechnic composition during a test.

It should be noted that the reported sample temperatures during a test have been based on calibration with sand, and no allowance for self heating prior to reaction has been made. It is expected that the error due to self heating at fast heating rates will be negligible but it may be several degrees C at the slow heating rates.

4. Results

4.1 Temperature Calibration

The temperature calibration curves for the SSCB at the fast and the two slow heating rates are shown in Figures 4, 5 and 6. The fast heating rate corresponds to a temperature rise of approximately 600°C in 16 minutes; the slow heating rates correspond to temperature rises of 600°C in 90 minutes (150 V) and 225°C in 41 minutes (120 V). The differences between the measured temperature (in the aluminium liner) and that experienced by the pyrotechnic composition varies with the measured temperature and the heating rate. The sample temperature measured from the calibration results will be inaccurate for several reasons -- differences in the thermal properties of the pyrotechnic compositions (heat capacity, thermal conductivity, thermal diffusivity), small variations in the heaters giving small variations in the heating rate, thermocouple accuracy, and data recording, i.e. readability/accuracy. However, it has been estimated that the measured temperature will be in error by no more than 5°C [8]. Also, the calibration runs were made using an inert sand filling and no allowance has been made for self heating from the pyrotechnic composition prior to reaction in the real test. This will be significant for the pyrotechnic compositions, particularly at the slow heating rates, and could lead to further errors of several degrees.

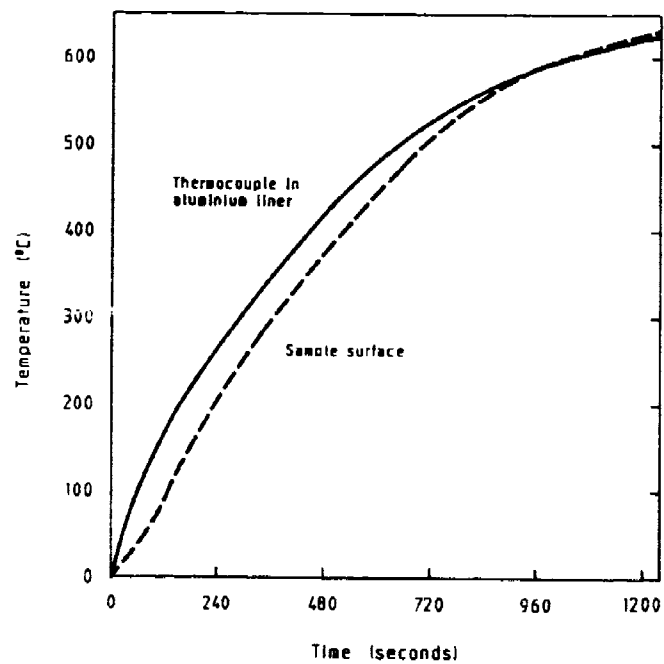


Figure 4: Temperature calibration curve for SSCB, fast heating rate.

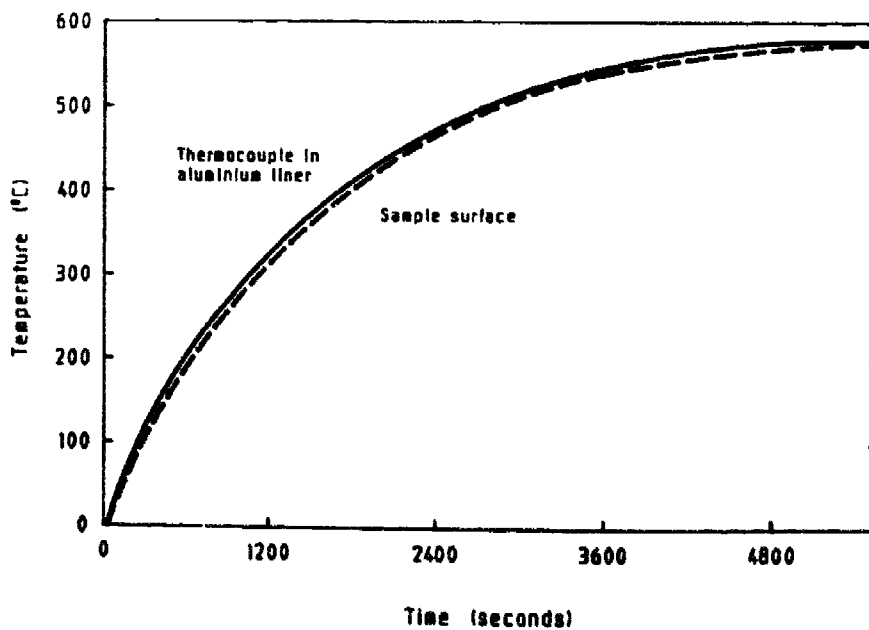


Figure 5: Temperature calibration curve for insulated SSCB, slow heating rate, voltage 150 V.

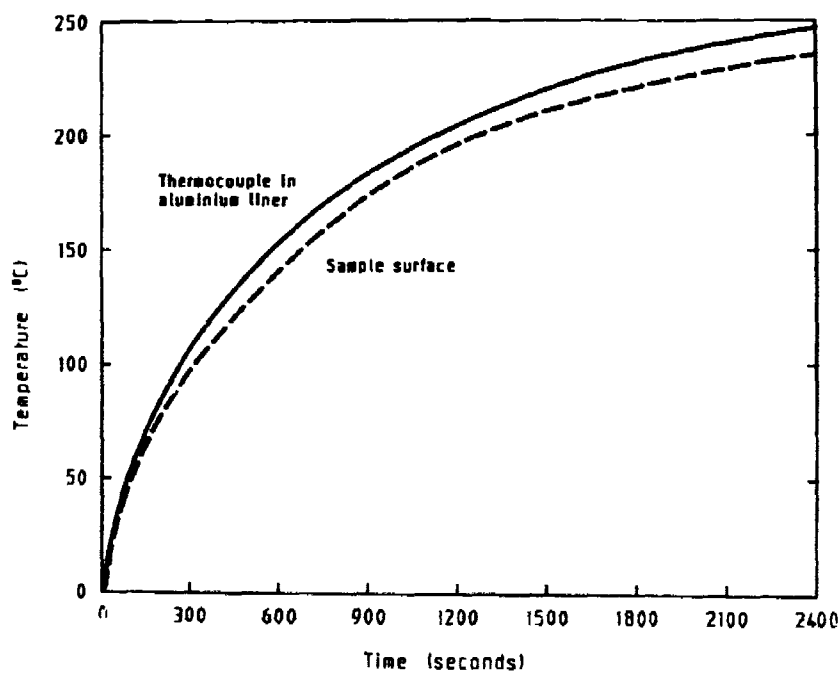


Figure 6: Temperature calibration curve for uninsulated SSCB, slow heating rate, voltage 120 V.

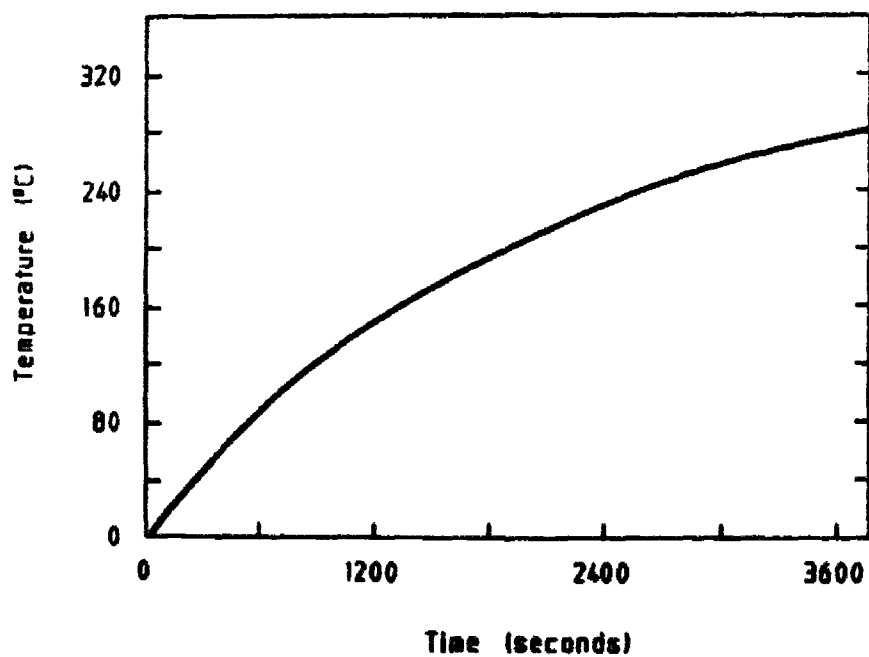


Figure 7: Temperature calibration curve for RARDE SSBC test, slow heating rate.

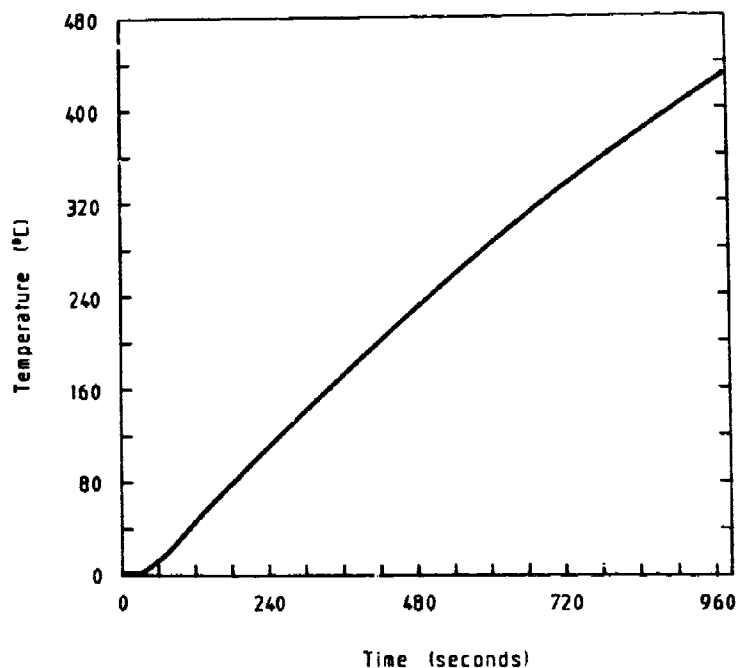


Figure 8: Temperature calibration curve for RARDE SSBC test, fast heating rate.

The temperature calibrations for the RARDE SSBC test are shown in Figures 7 and 8. The fast heating rate corresponds to a temperature rise of 450°C in 16 minutes and the slow heating rate corresponds to a temperature rise of 320°C in 60 minutes. Since the hardware is fully sealed with no thermocouple present during the test, the calibration curve is used to estimate, from the measured time to reaction, the approximate temperature inside the pyrotechnic sample prior to the reaction. Again, as with the SSCB test, errors of several degrees will be present due to thermal properties of the compositions, variation in the measuring equipment, self heating and the formation of hot spots.

4.2 SSCB Test

The results obtained for all the pyrotechnic compositions are presented in Table 2.

Table 2: Results of SSCB Tests on Pyrotechnic Compositions

Composition	Heating Rate	Temperature (°C)		Time (s)	Reaction
		Bomb	Pyrotechnic		
MSN, Grade 0 blown magnesium	Slow	525	510	3264	Mild burning
	Fast	545	490	786	Mild burning
MSN, Grade V cut magnesium	Slow	480	460	1992	Mild burning; erosion of outer container
	Fast	452	393	630	Mild burning; erosion of outer container
MSN, Type E magnesium	Slow	458	437	2040	Mild burning; erosion of outer container
	Fast	439	375	612	Mild burning; erosion of outer cylinder
OS	Slow	176	190	1170	Mild burning
	Fast	250	225	222	Mild burning
OSR	Slow	188	182	1020	Mild burning
	Fast	252	227	212	Mild burning
MSNE	Slow	456	448	2010	Mild burning
	Fast	485	418	702	Mild burning
APB	Fast	> 838	-	> 2040	No reaction
ACU	Fast	> 780	-	> 1740	No reaction
APP	Slow	> 670	> 655	> 5850	No result
	Fast	616	566	1104	Burning
MTV	Slow	> 530	> 513	> 2610	No reaction, heaters failed
	Fast	527	471	744	Mild burning
AAN	Fast	> 735	-	> 1494	No reaction

4.2.1 Flare Compositions

4.2.1.1 Magnesium/Sodium Nitrate Compositions (MSN)

Three different magnesium/sodium nitrate compositions, all ratio 50:50, were examined in this series of tests.

Using Grade 0 blown Mg powder (median particle size 250 μm , specific surface area 1.52 m^2/g) at the fast heating rate, the time to reaction was recorded as 786 s. The measured temperature was 545°C, corresponding to a sample temperature of 490°C. The SSCB apparatus showed no apparent

damage; no distortion of any components was recorded. The composition had reacted completely and was fully contained within the outer steel cylinder. The sealing plug on the top plate was intact but the thermocouple had been ejected. The underside of the top plate and the inner cylinders were coated with combustion products. At the slow heating rate, a reaction occurred at a recorded temperature of 525°C (3264 s) corrected to a sample temperature of 510°C. As with the result for the fast heating rate, there was no damage to the SSCB apparatus; the composition had completely reacted and was contained within the outer cylinder.

Using Grade 5 Mg powder (median particle size 50 μm , specific surface area 7.5 m^2/g) at the fast heating rate, reaction occurred at 452°C (630 s) corresponding to a sample temperature of 393°C. Again, the reaction was completely contained within the outer cylinder and no damage to the SSCB recorded.

At the slow heating rate reaction occurred at 480°C (1992 s) corresponding to a sample temperature of 460°C. The SSCB showed little damage but there was evidence of reaction products on the outside of the outer cylinder. There was also a hole in the top of the outer steel cylinder and the top portion of the band heaters were eroded. Figure 9 shows a photograph of the SSCB after the test.

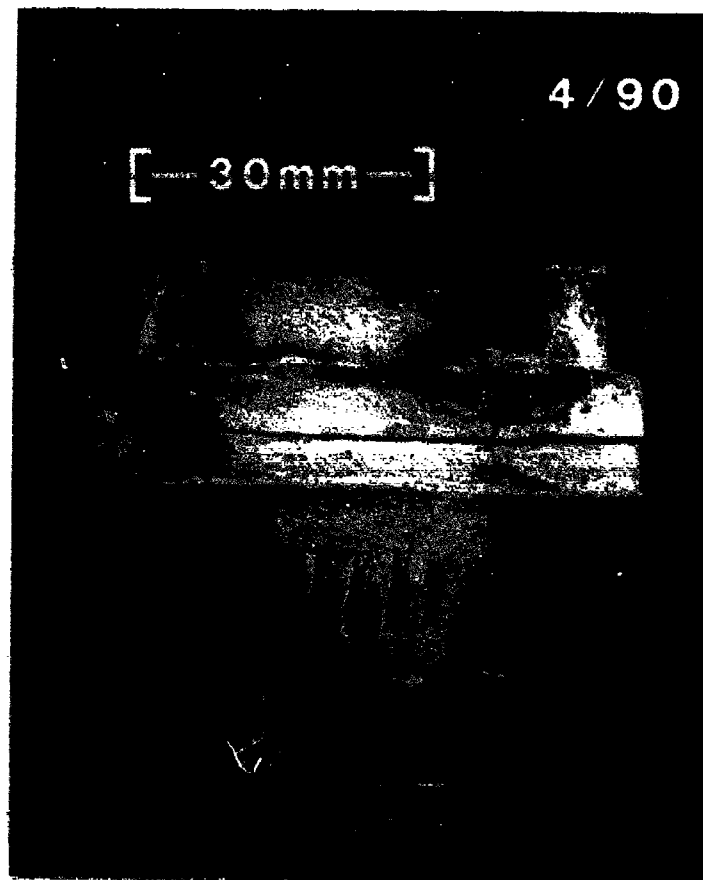


Figure 9: Erosion of the band heaters and outer steel cylinder of SSCB, magnesium/sodium nitrate, slow heating rate.

Using Type E Mg powder (median particle size 45 μm) at the fast heating rate produced a reaction of 439°C (612 s) corresponding to a sample temperature of 375°C. The SSCB was recovered intact but there was a hole in the top of the outer steel cylinder which allowed the reaction products to vent. The inner steel cylinders were intact but the aluminium liner had melted. The thermocouple plug had blown out but no reaction products were found on the top of the top plate.

At the slow heating rate reaction occurred at 458°C (2040 s) corresponding to a sample temperature of 437°C. The state of the SSCB hardware was similar to that observed at the fast heating rate but the outer steel cylinder was intact.

4.2.1.2 Magnesium/Sodium Nitrate/Binder (MSNE)

Only Grade V magnesium was used in these tests. At the fast heating rate, the reaction temperature was 485°C (702 s) which corresponds to a sample temperature of 418°C. The SSCB showed no physical damage and the reaction was completely contained. The thermocouple plug was blown out during the test.

At the slow heating rate the reaction temperature was 456°C (2010 s) corresponding to a sample temperature of 448°C. As for the fast heating rate, the SSCB was recovered intact and the reaction was complete and fully contained.

4.2.1.3 Magnesium/Teflon/Viton (MTV)

At the fast heating rate, a reaction was recorded at 527°C (744 s) which corresponds to a sample temperature of 471°C. The SSCB showed no damage and the thermocouple plug was intact. All the MTV composition was consumed and the reaction was fully contained in the outer steel cylinder.

At the slow heating rate, no reaction was recorded and the band heaters began to electrically short out at approximately 530°C corresponding to a sample temperature of 513°C. Although no combustion occurred, the MTV pellets in the inner steel cylinders had physically swollen by 1.2 mm.

4.2.2 Colored Smoke Compositions

4.2.2.1 Orange Smoke Compositions (OS)

At the fast heating rate the reaction commenced at a measured temperature of 250°C (222 s) corresponding to a sample temperature of 225°C. The SSCB showed no physical damage and the thermocouple plug was intact. There was evidence of sublimed dye on the outside of the outer steel cylinder indicating leakage of the smoke through the join between the outer cylinder and the top plate. All the smoke composition was consumed leaving a hard "clinker" residue, typical of pyrotechnic smoke compositions.

At the slow heating rate the reaction commenced at a measured temperature of 196°C (1170 s) corresponding to a sample temperature of 190°C. Again there

was no damage to the SSCB but there was some evidence of leakage of reaction products through the seal between the outer cylinder and the top plate.

4.2.2.2 Orange Smoke Composition/Flame Retardant (OSR)

The recorded reaction temperature, at the fast heating rate, was 252°C (212 s) corresponding to a sample temperature of 227°C. No damage to the SSCB was recorded and the thermocouple plug remained intact. At the slow heating rate, the reaction occurred after 1020 s at a recorded temperature of 188°C corresponding to a sample temperature of 182°C. The SSCB was undamaged and the reaction was fully contained.

4.2.3 Aluminium/Potassium Perchlorate (APP)

The flash composition showed a reaction at a recorded temperature of 616°C (1104 s) at the fast heating rate corresponding to a sample temperature of 566°C. The SSCB showed definite signs of damage due to the combustion reaction; the top plate of the SSCB had been blown off and the steel securing bolts were sheared off at the baseplate. The inner steel cylinders were not distorted but the inner aluminium liner had melted. There was evidence of molten aluminium on the underside of the top plate. Figure 10 shows a photograph of the SSCB after this test.



Figure 10: SSCB damage, aluminium/potassium perchlorate, fast heating rate.

At the slow heating rate the recorded temperature reached 670°C, corresponding to a sample temperature of approximately 655°C, before the band heaters shorted out. No reaction was recorded and the composition was recovered. The SSCB was recovered intact.

4.2.4 Miscellaneous Compositions

4.2.4.1 Aluminium/Copper Oxide (ACu)

A single test was conducted at the fast heating rate. No reaction was recorded up to the measured temperature of 780°C. Examination of the SSCB after the test showed that the composition had not reacted although the aluminium liner had melted.

4.2.4.2 Aluminium/Lead Chromate (APB)

This result was similar to the result for aluminium/copper oxide. At the fast heating rate no reaction was recorded and the test ceased at a measured temperature of 838°C. The pyrotechnic composition had not reacted but the aluminium liner had melted.

4.2.4.3 Aluminium/Ammonium Nitrate (AAN)

This result was similar to that recorded for aluminium/copper oxide and aluminium/lead chromate; at the fast heating rate no reaction was recorded and the test ceased at a recorded temperature of 735°C. The aluminium liner had melted.

4.3 Electrical Initiation of SSCB

4.3.1 Magnesium/Sodium Nitrate (MSN)

Three separate tests were conducted on this composition at three different pressing loads. Grade V cut magnesium (median particle size of 50 µm and a specific surface area of 7.5 m²/g) was used in these tests.

The first test used the same mass of MSN as for the normal SSCB test pressed into the inner steel cylinder at 1000 kg dead load to 76% TMD. On initiation, the top plate was violently blown off and the steel securing bolts were sheared off at the baseplate. The inner steel cylinders were not distorted but were damaged when they were ejected from the outer tube and impacted the concrete roof of the firing cell. The inner aluminium liner was split from top to bottom along the thermocouple slot but it was intact. There was no damage to the baseplate or the outer steel cylinder. All the pyrotechnic composition

was consumed. A photograph of the assembly after the test is shown in Figure 11.

In the second test, the pressing load on the MSN composition was increased to 3000 kg dead load to give approximately 80% TMD. The composition ignited and burnt to completion and the SSCB was undamaged. Some of the combustion products appeared to have vented through the hole in the top plate where the electrical wires to the fusehead passed. There was significant erosion of the top plate around this hole.

In the final test, the MSN composition was pressed at 6000 kg dead load (approximately 98% TMD). The reaction was the same as that recorded for the 80% TMD sample and the SSCB was undamaged.



Figure 11: SSCB damage, magnesium/sodium nitrate. 76% TMD, electrically initiated.

4.3.2 Orange Smoke Composition (OS)

After initiation of the fusehead the orange smoke composition reacted completely and was fully contained. There was some slight evidence of condensed dye on the outer steel cylinder. The SSCB was undamaged.

4.4 RARDE SSBC Test

4.4.1 Magnesium/Teflon/Viton (MTV)

This test was conducted at the fast heating rate only to ensure that a high enough temperature was reached. From the calibration graph the temperature reached by the sample was approximately 700°C before the reaction commenced. The hardware was not significantly damaged but there was evidence of the reaction products venting out through the thread between the top end cap and the outer steel tube. The reaction products solidified on the outside of the steel tube as shown in Figure 12.



Figure 12: Venting of MTV reaction products, RARDE SSBC test.

4.4.2 Orange Smoke Composition (OS)

This test was conducted at the slow heating rate only. The temperature reached by the sample was estimated from the calibration graph to be approximately 400°C. The reaction was fully contained and no leakage of reaction products was observed. There was no damage to the hardware from the reaction.

5. Thermal Analysis

5.1 Colored Smoke Compositions

The results of the DSC analysis of the colored smoke compositions with a range of additives are shown in Table 3. The DSC trace for the smoke composition with no additives (Fig. 13) shows two small endothermic peaks at 150°C (423 K) and 200°C (473 K). The first endothermic peak corresponds to the loss of one molecule of water of crystallization from the lactose fuel (α -lactose·H₂O → β -lactose). The second endotherm is associated with the melting of anhydrous β -lactose. A strong exothermic peak commences at approximately 207°C (480 K) corresponding to the smoke combustion reaction (lactose + potassium chlorate). A further small exotherm occurs at approximately 337°C (610 K) possibly due to a reaction between carbon (from the lactose) and residual potassium chlorate.

Results for the DTA/TG analysis of several of the smoke + additive compositions are presented in Table 4 and Figure 14. The colored smoke composition shows two exothermic peaks at 208°C (481 K) and 342°C (615 K) while the TGA results show a three stage weight loss process. There is an initial 17.8% loss corresponding to the first exothermic peak and a 9.3% weight loss associated with the second exothermic peak. A significant weight loss of 32.1% occurs between 230°C (503 K) and 310°C (583 K) which has no associated recorded heat flow. The first peak at 208°C (481 K) corresponds to the reaction of the lactose and the potassium chlorate. The theoretical weight loss associated with this reaction is 16.2%, close to that observed. The weight loss at 269°C (542 K) is the volatilization of the dye due to the heat generated by the chlorate/lactose reaction. Understandably, there is no associated heat flow. The loss of only 32.1% suggests that not all the dye was vaporized. This is not unexpected as the efficient combustion and volatilization of smoke compositions only occurs if the reaction is confined (pressurized). The final exotherm is associated with the oxidation of the carbonaceous organic residues (from the lactose) by the remaining potassium chlorate.

Table 3 shows that the addition of organic and inorganic flame retardants to the smoke composition had little effect on the thermal behaviour except for boric acid, aluminium hydroxide, ammonium polyphosphate, Amgard MC, and calcium borate. These additives caused a decrease in the calorific value of the main exotherm and boric acid caused an increase in the calorific value of the second exotherm. The onset temperature of the exotherms was not altered with any of the additives. Table 4 shows that the addition of the boric acid

resulted in a weight loss of 2.7% at approximately 118°C (391 K) with no associated heat flow. Also, the normal smoke composition initial exothermic peak at 208°C (481 K) was absent. None of the other additives had any significant effect on the DTA/TG response. The organic brominated additives hexabromocyclododecane and octabromodiphenyl oxide showed small additional exothermic peaks at 235°C (508 K) and 270°C (543 K) respectively.

Table 3: DSC Results for Orange Smoke Compositions with Flame Retardant Additives (5% w/w) Heating rate = 20 K/min⁻¹.

Additive	Exotherm 1		Exotherm 2	
	T_{onset} (°C)	ΔH (cal g ⁻¹)	T_{onset} (°C)	ΔH (cal g ⁻¹)
Nil	207	- 248.0	341	- 11.9
Aluminium hydroxide	209	- 142.5	340	- 16.9
Ammonium polyphosphate	199	- 174.2	341	- 12.4
Boric acid	241	- 122.5	340	- 85.6
Calcium borate	208	- 95.9	341	- 22.2
Zinc borate	206	- 222.0	340	- 9.2
Melamine hypophosphate	206	- 209.0	340	- 16.2
Ethylene bis tetrabromophthalamide	205	- 231.7	341	- 5.0
Hexabromocyclododecane	203	- 275.2	339	- 16.0
Ethylene bis dibromonorborane dicarboxamide	204	- 264.3	341	- 12.0
Floxan BL ¹	197	- 219.2	341	- 4.3
Amgard MC ²	200	- 179.8	338	- 9.1
Octabromodiphenyl oxide	214	- 242.8	347	- 9.1

¹ An Ammonium Polyphosphate

Table 4: DTA/TG of Colored Smoke Compositions with Flame Retardant Additives (5%) at a Heating Rate of $10^{\circ}\text{C min}^{-1}$.

Additive	Exotherm 1 ($^{\circ}\text{C}$)	Weight Loss (%)	Exotherm 2 ($^{\circ}\text{C}$)	Weight Loss (%)
Nil	208	17.8	342	9.3
Boric acid	118	2.7	341	15.9
Calcium borate	207	8.5	341	10.4
Zinc borate	210	15.9	340	7.5
Aluminium hydroxide	210	14.9	341	8.0
Hexabromocyclododecane	203	9.8	339	7.3
Octabromodiphenyloxide	204	16.2	339	7.3

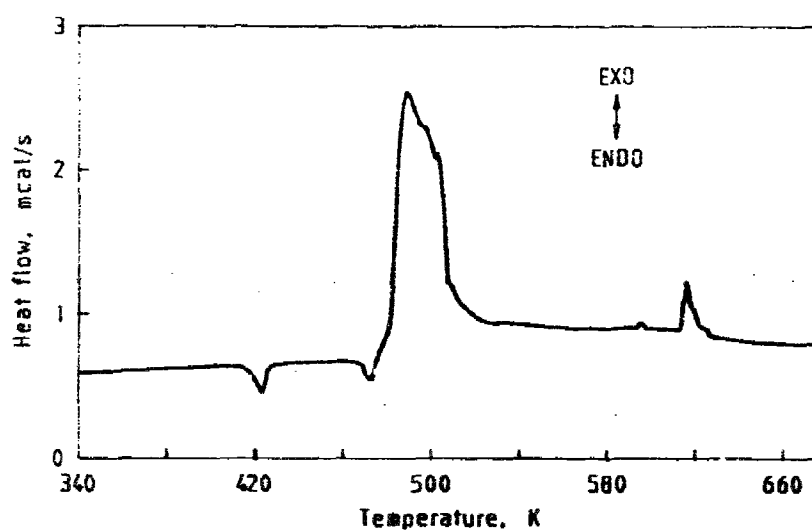


Figure 13: DSC curve for 0.49 mg of colored smoke composition, $20^{\circ}\text{C/min}^{-1}$ heating rate, in nitrogen.

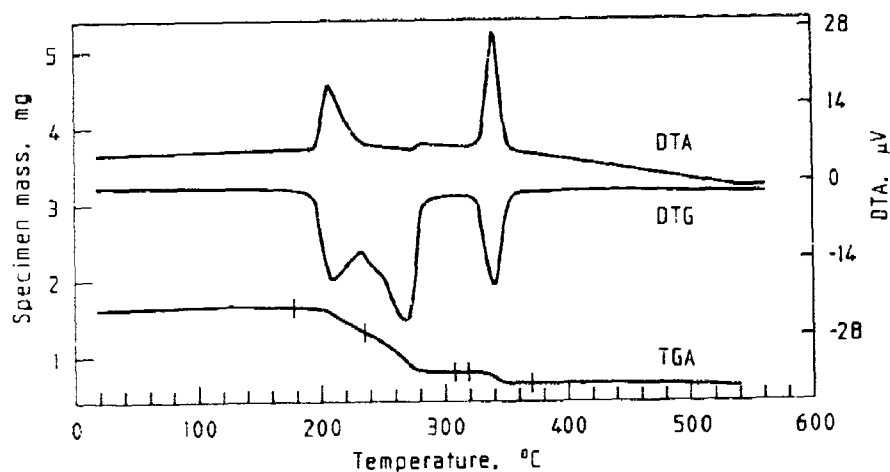
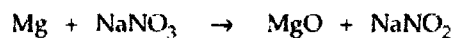


Figure 14: DTA/TGA curve for 1.6 mg of colored smoke composition, $10^{\circ}\text{C}/\text{min}^{-1}$ heating rate, in nitrogen

5.2 Other Compositions

DTA/TG analysis was carried out for the other pyrotechnic compositions tested in the SSCB apparatus. All the compositions showed no significant exothermic response when heated at $10^{\circ}\text{C}/\text{min}^{-1}$ from 0°C to 700°C . The exception was the MSN composition which showed a significant exotherm at 601°C (Grade 0 blown magnesium powder) and 539°C (Grade V cut magnesium powder). This exotherm corresponds to the reaction:



6. Discussion

6.1 SSCB Test and RARDE SSBC Test Response

The SSCB test can be used to assess the response of energetic compositions by the condition of the various parts of the SSCB apparatus at the completion of the test, e.g. the bulging of the base plate or the end plate, fragmentation of the inner cylinders, etc. A scale of test responses has been developed for explosives as a guide to the event severity [11]:

Response	Damage to SSCB
Mild Burning	Little or no damage - SSCB intact
Burning	Outer cylinder split, inner cylinder undamaged
Deflagration	Outer cylinder split, inner cylinder distorted
Explosion	Outer and inner cylinders fragmented/split, baseplate bulged
Detonation	Considerable fragmentation, baseplate holed

This scale lists the main points on which an assessment of the reaction should be based. However, there are no sharp distinctions between the various types of response and the SSCB is not intended to give an unequivocal definition of the materials response to cook off -- merely a guide to the reaction severity.

The RARDE SSBC test has a similar basis in that an estimate of the "explosiveness" of the explosive in a realistic geometry is determined from an interpretation of the number of fragments formed from the event. The advantage of this test over the SSCB is its enhanced confinement -- the threaded steel endcaps give almost total confinement, a significant increase over that of the sealing plates for the SSCB.

6.2 SSCB and RARDE SSBC Test Behaviour of Flare Compositions

The cookoff response of the MSN compositions was classed as mild burning in all cases and at all heating rates. The violence of the reaction was not altered by changes in the particle size of the magnesium powder.

It is generally accepted that the violence of the cookoff response for explosives is greater at the slow heating rate. However, as pointed out in [8], samples such as TNT based explosives which melted at temperatures considerably below the onset of reaction showed inconsistent responses due to the loss of sample from poor sealing of the SSCB and a reduction in density due to volumetric expansion of the composition. Table 2 shows that the temperatures at which reaction of the pyrotechnic sample occurred were above the melting point of sodium nitrate (mp 308°C). Examination of the SSCB apparatus after the test also showed that for the Grade V and Type E magnesium formulations some venting of the reaction products had occurred. Both these factors would reduce the severity of the response of the composition and correlation with a real life situation is questionable. However, similar low violence responses have been recorded in full munitions tests for illuminating flares [12, 13] which tend to support these findings. A major difference from cookoff behaviour of high explosives was that the temperature at which the pyrotechnic composition cooked off was lower at the fast heating rate than at the slow heating rate. This is the reverse of the behaviour usually observed with explosives [9]. This

result probably reflects the difference in reaction mechanisms between pyrotechnics and explosives.

The temperature at which the pyrotechnic composition undergoes cookoff decreased as the particle size of the magnesium decreased. This probably results from the greater ease of ignition with more intimate mixing of the fuel and the oxidant at smaller particle size. An analogous result is the increased impact sensitivity of pyrotechnic compositions as the particle size of the fuel/oxidant decreases.

Addition of a binder to the MSN composition (MSNE) had little effect on the reaction temperature and no effect on the level of response.

A reaction classed as mild burning was recorded at the fast heating rate and no reaction was recorded at the slow heating rate for the MTV flare composition. These results suggest that MTV does not represent a serious problem under these cookoff conditions. These results conflict with full scale munition tests reported by Seubert [13]; MTV filled stores gave a "non-detonation" response under fast cookoff conditions and "deflagration or partial detonation" under slow cookoff conditions, but only when the external temperature exceeds 430°C. Our results showed that no reaction occurs up to 513°C at the slow heating rate and only mild burning commenced at 471°C at the fast heating rate.

Widely varying responses between SSCB tests and full munitions has been noted for some explosives [14]. It is likely that MTV is another filling where correlation is poor. The much larger mass of the munitions relative to what the SSCB test used, permits buildup to a more violent event. In addition, the SSCB is not designed to provide a fully sealed environment for the material under test as noted above and the response observed may not necessarily correlate with results from a system with appreciable pressure confinement or from tests on complete ordnance items.

Further tests using the more confined RARDE SSBC test were unsuccessful as venting of the combustion products occurred through the end cap. The reaction response would be considered mild burning but the premature venting may have reduced the event severity.

6.3 SSCB and RARDE SSBC Test Behaviour of Smoke Compositions

The reactions observed for the orange smoke composition were classed as mild burning at both heating rates in the SSCB test. The SSCB hardware was undamaged but there was evidence of sublimed dye on the outside of the SSCB. These results again conflict with those recorded from full scale munitions tests by Seubert [13]. He found that smoke compositions do not present a hazard under fast cookoff conditions but that slow cookoff response was energetic ... "either deflagration or partial detonation when the exposure temperature exceeded 121°C and the munition did not include a vent or pressure relief device." Chin *et al.* [15] also showed that smoke compositions pressed into standard hardware and placed in a sealed steel magazine box, showed violent responses when radiatively heated. Two differences are apparent between our tests and those of Chin and Seubert; firstly, the degree of confinement and

secondly, the use of complete ordnance containing the full ignition system.

In an attempt to increase the confinement, the smoke composition was tested using the RARDE SSBC test hardware. However, a low level response classed as mild burning was again recorded and the reaction was fully contained. There was some evidence of small quantities of sublimed orange dye on the outside of the test hardware indicating that the system was not completely sealed.

The addition of a brominated binder (flame retardant) had little effect on the behaviour in the SSCB hardware. At both heating rates, the response was mild burning and no damage was observed. The reaction was fully contained and neither venting nor evidence of reaction products were observed on the hardware.

The temperature at cookoff of the smoke compositions was found to be greater at the fast heating rate than at the slow heating rate. Conkling [16] notes that for most pyrotechnics the temperature of ignition either increases with heating rate or remains constant. However, Barton's results [12] indicate that the temperature may increase or decrease depending on the particular composition.

From these results, the colored smoke compositions would not be considered as hazardous under our test conditions.

6.4 SSCB and RARDE SSBC Test Results for Other Pyrotechnics

6.4.1 Aluminium/Potassium Perchlorate (APP)

The response of the APP "flash composition" at the fast heating rate was classed as burning. The outer cylinder was not split but the SSCB hardware was damaged significantly as shown in Figure 10. At the slow heating rate, no reaction was recorded up to a temperature of 655°C.

Photoflash cartridges containing flash compositions based on either magnesium or aluminium as the fuel have exhibited a detonating hazard when exposed to either fast or slow cookoff conditions [13]. Tulis *et al.* [18] succeeded in detonating APP compositions with a detonator/booster but only as long as the particle size of the fuel and the oxidant were sufficiently small (generally below 10 µm and preferably in the range 1 µm). If the particle size was not sufficiently small, then the particles cannot be heated and chemically reacted rapidly enough to support propagation of a detonation wave. For our tests, the mean particle diameter of the aluminium and the potassium perchlorate were 20 µm and > 20 µm respectively, significantly larger than that needed for detonation.

The temperature at which a response was recorded at the fast heating rate was 566°C; the DSC/DTA results confirm this result with an exothermic reaction at 557°C (830 K) and a corresponding 25.4% weight loss. These temperatures differ significantly from those recorded by Seubert [13] where the APP composition "detonated" above 204°C. This composition would be classed as hazardous under fast cookoff conditions but non hazardous under slow cookoff conditions.

6.4.2 Aluminium/Ammonium Nitrate, Aluminium/Copper Oxide, Aluminium/Lead Chromate

These compositions were studied to examine the relationship between the melting point of the oxidizer and the response of the pyrotechnic composition. However, no reactions were recorded for any of the compositions at either heating rate over the temperature range available. The lack of thermal response was confirmed by DSC/DTA analysis. These compositions would not be classed as hazardous under cookoff conditions.

6.5 SSCB with Electrical Initiation

For the MSN compositions initiated electrically in the SSCB hardware, the responses were variable. Those compositions pressed to 98% and 80% TMD exhibited reactions classed as mild burning. The response of the sample pressed to 75% TMD would be classed as burning; the hardware was significantly damaged but the outer cylinder was not split or damaged (Fig. 11).

Comparison between this result with that from thermal cookoff initiation (Section 6.2) suggests that porosity or permeability may play a significant role in determining the response of pyrotechnics to cookoff conditions. The burn rate of a pressed pyrotechnic composition will increase as the pressed density decreases due to increased permeability with resultant thermal heating of the unburnt composition ahead of the burning front. As the gas volume increases, the pressure increases along with the burn rate. This generates more gas and the whole process continues until the pressure from the accelerating burning process causes either an uncontrolled burn, a pressure burst, a deflagration or, in rare instances, a detonation. The rate of the temperature rise in the composition ahead of the burning front is also affected by the thermal conductivity of the fuel and oxidizer used.

The SSCB or the RARDE SSBC hardware delivers predominantly conductive heating. As the temperature slowly increases, the oxidizer begins to melt once the temperature exceeds its melting point. Comparison of Tables 2 and 5 show that for all the formulations examined (with the exception of the colored smoke) the oxidizer would have melted before the reaction temperature was reached and the reaction commenced. The molten oxidizer flows into the sample pores and, via surface tension and coalescence, decreases the porosity. Once this occurs, the combustion gases and hot decomposition products cannot rapidly percolate through the composition ahead of the main reaction front and the pre heating is significantly reduced. This slows the burning rate and with it the violence or explosiveness of the reaction. Also, after the oxidizer has melted, some decomposition may occur before the reaction commences. This produces a back pressure to the advancing burning front and the pre heating gases, further reducing the pre heating effect, the burning rate and the reaction severity.

Table 5: Melting Points of Oxidizers and Fuels used in Pyrotechnic Compositions

Fuel or Oxidizer	mp (°C)	
Sodium nitrate	308	
Potassium chlorate	356	Decomposes $\approx$ 400°C
Lead chromate	844	
Copper oxide	1326	
Potassium perchlorate	610	Decomposes $\approx$ 400°C
Teflon	323	
Ammonium nitrate	169	
Lactose	202	
Magnesium	649	
Aluminium	660	

If however the sample is initiated with a conventional ignition system (fusehead and a priming composition) and the composition is pressed to $\ll$ 100% TMD, pre heating will occur as the porosity does not have enough time to be altered significantly once the reaction commences. As the burn rate increases due to the pre-heating, the severity of the reaction increases. This is confirmed by our results. Thermal initiation of the magnesium/sodium nitrate composition at the lowest %TMD resulted in only mild burning. Using exactly the same hardware but electrically initiating the composition resulted in a more vigorous reaction classed as burning and caused physical damage to the hardware. If the sample density was further increased and electrically initiated, the severity decreased to simple burning; the decrease in porosity reduced the burning rate and the reaction severity.

Both MTV and colored smoke composition have been reported to produce explosive type reactions more severe than those recorded here [12]. Few details of the experimental apparatus are given in [12] but in our arrangement the melting of the oxidizer appears to be important in the level of response. For MTV, the Teflon melts at 323°C, well below the reaction temperature of 471°C. For the smoke composition, although the melting point of the potassium chlorate is greater than the temperature of the reaction (356°C compared to 227°C), the lactose melts at less than 227°C and potassium chlorate is soluble in molten lactose [19]. It seems probable that the loss of porosity due to oxidant melting could explain the lower level of response in our test. The differences between our test results and those of others could be due to their use of full scale ordnance in their testing and the presence of ignition and priming systems which initiate the reaction before significant porosity changes occurs.

6.6 Thermal Analysis

The thermal analysis of the pyrotechnic compositions was conducted to support analysis of the behaviour of the compositions in the SSCB and the RARDE SSBC test and to examine the effect of flame retardant additives on thermal output. The DTA and DSC results for the colored smoke compositions showed that the main combustion reaction commenced at approximately 210°C which agrees closely with the temperatures recorded in the SSCB test. The magnesium/sodium nitrate composition also showed good agreement between the DTA result and the SSCB result. All the other compositions showed minimal exothermic reaction over the temperature range 100 to 550°C which does, to a certain degree, confirm the lack of response recorded in the SSCB test.

The use of flame retardants to modify the response of colored smoke compositions has been reported by Chin *et al.* [15, 20]. They proposed that the addition of small amounts (5%) of flame retardant to the colored smokes desensitized the smokes at slow heating rates; a smaller exotherm from their DTA analysis was reported as confirmation of this result. However, our results are significantly different. Table 3 shows that in our tests the addition of organic flame retardants have no effect on the size or the temperature of the two exotherms. Of particular interest are the results for hexabromocyclododecane and octabromodiphenyl oxide as they are claimed to desensitize smoke compositions to slow cookoff [15, 20]. Our results showed that both additives have no effect on the exotherms. This result is confirmed by the DTA/TG results which also show no change in the observed response for the smoke composition with flame retardant.

Table 3 shows that some of the inorganic additives alter the size of the exotherms. Boric acid, aluminium hydroxide, calcium borate, ammonium polyphosphate and Amgard MC appear to be effective in reducing the size of the major exotherm but none of the additives alter the temperature of the exotherms. Interestingly, several of these additives were tested in [15, 20] but were found to be ineffective.

Differences between our results and other published results may be due to the different heating rates employed. Chin [15, 20] used heating rates of 0.1, 1.0, 10.0 and 70.0°C/min⁻¹ and found that the combustion reaction was reduced at heating rates of 0.1 and 1.0°C/min⁻¹ but not at 10 or 70°C/min⁻¹. Our initial studies were conducted at 20°C/min⁻¹ (for practical reasons) but further studies at other heating rates (Table 6) showed that generally, as the heating rate was reduced the temperature of the major exotherm decreased and the thermal output decreased. Table 6 shows the DSC results at a reduced heating rate of 1.25°C/min⁻¹. The size of the major exotherm for the smoke composition with aluminium hydroxide or boric acid additives increased significantly at the lower heating rate compared to the values recorded at a heating rate of 20°C/min⁻¹. This result is unusual and, although triplicate DTA's were conducted, similar results were recorded for all repeat tests. No obvious explanation can be offered. The results for calcium borate and Amgard MC (ammonium polyphosphate) are more encouraging as they show a significant decrease in the size of the major exotherm at the lower heating rate of 1.25°C/min⁻¹.

Table 6: T_{onset} and ΔH values for colored smoke and additive compositions from DSC analysis at 20 K min^{-1} and 1.25 K min^{-1} heating rates

Additive	Heating Rate (K/min^{-1})			
	20	20	1.25	1.25
	$T_{onset} \text{ (C)}$	$\Delta H \text{ (cal g}^{-1}\text{)}$	$T_{onset} \text{ (C)}$	$\Delta H \text{ (cal g}^{-1}\text{)}$
Nil	207	- 248	187.0	- 238.9
Al(OH)_3	209	- 142	192.6	- 214.4
Boric Acid	241	- 122.5	157.9	- 199.4
Calcium Borate	208	- 95.9	194.8	- 87.9
Zinc Borate	206	- 222.0	186.9	- 207.4
Hexabromocyclododecane	203	- 275.2	177.4	- 189.7
Octabromodiphenyl oxide	214	- 242.8	187.4	- 228.6
Amgard MC	200	- 179.8	186.2	-105.3

7. Conclusions

Using the SSCB and the RARDE SSBC explosive test hardware to study the slow and fast cookoff response of pyrotechnic compositions showed that only the aluminium/potassium perchlorate composition produced a hazardous response under the test conditions. Mild burning reactions (non explosive) were recorded for all the other compositions including MTV and colored smoke compositions. These results differ in some cases from full scale munition tests [12, 13]. This difference is probably due to the smaller sample mass used in the SSCB/SSBC test coupled with venting of the combustion products. However, this study suggests that the RARDE SSBC test is more useful than the SSCB test as the sample is more confined and reduces venting of the reaction products.

The porosity of the composition and the method of heating appear to strongly influence the severity of the response. If the composition is initiated electrically under confinement in the SSCB the response may be severe. But, the response may be significantly reduced when conductively heated. This effect is due to change in the porosity of the composition with fuel/oxidant phase changes. Similarly, increasing the sample density reduces the response.

Analysis using DSC/DTA/TG techniques provided information on the thermal response and temperature of ignition of the composition. There is no direct measure of the severity of the response but the size of the main exotherm may be used to examine changes in the response of the compositions. The addition of flame retardant to colored smoke compositions has little effect on

the thermal output with the exception of calcium borate and ammonium polyphosphate.

This study does, however, suggest that to assess the response of pyrotechnic composition to slow and fast cookoff, full munitions rather than small scale tests need to be conducted except where there is no obvious hazard or the response is classed as low level.

8. Acknowledgements

The authors would like to thank Mr John Bentley and Dr Robert Spear for several useful discussions. Also Mr Mark Fitzgerald for the DSC/DTA analysis.

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SECURITY CLASSIFICATION OF THIS PAGE

UNCLASSIFIED

DOCUMENT CONTROL DATA SHEET

REPORT NO.
MRL-TR-91-44AR NO.
AR-006-842REPORT SECURITY CLASSIFICATION
Unclassified

TITLE

Cookoff behaviour of pyrotechnics

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DSTO Materials Research Laboratory
PO Box 50
Ascot Vale Victoria 3032REPORT DATE
February, 1992TASK NO.
DST 89/142SPONSOR
DSTCFILE NO.
G6/4/8-4048REFERENCES
20PAGES
38

CLASSIFICATION/LIMITATION REVIEW DATE

CLASSIFICATION/RELEASE AUTHORITY
Chief, Explosives Ordnance Division

SECONDARY DISTRIBUTION

Approved for public release

ANNOUNCEMENT

Announcement of this report is unlimited

KEYWORDS

Insensitive Munitions
Super Small Scale Cookoff BombSSCB
SCBSmall Scale Cookoff Bomb
Pyrotechnics

ABSTRACT

The US Navy has officially adopted a policy of Insensitive Munitions (IM) and the Australian Defence Forces are currently considering adoption of a similar IM policy. One major area of uncertainty is whether pyrotechnic stores respond in an unacceptably violent manner to IM threat scenarios, and whether they should be subjected to rigorous IM testing. At present there is only a limited amount of information available on the response of pyrotechnics to IM threat scenarios. The study reported in this paper generates some much needed data on the cookoff behaviour of pyrotechnics.

The results of the response of several pyrotechnic compositions to both fast and slow cookoff using the Super Small Scale Cookoff Bomb (SSCB) and the Royal Armament Research and Development Establishment (RARDE) Small Scale Booster Cookoff Test (SSBCT), supported by Differential Scanning Calorimetry/Differential Thermal Analysis (DSC/DTA) data, are presented. The results suggest that most pyrotechnic compositions do not present a serious threat in terms of the level of response to these test stimuli.