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Photo of Dr. Shimizu taken at the fireworks plant on April 11, 1998.



Cherry trees in bloom at the entrance to the fireworks plant [April 11, 1998].



The Critical Burning of Pyrotechnic Compositions

Takeo Shimizu
Koa Fireworks Company, Japan

Introduction

The author attempts to establish a general theory summarizing the phenomena related to the chemical reactions occurring inside pyrotechnic compositions.

There are three types of reactions: smoldering, burning and detonation. In addition, there are several interesting variations like sparking, flashing [strobing] and pyrotechnic whistling. These phenomena fall between smoldering and burning or between burning and explosion and should be referred to as "critical burning". The theory must include these phenomena.

General Reaction Mechanism of Pyrotechnic Compositions

Smoldering refers to the slow reaction of a composition generating a slight heat build-up and no flames, for example, smoke being gen-

erated by a colored-smoke composition. Burning is associated with greater heat build-up and with flames. Upon dying of the flame, burning may change to smoldering or stop. This, for example, can be seen in a flare. An explosion is a very rapid reaction (e.g., an explosive charge) associated with heat build-up, generating a shock wave inside the charge and in its surroundings. Unlike an explosion, which generates great pressure, the reactions during smoldering and burning occur almost at ambient pressure. Generally, the reaction mechanisms in each case are different.

Smoldering or burning begins when part of a composition is heated and the composition-specific ignition temperature is exceeded.

Continuation of the reaction is ensured by the heat of reaction, the heat radiated by the flame or by any other source of heat supplied (Figure 1). The reaction can be imagined as progressing in two directions: along the surface (surface reaction) and perpendicular to the reac-

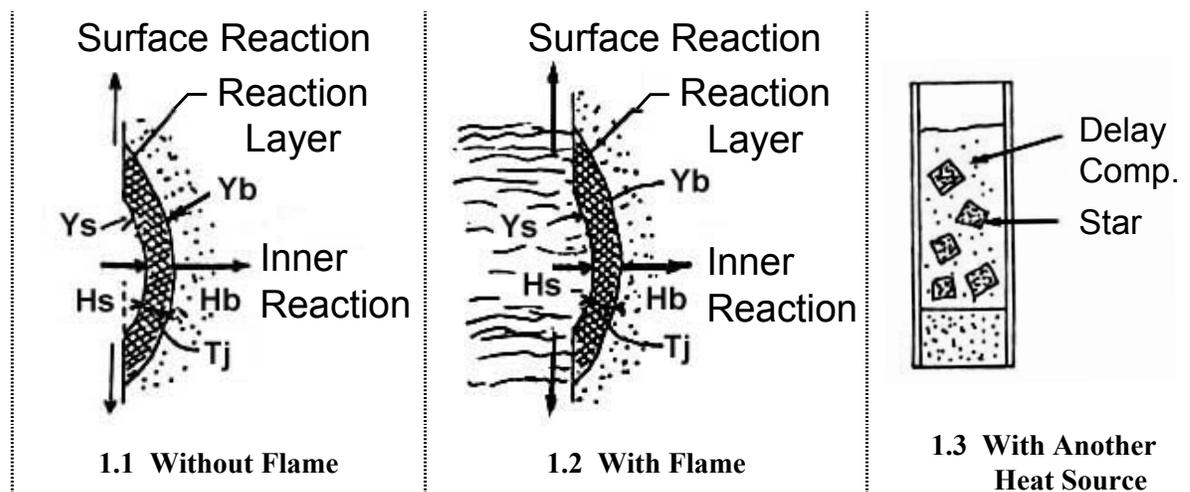


Figure 1. Types of burning reaction (1.1, 1.2, 1.3).

tion surface (inner reaction).^[1]

The reaction zone has a volume in which the reaction occurs, which means that a reaction layer is formed. This layer is bounded by the starting surface Y_b and the end surface Y_s . The distance between them is T_j . In the course of the reaction, the starting surface moves inward at a speed of H_b and the end surface at a speed of H_s . Whenever the reaction time is constant everywhere inside the composition, H_b equals H_s , and the constant value of T_j is determined by the reaction time. Especially in the case of reactions involving gas or flame formation, the reaction time is influenced by an increase in ambient pressure, which decreases T_j while increasing H_b and H_s .

When the reaction time is not constant, as it is with some kinds of smoke mixture, H_b exceeds H_s and T_j increases with time. Heat gradually increases the temperature at any given point inside the reaction layer from its initial temperature T_0 , first, to the ignition temperature T_1 and then to the burning temperature T_2 (Figure 2).

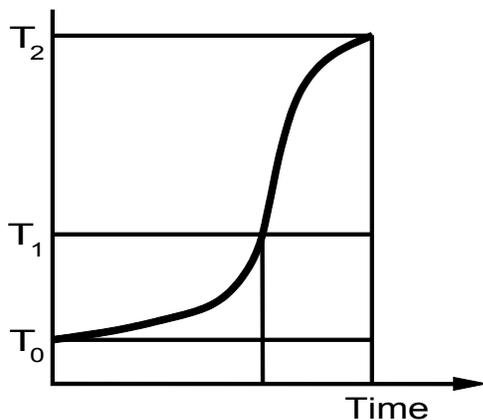


Figure 2. Reaction temperature at a given point inside the reaction layer as a function of time.

The reaction surface is not uniform. Often, several red-hot spots can be seen with the naked eye (Figure 6.1).

The various temperatures inside the reaction layer at a given time are shown in Figure 3.

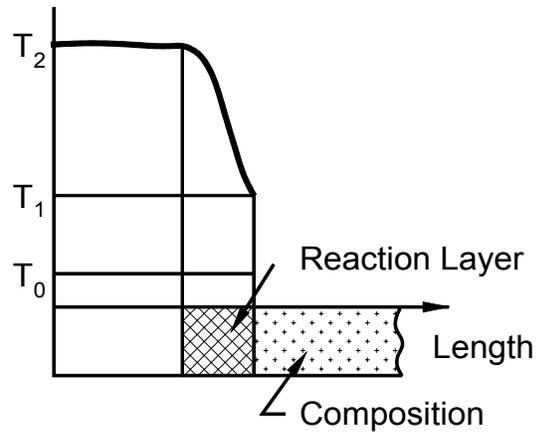


Figure 3. Temperatures inside the reaction layer at a given point in time.

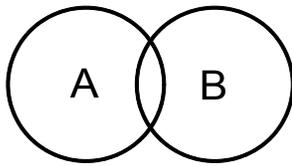
The surface reaction is a function of the surface conditions and the surroundings of the charge. As a rule, it progresses faster than the inner reaction.^[2]

Detonation reactions occur inside a reaction layer under high pressure.

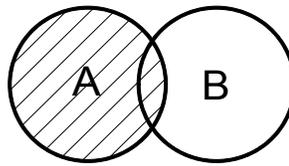
Two Ignition Temperatures

Generally, pyrotechnic compositions consist of several components. If a composition consists of two sets of components A and B, it has two different ignition temperatures T_a and T_b and the possibility to react in various ways. Mathematically, this circumstance can be expressed by the formula $A \cup B$, the symbol \cup indicates that set A and set B have common components and all of them react with each other at the same time (Figure 4.4). A different symbol \cap indicates only the set of the common components react (Figure 4.5). ("Set" is a mathematical term which means a collection of components.)

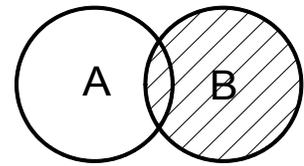
So, how do the reactions progress? If T_a is lower than T_b , reaction of A occurs first during ignition. If the heat generated by this reaction is low, or if too much heat is lost to warm the charge and its surroundings, ignition temperature T_b will not be reached. Only reaction of A will occur, leaving some of the components behind unchanged (Figures 4.2 and 5.1).



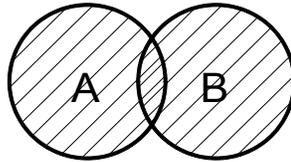
4.1 Set A and Set B with Common Components



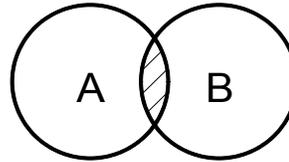
4.2 Only set A reacts.



4.3 Only set B reacts.

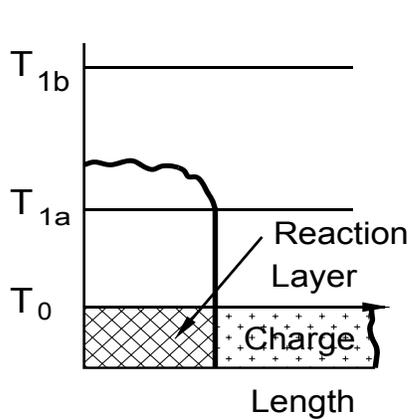


4.4 Set A and Set B both react ($A \cup B$)

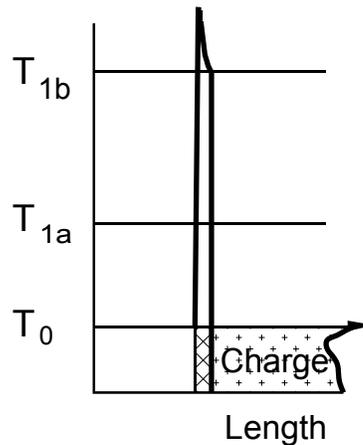


4.5 Only the common part of Set A and Set B react ($A \cap B$)

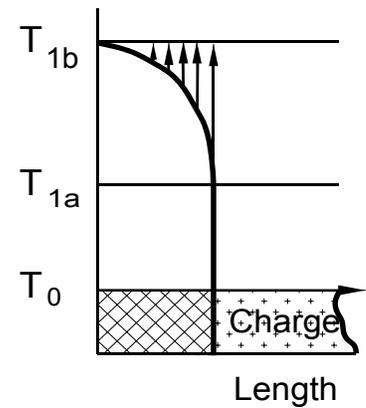
Figure 4. Sets of components in a charge for which a two-phase reaction is possible.



5.1 Slight Heat Generation



5.2 Strong Heat Generation



5.3 Medium Heat Generation

Symbols $\left\{ \begin{array}{l} T_{1a} : \text{ignition temperature of Set A} \\ T_{1b} : \text{ignition temperature of Set B} \end{array} \right.$

Figure 5. Reactions at various reaction heats of compositions with two ignition temperatures (5.1, 5.2, 5.3).

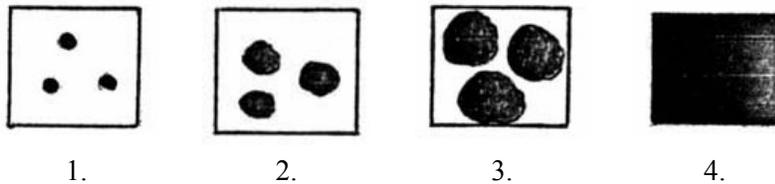


Figure 6. Development of red-hot spots on the burning surface left behind by reaction A.

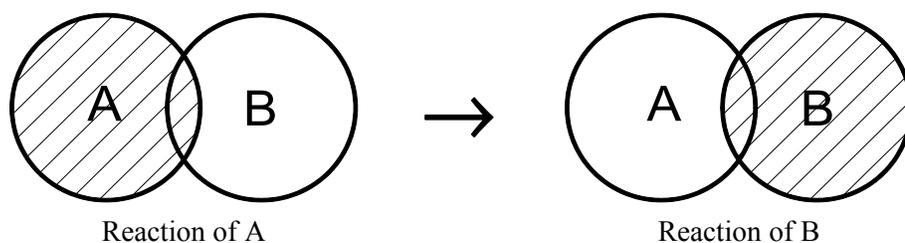


Figure 7. Two-phase reaction.

If the heat of reaction A is high, or if sufficient heat is generated by ignition, the temperature of the ignited part will immediately increase to temperature T_{1b} , generating reaction $A \cup B$ (Figures 4.4 and 5.2). If medium heat is generated, the reaction will continue, and some of the components, namely, of the set B, will be left behind unchanged (Figure 4.2 and 5.1). So, initially, reaction A occurs. The reaction heat of A slowly increases the temperature of component B until several red-hot spots appear and increase in size (Figures 4.2 to 4.3, 5.1 to 5.3, and 6).

I will refer to this phenomenon as “heat accumulation” here. At one point, temperature T_{1b} has finally been reached, and reaction B occurs by generating heat. Part of component B now reacts with a faster reaction speed, resulting in a flash or, frequently, an explosion. The fast reaction is caused by the fact that component B, due to its previous heating, is very sensitive to any additional heating or shock, so that even slight

heat will initiate reaction B. I will call this reaction a “two-phase reaction” here and the time between the beginning of reaction A and the beginning of reaction B the “delay” (Figure 7).

Normally, at the end of reaction B, the two-phase reaction is completed, since reaction B occurs so quickly that it does not transfer any excitation energy. However, it is also possible that the reaction continues, provided that energy is transferred to the adjacent layer. For example, it is not rare that a part of composition A, which belongs to the set A but did not take part in the reaction B due to its lower temperature, remains on the burning surface and its reaction heat causes the reaction of the adjacent layer. In this way, the reaction is repeated^[3] (Figures 8 and 9.1). The subsequent reaction A may also be caused by shock, pressure or heat transferred from the advancing violent reaction (Figure 9.2). Reactions repeating themselves are called flashing [strobing] reactions (Figure 9).

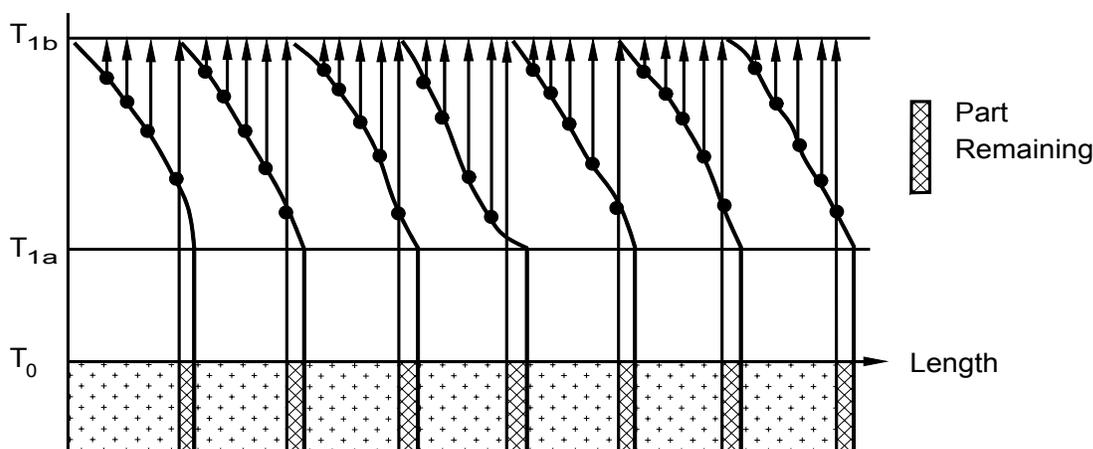


Figure 8. Repetition of two-phase reaction.

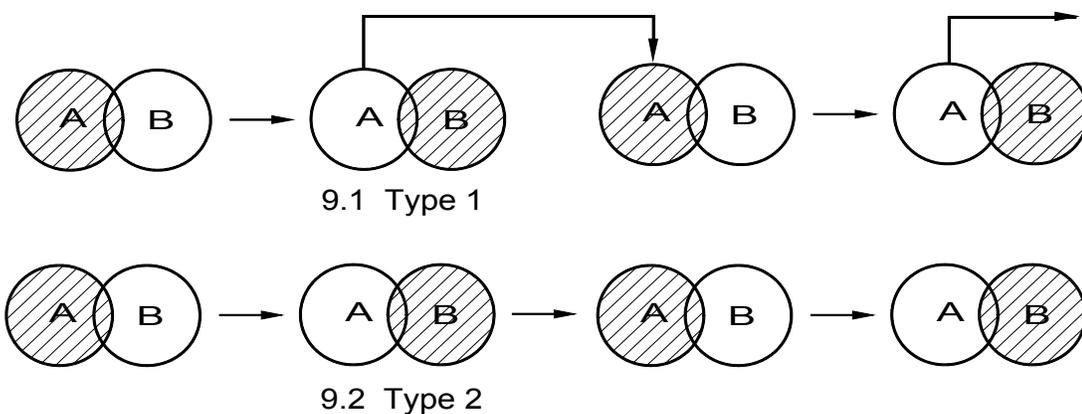


Figure 9. Flashing (strobe) reactions.

Two-phase reactions also progress along the surface of the composition and are greatly dependent on temperature and ambient pressure.

The above-described theory is summarized in Figure 10. K is a measurement for the degree of sensitivity of the charge to the temperature increase from T_0 to T_a , while F is the delay between the beginning of reaction A and the beginning of reaction B. E is the excitation energy for the next layer in the composition. So, K indicates how easily or difficult it is to ignite the composition; $1/F$ is a measurement for the speed with which reaction A occurs; and E is the heat or shock energy released by reaction B. The supply of thermal energy or an increase in ambient pressure, shorten delay F and increase excitation energy E .

To prove the above theory, several tests will be conducted.

Two-Phase Reaction

In certain compositions, a two-phase reaction is possible only here and there, that is, within isolated individual pellets or drops. The reaction does not occur otherwise, (i.e., in unisolated condition) since a large portion of the heat

generated during ignition is absorbed within the composition.

Test 1

50 g of a mixture of 43% magnalium and 57% barium nitrate are mixed with 10 g of 10% nitrocellulose solution in amyl acetate. Using a wooden roller, the mixture is broken up into angular pellets, and pellets between 1.5 and 3 mm in size are screened out. One pellet is placed inside a platinum-wire hoop and held into the flame of an alcohol burner. After about six seconds in the reduction flame (approx. 800 °C) or about 8 seconds in the oxidation flame (approx. 1000 °C), the color of the pellet changes from gray to black at about 600 °C. This shows that the pellet ignites at a temperature T_a and reaction A (smoldering) begins. At once the pellet is taken out of the flame of the burner. It becomes red-hot without any help of heat source, generating an odor of NO_2 . Here, we are dealing with heat accumulation caused by reaction A. After about 3 seconds, the temperature of the pellet has risen to T_b (approx. 800 °C), and the pellet burns violently with a bright flash. This reaction is shown in Figure 11 in the form of a diagram. The asterisk indicates a new compound created during reaction of A.

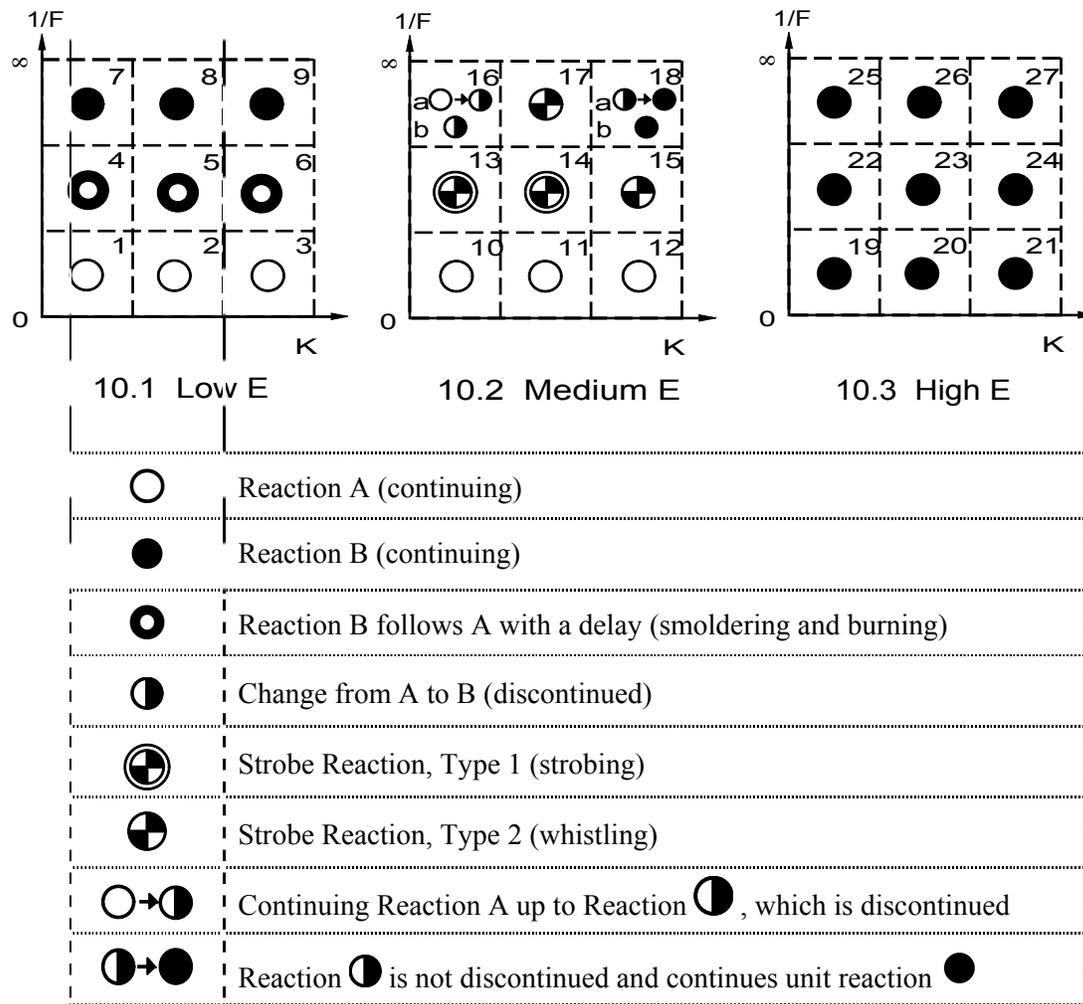


Figure 10. Possible reactions in compositions with two ignition temperatures.

If the barium nitrate in the mixture is replaced by strontium nitrate, then at a temperature T_a of about 500 °C, only reaction A occurs, leaving behind a black residue. When the pellet is heated in the flame, both reaction A and B occur.

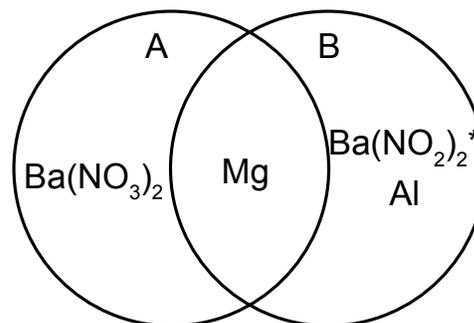


Figure 11. Two-phase reaction of a charge consisting of $Ba(NO_3)_2$ and magnesium.



Figure 12.1. Two-phase reaction of a composition consisting of $Ba(NO_3)_2$ and magnesium.

Test 2

The pellets made in Test 1 are mixed with a black powder mixture (50% KNO_3 , 37.5% pine charcoal, 12.5% sulfur) at a weight ratio of 3:7. The mixture is placed into a Kraft-paper tube which has a diameter of 11 mm, a wall thickness of 1 mm and a length of 60 mm and which is plugged at one end with clay. The other end is plugged with paper and fitted with a fuse. The tube is mounted about 1.5 m high, at a firing angle of 5° . When ignited at night, many bright flashes are seen, accompanied by crackling noises. The color of the flashes generated by the barium nitrate mixture is white, that of the strontium nitrate mixture pink (Figures 11, 12.1, and 12.2).

$[Ba(NO_3)_2, MgAl, S]$ and $[Sr(NO_3)_2, MgAl, S]$ compositions also result in two-phase reactions. The former composition is used in China



Figure 12.2. Two-phase reaction of a composition consisting of $Sr(NO_3)_2$ and magnesium.

for small fireworks. The effective area of each mixture is shown in Figure 13.^[4]

Test 3

When igniting a No. 6 electric detonator, which does not contain a delay, the change in voltage between the cap and the ground is observed photographically by means of an electrical device.^[5]

The curve recorded photographically indicates ignition of the igniting composition by a sharp peak and, after a certain period, detonation of the explosive by a steep change in voltage, which indicates that the composition underwent a two-phase reaction. Otherwise, there would have been no delay (Figure 14).

The following delays were recorded: 4.7, 5.3, 6.1, 6.1, 7.7, 9.2, 10.1, 11.9, and 13.0 milliseconds.

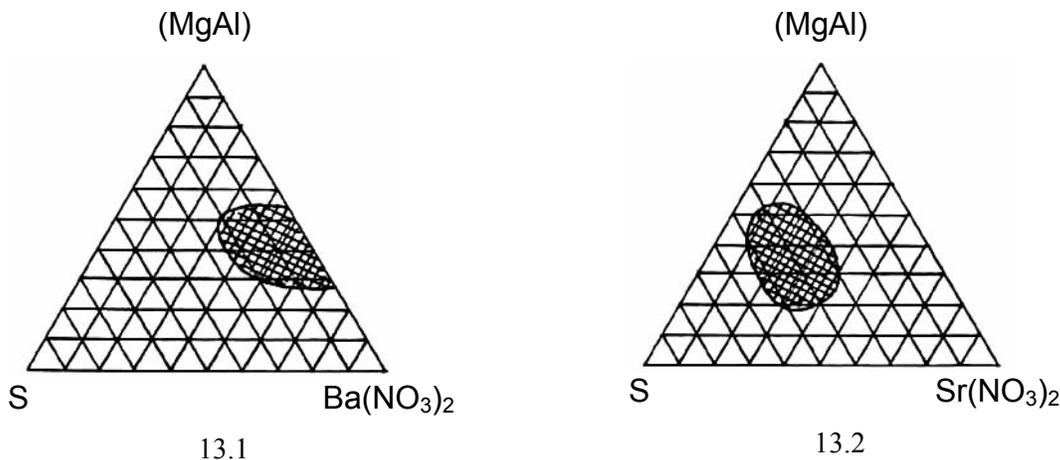
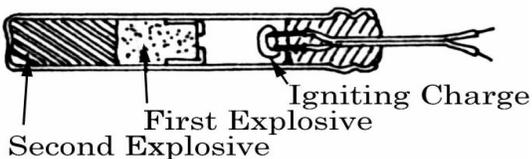


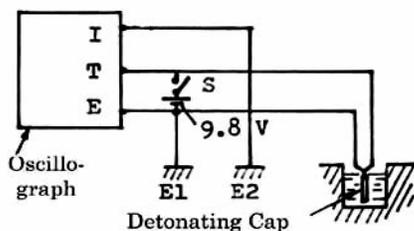
Figure 13. Effective area of two-phase reactions for tri-component mixtures.

In the manner described above, we observed ignition by means of an electric ignitor of salute composition consisting of 72 weight % of potassium chlorate and 28 weight % of fine flake aluminum powder. The following delays were recorded: 4.4 and 8.6 milliseconds (Figure 15).

Based on the aluminum spectrum observed, we suspect a two-phase reaction here, as shown in Figure 15.3. In set A, KCl^* , which is formed during the reaction of $KClO_4$ with Al, will promote decomposition of the $KClO_4$.^[6] Over the course of the reaction, the quantity of KCl increases in set A and it helps the heat accumulation.

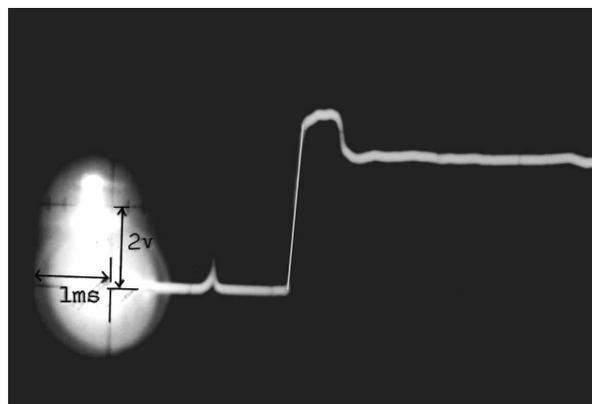


14.1 Detonating Cap.



I : Input
T : Trigger
E : Ground
S : Switch

14.2 Electric Circuit.



14.3 Electrical-voltage differential between detonating cap and ground.

Figure 14. Measuring of delays for detonating caps.

Test 4

A flare with a diameter of 27 mm, a length of 20 mm and a weight of 20 g, consisting of potassium perchlorate, strontium nitrate, polyvinyl chloride, etc. is fired from a mortar. Burning, the flare reaches a height of 25 m and then drops to the ground. At the very moment the flare reached the ground, a very loud bang is produced from the flare interrupting its burning. We are dealing with a surface explosion here. The reacting thin layer covering the flare, which is highly sensitive, explodes upon hitting the ground. This high degree of sensitivity is the result of the high temperature during burning. Except for its surface, the flare exhibits low temperatures and is left behind without explod-

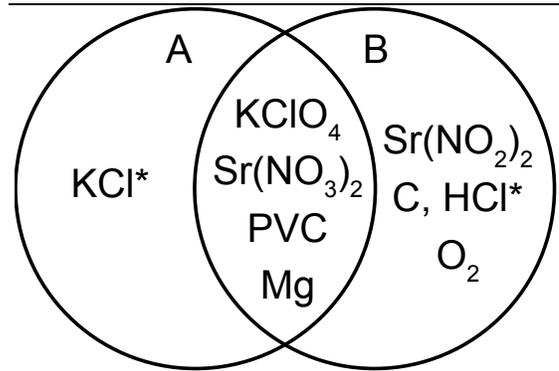
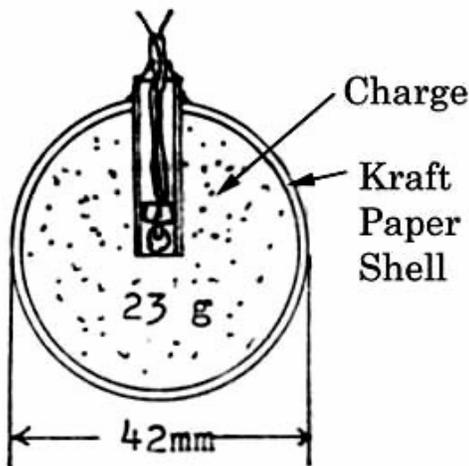
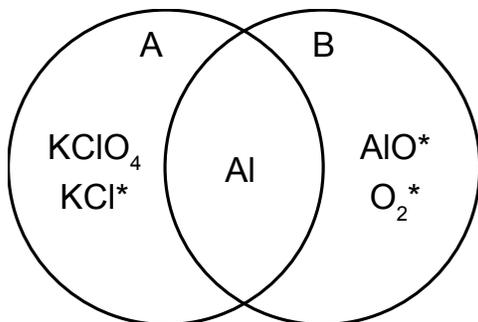


Figure 16. Sets involved in the two-phase reaction of a composition used for a flare.

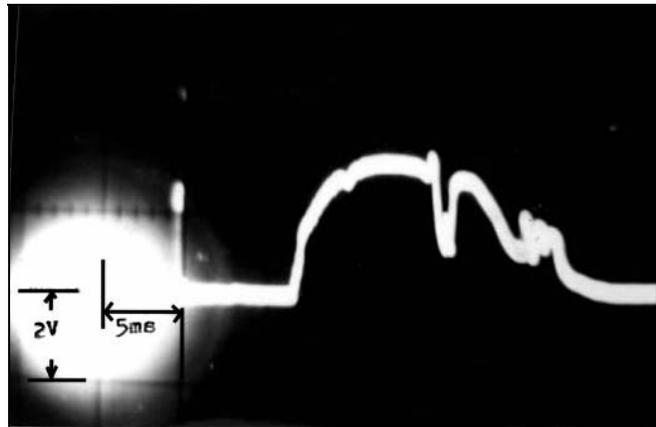
ing. We must be dealing with a two-phase reaction, involving the sets shown in Figure 16.



15.1 Sample of a salute charge.



15.3 Sets involved in the two-phase reaction of an explosive charge.



15.2 Electrical-voltage differential between sample piece and ground.

Figure 15. Measuring the delay for an explosive composition.

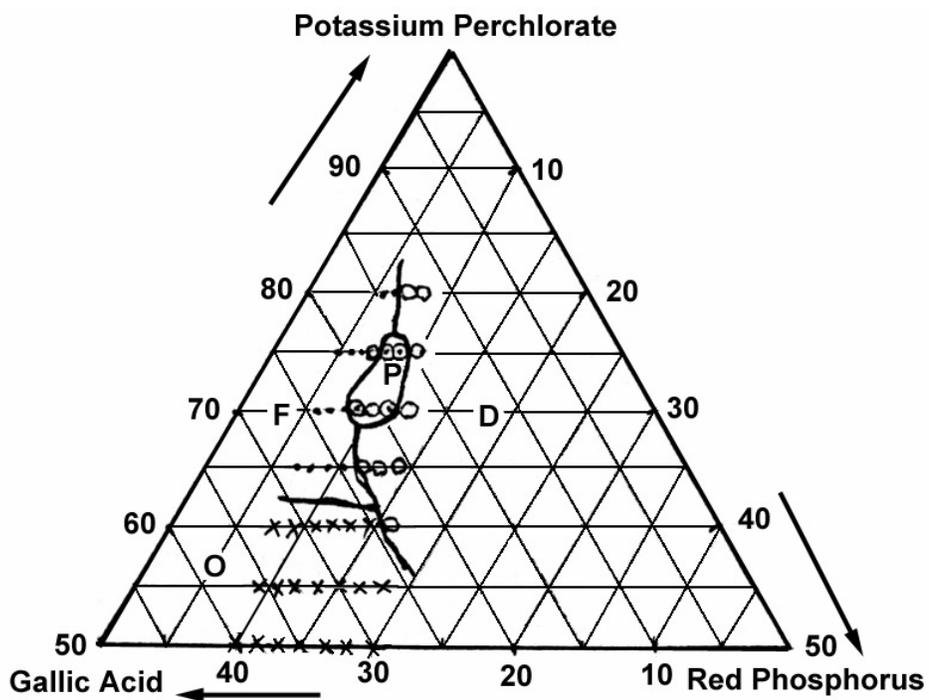


Figure 17. Whistling using A_1 ($KClO_4$, gallic acid, red phosphorus).

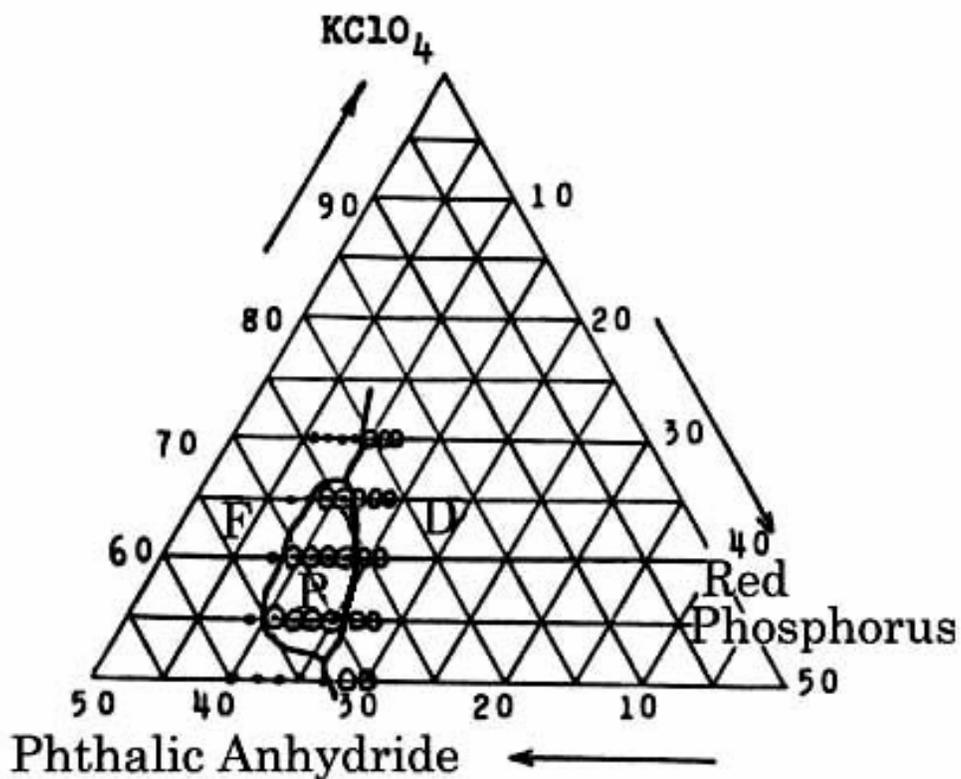


Figure 18. Whistling using A_2 ($KClO_4$, phthalic anhydride, red phosphorus).

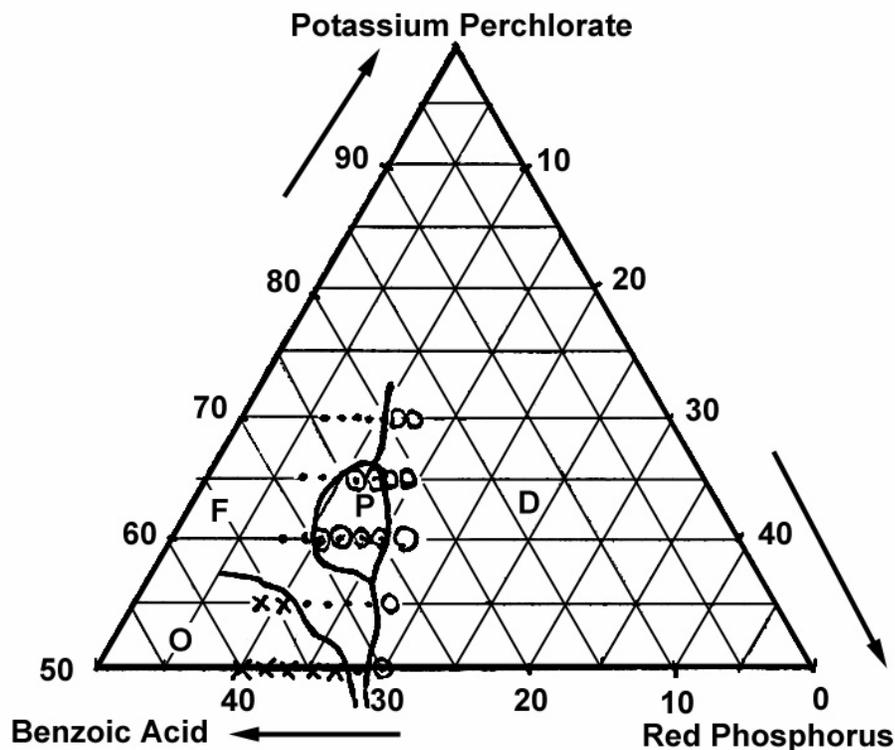


Figure 19. Whistling using A_3 ($KClO_4$, benzoic acid, red phosphorus).

We also examined compositions consisting of potassium perchlorate or potassium chlorate and resin (polyester, etc.) for their suitability as rocket fuels. Such compositions are shaped into one piece, without inhibitor, permitting all surfaces to be ignited. Upon ignition in a rocket mortar, surface explosion as described above occurs. However, if the potassium perchlorate or the potassium chlorate are replaced by ammonium perchlorate, no surface explosion occurs. The surface explosion is caused by the pressure surge of ignition. This reaction is also part of the two-phase reaction.

Flashing Reactions (Oscillating Reactions)

There are two representative types of flashing reactions: the strobe star and the pyrotechnic whistle. The former has already been described in *Pyrotechnica VII*^[7] and falls under reactions 13 and 14 shown in Figure 10.2. Here, we will

describe the pyrotechnic whistle, which falls under reactions 15 and 17 in Figure 10.2.

Test 5

A Kraft-paper tube with an inner diameter of 12 mm, a wall thickness of 1.2 mm and a length of 76 mm is plugged with 1.5 g of clay at one end. Using a hand press, at a pressure of 1200 kg/cm², the tube is loaded with 2 g of a whistling composition. The whistling compositions used consist of mixtures A_{1-4} (potassium perchlorate, one aromatic compound, red phosphorus)—the red phosphorus sensitizes the composition. Gallic acid $C_6H_2(COOH)(OH)_3 + H_2O$, phthalic anhydride $C_6H_4(CO)_2O$, benzoic acid C_6H_5COOH or anthracene $C_{14}H_{10}$ are used as the aromatic compound. Upon ignition by means of a fuse, the following effects are observed, ● indicating burning, ○ detonation, ⊙ whistling and × discontinuation of burning or no ignition. The areas of the various phenomena are designated F, D, P or O (Figures 17–20).

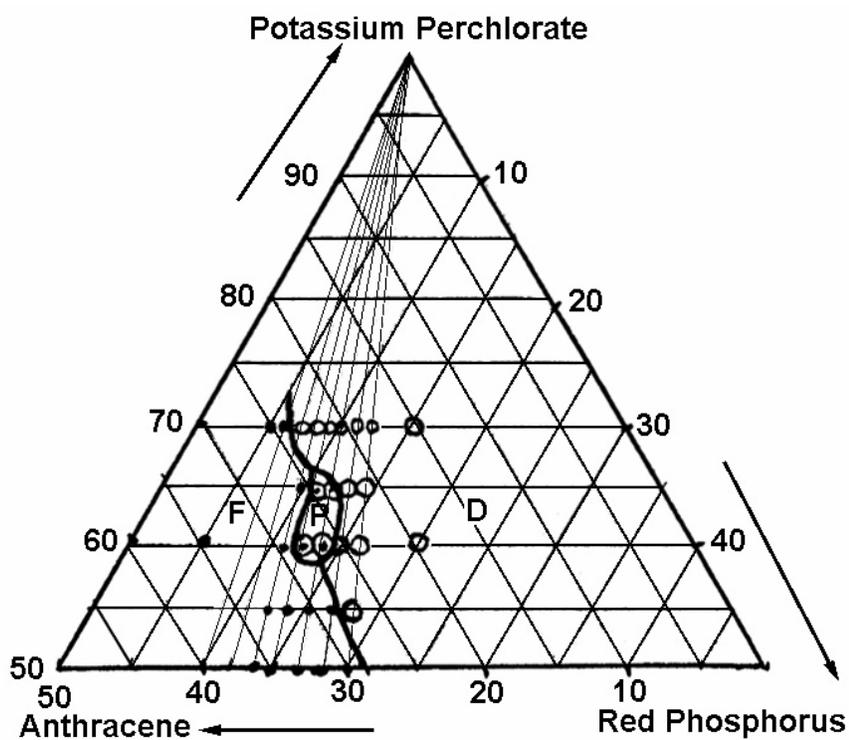


Figure 20. Whistling using A_4 ($KClO_4$, anthracene, red phosphorus).

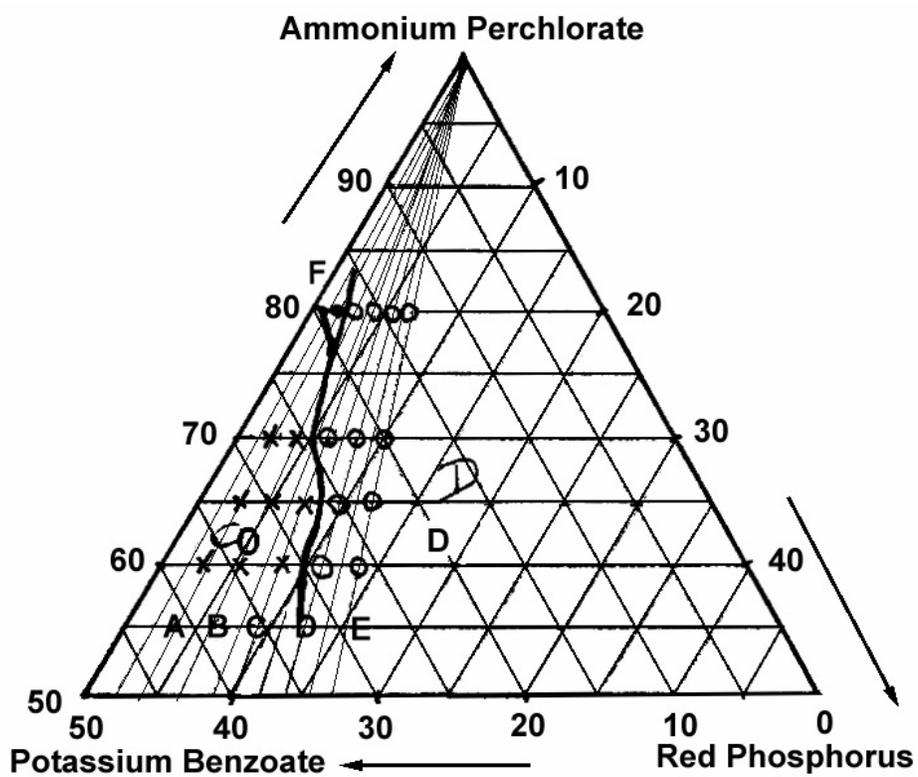


Figure 21. Whistling using A_5 (NH_4ClO_4 , potassium benzoate, red phosphorus).

Table 1. Two-Component Mixtures.

A↓ \ B→	Potassium picrate	Gallic acid	Potassium benzoate
KClO ₃	0/100** : D	<u>75/25</u> , 70/30: P	75/25, 70/30, <u>65/35</u> : P
KClO ₄	40/60: P*	75/25: F	80/20, <u>75/25</u> , <u>70/30</u> , 65/35, 60/40** : P
KNO ₃	5/95**, 10/90**, 15/85**, 20/80**, 25/75**, 30/70, 35/65, <u>40/60</u> , 45/55, 50/50: P	75/25: F	70/30: F
NH ₄ ClO ₄	40/60: F(still)	75/25: O	80/20: F(still) 75/25, 70/30, 65/35: O
Glass powder	20/80: P, 40/60: F	—	—
Strontium carbonate	20/80: P, 40/60: F	—	—

In this table, 60/40, for example, indicates the weight ratio of substances A and B.

F = burning; D = detonation; P = whistling; O = discontinuation of burning or no ignition;

* = a rasping sound and ** = the generation of black smoke.

Regular whistling charges are underlined

For comparison purposes, a mixture of NH₄ClO₄, potassium benzoate and red phosphorus was examined in the same manner (Figure 21). In this case, we did not observe whistling.

The two-component mixtures shown in Table 1 were also examined. In this table, 60/40, for example, indicates the weight ratio of substances A and B; F = burning; D = detonation; P = whistling; O = discontinuation of burning or no ignition; * = a rasping sound and ** = the generation of black smoke. Regular whistling charges are underlined.^[8]

Figures 17 through 20 show that whistling occurs in the range between burning and explosion. Namely, in each triangle graph, the whistling area P is surrounded by areas of burning F and detonation D like an island. Therefore, whistling must be explainable by a reaction mechanism during which burning and explosion alternate. Whistling is a function of the composition's degree of sensitivity, which is determined by the amount of red phosphorus (15 and 17 in Figure 10.2). Consequently, we are dealing with a flashing reaction.

Figure 21 shows that a mixture of NH₄ClO₄, potassium benzoate and red phosphorus does not result in whistling. Table 1 also shows that there is no whistling when NH₄ClO₄ is used.

In a mixture of KNO₃ and potassium picrate, KNO₃ is not required to produce whistling. It may be replaced by inert substances like glass powder or strontium carbonate, which produces a nice sound. This shows that such substances inhibit the decomposition of the potassium picrate and delay explosion (Table 1).

M. Kusakabe and N. Ishikawa report effects that were produced using a 5 kg hammer.^[9] Picric acid, TNT, tetryl and PETN were examined; yet, dual detonations with intervals of 1.3 to 2.3 ms per pulse (Figure 22) were observed for picric acid only. We are dealing here with a reaction during which explosion and burning alternate, and the resulting effect partially resembles whistling.

From the results of above experiments, the sets of vibrational reactions are thought to be as follows (Figure 23). KCl* or K₂O*, the latter of which comes from KNO₃, suppresses reaction B, while KCl* promotes the decomposition of KClO₄. Whistling occurs whenever reaction A is suitably promoted and reaction B suitably inhibited.

E.R. Maxwell^[8] reports that whistling compositions burn close to the surface. Therefore, each composition burns with a certain frequency, which is independent of the length of the paper tube or the frequency of the whistling sound. To prove this, we examined the relation-

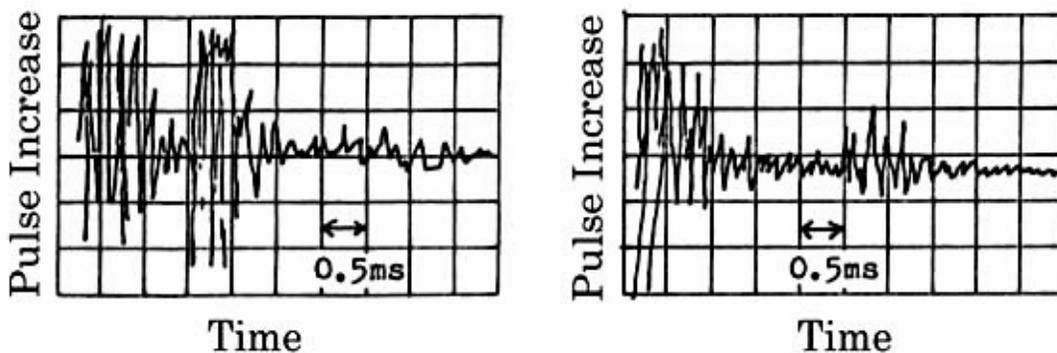


Figure 22. Oscillograms prepared by M. Kusakabe and N. Ishikawa^[9] showing the effects produced by a pulse sample containing picric acid.

ship between the frequency of the sound and the frequency of the thrust waves created by the burning of the composition.

Test 6

A sample piece which, except for a different length, corresponds to that used in Test 5, is connected to a carbon recipient, which receives the thrust waves created by the burning of the composition. An electromagnetic microphone (SONY, Model F-96) is positioned at a distance of 30 cm from the test piece. Both voltages are recorded by an oscillograph (Iwatsu Electric Co., SS4200M) without amplifier (Figures 24, 25, 26). For testing, we used the customary compositions A₅ (70% KClO₄, 30% potassium benzoate), A₆ (75% KClO₃, 25% gallic acid) and A₇ (37% KNO₃, 63% potassium picrate).

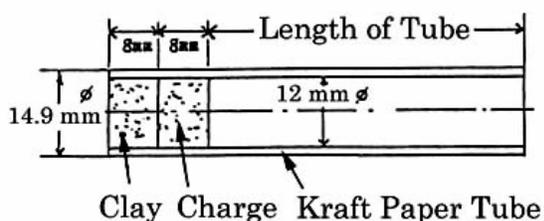


Figure 24. Sample piece.

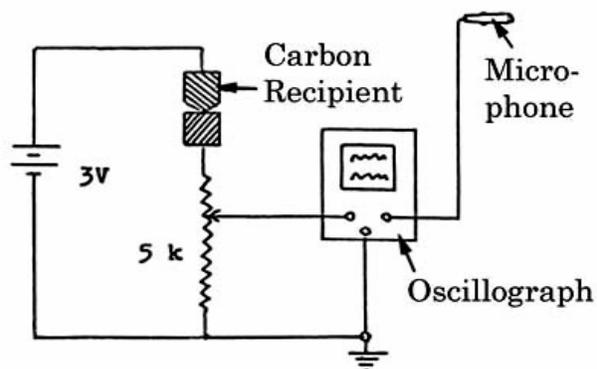


Figure 25. Assembly for measuring thrust waves and sound waves.

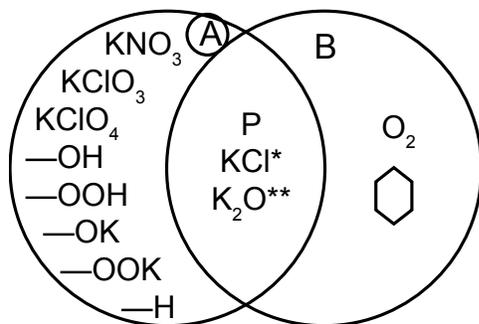


Figure 23. Probable sets involved in oscillating reactions of whistling compositions.

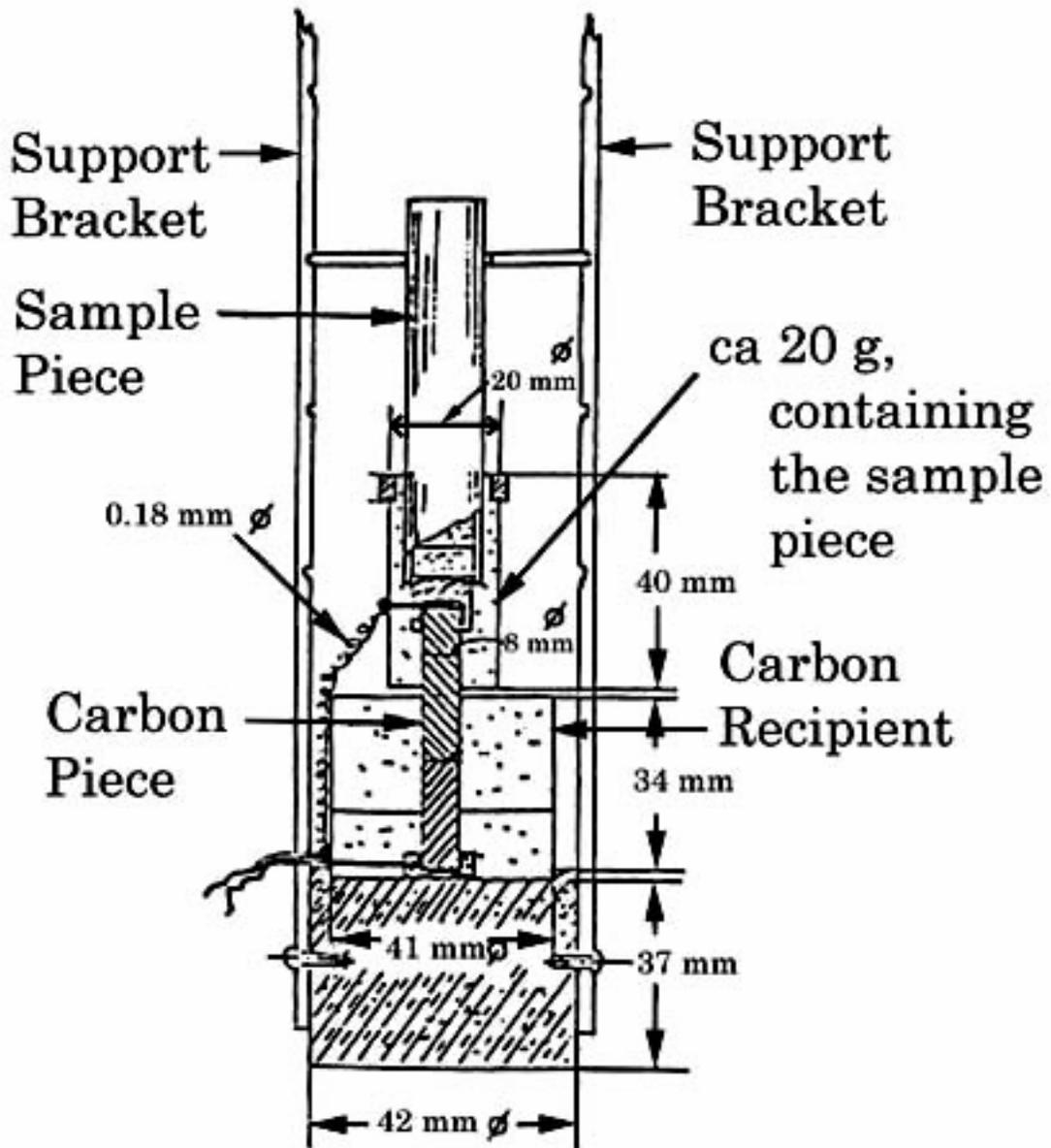


Figure 26. Assembly for measuring thrust waves.

Figure 27 shows the correlation between the length of the tube and the frequency of the sound. It can be seen that this correlation is almost entirely independent of the type of composition used.

Figures 28 and 29 show the correlation between thrust waves and sound waves. The thrust curves are explained in Figure 30.

In each oscillogram, the correspondence between the beginning of each thrust wave and

each sound wave is examined. The results are shown in Figures 31 through 34. The mark • in each curve indicating the beginning of a given thrust wave.

Good correlation exists only for Nos. 281 (A_5), 276 (A_6) and 279 (A_7). Fairly good correlation is also observed for No. 288, the frequency being half that of No. 276.

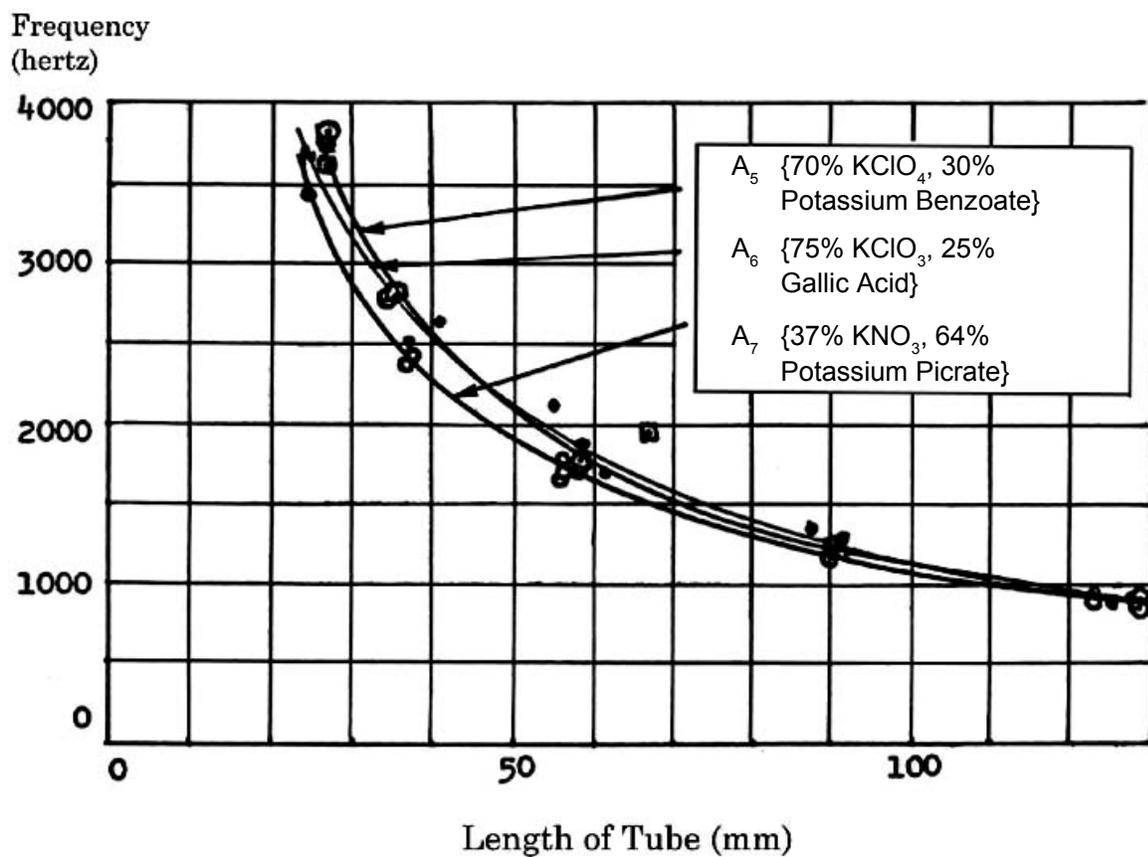


Figure 27. Frequency of the sound as a function of the length of the tube.

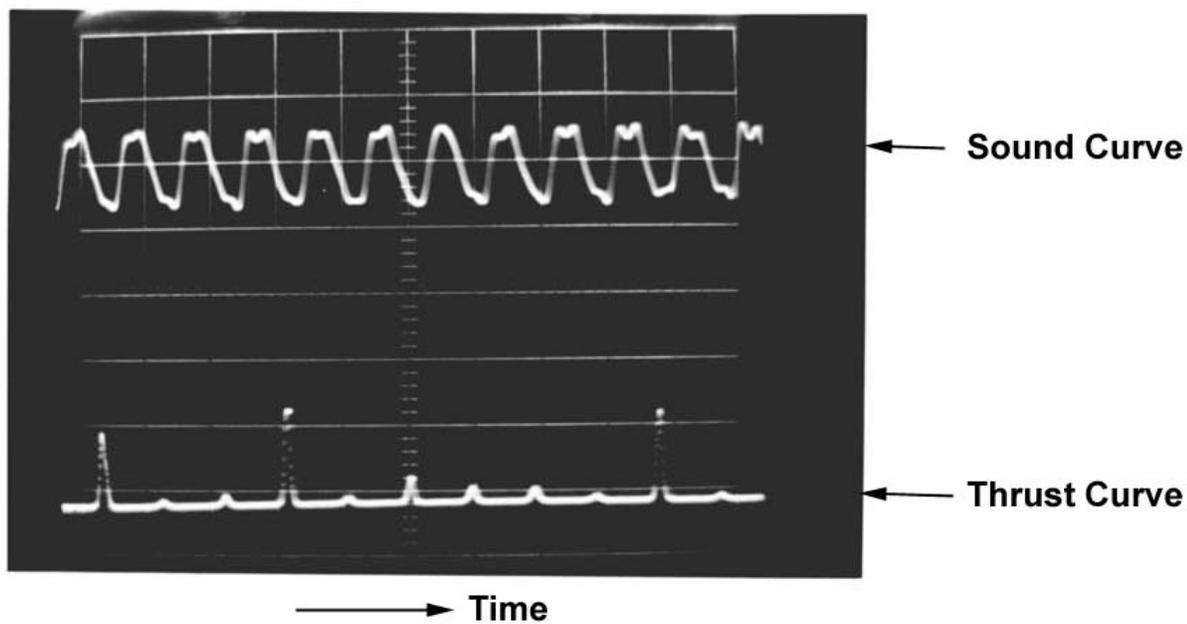


Figure 28. Effects of sound waves (top) and thrust waves (bottom); composition A_6 : length of tube = 56 mm; horizontal section = 0.5 ms; vertical section = 1 V (top) and 0.2 V (bottom).

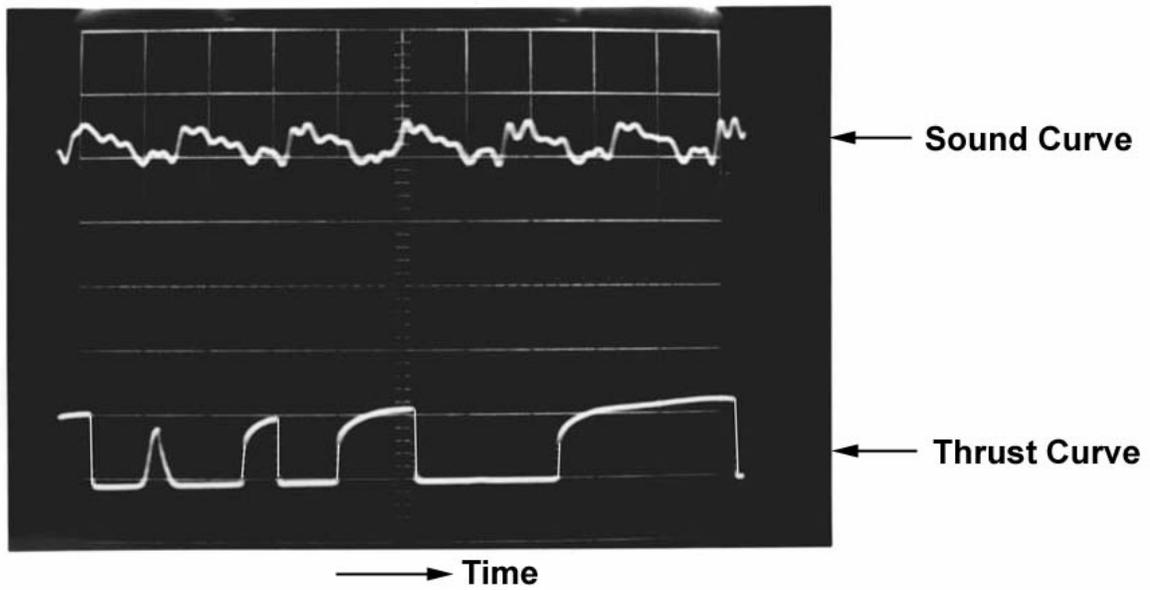


Figure 29. Effects of sound waves (top) and thrust waves (bottom); composition A_7 : length of tube = 91 mm; horizontal section = 0.5 ms; vertical section = 1 V (top) and 0.2 V (bottom).

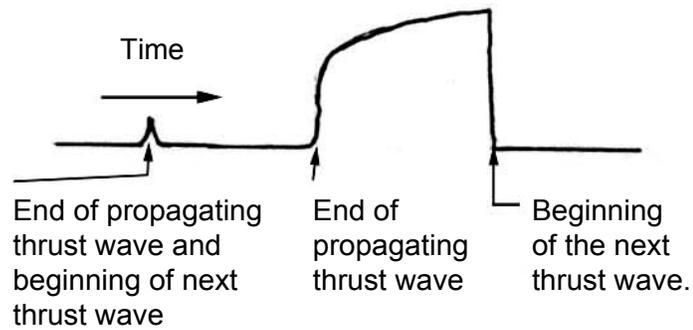


Figure 30. Significance of thrust curves.

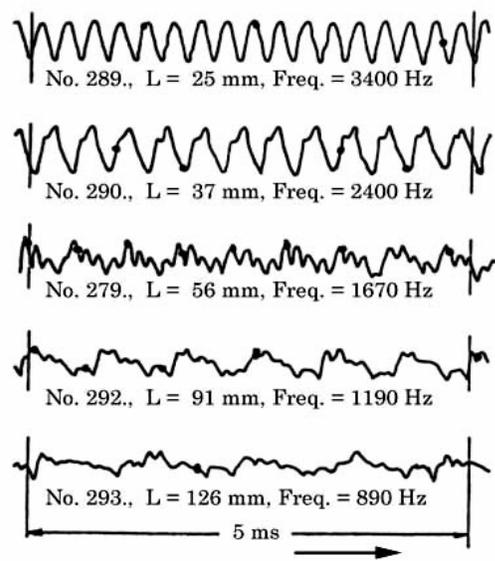
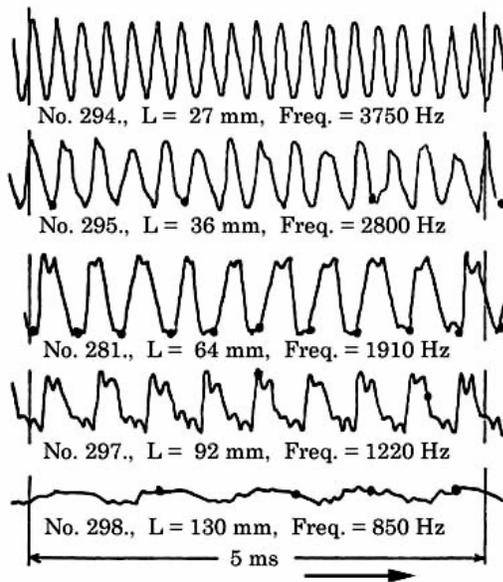


Figure 31. Sound curve of A_5 ; L = length of tube; Figure 33. Sound curve of A_7 .
 Freq. = periodic number of waves.

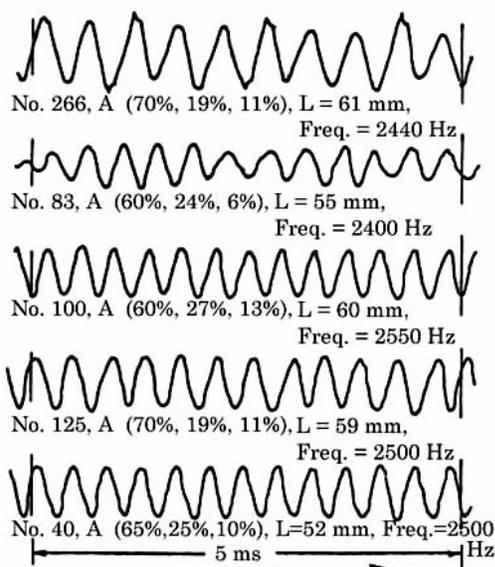
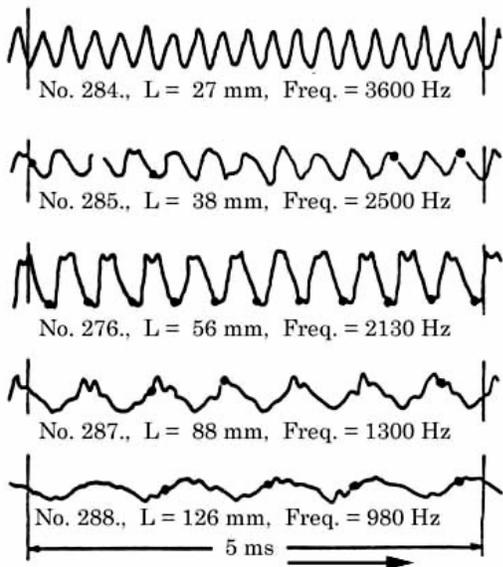


Figure 32. Sound curve of A_6 .

Figure 34. Sound curve of A_1 , A_2 , A_3 and A_4 (See Figures 17, 18, 19 and 20).

The results suggest that the reaction phenomena of the composition, that is, the alternating reactions of burning and explosion, have a specific frequency that is independent of the length of the tube or the frequency of the sound. Only if the frequency of the reaction and the sound correspond to the length of the tube, will the thrust waves have the same frequency. The specific periodic numbers are very similar (Table 2).

Figure 34 shows the sound curves for A_1 through A_4 , which are similar to the curves of Nos. 281, 276 and 279.

Table 2. Specific Periodic Numbers of Compositions in the Case of Whistling Reactions.

No.	Composition	Specific Periodic Number
281	A ₅ {70% KClO ₄ , 30% potassium benzoate}	1910 hertz
276	A ₆ {75% KClO ₃ , 25% gallic acid}	2130 hertz
279	A ₇ {37% KNO ₃ , 63% potassium picrate}	1670 hertz

Miscellaneous

Figure 35 shows only the principal reaction.

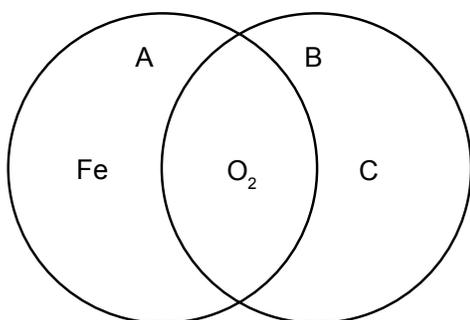


Figure 35. The principal reaction involved in the sparking of iron.

There are also $A \cup B \cup C$ three-phase reactions, such as in Figure 36.

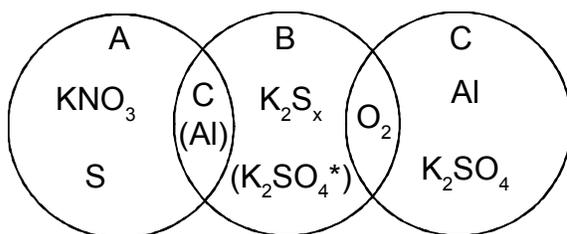


Figure 36. Three-phase reaction. (*) indicates that the substance is not involved in the reaction.

Conclusion

The set of reactants contains all the substances that are initially involved in the reaction. The substances created during reaction A are contained in the set of the substances reacting in the second reaction B.

As a rule, attention is paid to only those components whose reaction is known. This can be avoided by expressing a given reaction by means of mathematical sets. To explain a complicated reaction, the set must be determined by conducting various tests. Often, during such testing, one will become aware of certain circumstances which were previously unnoticed.

This method, which concerns mainly two-phase and multi-phase reactions, will be useful for solving problems related to accident prevention, the design of pyrotechnic compositions, etc. For example, the fact that the burning of a composition often turns into an explosion can be explained by this theory of the two-phase reaction. If this method is to be applied to new reactions, these reactions will have to be categorized as shown in Figure 10, according to their course of reaction.

Finally, I would like to thank Dr. Robert G. Winokur, USA, and Selçuk Öztap, Turkey, for their suggestions regarding testing.

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- 1) T. Shimizu, *Fireworks* (1976) p. 11.
 - 2) *Ibid.*, p. 12.
 - 3) T. Shimizu, "Studies on Strobe Light Pyrotechnic Compositions", *Pyrotechnica* VIII (1982) p. 7.
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 - 7) T. Shimizu, "Studies on Strobe Light Pyrotechnic compositions", *Pyrotechnica* VIII (1982) p. 5.
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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.

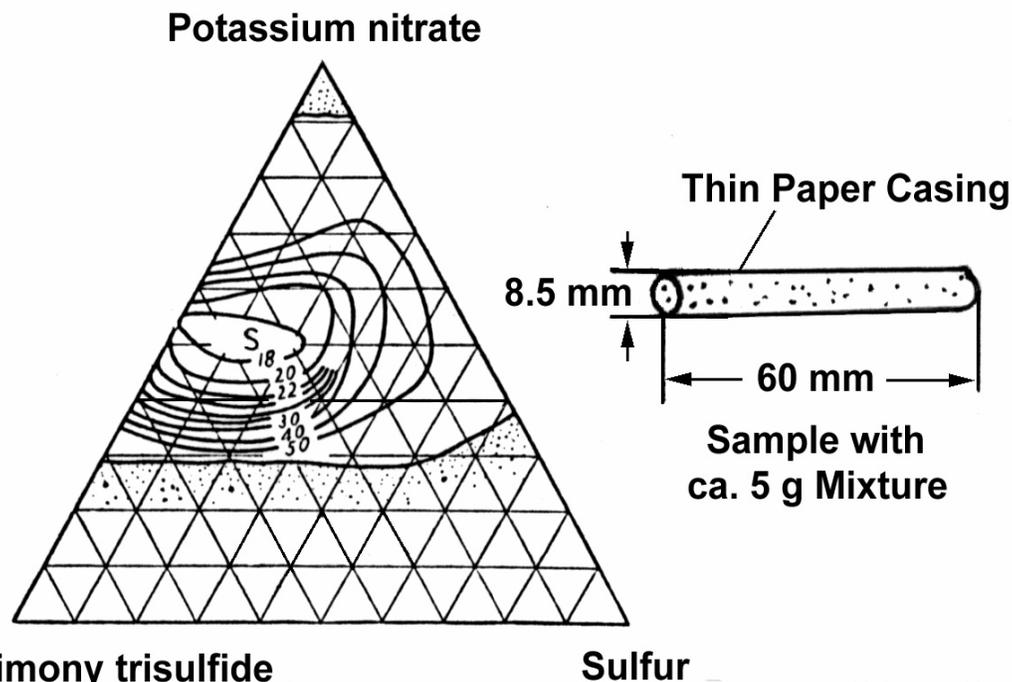


Figure 1. The duration of burn of the composition potassium nitrate + antimony sulfide + sulfur.

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, Pb₃O₄ + Ferrosilicon

	No. 31	No. 32	No. 33	No. 34	No. 35	No. 36	No. 37
Red lead, Pb ₃ O 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	4	4	4	5
			Yellow smoke	Yellow smoke	Yellow smoke	Yellow smoke	

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

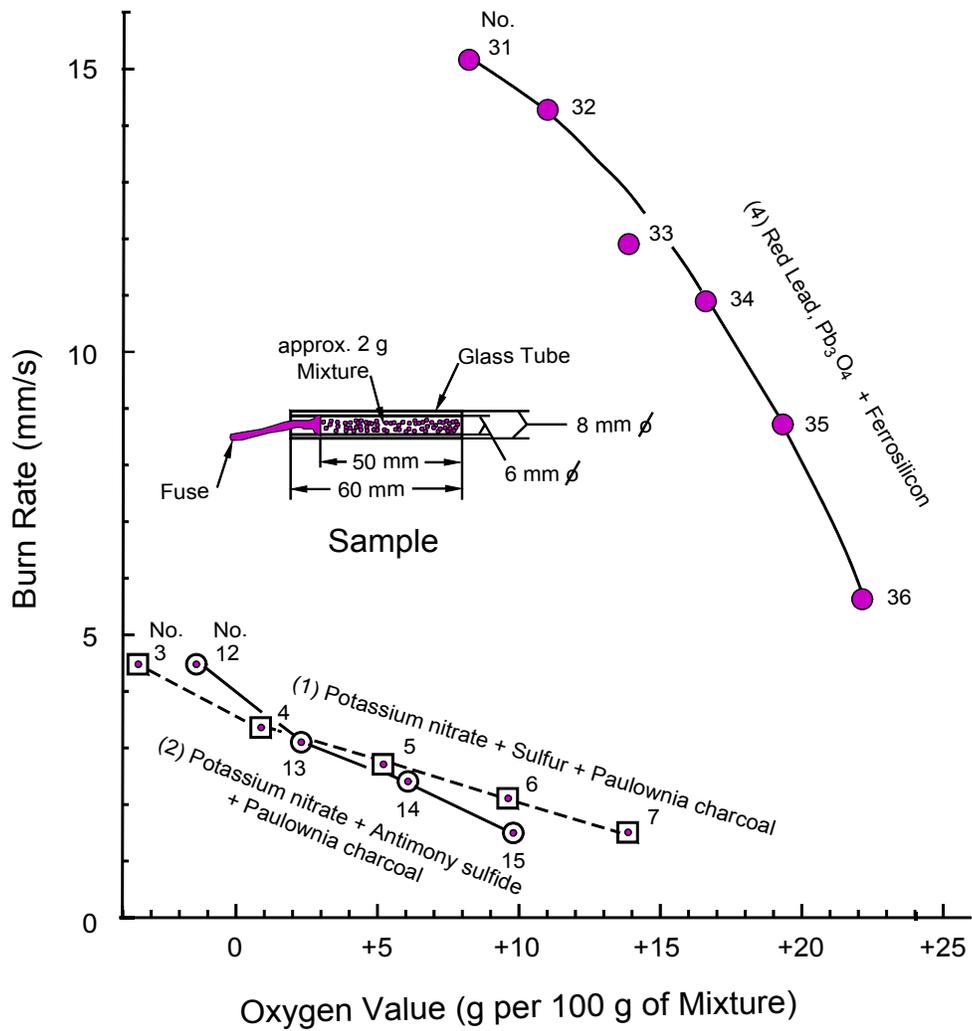


Figure 2. Burn rates of mixtures having a positive oxygen value.

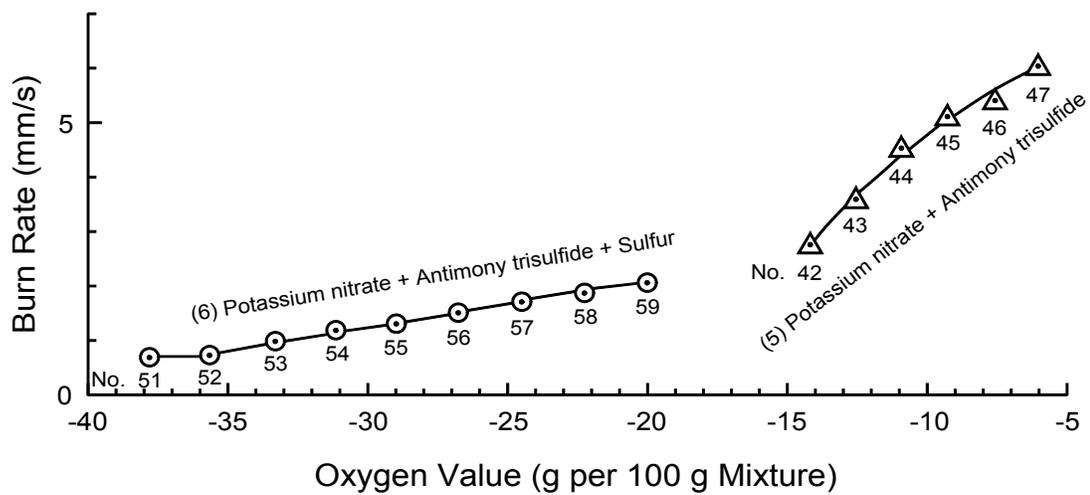


Figure 3. Burn rates of mixtures having a negative oxygen value.

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]

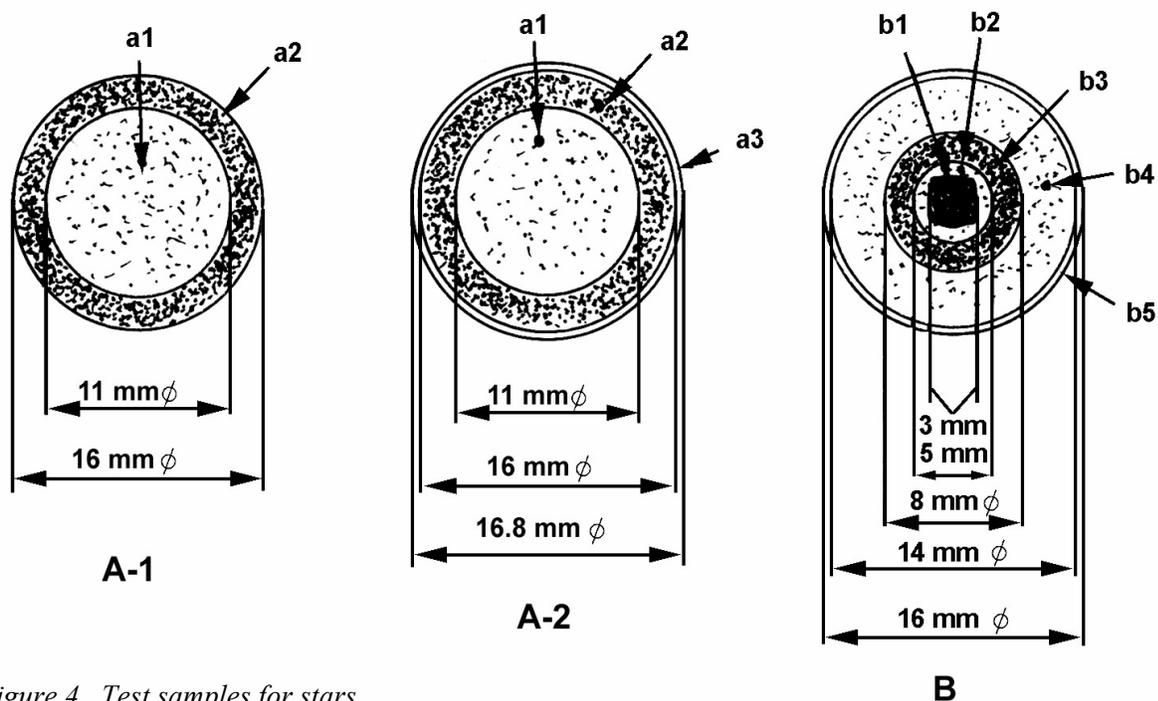


Figure 4. Test samples for stars.

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% BaSO₄, 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.

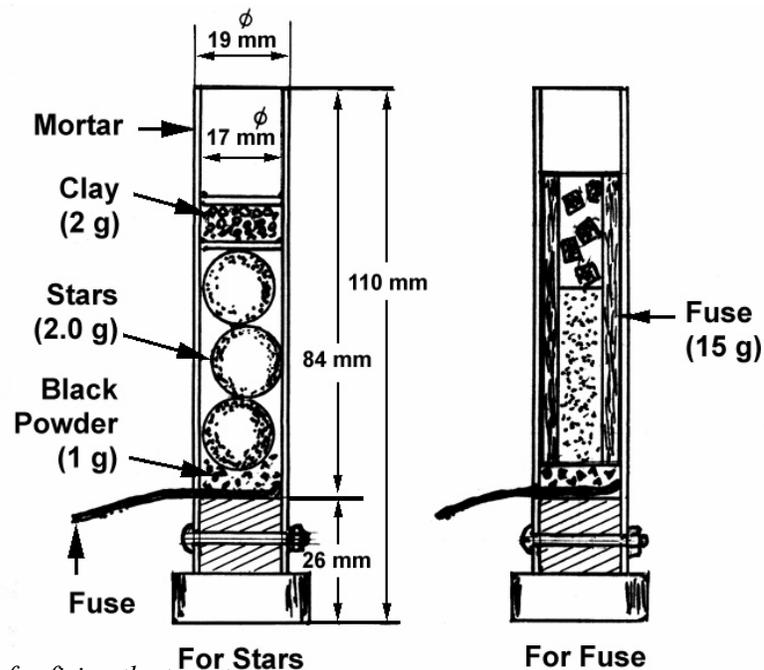


Figure 5. Device for firing the test stars.

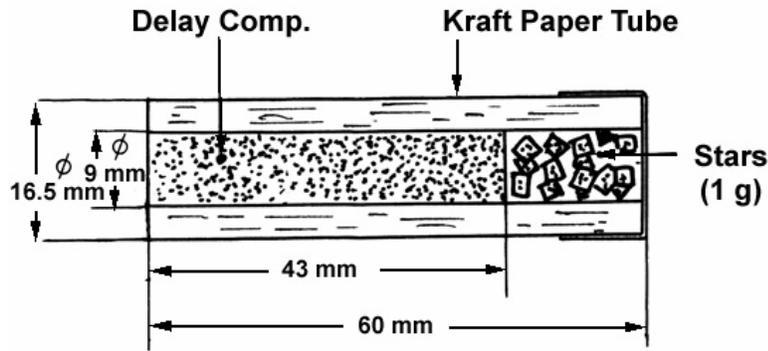


Figure 6. Sample of quick match.

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	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 ₂ S ₃
Mg	sl. Rxn., inert	gr. Rxn., H ₂ S, More active	gr. Rxn., H ₂ S Violent
Mg + 5% K ₂ Cr ₂ O 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 ₂ S
Mg/Al (50:50) + 5% K ₂ Cr ₂ O ₇	sl. Rxn., very inert	X	X
Fe	sl. Rxn., inert	gr. Rxn., H ₂ S	X
Fe + 5% K ₂ Cr ₂ O 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) H₂, NH₃, NO_x, or H₂S: 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.

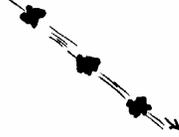
 <p>a weak flame, no sparks</p> <p>A1 Mg/Al with small particles</p>	 <p>a large, white flame with weak red sparks, which are not visible from a distance</p> <p>AB1 Mg/Al with small particles</p>
 <p>flashing light</p> <p>A2 Mg/Al, with large particles</p>	 <p>only a white flame with thin red sparks</p>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

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 ₃ O ₄	89
Magnalium (Mg/Al:50/50) (100-mesh)	11

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

Ingredient	(weight %)
Red lead, Pb ₃ O 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, Pb₃O₄, and atomized aluminum in various particle sizes, as follows, in the weight ratio Pb₃O₄/Al : 90.5/9.5.

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:

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

AgNO₃, HgO, Fe₂O₃, Fe₃O₄, BaO₂, Cu₂O, PbSO₄, PbO or PbO₂ instead of red lead, Pb₃O₄. Only PbO and PbO₂ 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, Al₂O₃. On the other hand, upon heating, the lead oxide Pb₃O₄ or PbO₂ 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.



In the case of the larger particles, however, a short delay is noted before the explosion. This means that the layer of aluminum oxide, Al₂O₃, 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 Al₂O₃ to rapidly react with the already melting aluminum to produce an explosion. That would be the origin of the bang.

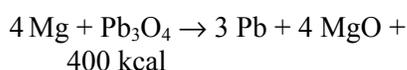
For the practical use of these mixtures, it is better to add a small amount of magnesium to the compositions to permit the dark reaction to take place without being extinguished.

Red Lead Explosive Composition IV

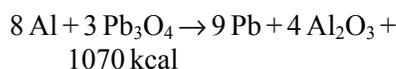
Ingredient	%
Red lead, Pb ₃ O ₄	90%
Aluminum, atomized (0.15–0.3 mm)	8%
Magnesium (0.15–0.25 mm)	2%

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:

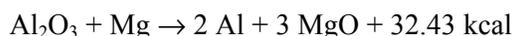
Reaction 2:



Reaction 3:



Reaction 4:



Reaction 4 proceeds slowly from left to right and not from right to left, as was experimentally determined. When the mixture of red lead, Pb₃O₄, 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, Al₂O₃, 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.

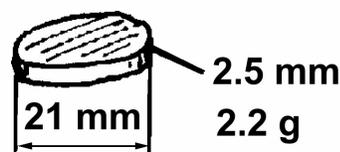


Figure 8. Sample from Table 12. The sample was placed on the ground and ignited using a piece of fuse and magnesium powder.

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.

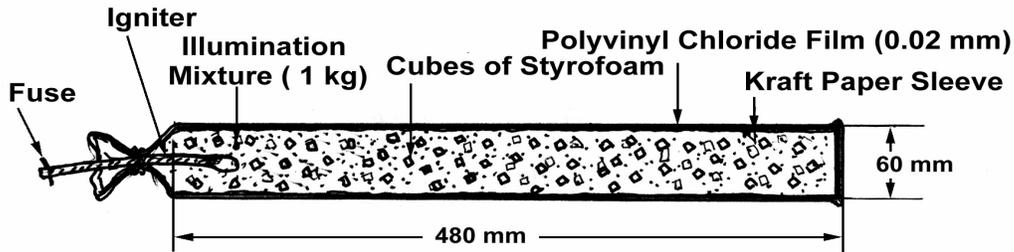
Sample No.	Mg/Al	Particle Size (mm)	Report	Effect
1	65/35	< 0.07	none	(by M. S. Swisher)
2	60/40	0.05–0.25	produced	small noise
3	50/50	0.005–0.09	produced	explosion
4	40/60	0.005–0.10	produced	crackling
5	30/70	0.001–0.05	produced	explosion (very loud bang)

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

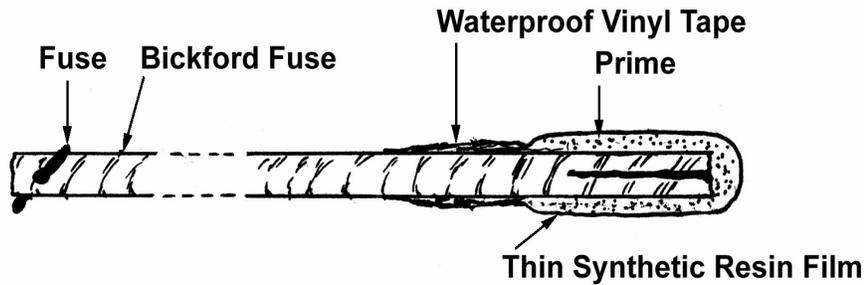
an emergency signal for use at sea.

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).

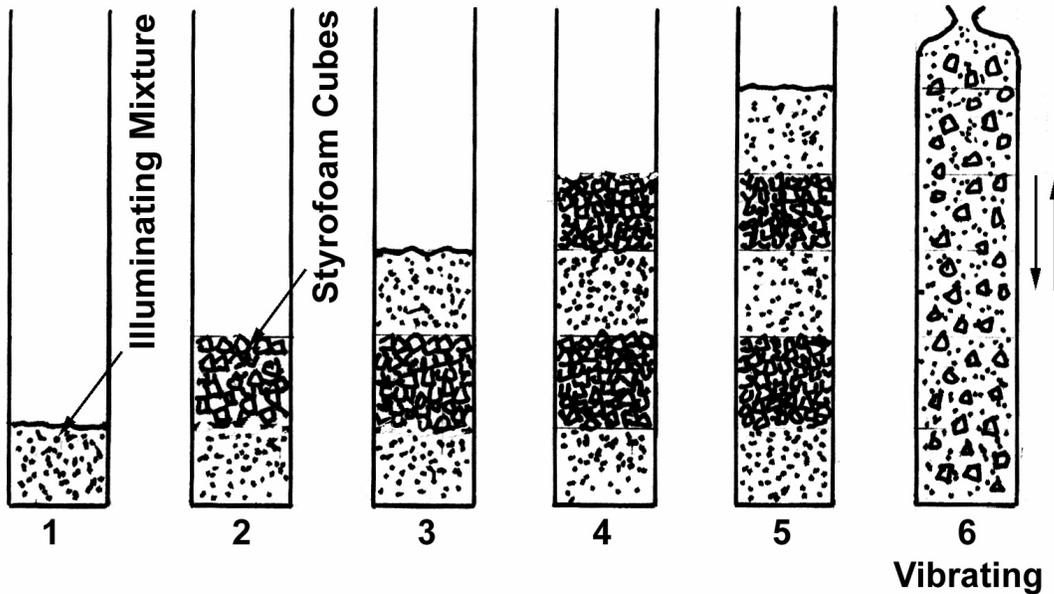
One end of the device was provided with a piece of Bickford fuse. At the end of the fuse inside the mixture, a certain amount of a mixture of red lead and ferrosilicon was added as the prime (4 g prime, Pb_3O_4 /ferrosilicon: 92/8).



1. Cross section of water flare



2. Igniter



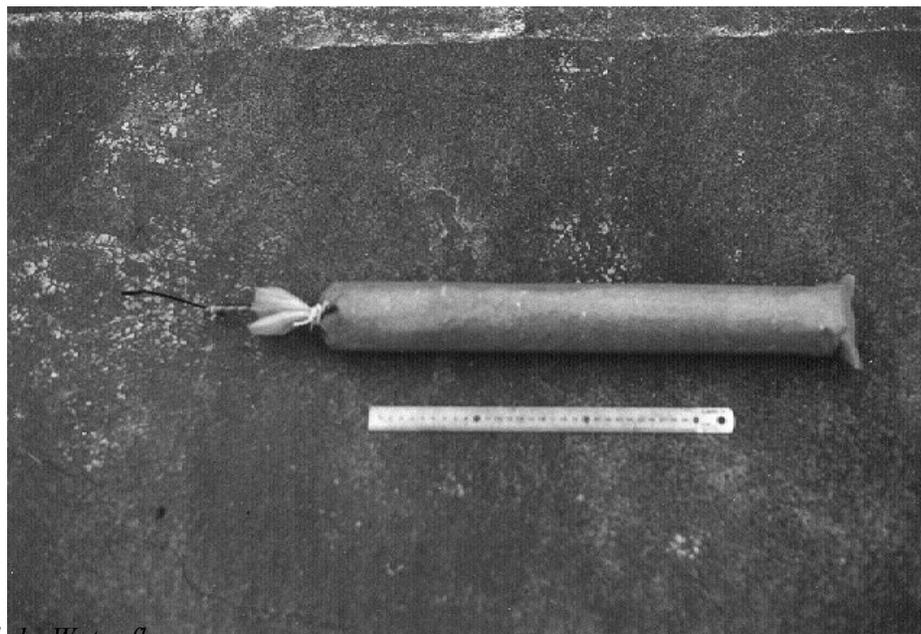
3. Illumination mixtures

Figure 9. Water flare.

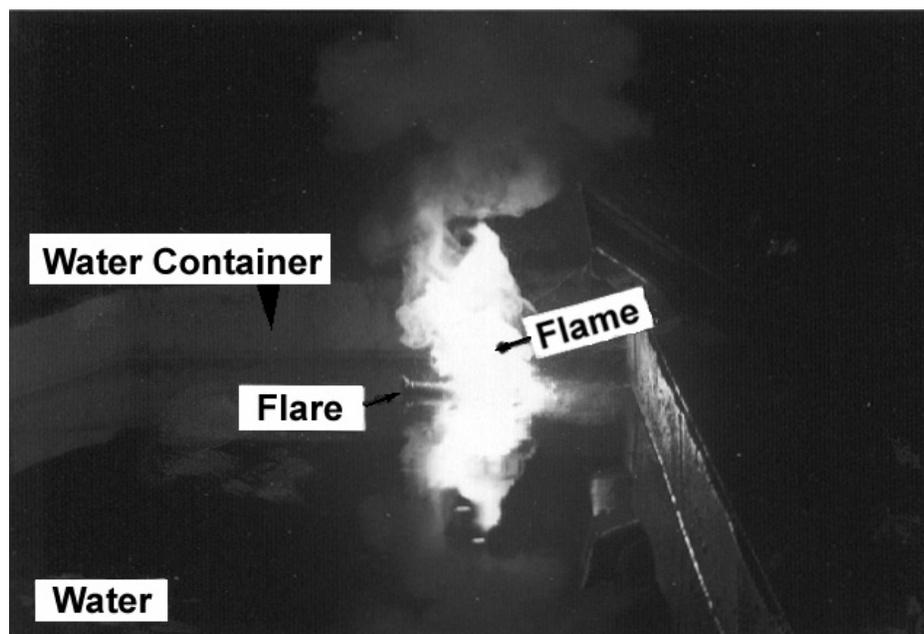
To prevent the device from sinking in the water, I had previously mixed some cubes of polystyrene foam (styrofoam) measuring approx. 10 mm along the edges into the illuminating mixture, so that the typical weight per unit volume of the device was on average 0.74. The method of loading the illuminating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

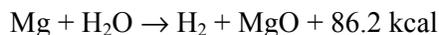


Photograph 2. The burning water flare.

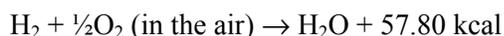
Table 13. Effective Dark Charges for a Negative Oxygen Value:

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.



Reaction 6.



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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Research on the Most Appropriate Method for the Pyrotechnic Industry To Determine the Sensitivity of Compositions

Takeo Shimizu

KOA KAKO CO., 801-1 Kamikayama, 350-12 Hidaka-shi, Saitama-ken, Japan

SUMMARY

Those of us who work in the pyrotechnic industry have three requirements to obtain data concerning the sensitivity of mixtures:

- 1) establish the starting point of no-ignition
- 2) understand the possibility of propagation of the ignition to combustion or explosion
- 3) clarify the variation of the sensitivity, which is dependent on the materials that we have used for tools

The methods used up to now have not satisfied our requirements.

The sensitivity was determined with a drop test using a steel ball onto a sample placed on an anvil. The sample used was molded as a thin round disk. This method was used to establish the propagation of ignition.

Initially, the experiment was conducted using the up-and-down method so as to compare with that described below. The data obtained on a salute composition did not indicate a normal probability distribution. This method does not give an exact result, without having some prior test data.

The experiment was then conducted using the descending-method, which I use regularly at the factory. The height of no-ignition was determined on 50 trials with the salute composition and with the composition CuO–Al.

It was possible to determine the influence of the material of the anvil on the sensitivity of the mixture and substituting aluminum for the steel.

1. Introduction

This report concerns the test method used to determine the sensitivity of pyrotechnic compositions. We who work in a pyrotechnic factory have three requirements to obtain the sensitivity data on compositions.

- 1) establish the point of no ignition
- 2) understand the possibility of propagation of the ignition to explosion
- 3) clarify the variation of the sensitivity, which is dependent on the materials that we have used for tools

Up to now, no methods have satisfied the requirements.

2. Equipment

The sensitivity was determined with a drop test using a steel ball onto a sample. The ball has a diameter of 76 mm and a mass of 1.8 kg. A small amount of pyrotechnic composition was placed on an anvil (Figure 1). This method permitted us to determine the propagation of the ignition to combustion, to explosion, or to non-propagation.

3. Testing

3.1 By the Up-And-Down Method

The first series of tests were performed using the up-and-down method. A description of this method follows.

Place the ball at an initial height and allow it to fall on the sample on the anvil. If the sample does not ignite, the ball is dropped from a higher,

predetermined level. If the composition does ignite, the ball is dropped from a shorter, predetermined level. The process is then repeated.^[1]

The sample of salute composition consisted of 64% potassium perchlorate, 23% aluminum and 13% sulfur and is more sensitive than the usual compositions.

Using a manual method,^[2] one establishes the level for the next test by basing it on the

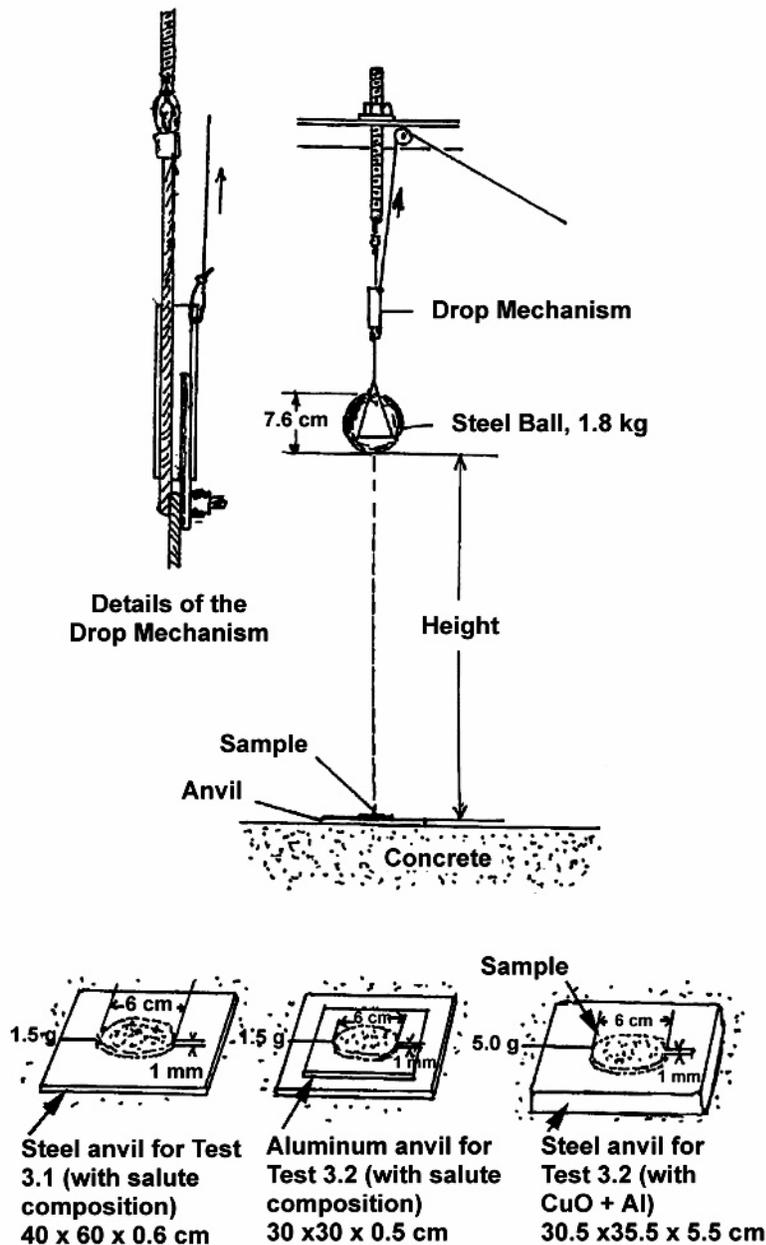


Figure 1. Equipment for the tests.

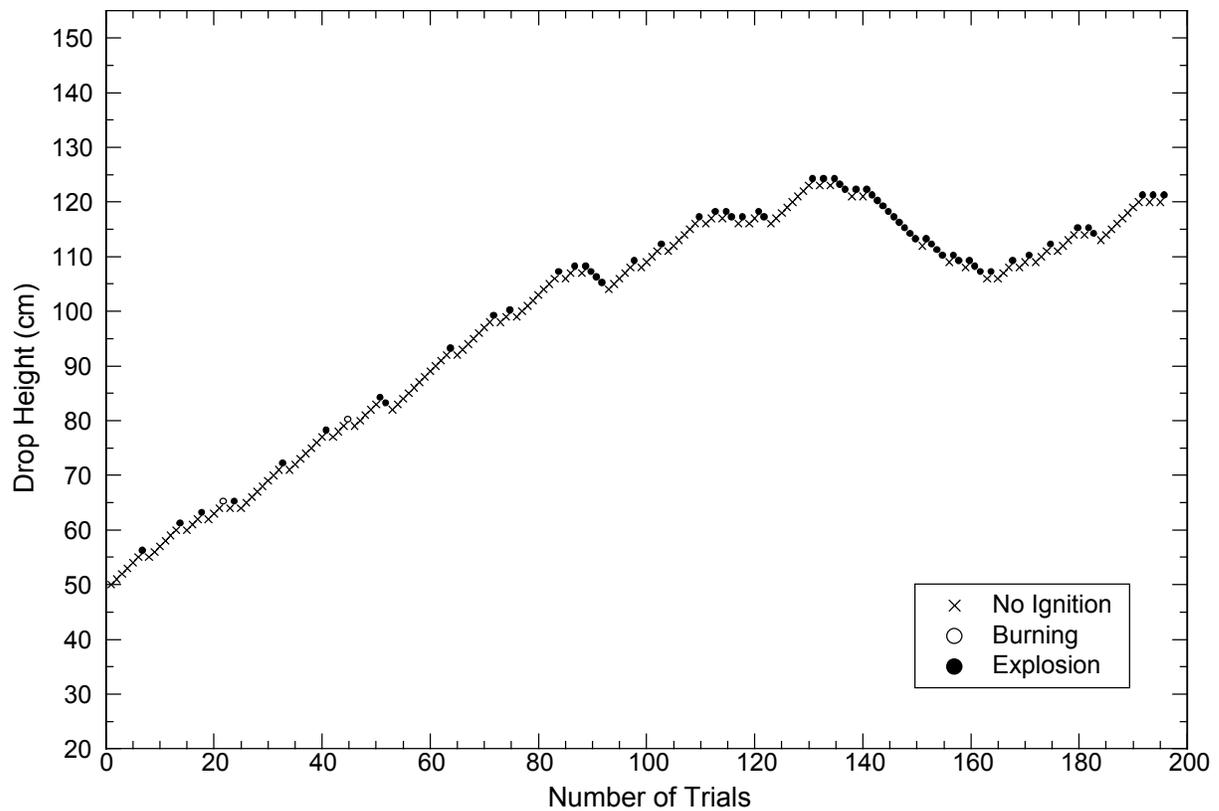


Figure 2. Test results for the up-and-down method with the salute composition.

results of the previous one. However, it was impossible to do this since I did not have the first data point nor could I obtain it using this method. I, therefore, chose a value of 1 cm. The results are shown in Figure 2.

As indicated by the curve, the data does not define a normal distribution, which is essential to obtain the exact, 50% height for ignitions.

That is to say that the up-and-down method does not give exact results, if we do not have sufficient previous test results.

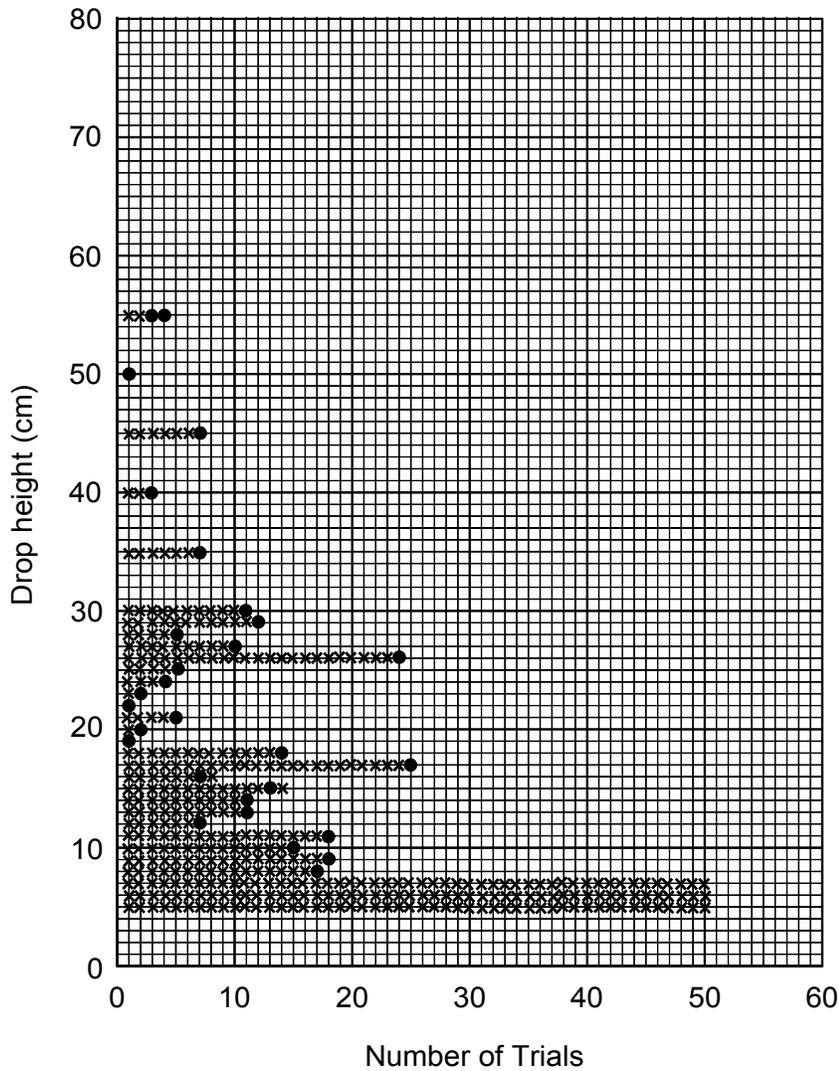


Figure 3. Test results for descending method with salute composition.

3.2 Descending-Method

The testing process was performed by using the descending-method, which I have used successfully. We place the ball at a first height and we drop the ball many times until an ignition occurs. After, we decrease the height from which the ball is dropped and we repeat the process.

One test was performed using this method with the same sample of salute composition. The results are shown in Figure 3. With 50 trials, a height of 7 cm was obtained as the no-ignition value.

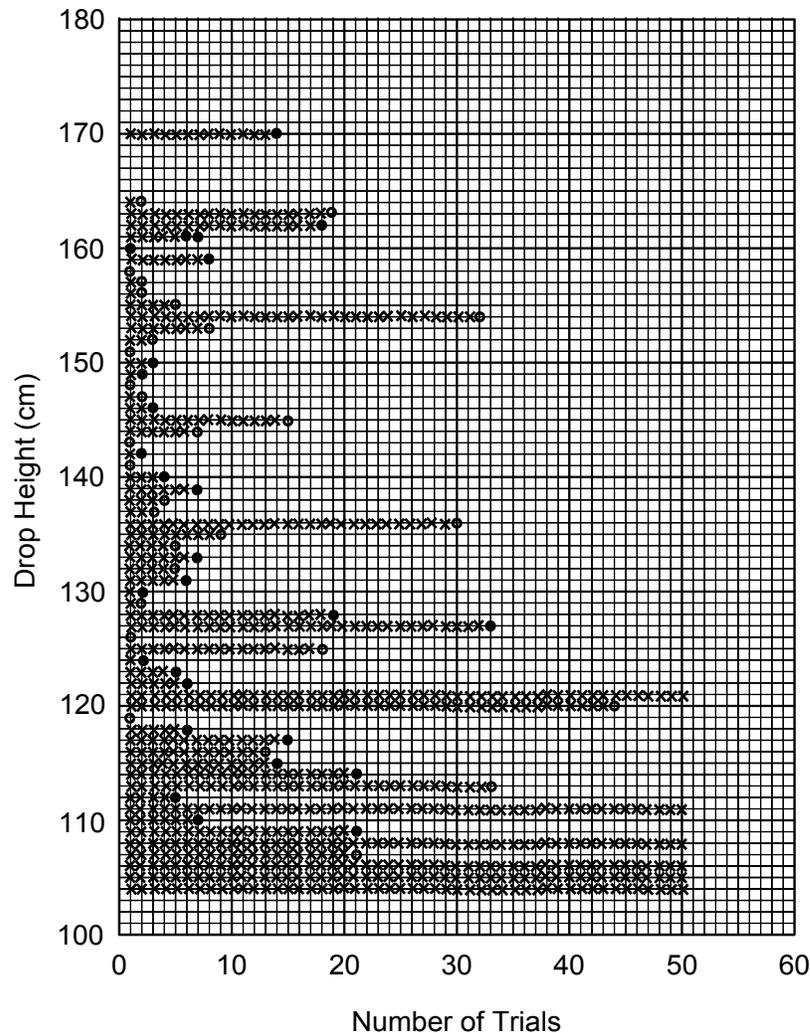


Figure 4. Test results for the descending method with the CuO + Al composition.

Figure 4 shows results for a recent composition, 80% CuO + 20% Al (atomized, Yamaishi VA 2000).^[3] This composition is very efficient as a bursting charge for firework shells.

The height for no-ignition, determined with 50 trials, was determined as 106 cm.

The same tests with the salute composition was repeated on an aluminum anvil instead of the one of steel. The 50 trials at a height of 170 cm did not result in any ignitions.

4. Discussion

The effect of the propagation is indicated as a no-ignition (x), ignition without propagation

(Δ), combustion (O), or explosion (•). This can be seen with the symbols in Figure 2, 3, and 4. The effect of ignition without propagation was not demonstrated by our compositions, but I have frequently seen it with other compositions. The salute composition has always given an explosion, but the CuO–Al composition sometimes results in combustion and sometimes in explosion. It seems to be due to the strong shock waves created by the ignition. We can obtain the effects of the propagation of the ignition by this method.

As indicated by the curve in Figure 2, the 50% height for ignition was not obtained because the results are not normally distributed. Certainly, the initial test height was incorrectly

chosen. It is believed that it is not possible to obtain good results by the up-and-down method without prior experience with the method, the composition, and the test apparatus.

Also, this method cannot provide the height of no-ignition that we fervently require at our factory. Moreover, even if we have obtained good results by this method, we could not determine this height with sufficient precision because of insufficient trials. This is why the up-and-down method is inadequate for our factory.

We find from Figure 3 that it is possible to obtain the height of the no-ignition using the descending method. This height was determined from the no-ignition of 50 trials at each of three, adjacent, descending heights. This method assumes that testing begins at an arbitrary height. Furthermore, the distance between test levels is chosen according to the precision desired. Another advantage of the descending method is that the number of times that a trial results in combustion or explosion are very few. This reduces the amount of damage to the equipment. The height of no-ignition for the salute composition using this method, was found to be 6 cm.

Figure 4 gives a result of the mixture CuO–Al using the same method, which finally will give us an acceptable method. The results are shown in the following Table 1.

Table 1. Number of Non-Ignitions at Various Heights.

Sample	Height(cm)	Number of Non-Ignitions
a)	121	50
	120	43
	119	0
b)	111	50
	110	6
c)	108	50
	107	20
d)	106	50
	105	50
	104	50

It is not possible to determine the no-ignition height of a), b) or c) with 50 trials at the same test height. Confirmation of the results at three adjacent heights, such as those in d), is necessary. These tests have resulted in a no-ignition height of 106 cm for the composition.

It is possible to establish the effect of the anvil material by changing it. As already mentioned, using the descending method, the no-ignition height for the salute composition was 7 cm for the steel anvil and 170 cm for the aluminum anvil.

5. Conclusions

A simple method was evaluated, whereby, a steel ball was dropped onto molded, thin disk sample placed on an anvil. Using this method it is possible to determine the point of no-ignition, ignition, or the propagation of ignition to combustion or to explosion. Moreover, it is possible to establish the sensitivity of the composition as a function of the anvil material.

The up-and-down test method does not provide useful information for our factory. It is very difficult to obtain a good normal distribution.

The descending method have given us good results, which can be used in our factory. However, confirmation of the effect at three different height with 50 trials at each height is necessary to obtain exact results.

6. References

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Study on the Reaction Mechanism of Black Powder and Its Applications

Takeo Shimizu

KOA Fireworks Company, 350-12 Hidaka-shi, Japan

ABSTRACT

Black Powder is said to be the oldest explosive. At present, it is one of the most important explosives. However, the burning reaction mechanism of materials in the mixture is still obscure. The purpose of this study is to clarify this mechanism and illustrate some applications of Black Powder.

The burning reaction of Black Powder has been denoted for a long time by various formulae that include potassium carbonate or sulfate, which is found in the ash. The author has endeavored to clarify the formation of such materials during burning, in an effort to shed light on the burning reaction mechanism.

Through his experiments, the author found that potassium carbonate or sulfate is formed not only in the case of Black Powder, but also in the case of mixtures of potassium nitrate and charcoal or potassium nitrate and sulfur. It is clear that the formation of potassium carbonate or sulfate is not peculiar to Black Powder, but to nitrate.

The ash contains both of these substances. The formation reaction takes place not in a gaseous, but rather in a solid or liquid state. Such a reaction would explain the excellent ignition characteristics of Black Powder.

Other applications of the burning reaction mechanism of Black Powder could be found to

make ignition of other compounds more effective.

1. Introduction

Black Powder is the oldest and best known explosive. However, since the discovery of smokeless powder, studies on this explosive have been neglected. Nevertheless, even today, Black Powder is renowned for properties that make other explosives ineffective substitutes. For example, it ignites well, burns vigorously, and its flame is very difficult to extinguish.

The purpose of this study is to clarify Black Powder's obscure burning mechanism and find other applications for it.

This problem was studied by several scientists in the 19th century: Bunsen-Schischkoff, Links, Karolyi, Noble-Abel, Sarrau, Berthelot, Debus, and so on. In Japan in 1940, Dr. N. Yamaga strove to calculate typical values for ballistics.

2. Analyses of the Combustion Products of Black Powder, Conducted by Bunsen, Karolyi and Noble-Abel, and an Explanation of the Burn Mechanism by N. Yamaga.

The chemical compositions tested by Bunsen, Karolyi and Noble-Abel are illustrated in Figure 1.

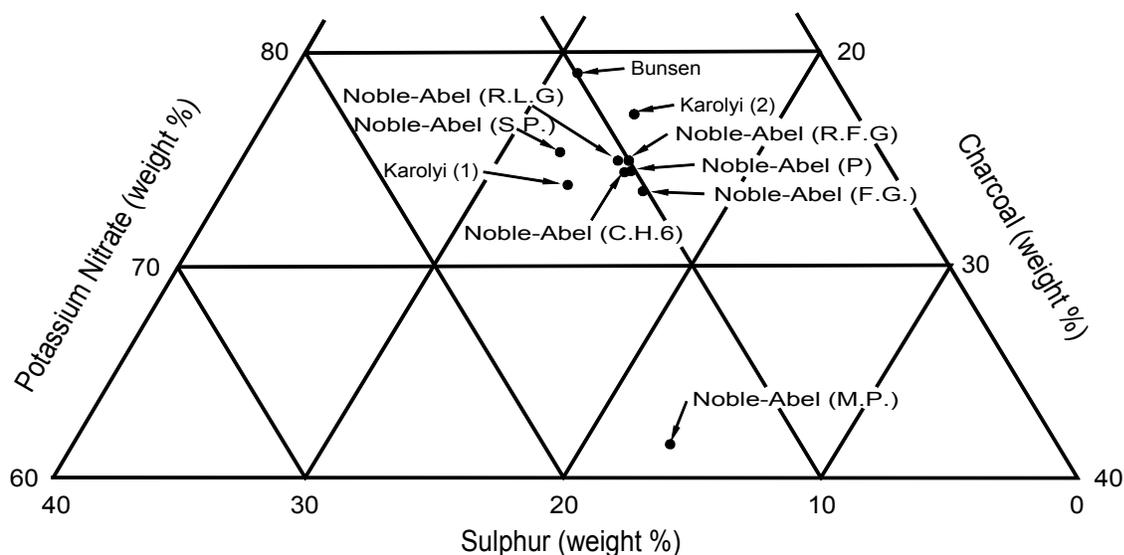


Figure 1. Test powder used by Bunsen, Karolyi and Noble-Abel^[1,2,3].

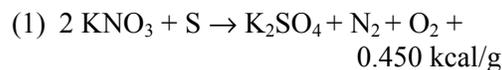
Symbols:

P	Waltham-Abbey pebble powder	S.P	Spanish spherical pebble powder
R.F.G.	Waltham-Abbey rifle fine grain	C.H.6	Curtis Harvey No. 6 sporting powder
R.L.G.	Waltham-Abbey rifle large grain	M.P	Mining powder
F.G.	Waltham-Abbey fine grain		

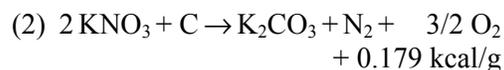
Figure 2 illustrates the results of the testing. The symbols on the curves represent the primary products. There were others, such as $K_2S_2O_3$, $(NH_4)_4H_2(CO_3)_3$ or $KSCN$, but in very small quantities. When the curve for total percentage of ash by weight is compared to the curve for the gases, we see that there were more ashes than gases, except in the case of the mining powder. Of all the powders, this one contained the smallest amount of potassium nitrate. Consequently, its burning mechanism may be different from that of the other powders. In Figure 2, we have CO_2 , CO , N_2 and H_2S as gases, which can be found in customary burning reactions. On the other hand, we have K_2CO_3 , K_2SO_4 and K_2S as ash, which is not readily found in combustion reactions. As a result, an examination of the formation reaction of K_2CO_3 , K_2SO_4 and K_2S would be the most effective key to clarifying the burning mechanism of Black Powder.

Dr. Yamaga^[4] explained the burning mechanism as follows:

First, the sulfur is oxidized by the potassium nitrate:



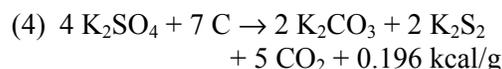
When the sulfur is used up, the charcoal is then oxidized by the potassium nitrate:



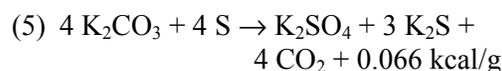
The oxygen from reactions (1) and (2) oxidizes the charcoal:



If the charcoal is not used up, the sequence is as follows:



If the sulfur is not used up, the sequence is as follows:



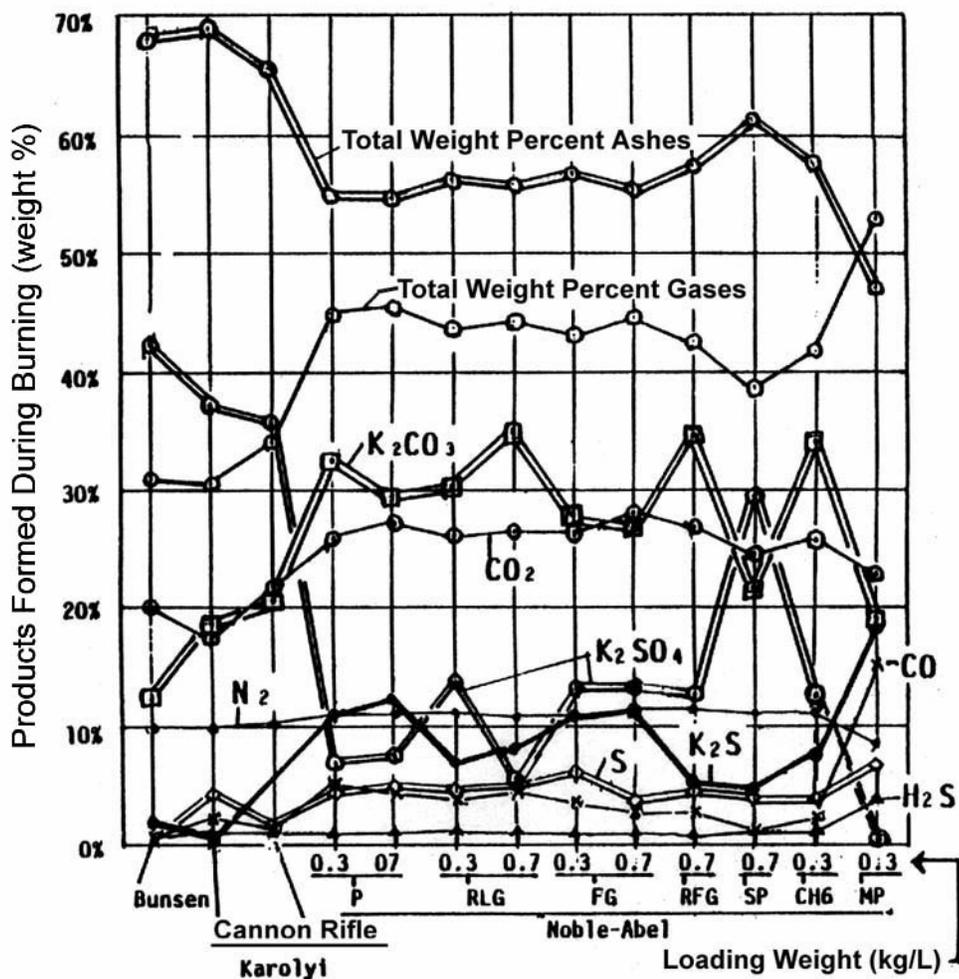
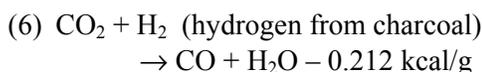
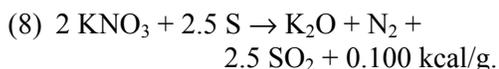
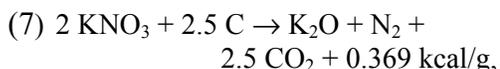


Figure 2. Primary products on burning of the test powder by Bunsen, Karolyi and Noble-Abel.

If charcoal remains, the sequence is as follows:



Besides equations (1) to (6) above, the following equations (7) and (8) are generally used to calculate the oxygen saturation point of a reaction.



The most noticeable thing here is that there is no potassium oxide (K_2O), despite very careful analyses by scientists (Figure 2).

3. Experiments

The author's experiments were conducted outdoors to be able to observe the burning phenomena well. The types of products in the air (Bunsen) are identical to those in a high-pressure environment (Karolyi and Noble-Abel) (Figure 2). Consequently, the burning mechanism in a lower air pressure environment is not that different from that observed in a higher air pressure environment.

First question: Compounds, such as potassium carbonate and potassium sulfate, which are not readily obtainable on burning the other powders, are easily obtainable in the case of Black Powder, as illustrated in Figure 2. Is the formation of the compounds peculiar to Black Powder, which is a mixture of potassium nitrate, charcoal and sulfur?

Table 1. Burning of the Mixtures of Nitrates and Carbon-Containing Substances (Acaroid Resin or Charcoal).

Fuel ↓	Nitrate	KNO ₃	NaNO ₃	Ba(NO ₃) ₂	Sr(NO ₃) ₂	NH ₄ NO ₃
Acaroid resin						
(a) Amount of mixture		9.65 g	10.14 g	10.06 g	10.27 g	9.70 g
(b) Amount of ash		5.61 g	5.00 g	6.23 g	—	—
Ratio of (b)/(a)		58.1%	49.3%	61.9%	—	—
Duration of burning		19.4 s	18.5 s	19.2 s	—	—
Appearance of flame		Slow, with yellow flame	Slow, with orange flame	Slow, with yellow flame	Did not burn	Did not burn
Carbonate found in ash		K ₂ CO ₃	Na ₂ CO ₃	BaCO ₃	—	—
Charcoal (Paulownia)						
(a) Amount of mixture		10.14 g	10.61 g	9.85 g	10.76 g	10.13 g
(b) Amount of ash		3.65 g	1.10 g	2.28 g	—	0.53 g
Ratio (b)/(a)		36.0%	10.4%	23.1%	—	5.2%
Duration of burning		34.2 s	16.2 s	42.3 s	—	21.5 s
Appearance of flame		Slow, with orange flame	Slow, with yellow flame	Very slow, with weak flame	Did not burn	Slow, with transparent flame
Carbonate found in ash		K ₂ CO ₃	Na ₂ CO ₃	BaCO ₃		

Remarks for Tables 1 and 2:

- (1) Weight ratio nitrate/fuel = 80:20 (Tables 1 and 2).
- (2) Weight ratio nitrate/sulfur/charcoal = 80:20:5 (Table 2), where the 5 is an additional percent.
- (3) Analysis of charcoal (Paulownia): water content: 7.09%, ash: 4.92%, in which 14.18% Ca and 13.63% K were contained for 100% ash.

To answer this question, the author conducted an experiment using mixtures of oxidizing substances (potassium, sodium, barium, strontium or ammonium nitrate) and fuels (acaroid resin, charcoal, sulfur, or sulfur + charcoal). See Tables 1 and 2, as well as Figure 3.

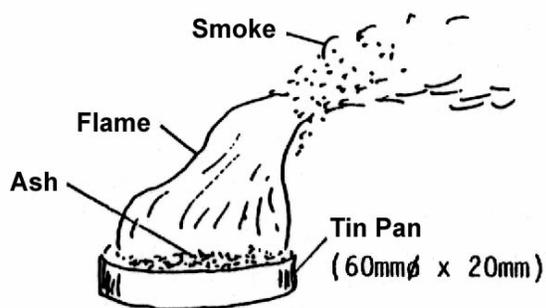


Figure 3. Burning phenomenon of test mixture in air.

Table 2. Burning of Mixtures of Nitrates and Sulfur or of the Same Mixtures, to Which a Small Amount of Charcoal Was Added.

Fuel ↓	Nitrate	KNO ₃	NaNO ₃	Ba(NO ₃) ₂	Sr(NO ₃) ₂	NH ₄ NO ₃
Sulfur						
(a) Amount of mixture		9.53 g	9.95 g	10.58 g	10.30 g	9.76 g
(b) Amount of ash		4.73 g	9.44 g	6.82 g	10.21 ?	9.00 ?
Ratio of (b)/(a)		49.6%	94.9%	64.5%	—	—
Duration of burning		69.5 s	More than 120 s	36.0 s	—	—
Appearance of flame		Very slow, with very white flame	Very slow, with transparent flame	Slow, with white flame	Difficult to burn	Did not burn
Sulfate found in ash		K ₂ SO ₄	Na ₂ SO ₄	BaSO ₄	—	—
Sulfur with charcoal (Paulownia) added						
(a) Amount of mixture		10.39 g	11.13 g	10.20 g	9.94 g	
(b) Amount of ash		4.26 g	6.16 g	5.17 g	—	
Ratio (b)/(a)		40.6%	55.4%	33.5%	—	
Duration of burning		4.0 s	12.0 s	15.5 s	—	
Appearance of flame		Very fast, vigorous, with large, white flame	Vigorous, with yellow flame	Vigorous, white flame	Did not burn	
Sulfate found in ash		K ₂ SO ₄	Na ₂ SO ₄	BaSO ₄		

As indicated in Table 1, the general chemical trend is for carbonate to form when a mixture of nitrate is burned not only with charcoal, but also with a carbon-containing substance. The short burn duration of each mixture shows that the carbonate is formed very readily. In Table 2, we see that a sulfate is not readily formed when a mixture of nitrate and sulfur is burned, as demonstrated by the very long burn durations. However, even when a small amount of charcoal is added to the mixture, sulfate forms quite readily.

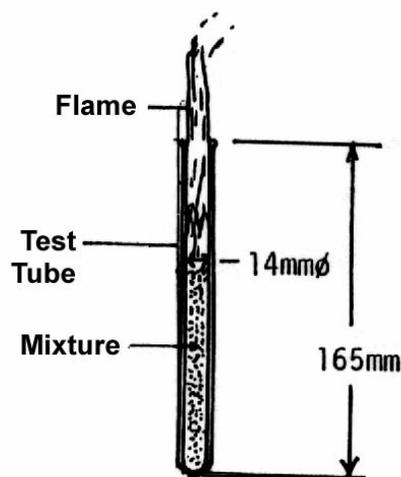


Figure 4. Method for collecting ashes.

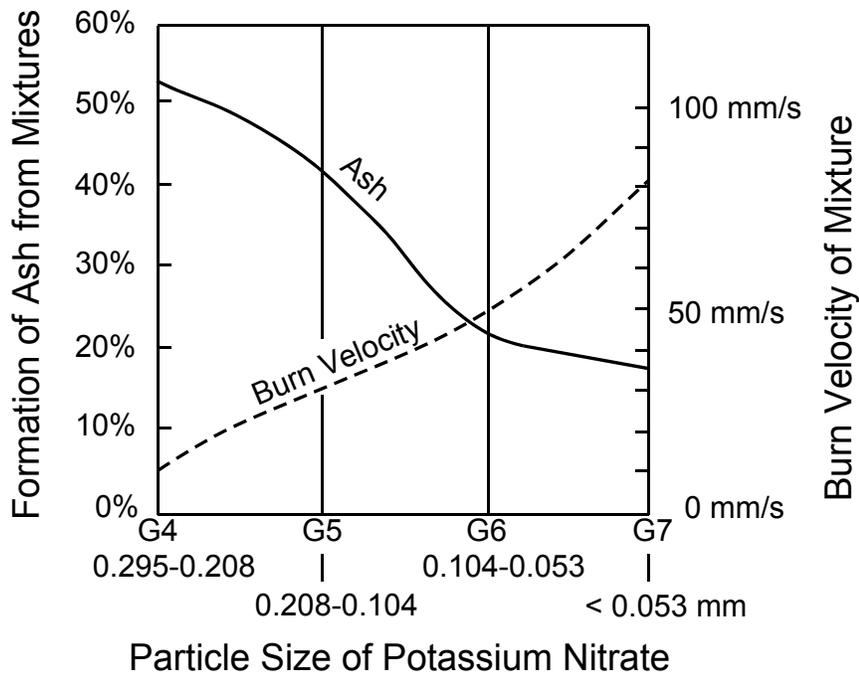


Figure 5. Burn effects with particle sizes of potassium nitrate I: Burn velocity and amount of ash produced.

Second question: In what state does Black Powder burn? As shown in Figure 3, a very large quantity of ash remains on the burn sur-

face. The ash must come from a solid or liquid state, because if the ash comes from a gaseous state, the ash must escape as smoke from the

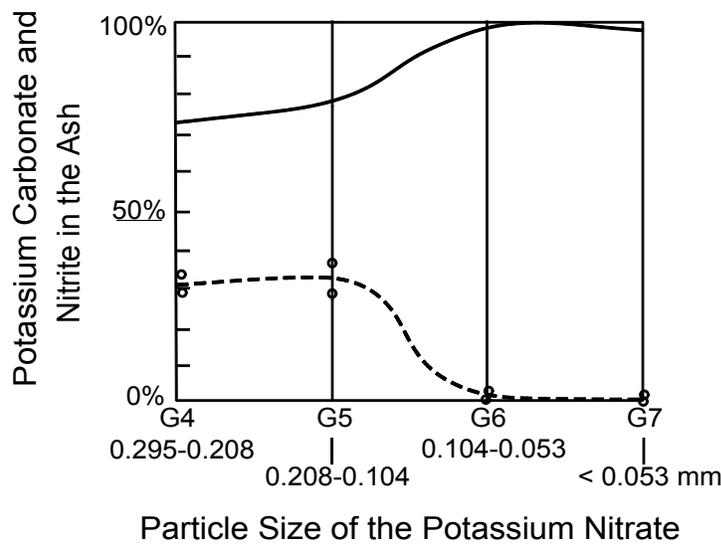


Figure 6. Burn effects with particle sizes of potassium nitrate II: Potassium carbonate and potassium nitrite content in the ash.

Table 3. Burning of Mixtures Originating from Charcoal (Paulownia) And Potassium Nitrate of Various Particle Sizes.

Particle size of nitrate	G4		G5		G6		G7	
Amount of mixture (a)	22.46g	21.81g	23.78g	21.22g	20.20g	21.70g	19.88g	19.23g
Length of mixture	95 mm	93 mm	100 mm	87 mm	88 mm	98 mm	94 mm	88 mm
Burn velocity (mm/s)	0.84	1.07	3.14	2.93	4.86	5.10	8.39	8.30
Amount of ash (b)	12.41g	11.01g	9.38g	9.26g	4.66g	4.64g	4.31g	2.94g
(b)/(a)	55.3%	50.5%	39.4%	43.7%	23.1%	21.4%	21.7%	15.3%
Potassium carbonate in ash (c)	8.66g	8.81g	6.96g	8.01g	5.19g	4.79g	4.27g	2.86g
(c)/(b)	71.0%	65.9%	63.0%	73.1%	99.8%	96.6%	96.8%	99.3%
Potassium nitrite in ash (d)	3.53g	4.56g	4.08g	2.95g	0.01g	0.17g	0.14g	0.02g
(d)/(b)	29.0%	34.1%	37.0%	26.9%	1.5%	3.4%	3.2%	0.7%

Remarks:

(1) Particle sizes are indicated as follows:

Symbol	Screen opening
G4	0.295 – 0.208 mm
G5	0.208 – 0.104 mm
G6	0.104 – 0.053 mm
G7	<0.053 mm

(2) Weight ratio of potassium nitrate to carbon in mixtures is 8:2.

(3) Particle size of charcoal: G7.

flame into the air (see also Figure 2 and Table 2). Thus, roughly half of the Black Powder burns in a solid state and roughly half burns in a liquid state. This means that Black Powder burns with less heat loss. This is why Black Powder is easy to ignite.

Third question: Why is it necessary to apply pressure and friction to the mixture during the manufacture of Black Powder? Potassium nitrate from four particle size categories was prepared [see remarks (1) and (2) in Table 3]. The mixtures of potassium nitrate and charcoal (Paulownia) were burned and the ashes analyzed (Table 3, Figures 5 and 6).

As can be seen in Figures 5 and 6, the smaller the particle size of the potassium nitrate, the faster it burns, the less ash is produced, the more potassium carbonate is formed, and the less potassium nitrite is contained in the ash. This shows that the burn reaction is complete

when the components are in direct contact with each other. This reaction is characteristic especially of a burn reaction in a solid state. Hence, the necessity of the pressure and friction process during the manufacture of Black Powder becomes clear.

Fourth question: Where does Black Powder get its excellent ignition and/or burn quality? In the experiment, 7 mm cubic stars were made, consisting of different chemical compounds. Three test stars were placed each time in a small mortar and ignited (Figure 7). The number of stars that were ignited is indicated (Tables 4–9, also see second question!).

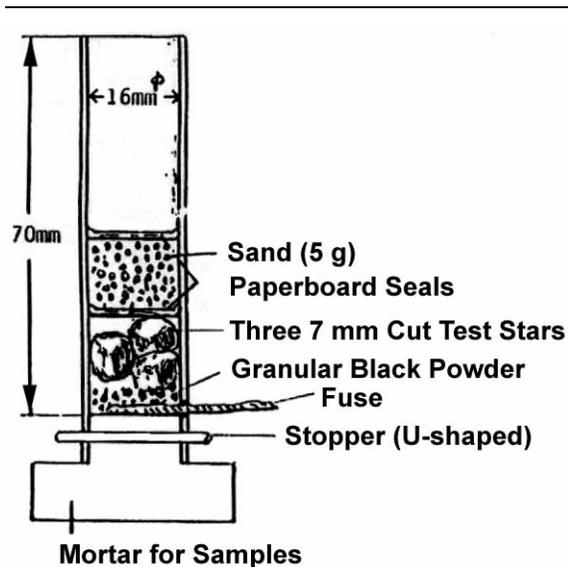


Figure 7. Assembly for ignition tests for test stars.

Remarks regarding Tables 4–9:

- (1) The first row indicates the symbols for the mixtures.
- (2) The second row indicates the weight ratio of the chemical compounds of the mixtures.
- (3) The third row indicates the number of stars that were ignited when they were fired: the symbols or digits \times , 1, 2, 3 each show none, one, two and three ignited stars of the three. The * symbol means delayed ignition.
- (4) The words “coated on” in the third and fifth rows of Table 9 refer to a test star design, such as illustrated in Figure 8.

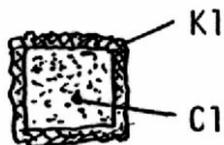


Figure 8. Star C1 coated with a mixture K1.

The answer is directly or indirectly indicated by the results in Tables 4 to 9.

Table 4: The addition of some potassium nitrate yields very good ignition of the stars being used (A2 and C2). The addition of sulfur reduces the ignition effect (C3 and C4). The addition of barium nitrate is invalid (B2).

Table 5: No good effect found.

Table 6: The addition of potassium carbonate produces a better effect, but sodium carbonate yields the best effect (E6 and E11).

Table 7: Black Powder produces the best ignition effect (FS1 and FS2). The fact that a mixture of potassium perchlorate, potassium nitrate and acaroid resin (H1) produces a better ignition effect is noteworthy.

Table 8: A few mixtures of nitrate and charcoal produce a better ignition effect (I1 and I3, which contain potassium nitrate or barium nitrate). Mixtures containing nitrate and sulfur do not produce a good effect.

Table 9: Black Powder K1 on C3 or a mixture of barium nitrate and charcoal K4 on C1 or C3 produce a better effect. However, K4 delays ignition.

In view of the above results, we see that a mixture of potassium nitrate, charcoal and sulfur produces the best ignition or burn effect. However, we also see that another mixture of potassium nitrate and charcoal produces a better effect, but such is not the case with another mixture of potassium nitrate and sulfur.

Table 4. Ignition Tests for Stars in Use: Effects of the Addition of Nitrate.

	A1	A2	B1	B2	C1	C2	C3	C4
KClO ₄	66	66	60.8	60.8	68	68	68	68
KNO ₃	—	5	—	—	—	11	—	10
NaNO ₃	—	—	—	—	—	—	—	—
Ba(NO ₃) ₂	—	—	—	5	—	—	—	—
Sr(NO ₃) ₂ •4H ₂ O	—	—	—	—	—	—	—	—
NH ₄ NO ₃	—	—	—	—	—	—	—	—
Charcoal	—	—	—	—	—	—	—	—
Acaroid resin	13	13	9.0	9.0	13	13	13	13
Sulfur	—	—	—	—	—	—	5	5
K ₂ CO ₃	—	—	—	—	—	—	—	—
Na ₂ CO ₃ •H ₂ O	—	—	—	—	—	—	—	—
BaCO ₃	—	—	—	—	—	—	—	—
SrCO ₃	12	12	—	—	12	12	12	12
CaCO ₃	—	—	—	—	—	—	—	—
CuCO ₃ •Cu(OH) ₂	—	—	12.3	12.3	—	—	—	—
CuO	—	—	—	—	—	—	—	—
K ₂ SO ₄	—	—	—	—	—	—	—	—
Na ₂ SO ₄	—	—	—	—	—	—	—	—
BaSO ₄	—	—	—	—	—	—	—	—
SrSO ₄	—	—	—	—	—	—	—	—
CaSO ₄ •½ H ₂ O	—	—	—	—	—	—	—	—
Vinyl chloride	2	2	—	—	—	—	—	—
Parlon	—	—	13.1	13.1	2	2	2	2
Glutinous Rice Starch	5	5	4.8	4.8	5	5	5	5
Test No.	Number of Ignitions							
1	x	3	x	x	x	3	x	1
2	1	2	x	x	x	3	x	x
3	x	3	x	x	x	2	x	1
4	x	2	x	x	x	3	x	x
5	1	3	x	x	x	3	x	1

Table 5. Ignition Tests of the Stars in Use: Effects of the Addition of Nitrate or Carbonate.

	D1	D2	D3	D4	E1	E2	E3	E5
KClO ₄	63	63	66	66	68	68	68	68
KNO ₃	—	—	—	—	—	—	—	—
NaNO ₃	—	—	—	—	—	—	—	—
Ba(NO ₃) ₂	—	11	—	10	—	—	—	—
Sr(NO ₃) ₂ •4H ₂ O	—	—	—	—	—	—	—	—
NH ₄ NO ₃	—	—	—	—	—	—	—	—
Charcoal	—	—	—	—	—	—	—	—
Acaroid resin	9	9	10	10	13	13	13	13
Sulfur	—	—	5	5	—	—	—	—
K ₂ CO ₃	—	—	—	—	—	—	—	—
Na ₂ CO ₃ •H ₂ O	—	—	—	—	—	—	—	—
BaCO ₃	—	—	—	—	—	—	—	—
SrCO ₃	—	—	—	—	—	—	—	12
CaCO ₃	—	—	—	—	—	—	—	—
CuCO ₃ •Cu(OH) ₂	13	13	—	—	—	—	—	—
CuO	—	—	13	13	—	—	—	—
K ₂ SO ₄	—	—	—	—	—	—	—	—
Na ₂ SO ₄	—	—	—	—	—	—	—	—
BaSO ₄	—	—	—	—	—	—	—	—
SrSO ₄	—	—	—	—	—	—	12	—
CaSO ₄ •½ H ₂ O	—	—	—	—	—	—	—	—
Vinyl chloride	—	—	—	—	—	—	—	—
Parlon	15	15	6	6	2	2	2	2
Glutinous Rice Starch	5	5	5	5	5	5	5	5
Test No.	Number of Ignitions							
1	1	1*	x	x	x	x	x	1
2	1	x	x	x	x	x	1	x
3	1	1*	x	x	1	2	x	x
4	1	x	x	x	x	x	x	x
5	1	x	x	x	x	1	x	2

Table 6: Ignition Tests of the Stars in Sample Mixtures: Effects of Carbonate or Sulfate with No Nitrate.

	E6	E7	E8	E9	E10	E11	E12
KClO ₄	68	68	68	68	68	68	68
KNO ₃	—	—	—	—	—	—	—
NaNO ₃	—	—	—	—	—	—	—
Ba(NO ₃) ₂	—	—	—	—	—	—	—
Sr(NO ₃) ₂ •4H ₂ O	—	—	—	—	—	—	—
NH ₄ NO ₃	—	—	—	—	—	—	—
Charcoal	—	—	—	—	—	—	—
Acaroid resin	13	13	13	13	13	13	13
Sulfur	—	—	—	—	—	—	—
K ₂ CO ₃	12	—	—	—	—	—	—
Na ₂ CO ₃ •H ₂ O	—	—	—	—	—	12	—
BaCO ₃	—	—	—	—	—	—	—
SrCO ₃	—	—	—	—	—	—	—
CaCO ₃	—	12	—	—	—	—	—
CuCO ₃ •Cu(OH) ₂	—	—	—	—	—	—	—
CuO	—	—	—	—	—	—	—
K ₂ SO ₄	—	—	—	—	12	—	—
Na ₂ SO ₄	—	—	—	—	—	—	12
BaSO ₄	—	—	12	—	—	—	—
SrSO ₄	—	—	—	—	—	—	—
CaSO ₄ •½ H ₂ O	—	—	—	12	—	—	—
Vinyl chloride	—	—	—	—	—	—	—
Parlon	2	2	2	2	2	2	2
Glutinous Rice Starch	5	5	5	5	5	5	5
Test No.	Number of Ignitions						
1	1	x	x	x	x	3	1
2	1	x	x	x	x	3	x
3	2	x	x	?	x	3	1
4	2	x	x	x	x	3	x
5	3	x	x	x	x	3	x

Table 7. Ignition Tests of Stars in Sample Mixtures: Effects of Black Powder Or Nitrates.

	FS1	FS2	H1	H2	H3	H4
KClO ₄	—	—	77	77	77	77
KNO ₃	75?	75	10	—	—	—
NaNO ₃	—	—	—	10	—	—
Ba(NO ₃) ₂	—	—	—	—	10	—
Sr(NO ₃) ₂ •4H ₂ O	—	—	—	—	—	10
NH ₄ NO ₃	—	—	—	—	—	—
Charcoal	15?	15	—	—	—	—
Acaroid resin	—	—	15	15	15	15
Sulfur	10?	10	—	—	—	—
Vinyl chloride	—	—	—	—	—	—
Parlon	—	—	2	2	2	2
Glutinous Rice Starch	6	6	6	6	6	6
Test No.	Number of Ignitions					
1	3	2	2	x	1	x
2	3	3	2	2	3	1
3	3	3	2	2	1	1
4	2	3	3	x	1	1
5	3	3	1	1	1	1

4. Discussion

From the above results in the experiments (Tables 4 to 9), we see that a mixture of potassium nitrate, charcoal and sulfur produces the best burn or ignition effect. Nevertheless, we also see that another mixture of potassium nitrate and charcoal yields the best effect. Sulfur is ineffective for burn or ignition purposes.

It can therefore be assumed that nitrate and carbon or carbonate, which forms as a solid during the burn reaction, are effective for burning or ignition. Sulfur or sulfate, which forms during the burn reaction, is only one source of heat, because sulfur, as it reacts with potassium nitrate, produces more heat than the carbon with potassium nitrate. The heat greatly accelerates the reaction of the carbon and potassium nitrate [formulae (1) and (2) and Table 2].

When employing the burn mechanism for Black Powder, the author suggests adding some nitrate or carbonate to the chemical composition (see Tables 4–9) to improve the ignition of a mixture.

Sulfur does not readily react with potassium nitrate [formula (1)]. On the other hand, char-

coal reacts very readily with potassium nitrate [formula (2)]. Thus, charcoal must react with the potassium nitrate first, followed by the sulfur.

As Black Powder burns, it is very difficult to extinguish its flame, owing to the active ash, which contains, among other things, potassium sulfide.^[5]

Table 8. Ignition Tests of Stars in Sample Mixtures Formed from Nitrates And Charcoal Or Acaroid Resin.

	I1	I2	I3	I4	J1	J2	J3	J4
KClO ₄	—	—	—	—	—	—	—	—
KNO ₃	80	—	—	—	75	—	—	—
NaNO ₃	—	80	—	—	—	75	—	—
Ba(NO ₃) ₂	—	—	80	—	—	—	75	—
Sr(NO ₃) ₂ •4H ₂ O	—	—	—	80	—	—	—	75
NH ₄ NO ₃	—	—	—	—	—	—	—	—
Charcoal	20	20	20	20	—	—	—	—
Acaroid resin	—	—	—	—	—	—	—	—
Sulfur	—	—	—	—	25	25	25	25
Glutinous Rice Starch	6	6	6	6	6	6	6	6
Test No.	Number of Ignitions							
1	x	2	3	1	x	x	x	x
2	3	1	2	1	x	x	x	x
3	3	1	2	1	x	x	x	x
4	3	2	3	1	x	x	x	x
5	3	1	3	1	x	1	x	x

5. Conclusion

Still one question remains unanswered from a chemical point of view, namely why a good ignition or burn effect can be had with a chemical composition, mostly by adding carbonate or through the formation of the latter.

Table 9: Ignition Effects of the Sample Mixtures with Which the Test Stars Were Coated.

Coated with→	K1	K2	K3	K4	K5
KClO ₄	—	—	—	—	—
KNO ₃	75	80	86	—	—
NaNO ₃	—	—	—	—	—
Ba(NO ₃) ₂	—	—	—	84	88
Sr(NO ₃) ₂ •4H ₂ O	—	—	—	—	—
NH ₄ NO ₃	—	—	—	—	—
Charcoal	15	20	—	16	—
Acaroid resin	—	—	—	—	—
Sulfur	10	—	14	—	12
Glutinous Rice Starch	5	5	5	5	5
Star C1		Number of Ignitions			
1	3	1	x	1*	2*
2	1	1	x	3*	3*
3	2	2	x	3*	2*
4	1	2	x	2*	x
5	1	1	x	3*	3
Star C3		Number of Ignitions			
1	1	3	x	3*	1
2	3	2?	1	2*	2
3	3	2?	2	3*	2
4	3	3	x	2*	2
5	3	2	2	1*	2

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Detection of Underwater Blasting Using Electrical Noise

T. Shimizu*

Koa Fireworks Ltd., Saitama Plant

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ABSTRACT

We conducted a small-scale experiment on soil simulating underwater blasting and studied the shape of waves as well as properties of electrical noises generated during blasting. From these noise waves, we wanted to detect any failure in initiation of the charge or blasting conditions, etc. It was observed that the main source of noise is the residual electricity in the exploder; the shape of noise waves is typical of blasting conditions of the charge. It enables us to detect blasting failure, or blasting of detonator touching the water, or detonation of charge, etc. from these noise waveforms. It was also confirmed that this method of detection can also be applied in double-hole or multi-hole blasting which follows stage explosion.

1. Introduction

No method is available for the correct detection of underwater explosion or residual failure within the range of theoretical considerations. In this study we have tried to develop a method to detect underwater blasting or failure thereof using the electrical noises generated during blasting. Although the experiment was conducted on soil, we tried to simulate the underwater conditions as far as possible by an electrical system.

So far, a number of methods have been proposed to detect failure in blasting such as: (a) magnetic detection, (b) detection from color of sea water using pigments or a buoy, (c) detection with sound generator, and (d) detection using earth vibration or underwater sound waves generated during blasting, etc. However, none of these methods can be employed easily because of the intricate technology and high costs

involved, particularly when the sea bed is very deep.

If we decide to use the proposed method, it is not necessary to use a special power supply, detectors, or other equipment. The method is equally easy for all depths, and all the above-mentioned problems faced in different methods can be resolved.

It is well known that some electrical noise is generated during blasting. This is the major hurdle while measuring the detonation velocity in a bore hole by a resistance wire method. Earlier efforts were directed at reducing this noise, whereas we have effectively turned the same noise to our own purpose.

2. Principle of Detection

It was observed that when a circuit is arranged as shown in Figure 1, a large electrical potential difference arises between grounds E_1 and E_2 as the cartridge explodes. This potential difference, when added to the input current of synchroscope, is seen in the form of noise waves changing with time. This waveform varies with the types of explosives and conditions of explosion. It is therefore quite useful, not only for the detection of failure in explosion, but also for the estimation of explosion conditions. This is the basic principle of this method.

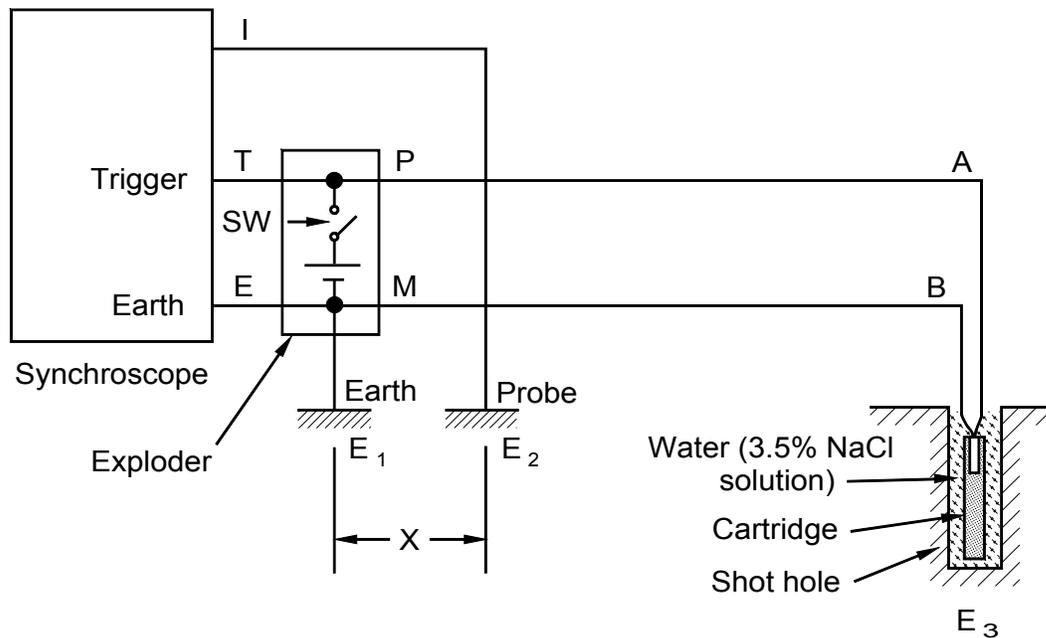


Figure 1. Circuit which produces a noise from one-hole blasting. $I = \text{input}$.

3. Apparatus, Material and Procedure (Figure 1)

1. *Synchroscope*. Iwasaki Tsushin Co.'s Junior II. Input impedance: $1\text{ M}\Omega$, 50 pF , parallel.
2. *Exploder*. Self-made, having a circuit diagram as shown in Figure 2.
3. *Grounds E_1, E_2* . Copper bar of 15 mm diameter and 345 mm length was buried into the soil to a depth of about 300 mm. The sum of individual contact resistance was $500\text{--}1,000\ \Omega$. Hereafter, E_2 refers to the probe and X to length of ground wire.
4. *Blasting bore E_3* . A bore of 8 cm diameter and about 80 cm deep was drilled in the soil. It was filled by 3.5% salt solution to simulate sea water conditions. The soft loamy soil of the Kanto area had an eroded surface layer.
5. *Blasting cable PA-BM*. We used two types of PVC coated cables: I—copper wire diameter 0.6 mm, total resistance $5.22\ \Omega$; II—copper wire diameter 1.6 mm, total resistance $1.77\ \Omega$. Corresponding types were selected, depending on the object of the experiment.
6. *Input wire $E_2\text{--}I$* . Shielded wire (coaxial cable). For lengths above 30 m, we used one strand of five-stranded cable.
7. *Trigger wire P-T*. This was usually connected between pressure distribution point of exploder P_2 and trigger terminal T (Figure 2).
8. *Types of explosives*. Ignition charge: $0.85 \pm 0.1\ \Omega$; detonator: No. 6 industrial detonator; instantaneous electrical detonator: No. 6, $0.95\ \Omega$. These last two are Nippon Yushi products.

Step blasting detonators were prepared using the above ignitor; delay element of minimum ferro silicate type; red explosive (potassium chlorate 65%, inert matter 35%, charge per detonator about 0.7 g); and a brass tube of diameter 6 mm, thickness 0.2 mm, and length 50 mm. A five-stage delay was obtained. The actual delay time was 4, 60, 200, 360 and 800 ms when about 5 A current was passed through it.

Explosive was potassium perchlorate 64%, aluminum flake 23%, sulphur 13%. This mixture was packed in 35 mm long, 20 mm ID, thick Kraft paper tube with a packing density of 0.85 g/cc . The above mentioned industrial or electrical detonator was fixed at the top or bottom depending on the object of the experiment.

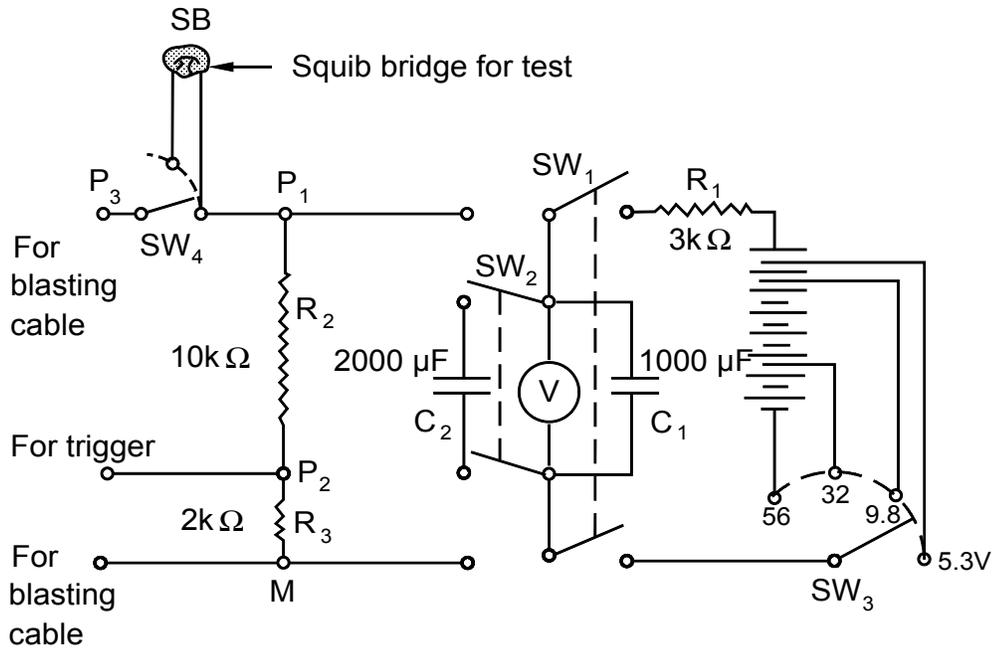


Figure 2. Circuit of exploder.

Then it was put into a thin polyethylene bag and sealed with vinyl tape to protect it from water. We used two types of cartridges. Short cartridge (explosive 177–190 g, length 220 mm) was used for simulation of half explosion, and long cartridge (charge 315–386 g, length 440–445 mm) for simulation of full explosion. Detonation velocity of this explosive was low, about 1,400 ms,^[3] which is about 5/23 the detonation velocity of underwater explosions used in Honshu Shikoku Bridge Works.^[5] However, it is convenient to simulate the actual explosive with the help of these small test cartridges. If we calculate the explosion time of charge using this detonation velocity, it comes to 0.16 ms for short cartridge and 0.32 ms for long cartridge.

A spherical capsule charge is made by adding some gum to the above explosive. The set material is made in the form of 4 mm ball wrapped in Kraft paper.^[3] The quantity of charge was 30–50 g. This has about 1 ms of burning time and can be used to simulate a condition where the explosive burns without explosion. Also, it takes about 6–9 ms for explosion after switching on and, hence, can be used as a delay element in the experiment. For igniting this charge, the ignition tubes as used in concrete

exploder (Asahi Chemical Co.'s CCR) were used.

4. Sources of Noise

There are two types of noise. One is due to the residual electricity in an exploder; the other is due to the explosion of charge. The latter is weaker than the former.

Figure 3a, “b” shows the experiment conducted with the electric detonator at comparatively low blasting voltage (9.8 V). If we insert detonator alone into the blasting hole E_3 and ignite it, then we get a noise pattern corresponding to input current, I , shown in “b”. The blasting voltage at the exploder terminal under this condition is shown in Figure 3a. Incidentally, if we use the squib SB, shown in Figure 2, in series (with detonator) and insert the detonator in blasting hole, then at blasting voltage above 50 V, the squib bridge would blow off before the detonator explodes,^[4] and the blasting circuit will be disconnected. As a result, residual current from the exploder would stop flowing. The noise pattern under this situation appears as in Figure 3c. In this case, the length of ground wire was 1 m, and the distance between blasting hole E_3 and synchroscope earth E_1 was 77 m.

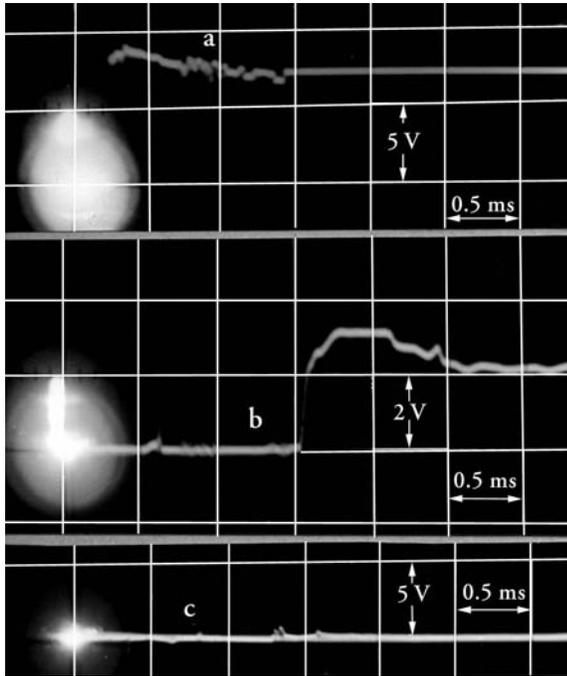


Figure 3. Noises from a detonator, a: blasting voltage for b; b: noise from a detonator; c: noise from a detonator under disconnection of blasting circuit.

The results of the explosion under a high explosion voltage (56 V) for a long cartridge are shown in Figure 4. The other conditions were the same as for Figure 3. Figure 4a indicates the blasting voltage at the exploder terminal, Figure 4b indicates noise from a charge, and Figure 4c indicates noise from a charge when residual electricity is disconnected.

In both the figures, the peak voltage in *b* is much higher than in *c*. Also, the voltage for *b* increases with the increase in ignition voltage, whereas voltage for *c* is independent of ignition voltage. This was also confirmed by another method described below.

Figure 5 shows the noise (c_2), when a short cartridge was exploded with industrial detonators or igniting wire without blasting electric detonator, and the noise (c_3), when a long cartridge is exploded with the blasting circuit totally made independent of measuring circuit and earth removed from the blasting circuit.

It can be seen that voltage of *c* wave-forms of Figures 3 and 4 and those of c_2 and c_3 (Figure 5) are around 0.5 V. (In case of c_3 , switching

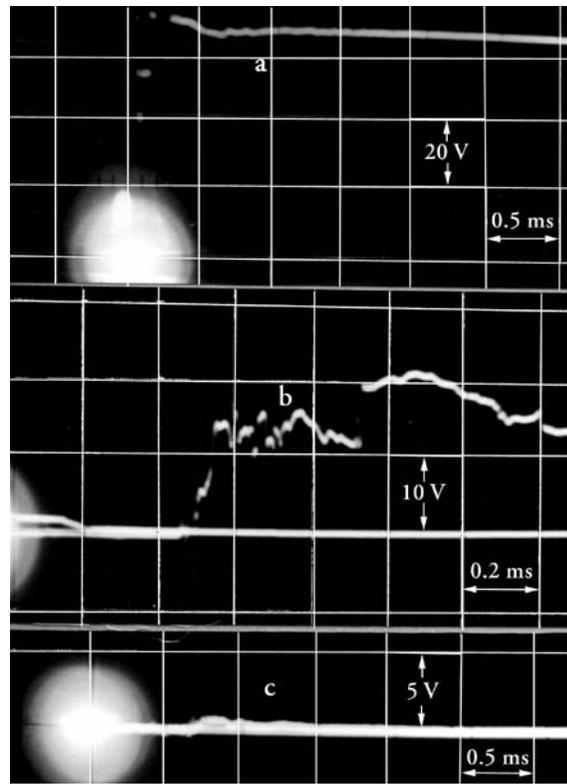


Figure 4. Noise from an explosive charge in a long cartridge (diameter: 35 mm, length: 440 mm, charge: 315–386 g, detonation velocity: 1400 m/s), a: blasting voltage; b: noise from a charge; c: noise from a charge under disconnection of blasting circuit.

voltage was 9.8 V.) The trigger signal of synchroscope was derived from c_2 , c_3 voltage directly. However, as this voltage was small, the trigger was 2/5 effective.

It was thus confirmed that noise *b* is generated due to the residual electricity of exploder, whereas a completely different source (the origin of which lies in the explosion phenomenon of the explosive) is responsible for *c*, c_2 and c_3 . If the ion gap is used for trigger signal, the

circuit remains the same as for the exploder. Hence, the power supply of the ion gap generates the same noise as *b*. In order to obtain noise due to residual electricity, it is necessary to use a common ground connection E_1 for the electric circuits of exploders and measuring circuit, but trigger wire *TP* is not that essential (Figure 1).

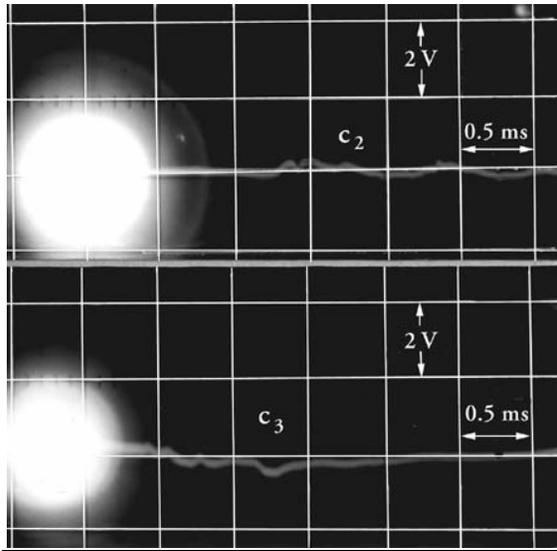


Figure 5 Noises from an explosive charge in a short cartridge (diameter: 35 mm, length: 220 mm, charge: 177–190 g, detonation velocity: 1,400 m/s), c_2 : noise from a charge without electric initiation; c_3 -noise from a charge with electric initiation, which is independent of the measuring circuit.

5. Location of Probe and Amplitude of Noise

Since the voltage of noise due to the residual electricity of the exploder is high, it can be used to detect the failure of explosion. We therefore discuss only this noise below.

During this study, we did not observe any correlation between the location of probe and amplitude of noise when the position of ground E_1 and shothole E_3 was constant. In other words, when an explosive is blasted off by electrical switching, the potential of the ground surface at certain points rises above (or goes below) E_1 . This fluctuation does not have a fixed relation with the distance from the shothole. The relation is shown in Figure 6. In this figure, we have assumed the distance between E_1 and E_3 as 53 m. The probe position E_2 was changed point by point along the line joining E_1 – E_3 , and the noise at each position was measured. The explosive sample was the detonator. Detonation wire II was used. The switching voltage from exploder was 9.8 V. In this figure, we have also

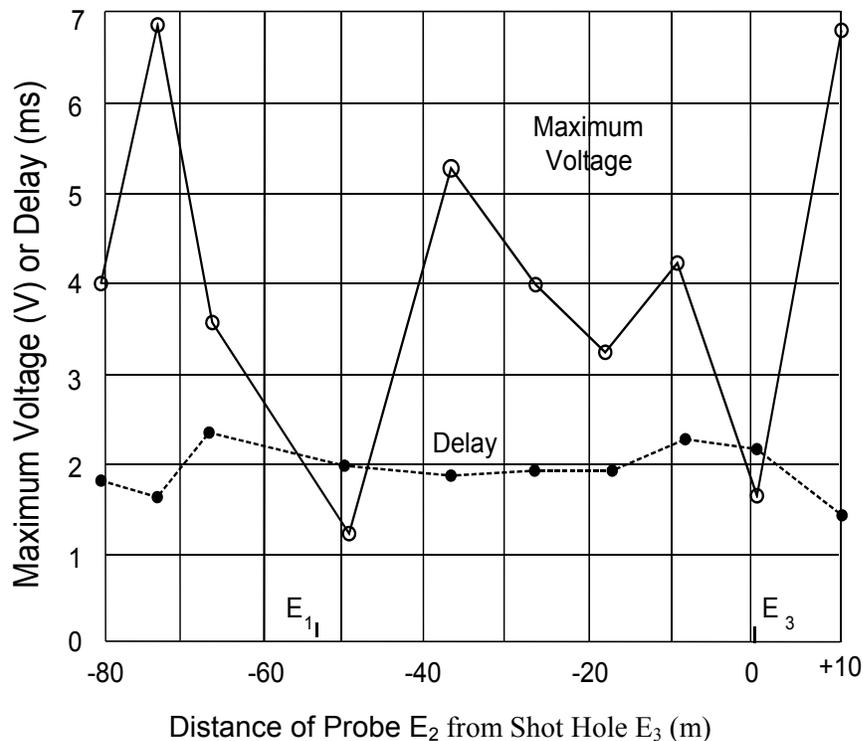


Figure 6. Influence of the position of the probe E_2 to the shot hole E_3 and to the ground of the exploder E_1 on the voltage of a noise. (Delay times from switching on to the initiation of a detonator are also shown.)

shown the time lag between the switching and rise of noise wave for the purpose of reference (dotted line).

From the above experiment, we can expect a high voltage noise even if ground E_1 and probe E_3 are placed very close to each other. The results of experiment were as follows. When the length of ground wire E_1E_2 at right angles with the direction of shothole E_3 was 1 m, the peak noise voltage was 4.3 V, 2.8 V. At 1 m in the direction of E_1 , it was 3.6 V, 3.3 V. For 50 cm distance at right angles, it was 3.2 V, 2.8 V, and at 50 cm in the direction, 4.2 V and 3.0 V; at 10 cm at right angle, 4.2 V and at 10 cm in the direction, 2.2 V. Thus, even if E_1 and E_2 are placed close, at 10 cm, noise voltage is still of considerable amplitude. In this case, the positioning of ground wire is immaterial as far as noise voltage is concerned. (The experimental conditions in this case are the same as for Figure 6, except for the change in probe position.)

6. Noise Waveform

The shape of the time-dependent noise voltage curve has the following characteristics for electric detonator alone or with explosive. Both forms can be easily distinguished. Also, when the explosive is used, there is a clear difference in the noise pattern when the probe is directly inserted into shot hole or when the two are separated.

1. *Blasting of electric detonator alone:* The noise wave was as shown in Figure 7. When the switching current was high (3.3 A), we observed an overshoot pulse in the beginning, followed by the mountain wave with some time gap (a). When the current is low (1.6 A), the pulse is immediately followed by mountain wave (b), or the pulse can also be seen between the mountain waves (c). In another case, pulse and mountain wave start simultaneously (d).

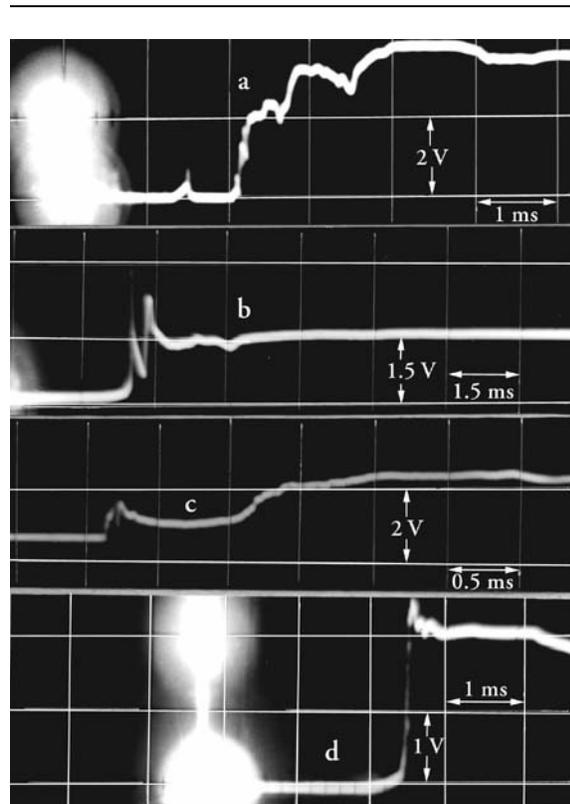


Figure 7. Noises from a detonator, blasting current: a = 3.3 A; and b, c, d = 1.6 A.

The pulse generation time is affected by the switching current and is probably due to blasting of ignitor bridge in the detonator.^[4] As the detonator body is metallic, the electrical path at the time of bridge blasting becomes somehow electrically connected with the exterior; this may be the source of noise. No such overshoot was observed for the cartridge where the detonator is fully covered. The mountain wave is generated when the electrical contact is established between the circuit and the exterior as the detonator is exploded; as such, the rise time of pulse indicates instant blasting of the detonator.

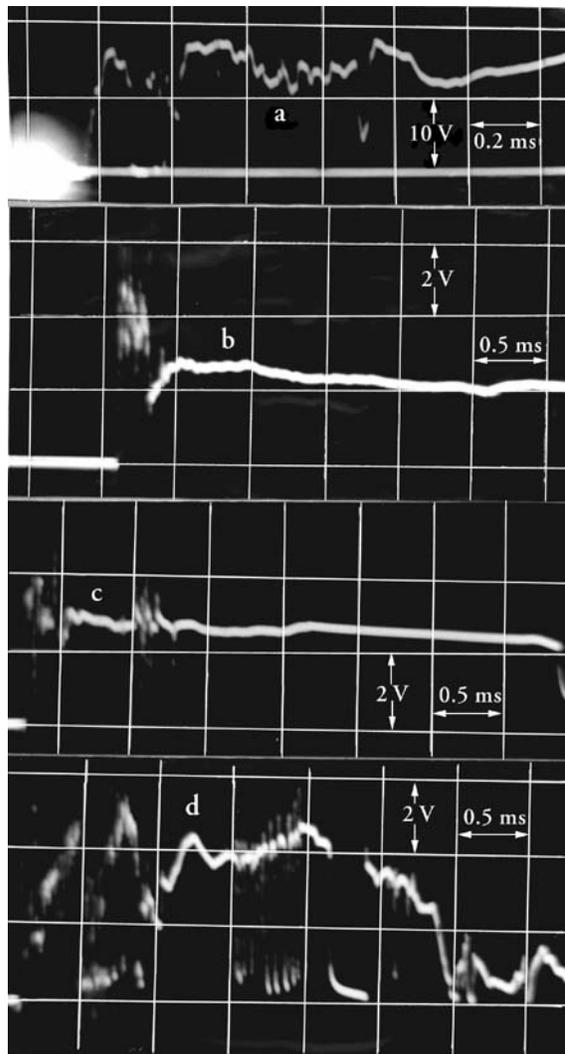


Figure 8. Noises from all explosive charge. The probe E_2 and the shothole E_3 are separated in the case of a, and connected, in the case of b, c, and d (long cartridges, see Figures 4 and 5).

2. *Blasting of cartridge*: This results in a representative noise waveform as shown in Figure 8. In Figure 8a, the length of ground wire $X = E_1E_2$ was taken as 1 m, distance between ground E_1 and shothole E_3 was 77 m, and a long cartridge with electrical detonator at top was used. Blasting voltage of the detonator was 56 V. Blasting starts 0.16 ms after switching on, and a comb-like waveform continues till 0.74 ms followed by mountain waves. The detonation time calculated from detonation velocity for long cartridge is 0.32 ms. This corresponds to the detonator termination point of falling pulse (Figure 8d). Figure 8b and following were ob-

tained when a 2.5 mm dia. PVC-coated copper wire was inserted into the shothole and the lower half of the wire was used as a probe. The distance between E_1 and E_3 was taken as 52 m. If a noise wave is thus picked up directly from the shothole, it is possible to read the detonation time quite clearly. In other words, noise generally consists of a smooth mountain waveform at the background and a high amplitude, high frequency shock wave at the foreground (Figure 8b). Another wave, which is just a reflection of the above, is also seen in Figure 8c. The *b* and *c* waveforms are obtained when an electric detonator is connected at the tail end of the long cartridge. Compared to this, the waveform in Figure 8d is obtained when an electric detonator is connected at the front end of cartridge. In this case, a lot of reflected noise is clubbed together, and it is difficult to distinguish the point *p* corresponding to the end of detonation. Here, one method to detect *p* is to note the gaps in background noise.

We picked up the noise wave directly from the shothole and measured the detonation time of sample by the photographic method discussed above. A comparison of these values with the values calculated from detonation velocity is shown in the following table. An adequate number of experiments have not been conducted for a situation where E_2 and E_3 are separated. In this condition the last pulse is not very clear. Therefore, the above method of detection of detonation time is not valid.

Time of the So-called "Shock Noises" Compared with the Time of Detonation.

Cartridge	Time of detonation (calculated) (ms)	Time of shock noise measured (ms)	Difference (ms)
Short	0.16	0.17	-0.01
Short	0.16	0.11	0.05
Short	0.16	0.18	-0.02
Short	0.16	0.10	0.06
Long	0.32	0.32	0.00
Long	0.32	0.36	-0.04
Long	0.32	0.31	0.01
Long	0.32	0.30	0.02

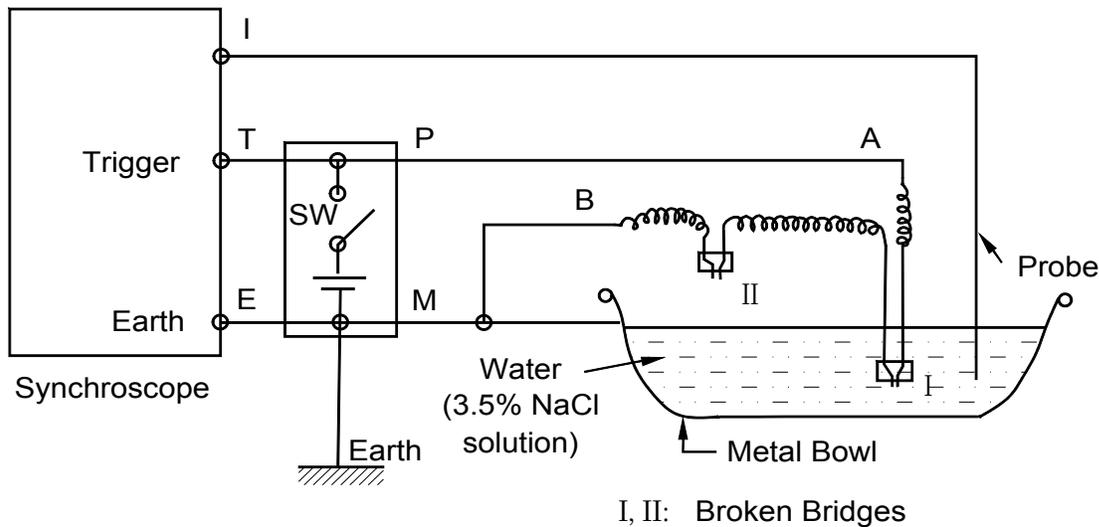


Figure 9. Circuit for imitation test of noises from double-hole blasting in a room. I = input, SW = switch in exploder.

3. *Explosive burning*: This used granular explosive in a spherical capsule. A condition was simulated in which the explosive burns instead of blasting. From the result of this experiment, we found that except for the rising instant, the noise wave does not have any overshoot.

7. Double-Hole and Multi-Hole Blasting

We first determined in a laboratory experiment the type of signals that are generated during double-hole blasting using the equipment and circuit diagrams shown in Figure 9.

A metallic bowl filled with a 3.5% salt solution can be considered as ground or sea water. I and II are the broken igniting bridges which can be freely submerged in the salt solution by moving up or down. If the synchroscope, exploder, ground, and probe are connected as shown above, and I and II are connected in series with the exploding circuit, we get a double-hole blasting circuit equivalent to Figure 1. In this condition, the resistance between I and E was 3,000 ohm. (There was no change in this value, even though probe position was varied.) The condenser of exploder has a capacitance of 3,000 μF and working voltage of 48 V. First, only bridge I on the right side of exploder wire

was immersed in water, and the circuit was switched on by activating the exploder. It was then possible to simulate a condition where I breaks first and establishes an electrical contact with water. Subsequently, II can be immersed in water. Therefore, II cracks with some delay after I and makes contact with water. The input waveform from the probe in this case is shown in Figure 10a.

It can be seen from this figure that a pulse indicating a second explosion appears on the minus side. If the sequence is reversed (i.e., bridge II on the minus side of exploder is first immersed into water followed by I), we get waveform *b*. Here, the pulse indicating a second explosion appears on the plus side. From these experiments, it was quite clear that during stage explosion for a double-hole blasting the two explosions can be easily distinguished. The direction of blasting pulse in the corresponding noise waveforms is minus if the first blasting wire is connected to pulse terminal, and it is plus in the other case. Hereafter, we have indicated the line connecting the plus terminal of exploder for first blasting as the plus wire, and the other wire in the opposite mode as the minus wire.

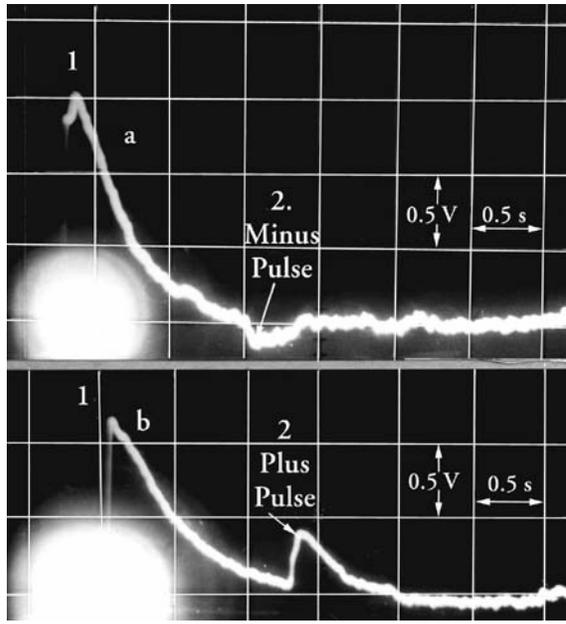


Figure 10. Noises from an imitation test, *a*: the plus terminal of the exploder is connected to the broken bridge, which is first put into the water, *b*: reverse of *a*.

Figure 11 shows the noise waveforms obtained when double-hole blasting was conducted in the field. Waveform *a* corresponds to the plus wire and *b* to the minus wire. For the first blasting, we used a detonator, whereas for the second blasting we used a spherical capsule which explodes with some delay. As this figure shows, in both *a* and *b*, an overshoot due to detonator is observed at 2.2 ms after the switching on; a mountain waveform rises at 2.4 ms, indicating where the detonator explodes (1). Subsequently, at about 10 ms, we observe another overshoot (2) which is on the minus side for *a* and on the plus side for *b*. Now, looking at the results of laboratory experiments, it is quite clear that in either case, this overshoot represents blasting of second stage explosive. The experimental conditions in this case were as follows: $E_1E_2=2$ m, gap between blasting holes 2 m, distance between E_1 and blasting hole about 50 m, exploder wire II was used, blasting voltage, 9.8 V, exploder condenser had a capacity of 1,000 μ F, and the series resistance between E_1E_2 , was 800 ohm.

The basis for the generation of blasting pulses for a multi-hole blasting is exactly identical as in double-hole blasting. Figure 12 shows

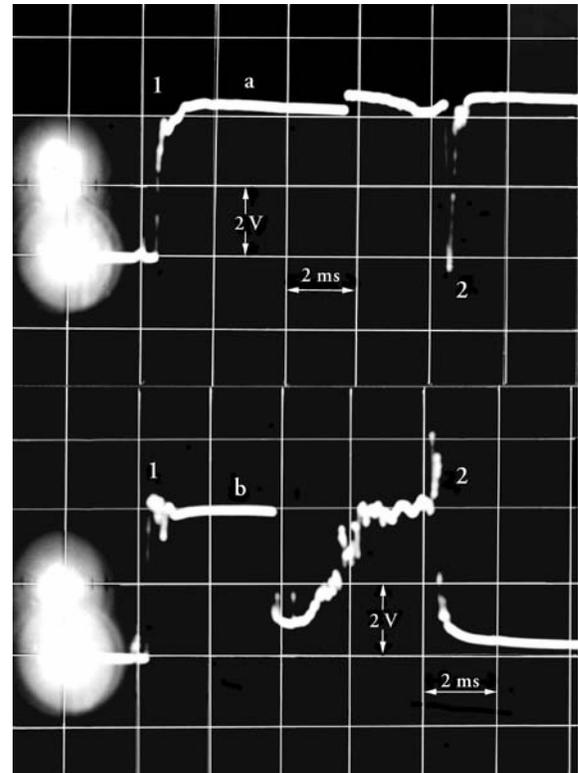


Figure 11. Noises from a double-hole blasting: *a* and *b* correspond to those in Figure 10 respectively. 1: from a detonator; 2: from a small cartridge which explodes with a delay.

the noise waves obtained when a multi-hole blasting was conducted in the field. Here, for step explosion, we used five self-made electrical detonators; they were connected to plus wire without the use of explosive cartridge. In this experiment, $E_1E_2=1$ m. All five blasting holes

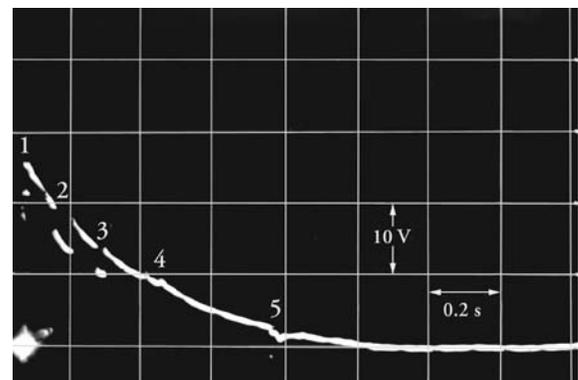


Figure 12. Noise from a five-step delay blasting using delay detonators.

were almost in a straight line having a gap of 2 m between two consecutive bores. Distance between E_1 and blasting hole group was about 75 m, exploder wire II was used, blasting voltage was 48 V, exploder condenser was of 3,000 μ F capacity, and series resistance between E_1E_2 was 750 ohm.

8. Conclusion

We have discussed the noise waveforms under different explosion conditions. The noise was extremely clear when the probe was inserted directly into the blasting hole but, actually, it is much more economical to keep the probe near the exploder. Detection of failure of explosion is comparatively simple but a lot of data needs to be collected for detection of explosion conditions. The special feature of this circuit is that one terminal of the exploder is connected directly to the ground of measuring equipment. This method can be used for underwater wired and step explosions equally well. Whether this method can also be used for underwater wireless explosions, or explosions on land, needs to be studied in the future.^[5]

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port in detail. We express our sincere thanks to them.

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