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Some Techniques for Manufacturing Fireworks

(1) Dark Delay Compositions

(2) The Use of Metal Powders

Takeo Shimizu

1. Introduction

In recent years I have studied the oxidation and reduction taking place between various substances in a mixture. I reported on some of these studies in a paper titled "A Concept of Negative Explosives" presented in 1986 at the *Eleventh International Pyrotechnics Seminar*[1] in Vail, Colorado, USA. In the present paper, I will be presenting the follow-up work which I have performed under the above title.

The work was carried out using the oxygen value of the mixture to clarify the burning effects. The oxygen value denotes the excess (positive) or inadequate (negative) amount of oxygen generated in grams per 100 grams of mixture during the burn.

The term "dark delay composition" refers to a mixture which does not form a flame or spark that is visible from a distance. The effect can be used to prevent the formation of the trail from a flying firework. It is referred to for short in the following as "dark composition".

When a metal is used as the component of a mixture, a special effect is generated. A report is given here on metal sparks, red lead explosive charges and water flares. The metals in question are magnesium, magnalium, aluminum, ferrotitanium and zirconium, whose effects are explained as a function of the properties of the metal, those of the oxygen carrier and the oxygen value of the mixture.

2. Dark Compositions

2.1 Previous Dark Compositions

There are two types of dark composition: One for fuses and the other for the transitional layer of color-changing stars. The compositions of the first type are, for example, as follows:[2]

I.	Potassium nitrate	36%
	Realgar	45%
	Paulownia charcoal	10%
	Sulfur	9%
	Oxygen value	–39.11 g/100 g mixture
	Burn rate	2.8 mm/s
II.	Potassium nitrate	56%
	Realgar	34%
	Paulownia charcoal	10%
	Oxygen value	–13.08 g/100 g mixture
	Burn rate	5.1 mm/s

These compositions are effective but each one contains realgar, which is not customarily used in Europe or the USA. By trial and error, I determined the composition of the second type of dark composition to be as follows:[3]

III.	Potassium nitrate	79%
	Potassium perchlorate	7%
	Accroides resin	2%
	Antimony trisulfide	3%
	Wood charcoal	9%
	Oxygen value	+6.58 g/100 mixture
	Burn rate	0.85 mm/s

This composition burns with a very weak flame while on the ground.

It was intended to improve compositions I–III. Compositions I and II each have a negative oxygen value while III has a positive oxygen value. This indicates that the most advantageous compositions lie within the negative or positive zones of the oxygen value.

2.2 Experiments

I therefore checked the oxygen value of the following compositions.

(1) Potassium nitrate + sulfur + Paulownia charcoal

(2) Potassium nitrate + antimony trisulfide + Paulownia charcoal

(3) Potassium perchlorate + accroides resin

(4) Red lead, Pb_3O_4 + ferrosilicon

(5) Potassium nitrate + antimony trisulfide

(6) Potassium nitrate + antimony trisulfide + sulfur

Compositions (5) and (6) were selected with the aid of the triangular diagram (Figure 1).[4] Compositions (1) to (4) are located almost in a zone where the oxygen value is positive, but (5) and (6) are in the negative oxygen value zone. The results for each composition are shown in Tables 1 to 6 and in Figures 2 and 3.

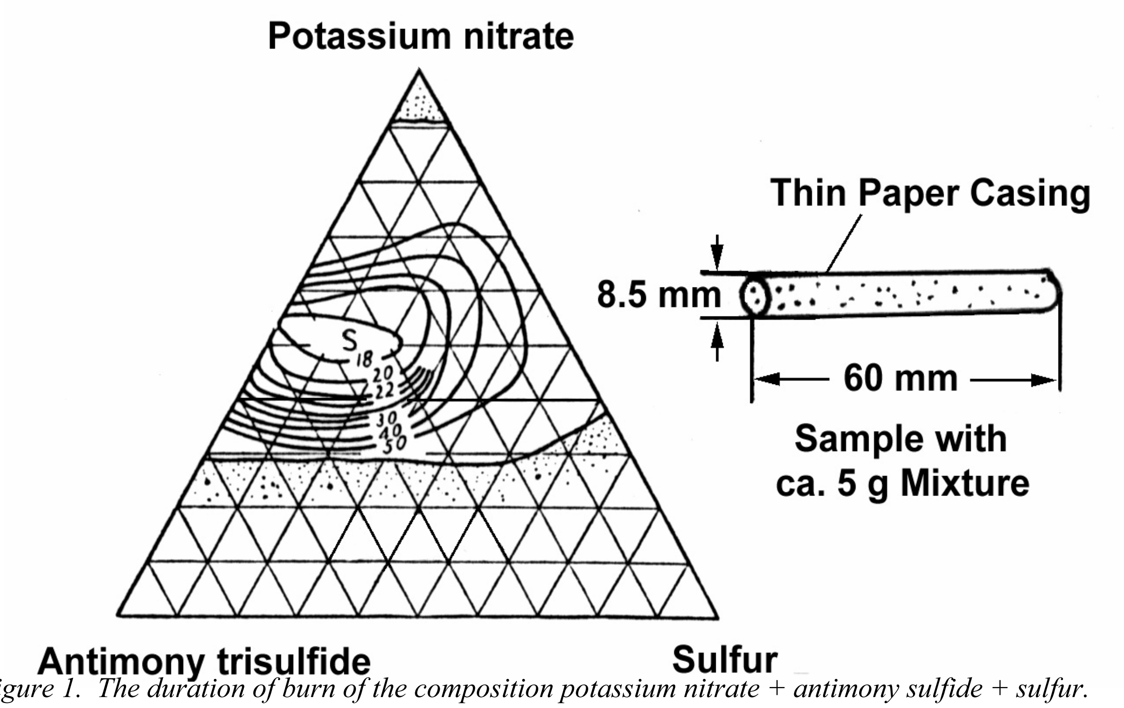


Figure 1. The duration of burn of the composition potassium nitrate + antimony sulfide + sulfur.

Table 1. Potassium Nitrate + Sulfur + Paulownia Charcoal.

	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8	No. 9
Potassium nitrate	76	78	80	82	84	86	88	90	92
Sulfur	12	11	10	9	8	7	6	5	4
Paulownia charcoal	12	11	10	9	8	7	6	5	4
Oxygen value (g/100 g mixture)	–12.1	–7.75	–3.45	+0.85	+5.16	+9.47	+13.77	+18.07	+22.38
Burn rate (mm/s)	7.6	6.1	4.6	3.5	2.8	2.2	1.6	—	—
Effect	1	1	2	2	3	3	4	5	5

Abbreviations for Effect:

1 long flame (approx. 6 cm) or spark

2 thin flame or spark

3 almost no flame or spark

4 small flame and spark

5 does not ignite or goes out

NOTE: These abbreviations are also used in the following Tables.

Table 2. Potassium Nitrate + Antimony Trisulfide + Paulownia Charcoal.

	No. 11	No. 12	No. 13	No. 14	No. 15	No. 19
Potassium nitrate	76	78	80	82	84	86
Antimony trisulfide	12	11	10	9	8	7
Paulownia charcoal	12	11	10	9	8	7
Oxygen value (g/100 g mixture)	–5.15	–1.41	+2.31	+6.03	+9.77	+13.5
Burn rate (mm/s)	6.3	4.6	3.1	2.5	1.6	—
Effect	1	1	2	3	5	5

Table 3. Potassium Perchlorate + Accroides Resin.

	No. 21	No. 22	No. 23	No. 24	No. 25	No. 26
Potassium perchlorate	76	78	80	82	84	86
Accroides resin	24	22	20	18	16	14
Oxygen value (g/100 g mixture)	—	—	—	—	—	—
Burn rate (mm/s)	1.4	1.4	1.5	—	—	—
Effect	1	1	1	5	5	5

Table 4. Red Lead, Pb_3O_4 + Ferrosilicon

	No. 31	No. 32	No. 33	No. 34	No. 35	No. 36	No. 37
Red lead, Pb_3O_4	86	88	90	92	94	96	98
Ferrosilicon (≈90% Si)	14	12	10	8	6	4	2
Oxygen value (g/100 g mixture)	+8.33	+11.08	+13.85	+16.61	+19.36	+22.12	+24.89
Burn rate (mm/s)	15.1	14.3	11.9	10.9	8.6	5.7	—
Effect	3	3	4 Yellow smoke	4 Yellow smoke	4 Yellow smoke	4 Yellow smoke	5

Table 5. Potassium Nitrate + Antimony Trisulfide

	No. 41	No. 42	No. 43	No. 44	No. 45	No. 46	No. 47	No. 48	No. 49
Potassium nitrate	30	32	34	36	38	40	42	44	46
Antimony trisulfide	70	68	66	64	62	60	58	56	54
Oxygen value (g/100 g mixture)	–15.84	–14.26	–12.68	–11.08	-9.50	-7.92	-6.34	-4.76	-3.16
Burn rate (mm/s)	—	2.8	3.6	4.6	5.2	5.4	6.1	5.9	6.4
Effect	5	4 smoke	4 smoke	3 smoke	3 smoke	2	1	1	1

Table 6. Potassium Nitrate + Antimony Trisulfide + Sulfur

	No. 51	No. 52	No. 53	No. 54	No. 55	No. 56	No. 57	No. 58	No. 59
Potassium nitrate	30	32	34	36	38	40	42	44	46
Antimony trisulfide	35	34	33	32	31	30	29	28	27
Sulfur	35	34	33	32	31	30	29	28	27
Oxygen value (g/100 g mixture)	–37.9	–35.7	–33.5	–31.3	–29.0	–26.8	–24.6	–22.4	–20.2
Burn rate (mm/s)	0.78	0.76	1.05	1.24	1.41	1.55	1.72	1.88	2.18
Effect	5	4 smoke	4 smoke	4 smoke	4 smoke	4 smoke	3	3	3

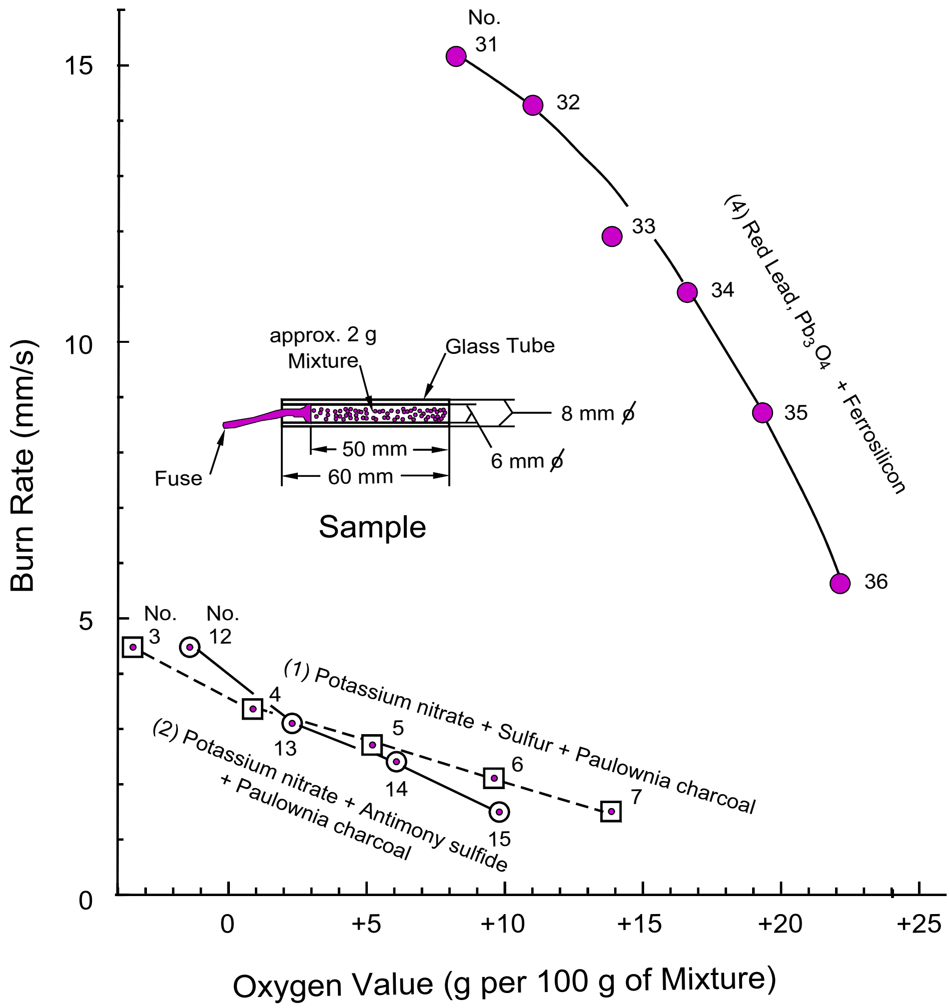


Figure 2. Burn rates of mixtures having a positive oxygen value.

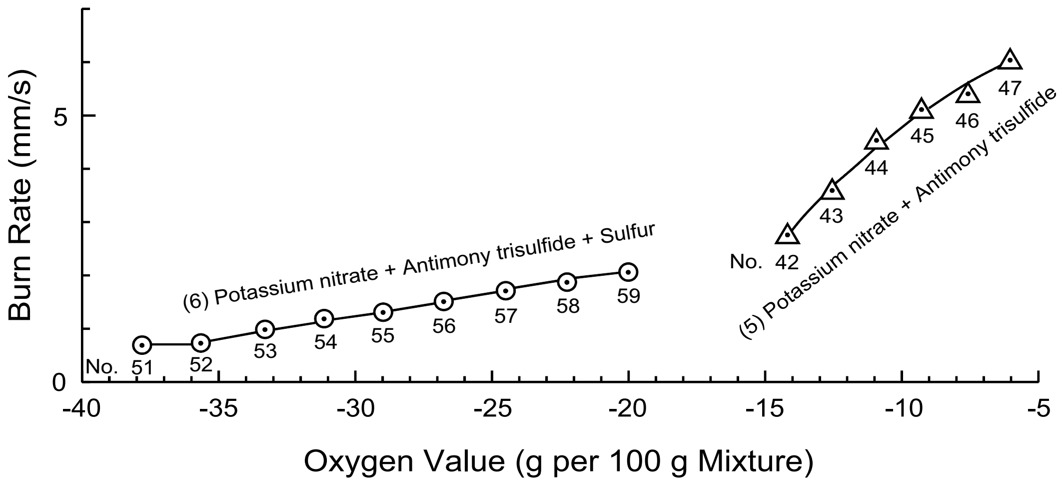


Figure 3. Burn rates of mixtures having a negative oxygen value.

From the results presented in these Tables and Figures, we can select some mixtures that are suitable for use as the dark composition:

From the compositions having a positive oxygen value:

(1) No. 5, No. 6, No. 7

(2) No. 14

(4) No. 34, No. 35, No. 36

From the compositions having a negative oxygen value:

No. 42, No. 43, No. 44

No. 52, No. 53, No. 54, No. 55, No. 56

Composition No. (3) is not suitable for the dark composition because the mixture always forms a bright flame.

The compositions, which have the positive oxygen value, are not suitable for fuse with a paper tube or a paper sleeve because the burning paper creates a flame that is visible from a distance. Therefore, the compositions can only be used as the transitional layer on color-changing stars. An experiment was conducted to determine its usefulness. For this purpose, three types of stars, as illustrated in Figure 4, were prepared.[6]

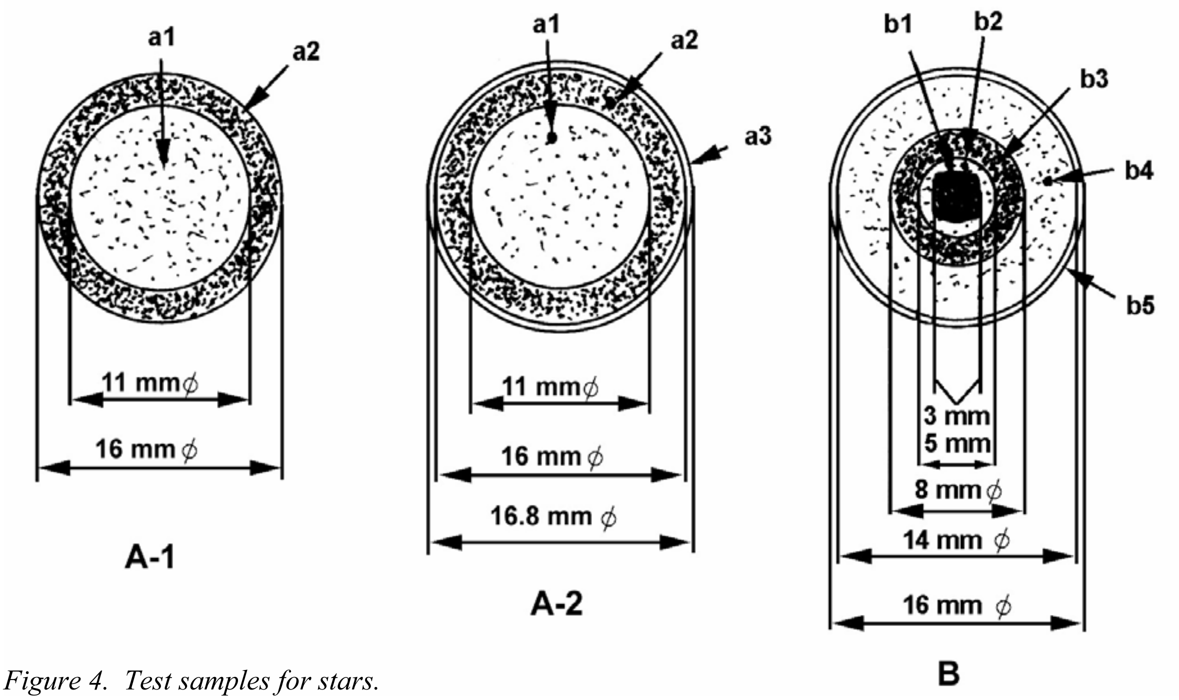


Figure 4. Test samples for stars.

Notes: The compositions of the stars are as follows:[5]

a1: Red (66% potassium perchlorate, 13% accroides resin, 2% lampblack, 12% strontium carbonate, 2% polyvinyl chloride, 5% glutinous rice starch)

a2: Dark composition (No. 5, No. 6 or No. 7 additionally containing 5% glutinous rice starch)

a3: Black powder (75% potassium nitrate, 15% wood charcoal, 10% sulfur, plus additional 5% glutinous rice starch): prime layer

b1: Strobe (70% $BaSO_4$, 25% Mg/Al (50/50), 5% glutinous rice starch)

b2: Prime (70% potassium perchlorate, 20% magnalium (Mg/Al: 50/50), 10% accroides resin, 5% additional glutinous rice starch)

b3: Dark composition (No. 5, No. 6 or No. 7 containing an additional 5% glutinous rice starch)

b4: Blue (60.8% potassium perchlorate, 9.0% accroides resin, 12.3% basic copper carbonate, 13.5% Parlon, 4.8% glutinous rice starch)

b5: Black powder, same as a3: prime layer

Table 7. The Results Obtained When Firing the Test Stars with a Dark Coating (Transitional Coating) Having a Positive Oxygen Value.

Sample No.	Test Star	Dark Composition of Dark Layer	Effect of Dark Layer		
			Ignition by a Leading Charge	Visibility of Flame or Spark	Ignition of Trailing Charge by Dark Composition
1	A-1 (without an ignition layer)	No. 5	Good	Not visible	Good
2		No. 6	Poor	—	—
3		No. 7	Poor	—	—
4	A-2 (with an ignition layer)	No. 5	Good	Not visible	Good
5		No. 6	Good	Not visible	Good
6		No. 7	Poor	—	—
7	B (with an ignition layer)	No. 5	Good	Not visible	Good
8		No. 6	Good	Not visible	Good
9		No. 7	Good	Visible	Good

These stars were fired from a small mortar and observed from a distance of 30 m. The results are given in Table 7.

From the results in Table 7, the compositions of the dark charges No. 5 and No. 6 were selected for the transition layer.

The compositions having a negative oxygen value would be suitable for fuses having a paper tube or a paper sleeve because, as the charge burns, the paper does not burn due to the "deficiency" of the compositions. The following experiment was therefore carried out [see Figure 6].

The test specimens were fired from the mortar shown in Figure 5. The results are given in Table 8.

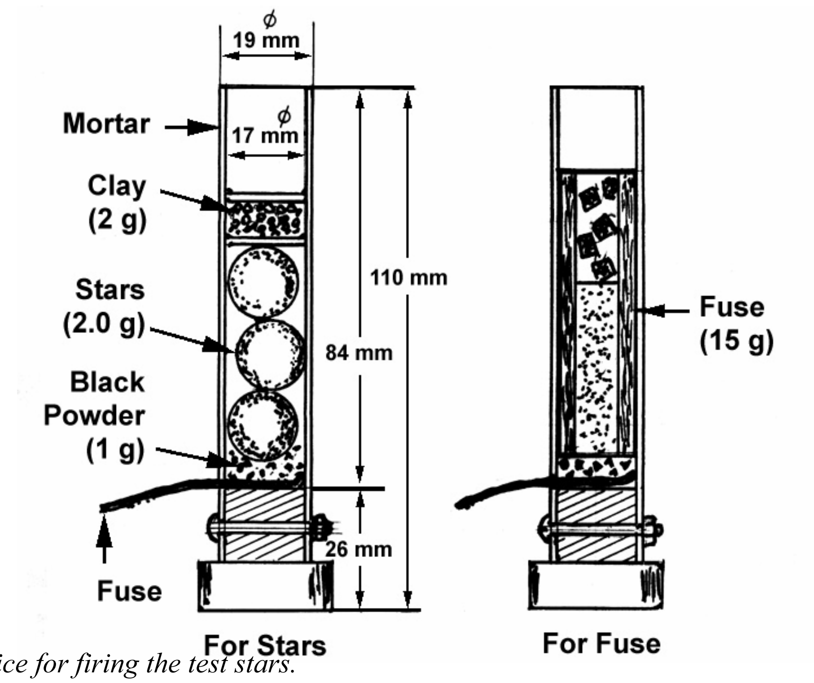


Figure 5. Device for firing the test stars.

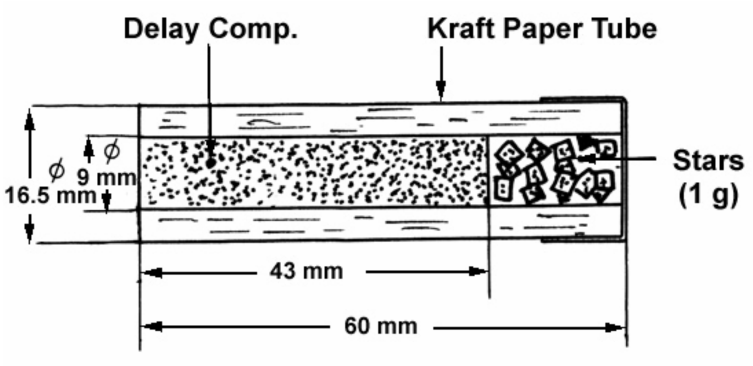


Figure 6. Sample of quick match.

Table 8. The Results Obtained When Firing Test Samples of Fuses Having a Dark Composition with a Negative Oxygen Value.

Sample No.	Dark Composition	Ignition of Fuse on Being Fired	Effect of Dark Charge: Visibility of Flame or Sparks	Effect of Dark Charge: Ignition of Trailing Stars by Dark Composition
1	No. 42	Ignites	Not visible	Good
2	No. 43	Ignites	Not visible	Good
3	No. 44	Ignites	Not visible	Good
4	No. 52	Does not ignite	Not visible	—
5	No. 53	Does not ignite	—	—
6	No. 54	Ignites	—	Good
7	No. 55	Difficult	Not visible	—
8	No. 56	Does not ignite	—	—
9	No. 57	Ignites	Visible	Good

3. The Use of Metal Powders

The following metal powders are dealt with in this paper:

- Magnesium, Mg
- Aluminum (atomized), Al
- Magnalium (magnesium and aluminum alloy), Mg/Al
- Ferrotitanium (sponge, approx. 20% Fe)
- Zirconium (sponge), Zr

3.1. The Chemical Stability of Metal Powders

For this case, the reaction tendencies between metals and potassium nitrate, sulfur or antimony trisulfide in a moist environment are important when one is planning a particular composition.

Table 9. The Reaction Tendency Between a Metal and Another Substance under the Effect of Moisture.

	KNO_3	S	Sb_2S_3
Mg	sl. Rxn., inert	gr. Rxn., H_2S, More active	gr. Rxn., H_2S Violent
Mg + 5% $K_2Cr_2O_7$	X	X	sl. Rxn, very inert
Al	gr. Rxn., H_2, NH_3, NO_x	X	X
Mg/Al (50:50)	sl. Rxn, NH_3	X	gr. Rxn, H_2S
Mg/Al (50:50) + 5% $K_2Cr_2O_7$	sl. Rxn, very inert	X	X
Fe	sl. Rxn, inert	gr. Rxn, H_2S	X
Fe + 5% $K_2Cr_2O_7$	sl. Rxn, very inert	X	X
Fe/Ti (20:80)	X	X	X
Zr	X	X	X

Notes:

(1) X : under the effect of moisture, no reaction tendency

(2) sl. Rxn.: under the effect of moisture, slight reaction tendency

(3) gr. Rxn.: under the effect of moisture, great reaction tendency

(4) H_2, NH_3, NO_x, or H_2S: the gas is generated during the reaction

(5) Iron, Fe, is indicated for information only

Table 10. Basic Compositions for Metal Powders.

	A	B	AB (½A + ½B)
Potassium nitrate	86%	34%	60%
Sulfur	7%	26%	16.5%
Antimony trisulfide	—	40%	20%
Paulownia charcoal	7%	—	3.5%
Rice starch (additional)	5%	5%	5%
Oxygen value (g per 100 g of mixture)	+3.57	–35.40	–15.92

It is worth noting in Table 9 that the magnalium, Mg/Al (50/50), does not have any tendency to react with sulfur and reacts only slightly with potassium nitrate. Ferrotitanium, Fe/Ti (20/80), and Zirconium, Zr, react only sluggishly with potassium nitrate, sulfur or antimony trisulfide in moist conditions.

3.2. Metal Sparks

3.2.1. Basic Compositions

The composition which forms metal sparks consists of a basic composition and an additional quantity of metal powder. In the present study, the basic compositions shown in Table 10 were used.

Table 11. The Metal Powders Used for Testing the Sparks.

	Small Grains		Large Grains	
	Sample No.	Grain Size	Sample No.	Grain Size
Magnalium, Mg/Al (50:50)	1	0.005–0.09 mm	2	0.25–0.5 mm
Ferrotitanium, Fe/Ti (20:80) (sponge)	3	0.002–0.005 mm	4	0.8–1.0 mm
Zirconium, Zr (sponge)	5	0.001–0.015 mm	6	0.1–0.3 mm

Type A is derived from composition No. 6 and Type B from composition No. 43, but the latter was improved by adding sulfur to counteract the excessive amount of antimony trisulfide. AB is the composition of a mixture consisting of half A and half B. In these compositions, potassium nitrate was used as the oxygen carrier because it is more effective in forming elegant sparks in a wider zone of the compositions than other substances. In this case, the burn reaction of the composition would not be as simple as the case of potassium chlorate or potassium perchlorate.

3.2.2. Experiment

A mixture of one of the basic compositions with an additional 5% of metal powder was kneaded with an amount of water and formed into cube-shaped stars measuring 10 mm along the edges. These stars were dried at room temperature. The metal powders used are listed in Table 11.[7]

Three sample stars of each composition were loaded into and fired from the same mortar as that shown in Figure 4. The results are explained in Figure 7 where, for example, the designation A1 denotes the star consisting of the basic composition A and magnalium No. 1.

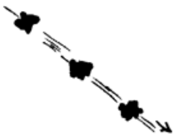
 a weak flame, no sparks A1 Mg/Al with small particles	 a large, white flame with weak red sparks, which are not visible from a distance AB1 Mg/Al with small particles
 flashing light A2 Mg/Al, with large particles	 only a white flame with thin red sparks AB2 Mg/Al, with large particles
 brilliant white sparks A3 Fe/Ti with small particles	 bright, pale-yellow sparks with thin red sparks AB3 Fe/Ti with small particles
 very beautiful, brilliant white sparks A4 Fe/Ti with large particles	 brilliant, pale-yellow sparks AB4 Fe/Ti with large particles
 brightly shining, short white sparks A5 Zr with small particles	 large white flame with thin red sparks AB5 Zr with small particles
 very beautiful, brightly shining white sparks A6 Zr with large particles	 white flame with a few sparks AB6 Zr with large particles

Figure 7. The results of the effects of metal spark charges on being fired.
NB: Not all the stars that contained basic charge B were ignited.

3.3. Red Lead Explosive Compositions

These compositions were developed in recent years in China and are mainly used as exploding micro-stars in small fireworks. The compositions are, for example, as follows:[8]

Red Lead Explosive Composition I (by Michael S. Swisher, USA)

Ingredient	%
Red lead, Pb_3O_4	89
Magnalium (Mg/Al:50/50) (100-mesh)	11

Red Lead Explosive Composition II (by Larry Stevens, USA)

Ingredient	(weight %)
Red lead, Pb_3O_4	10
Copper(II) oxide, CuO	7
Magnalium, Mg/Al	4
Potassium nitrate	1.5
Sulfur	1

Red Lead Explosive Composition III (by Peter Budarick, Australia)

Ingredient	%
Potassium nitrate	51.5
Sulfur	6.5
Charcoal	33.0
Dextrin	6.0
Aluminum, large flakes	3.0
Red lead/Magnalium, Mg/Al grains	25.0 (additional)
(prepared with N/C in acetone)	

I conducted experiments to determine how the explosion is caused. First of all, I studied the mixtures of red lead, Pb_3O_4, and atomized aluminum in various particle sizes, as follows, in the weight ratio Pb_3O_4/Al : 90.5/9.5.

Commercial Brand of Aluminum (from Yamaishi Metal Co.)	Particle Size (mm)
No. 1	0.0005–0.0009
No. 2	0.0005–0.004
No. 3	0.001–0.005
No. 4	0.012–0.08
No. 5	0.015–0.3
No. 6	0.1–0.5

Small amounts (10g) of the mixtures were placed in piles on the floor and ignited using a piece of fuse. The mixtures containing small particles such as No. 1, No. 2 or No. 3 did not produce any explosion, but those with larger particles such as No. 4, No. 5 or No. 6 did generate a crackling. On the other hand, I tested the mixtures of various types of oxygen carrier: $AgNO_3$, HgO, Fe_2O_3, Fe_3O_4, BaO_2, Cu_2O, $PbSO_4$, PbO or PbO_2 instead of red lead, Pb_3O_4. Only PbO and PbO_2 were effective in producing an explosion.

Therefore, it is clear that the generation of the explosion is a peculiar phenomenon associated with mixtures of lead(II) oxide and aluminum. The particles of aluminum are covered with a chemically-stable layer of aluminum oxide, Al_2O_3. On the other hand, upon heating, the lead oxide Pb_3O_4 or PbO_2 converts into PbO. The lead oxide PbO has a lower boiling point of 1470 °C. It was observed that there was no delay before combustion reaction when the mixture is ignited with small particle-size aluminum. The combustion reaction must be as follows:

Reaction 1.

$$3\,PbO + 2\,Al \rightarrow 3\,Pb + Al_2O_3 + 243\text{ kcal.}$$

In the case of the larger particles, however, a short delay is noted before the explosion. This means that the layer of aluminum oxide, Al_2O_3, impedes the combustion reaction and a dark reaction results. If the temperatures of the dark reaction exceed the boiling point of PbO, namely 1470°C, the PbO gas passes through the layer of Al_2O_3 to rapidly react with the already melting aluminum to produce an explosion. That would be the origin of the bang.

For the practical use of these mixtures, it is better to add a small amount of magnesium to the compositions to permit the dark reaction to take place without being extinguished.

Red Lead Explosive Composition IV

Ingredient	%
Red lead, Pb_3O_4	90%
Aluminum, atomized (0.15–0.3 mm)	8%
Magnesium (0.15–0.25 mm)	2%

In the mixtures developed in China, the main components used are red lead and magnalium, Mg/Al. The reactive tendency of magnesium and aluminum in the alloy is the problem. The respective reactions are as follows:

Reaction 2:

$$4\,Mg + Pb_3O_4 \rightarrow 3\,Pb + 4\,MgO + 400\text{ kcal}$$

Reaction 3:

$$8\,Al + 3\,Pb_3O_4 \rightarrow 9\,Pb + 4\,Al_2O_3 + 1070\text{ kcal}$$

Reaction 4:

$$Al_2O_3 + Mg \rightarrow 2\,Al + 3\,MgO + 32.43\text{ kcal}$$

Reaction 4 proceeds slowly from left to right and not from right to left, as was experimentally determined. When the mixture of red lead, Pb_3O_4, and magnalium, Mg/Al, burns, the magnesium in the magnalium is first oxidized by the lead oxide, leaving the aluminum unoxidized. This means that Reaction 2 occurs and Reaction 3 does not. If Reaction 3 were to take place, the aluminum oxide, Al_2O_3, formed would be reduced by magnesium to aluminum, Al, as shown in Reaction 4, until the magnesium was used up by Reaction 2. In fact, magnesium blocks the reaction of the aluminum. When the magnesium in the magnalium is completely used up, the aluminum left behind is oxidized suddenly, with the action of the gas of PbO, and an explosion occurs with a bang.

The second problem is the ratio between the partial amounts of magnesium and aluminum in the alloy. The experimental results regarding the effects are listed in Table 12.

Excessive partial amounts of magnesium in magnalium, Mg/Al, prevent explosion. The reaction taking place when lead oxide and magnesium burn together is very violent. If the proportion of magnesium is too high, the reaction temperatures will immediately shoot up too high. In this case, the effect of magnesium preventing the oxidation of aluminum is weak, because Reaction 4 is relatively slow, as mentioned above. Therefore both magnesium and aluminum burn simultaneously without a dark reaction and no bang is generated.

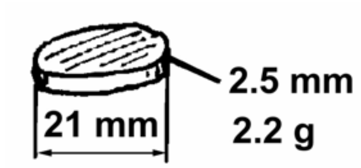


Figure 8. Sample from Table 12. The sample was placed on the ground and ignited using a piece of fuse and magnesium powder.

3.4. Water Flare

It has long been one of my wishes to use water as the oxygen carrier for fireworks.

I have found that a flare, as shown in Figure 9, would be effective as a water firework or as

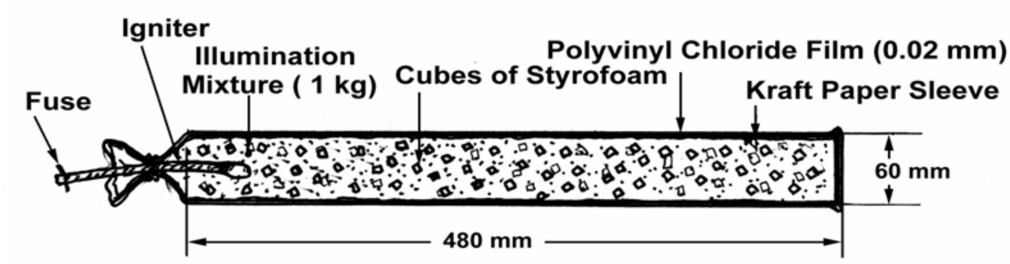
Table 12. The Effects of the Explosion Given Various Amounts of Magnesium and Aluminum in Magnalium.

Sample No.	Mg/Al	Particle Size (mm)	Report	Effect
1	65/35	< 0.07	none	(by M. S. Swisher)
2	60/40	0.05–0.25	produced	small noise
3	50/50	0.005–0.09	produced	explosion
4	40/60	0.005–0.10	produced	crackling
5	30/70	0.001–0.05	produced	explosion (very loud bang)

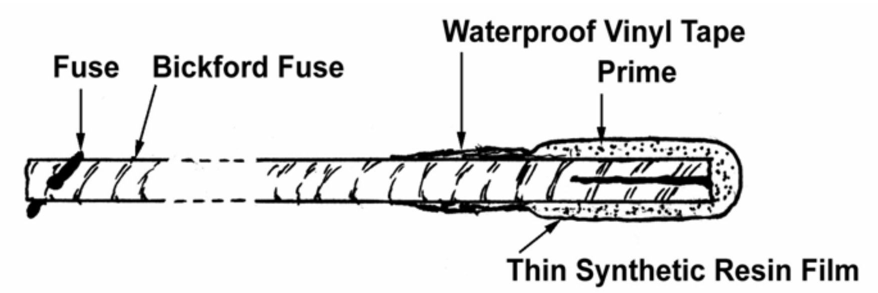
Note: The specimens were compacted with N/C (nitrocellulose) binder.

an emergency signal for use at sea.

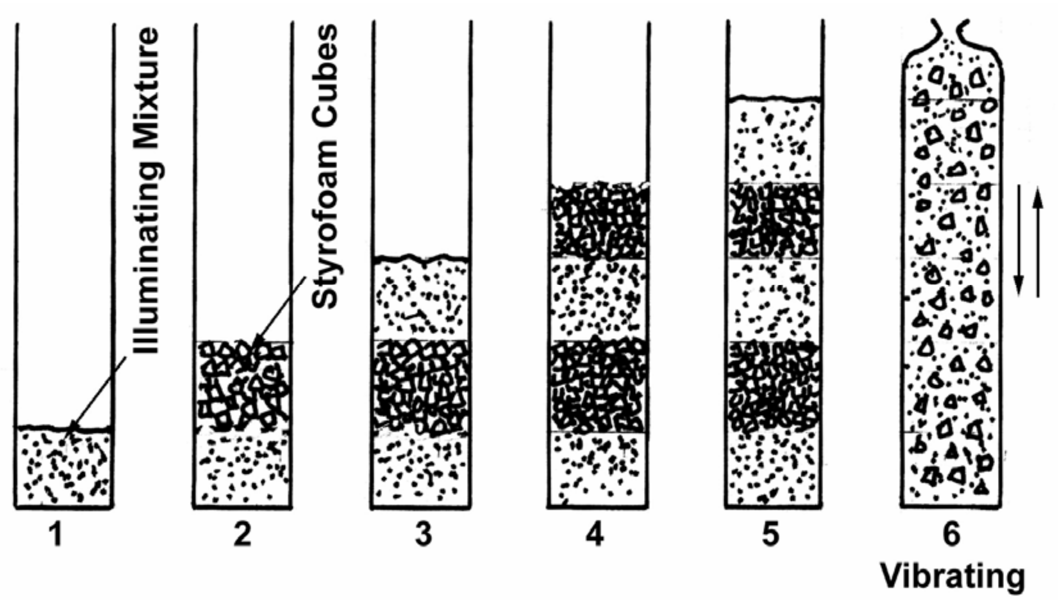
A mixture of 95% magnesium and 5% cryolite powder, which is effective in generating a very strong flame, was loaded into a long Kraft paper tube having an outer water-protective coating of vinyl chloride film (0.02 mm thick). One end of the device was provided with a piece of Bickford fuse. At the end of the fuse inside the mixture, a certain amount of a mixture of red lead and ferrosilicon was added as the prime (4 g prime, Pb_3O_4/ferrosilicon: 92/8).



1. Cross section of water flare



2. Igniter



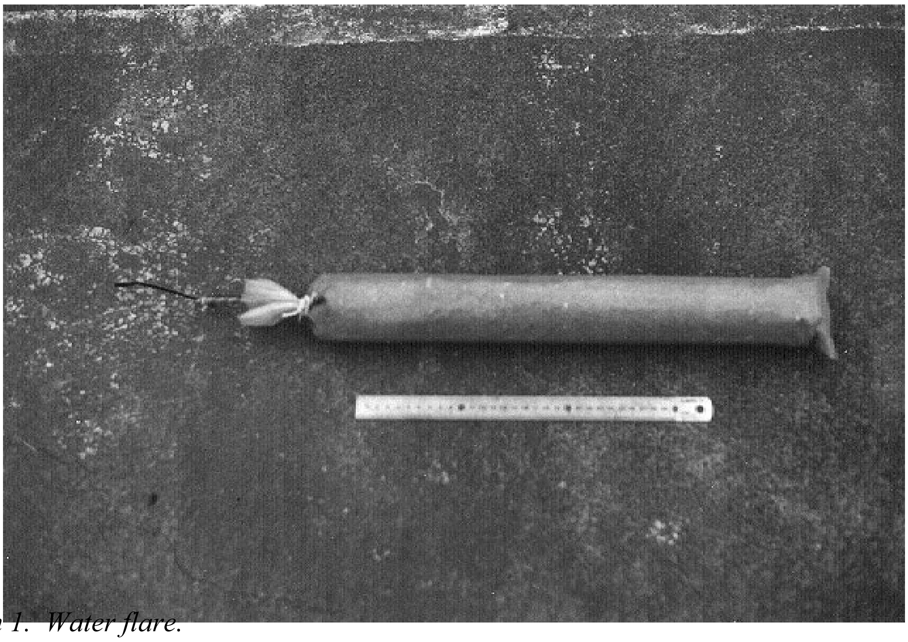
3. Illumination mixtures

Figure 9. Water flare.

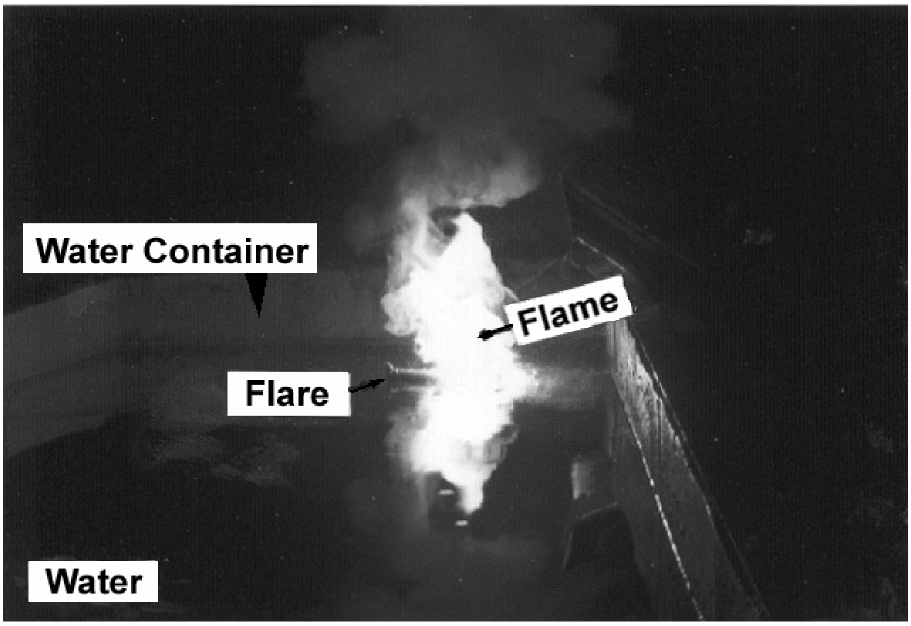
To prevent the device from sinking in the water, I had previously mixed some cubes of polystyrene foam (styrofoam) measuring approx. 10 mm along the edges into the illuminating mixture, so that the typical weight per unit volume of the device was on average 0.74. The method of loading the illuminating mixture is shown in Figure 8-3.

The device was ignited at the end of the fuse and thrown into the water. It worked well. The maximum luminosity of the flame was 430,000 cd and the burn lasted 150 s (Photos 1 and 2).

The flame is produced by the reaction between magnesium and water:



Photograph 1. Water flare.



Photograph 2. The burning water flare.

Table 13. Effective Dark Charges for a Negative Oxygen Value:

Ingredient	No. 42	No. 43	No. 44	No. 55
Potassium nitrate	32%	34%	36%	38%
Sulfur	—	—	—	31%
Antimony trisulfide	68%	66%	64%	31%
Oxygen value (g per 100 g mixture)	-14.26	-12.68	-11.08	-29.03

Reaction 5.

$Mg + H_2O \rightarrow H_2 + MgO + 86.2$ kcal

Reaction 6.

$H_2 + \frac{1}{2}O_2$ (in the air) $\rightarrow H_2O + 57.80$ kcal

The heat produced per 1 g of magnesium is 5.9 kcal.

3.5. Safety Warning

When metal powder is added to a composition, in general, this greatly increases the sensitivity of the composition, and, in particular, the presence of aluminum or lead oxide increases this tendency.

From this standpoint, the water flare is safer than other firework devices, because the flare does not have any oxygen carrier in the composition.

4. Summary and Discussion

Using chiefly the oxygen value of the mixture, studies were carried out on the dark delay compositions and on the use of certain metal powders.

As dark compositions, it was found that the following compositions are suitable for the transitional layer on the color-changing stars:

For positive oxygen value:

Ingredient	No. 5	No. 6
Potassium nitrate	84%	86%
Sulfur	8%	7%
Paulownia charcoal	8%	7%
Oxygen value (g per 100 g mixture)	+5.16	+9.47

The use of these compositions with a paper tube or sleeve is not advisable as a visible flame is formed because of the excess oxygen. It is necessary to add a certain amount of binding agent such as glutinous rice starch to the composition for use as the transitional layer. However, not too much must be added otherwise the binding agent causes oxygen deficiency and a visible flame is formed.

Table 13 lists effective dark charges to use in fuses.

These compositions are a reworking of the traditional compositions in which realgar is replaced with antimony trisulfide. Antimony trisulfide is more popular than realgar. These compositions have a negative oxygen value. Therefore the ignition effect of the compositions on others is weak. Therefore these compositions are not suitable for the transition layer.

When using metal powders, it is worth noting that in moist conditions magnalium is resistant to sulfur and it is more resistant than aluminum to potassium nitrate (Table 9). The properties of magnalium are useful for the prime if it comes into contact with black powder, for example:

Magnalium Prime

Ingredient	%
Potassium perchlorate	70
Magnalium (0.005-0.09 mm)	20
Accroides resin	10

Two effective compositions were given (Table 10) for the basic charges used for forming metal sparks:

Ingredient	A	AB
Potassium nitrate	86%	60%
Sulfur	7%	16.5%
Antimony trisulfide	—	20%
Paulownia charcoal	7%	3.5%
Rice starch (added)	5%	5%
Oxygen value	+3.57	-15.92

Composition B, whose oxygen value is less than –15 g per 100 g of mixture, was not effective. Because of their positive oxygen values, the A mixtures form bright, white sparks. On the other hand, the AB mixtures, with negative oxygen values, form pale yellow sparks. This means that it is possible to delicately regulate the color of the sparks, by mixing A and AB in a ratio (i.e., by modifying the oxygen value).

Magnalium does not produce good sparks, however, ferrotitanium and zirconium produce a very good effect, especially when large particles are used. The effect of ferrotitanium is almost the same as that of zirconium, but the sparks from zirconium are brighter than those of ferrotitanium.

The following important comments need to be made about the red lead explosive compositions:

(1) The oxygen value of the charge should be zero to produce the loudest bang.

(2) The bang is produced by the explosion of the aluminum particles in the composition. There is a slight delay prior to explosion.

(3) The delay occurs in two cases:

1. With aluminum-red lead mixtures containing large aluminum particles:

   The delay is caused by the layer of aluminum oxide on each particle that prevents the oxidation effect of the red lead, thus producing a dark reaction.

2. With the magnalium-red lead mixture:

   The delay is caused by the blocking of the reducing effect of magnesium in each particle of the magnalium, thus producing a dark reaction as above.

(4) When the temperatures of the dark reaction of (2)-1 or (2)-2 rise above 1470 °C, the lead oxide, PbO, formed in each composition is volatilized and the gas acts on the molten aluminum left behind in each particle to produce an explosion.

(5) The addition of the other substances, such as copper oxide, CuO, sulfur, potassium nitrate, etc., to the red lead explosive composition would be effective to facilitate ignition of the explosive composition, especially in the microstars.

The water flare is an example of the use of magnesium. Magnesium has a very strong reducing effect on oxygen-containing substances. Therefore, magnesium also burns with earth, producing a beautiful orange flame.

The first problem when planning the flare was to ensure that the igniter works reliably in water. A simple igniter, as shown in Figure 8–2, proved very successful. The second problem was to allow the water to penetrate through the burning surface of the flare. For this purpose, the particle size of the magnesium and of the admixed substances should not be too fine.

In conclusion, with respect to the red lead compositions I would like to thank Mr. Robert G. Cardwell, Mr. Michael S. Swisher, Dr. Robert M. Winokur, in the USA; as regards the sample materials, I am grateful to Mr. H. Murai, Daichi Yakuhin Co., and Mr. M. Koitabashi, Mitsuwa Kinzoku Co., in Japan. My thanks are also due to Mr. David Allen in the USA for providing me the zirconium sample.

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