POTENTIAL FIRE AND EXPLOSION HAZARDS OF A RANGE OF LOOSE PYROTECHNIC COMPOSITIONS

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Summary:

An earlier paper presented the results of burning trials on 1-25 kg quantities of a range of pyrotechnic substances, under the conditions of self confinement. In particular, information was given on fireball size, duration and thermal radiation output. In some instances the compositions burned so quickly, and the quantity of material present provided sufficient self-confinement, to cause explosion. This paper considers how the previously reported information can be used to estimate the potential fire and explosion hazards which these materials may present when handled (for example in a workroom).

1. Introduction:

Most pyrotechnic substances are generally recognised to be much more sensitive to accidental initiation than conventional secondary high explosives. In recent years there have been a number of serious accidents reported from different countries that have involved pyrotechnic substances and articles, particularly during their manufacture. Whether or not a particular pyrotechnic substance will burn or explode when initiated, depends upon a number of factors such as how energetic the material is and how much confinement is present. The potential blast effects from flash composition are well illustrated by the reported[1] demolition of a two storey brick-built house following initiation of 5 kg of flash composition. Although it is difficult to accurately predict whether, and how vigorously, a pyrotechnic substance under particular circumstances will either burn or explode, quantification of the potential hazards of these materials can be used to aid the selection of appropriate protective measures.

Whilst there is some limited information in the literature on fireball size and burning rates for high explosives, there is little information available for pyrotechnic substances, and particularly for their thermal radiation outputs.

2. Trials Results:

Experiments to measure the thermal radiation hazards from a range of pyrotechnic compositions have been carried out[2]. Details of these compositions are given at Appendix 1. Table 1 summarises the burning rates, fireball diameters, etc from the trials measurements.

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Table 1: Trials results on pyrotechnic compositions.

PYROTECHNIC	SAMPLE MASS (kg)	MEAN DIAM. EQUIV. SPHERE (m)	MEAN DURATION (s)	MASS BURNING RATE (kg/s)	MEAN PEAK SEP (kW/m^2)
Gunpowder	1.000	3.200	1.000	1.040	230.000
	5.000	4.800	1.400	3.640	250.000
	25.000	9.000	1.600	15.630	320.000
Flare Comp. 1	1.000	1.200	25.600	0.040	250.000
	5.000	1.200	50.400	0.100	250.000
	25.000	2.400	54.000	0.460	270.000
Flare Comp. 2	1.000	2.000	7.400	0.140	580.000
	5.000	3.200	10.500	0.480	670.000
	19.000	4.800	12.300	1.540	1010.000
Star Comp. 1	1.000	3.400	1.400	0.760	1010.000
	5.000	7.000	2.300	2.180	1000.000
	25.000	explosion	explosion	explosion	explosion
Star Comp. 2	1.000	1.600	6.200	0.160	380.000
	5.000	2.800	10.700	0.470	430.000
	25.000	4.200	13.000	1.920	600.000
Priming Comp. 1	1.000	0.800	7.900	0.130	360.000
	5.000	1.000	12.500	0.400	430.000
Priming Comp. 2	1.000	2.400	1.700	0.610	400.000
	5.000	4.400	2.400	2.260	360.000
	25.000	5.800	3.600	6.940	370.000
Delay Comp.	1.000	too weak to measure			
	5.000	1.000	26.100	0.190	150.000
	25.000	1.600	30.000	0.830	260.000
Flash Comp. 1	1.000	5.000	0.400	2.330	
	5.000	explosion	explosion	explosion	explosion
Flash Comp. 2	1.000	explosion	explosion	explosion	explosion

Note: SEP = surface emissive power

In all instances it was possible to define the relationship between fireball diameter (D) and mass (M) by $D = a M^b$. Values for the constants a and b are given in Table 2.

Table 2: Flame diameter (D) and charge mass (M) parameters ($D = aM^b$)

Composition	a	b
Gunpowder	3.100	0.279
Flare Composition 1	1.060	0.209
Flare Composition 2	1.890	0.323
Star Composition 1	3.300	0.400
Star Composition 2	1.540	0.327
Priming Composition 1	0.740	0.171
Priming Composition 2	2.520	0.292
Delay Composition	0.530	0.325

3. Estimates of the Potential Thermal Radiation Hazards:

3.1 Methodology:

When a pyrotechnic composition burns, the amount of thermal radiation received by someone nearby will depend upon a number of factors, such as how much thermal radiation is emitted from the surface of the flame/fireball, the size of the flame/fireball, how close the worker is to the event, and how long it burns. If the composition starts to burn relatively slowly and then builds up steadily to its full potential, people in the immediate vicinity of the fire may have sufficient time to evacuate the area before injury occurs. On the other hand, people are generally unable to respond quickly enough to a short duration fireball; i.e the event could be over before the person facing the fireball senses it and turns away to escape. A minimum response time of 5 seconds is quoted in the literature[3].

The effects of received radiation on the human body are dependent on a number of factors including age of the person, amount of exposed skin, and type of clothing. In the literature Hymes et al[3] give some limits for the effects of received thermal radiation doses:

Table 3: Effects of thermal radiation doses on human body.

Thermal Radiation Dose $(kW/m^2)^{4/3}$ s	Effect
10,000-3,000	Spontaneous ignition of clothing
4,000-1,100	Piloted ignition of clothing
3000[a]	Third degree burn
2300	50% mortality[b]
1800	Deep second degree burn
1200[c]	Second degree burn
1060	1% mortality[b]
700[d] -210	Threshold of blistering

Notes: a. Third degree burns with burn depth of 2 mm. b. These mortality thresholds relate to 'ordinary' clothing.
c. Second degree burns with burn depth of 0.1 mm. Burn depth increases linearly up to a value of the thermal dose at 2600 dose units.
d. There is evidence for a region of constant injury between these limits

Calculation[3] of the received thermal radiation dose, V ((kW/m^2)$^{4/3}$ s), at a distance X (m) from the centre of a fireball is possible using $\mathbf{V = (I^0 \times F)^{4/3}\, t}$

where I^0 = source heat flux (kW/m^2)
F = configuration factor
and F, for a spherical fireball[4] = $(R/X)^2$
R = radius of fireball (m)
and t = the exposure time (seconds)

3.2 Thermal Dose Calculations:

Using the methodology given above, information from the burning trials can be used to calculate the distances to some of the 'thermal radiation dose' (burn) criteria given in Table 3. The results of this are given in Table 4.

Table 4: Distances from burning pyrotechnic to levels of harm.

Pyrotechnic	Quantity (kg)	Fireball Radius (m)	Distances (m) from centre of flame/fireball to levels of harm:			
			3rd Degree Burns / Spontaneous Ignition of Clothing (3000 (kW/m^2)$^{4/3}$s)	**Deep 2nd Degree Burns** (1800 (kW/m^2)$^{4/3}$s)	**2nd Degree Burns.** (1200 (kW/m^2)$^{4/3}$s)	**Blister Threshold** (210 (kW/m^2)$^{4/3}$s)
Gunpowder (3/7 Grist)	1 5 25	1.6 2.4 4.5	1.6 2.4 4.8	1.6 2.6 5.8	1.7 3.0 6.7	3.3 5.8 12.9
Flare Comp 1	1 5 25	0.6 0.6 1.2	0.9 (5 s) 0.9 (5 s) 1.8 (5 s)	1.0 (5 s) 1.0 (5 s) 2.2 (5 s)	1.2 (5 s) 1.2 (5 s) 2.5 (5 s)	2.3 (5 s) 2.3 (5 s) 4.9 (5 s)
Flare Comp 2	1 5 19	1 1.6 2.4	2.2 (5 s) 3.8 (5 s) 6.9 (5 s)	2.7 (5 s) 4.6 (5 s) 8.4 (5 s)	3.1 (5 s) 5.3 (5 s) 9.8 (5 s)	5.9 (5 s) 10.2 (5 s) 18.8 (5 s)
Star Comp 1	1 5 25	1.7 3.5 explosion	3.0 7.5 explosion	3.7 9.1 explosion	4.3 10.6 explosion	8.3 20.4 explosion
Star Comp 2	1 5 25	0.8 1.4 2.2	1.4 (5 s) 2.6 (5 s) 4.9 (5 s)	1.7 (5 s) 3.2 (5 s) 5.9 (5 s)	2.0 (5 s) 3.7 (5 s) 6.9 (5 s)	3.8 (5 s) 7.2 (5 s) 13.3 (5 s)
Priming Comp1	1 5	0.4 0.5	0.7 (5 s) 0.9 (5 s)	0.8 (5 s) 1.1 (5 s)	1.0 (5 s) 1.3 (5 s)	1.9 (5 s) 2.6 (5 s)
Priming Comp2	1 5 25	1.2 2.2 2.9	1.5 2.9 4.5	1.8 3.5 5.4	2.1 4.1 6.3	3.9 7.8 12.1
Delay Comp	1 5 25	n.a 0.5 0.8	n.a 0.6 (5 s) 1.2 (5 s)	n.a 0.7 (5 s) 1.4 (5 s)	n.a 0.8 (5 s) 1.7 (5 s)	n.a 1.5 (5 s) 3.2 (5 s)
Flash Comp 1	1 5	2.5 explosion	n.a explosion	n.a explosion	n.a explosion	n.a explosion
Flash Comp 2	1.000	explosion	explosion	explosion	explosion	explosion

Notes: **n.a** - means 'not available'
(5 s) - means that pyrotechnic burned for more than 5 seconds, but calculation assumes that person escapes after this time.

4. Estimates of the Potential Explosion Hazards:

4.1 Methodology:

Blast predictions for high explosives are usually made using a TNT-equivalence approach[5], and it is known that compositions containing mixtures of aluminium and potassium perchlorate (such as are used for producing light and sound effects), can also explode and produce blast waves similar to TNT[1]. In general, lower energy pyrotechnics which can explode do so much more slowly than conventional high explosives. A result of this is that the corresponding shock wave is usually initially of much lower amplitude and much longer duration. Information on the blast parameters from pyrotechnic compositions is somewhat limited, and although the ability for pyrotechnics to cause blast damage is different to TNT type explosions, it is still usual and convenient to equate them all to TNT.

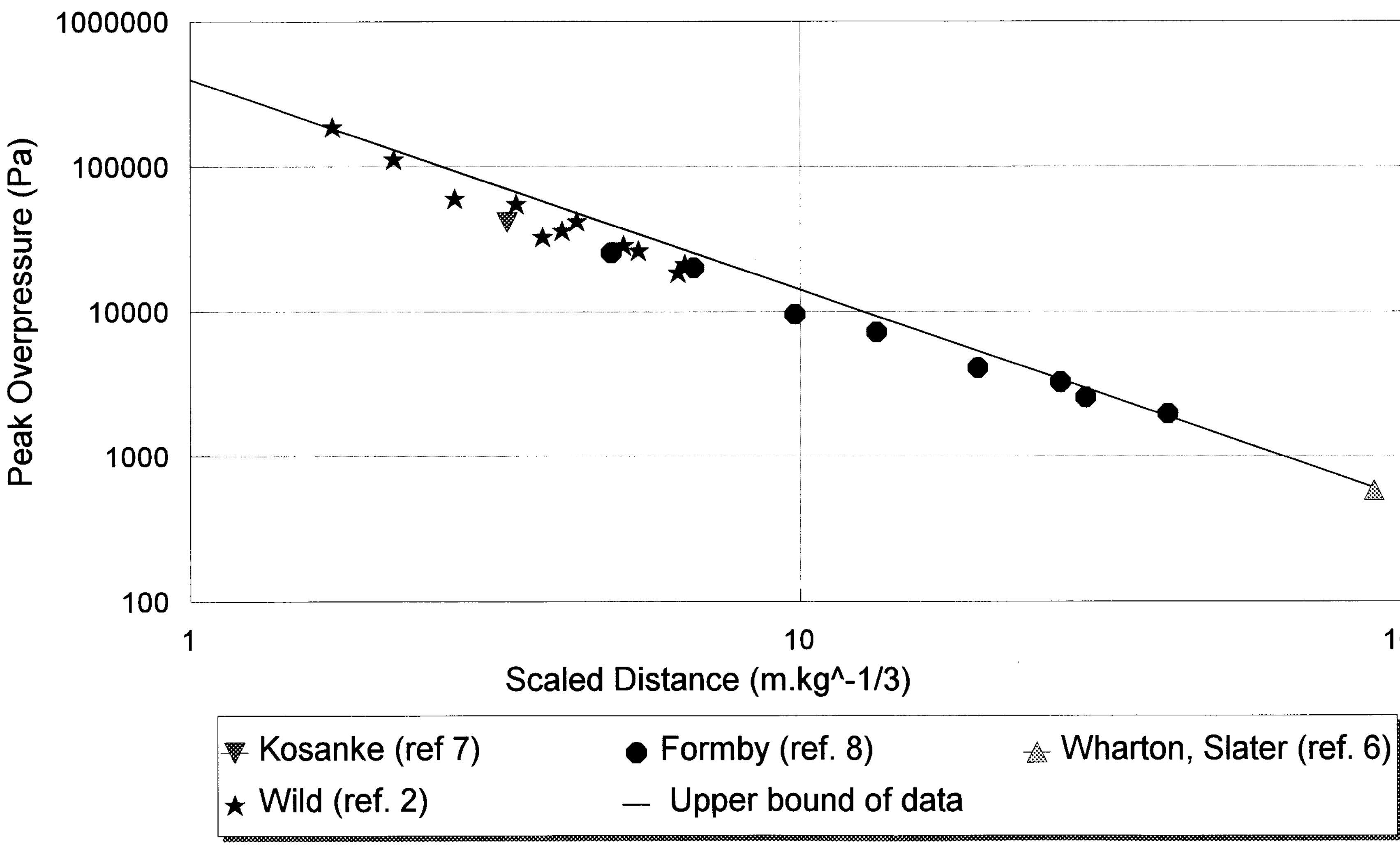
Of the compositions tested, the flash compositions presented the greatest explosion hazard. Blast data[1, 6, 7, 8] for small quantities of a flash composition very similar to the second of the two considered here (i.e 30% Al / 70% $KClO_4$), provided the results in Table 5.

Table 5: Compilation of blast data for Flash Composition

Confinement	Mass of Flash Composition (g)	Distance (m)	Peak Overpressure (kPa)	TNT Equivalence	Ref.
as a firework	5	15.000	0.600	0.400	6.000
polythene bottle with metal screw cap	50	1.200	41.400	0.400	7.000
thin cardboard box	50 50 50 100 100 100 200 200 200 500 500	1 1.5 2 1 2 3 1 2 3 3 5	60.4 36.3 26.4 112.6 42.1 21.3 188.0 55.2 28.7 32.8 18.5	0.6 0.8 1.1 0.8 1.3 1.3 0.8 1.0 1.1 0.6 0.9	1.000
plastic maroon shell	400 400 400 400	5 10 20 30	19.9 7.2 3.3 2.0	0.8 0.7 0.7 -	8.000
double plastic bag	1000 1000 1000 1000	5 10 20 30	25.6 9.6 4.1 2.6	0.5 0.6 0.5 -	8.000

Figure 1 illustrates data from Table 5 and indicates that a common dependence links overpressure with scaled distance. The line shown indicates the maximum overpressure expected, and could be used as a

Figure 1: Peak Overpressure (Flash Composition)



basis for predicting potential blast overpressures at distance for different quantities of flash composition. The equation of this line is:

$$\log_{10}[\text{blast overpressure (Pa)}] = 5.6 - 1.45 \log_{10}[\text{scaled distance (m. kg}^{-0.333})]$$

The most sensitive and vulnerable human organ to blast overpressure is the ear. The potential for causing damage to the eardrum[5] is shown in Table 6.

Table 6: Variation of eardrum rupture with blast overpressure.

Blast Overpressure (kPa)	% Eardrum Rupture
35.6	5
45.4	10
67.7	25
105	50
163	75
243	90

4.2 Eardrum Rupture Calculations:

Using the methodology described in 4.1 above, estimates of the extent of eardrum rupture from the blast from quantities of flash composition at distances typical of pyrotechnic processing operations are presented in Table 7.

Table 7: Estimates of the extent of eardrum rupture from the blast from flash composition.

Mass of Composition (g)	% Eardrum rupture at	
	1 m	3 m
50	40	<1
100	60	<1
500	90	20
1000	100	35

5 Observations:

- **Gunpowder:** None of the gunpowder samples exploded. They all burned extremely rapidly, and even at the 25 kg size, the gunpowder was consumed in 2 seconds. In an accident situation involving up to 25 kg of loose material, the event would be over before anyone in the vicinity had time to take evasive action. It is interesting to note that outside the fireball the potential for serious burns falls away very rapidly with distance. Even the threshold for second degree burns is very close to the surface of the fireball.

- **Flare Compositions:** Flare compositions are intended to burn brightly for long periods of time. This is reflected in the measured very high surface emissive powers of Composition 2, and the long burn time. In an accident situation this means that the hazardous 'zones' will extend well outside the flame diameter. For 5 kg of Composition 2 for example, the fireball radius is 1.6 m, whilst the distances to 2nd and 3rd degree burns are 5.3 and 3.8 m, respectively.

- **Star Compositions**: Star Composition 1 exploded violently only at the 25kg test size. This does not mean that the smaller quantities would not have exploded if, for example, more confinement was present in the form of packaging. Also other star compositions not tested might be even more hazardous. The 5 kg trial on Star Composition 1 gave the largest fireball and also the greatest potential for burns injuries outside the fireball, i.e distances of 20 m, 11 m, and 8 m to the blister threshold, 2nd and 3rd degree burns, respectively. These distances were reduced by a factor of approx. three for the 1 kg quantity.

- **Priming Compositions:** The second Priming Composition was the more energetic of the two, with fireball dimensions less than gunpowder, but outside the flame the potential for serious burns fell away less rapidly with distance.

- **Delay Compositions:** The one Delay Composition tested burned relatively slowly and with small flame dimensions.

- **Flash Compositions**: Flash Composition 2 presented the greatest explosion hazard. Associated with each explosion is a fireball; but these were not quantified in terms of fireball diameter and duration. Flash Composition 1 was slightly less energetic in that the 1kg test sample did not explode, but gave a very large fireball (5 m diameter).

- Table 5 indicates that there is a variation in behaviour of flash composition depending on confinement; and that the TNT equivalence varies with the quantity of material and distance from the explosion source

- Table 7 shows that the potential for causing eardrum damage falls away rapidly with distance from the source. This can be compared with the fireball diameter of 2.5 m for 1 kg of Flash Composition 1; (- fireball dimensions for Flash Composition 2 were not measured).

6. Conclusions:

- Considering the most energetic/hazardous result from each 'pair' of compositions tested; the order by which the compositions present the potential for causing the greatest injury (blast and/or thermal effects) were as follows:

  Flash > Star > Flare > Gunpowder > Priming > Delay

  Only the flash and the one star compositions exploded as tested. This does not mean that none of the other compositions can explode violently if more material is present, or if additional confinement is provided. McIntyre[9] for example, quotes TNT equivalences of up to around 50% for some flare compositions.

- The likelihood of explosion of the Flash and Star compositions in less than 1 kg quantities is not clear, although with flash composition evidence of violent reactions was obtained[8] with quantities as low as 5g contained in small stoppered glass bottles. Accidental initiation of pyrotechnic compositions is clearly most likely to occur when they are being handled, and explosions of 1 kg of Flash or Star composition would at the very least, almost certainly cause serious eardrum damage. Whether or not the mixture burned rapidly or exploded, the process worker would be engulfed in a fireball.

♦ Engulfment of a person inside a fireball produced from either burning or exploding pyrotechnic composition would cause severe burns to any exposed part of the body, and possibly any part not adequately protected by suitable, and possibly special, fire protective clothing.

♦ For Gunpowder (1 - 25 kg) and compositions with similar burning characteristics, the potential for causing serious burns falls away rapidly outside the fireball.

♦ Flare compositions burn intensely for long periods of time, giving rise to the potential for serious burns well outside the flame diameter.

♦ The priming compositions tested gave fireball dimensions less than Gunpowder. Outside the flame associated with Composition 2, the potential for serious burns fell away less rapidly than gunpowder.

♦ The one Delay Composition tested burned relatively slowly and with small flame dimensions.

♦ The first step towards providing effective safeguards against the risks associated with pyrotechnics handling is the quantification of potential hazards. This paper presents a summary of potential thermal and explosion hazards from typical quantities of pyrotechnics that could be encountered in industrial manufacturing, handling and processing situations. It is hoped that the information in this paper may prove useful in providing a basis for assessing the safety of these operations.

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APPENDIX 1

List of pyrotechnic substances and ingredients.

PYROTECHNIC	INGREDIENTS	%
Gunpowder 3/7 Grist	Potassium Nitrate Carbon Sulphur	75.0 15.0 10.0
Flare Composition 1	Magnesium Lithographic Varnish Sodium Nitrate Calcium Oxalate PVC Powder	26.0 4.0 42.0 16.0 12.0
Flare Composition 2	Magnesium Lithographic Varnish Sodium Nitrate Calcium Oxalate	49.0 4.5 39.5 7.0
Star Composition 1	Magnesium Boiled Linseed Oil Barium Nitrate Potassium Perchlorate PVC Powder	42.0 6.0 17.0 27.0 8.0
Star Composition 2	Gunpowder Potassium Nitrate Dextrin Binder Aluminium	55.6 18.5 7.4 18.5
Priming Composition 1	Potassium Nitrate Silicon Powder Gunpowder Sulphurless mealed	40.0 40.0 20.0
Priming Composition 2	Gunpowder Potassium Nitrate Silicon Dextrin Binder	68.0 14.6 14.6 2.8
Delay Composition	Potassium Nitrate Charcoal Acaroid Resin Gunpowder	66.7 11.1 11.1 11.1
Flash Composition 1	Magnesium Potassium Perchlorate Graphite	57.0 37.0 6.0
Flash Composition 2	Aluminium Potassium Perchlorate	33.3 66.7