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The Critical Burning of Pyrotechnic Compositions

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Introduction

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

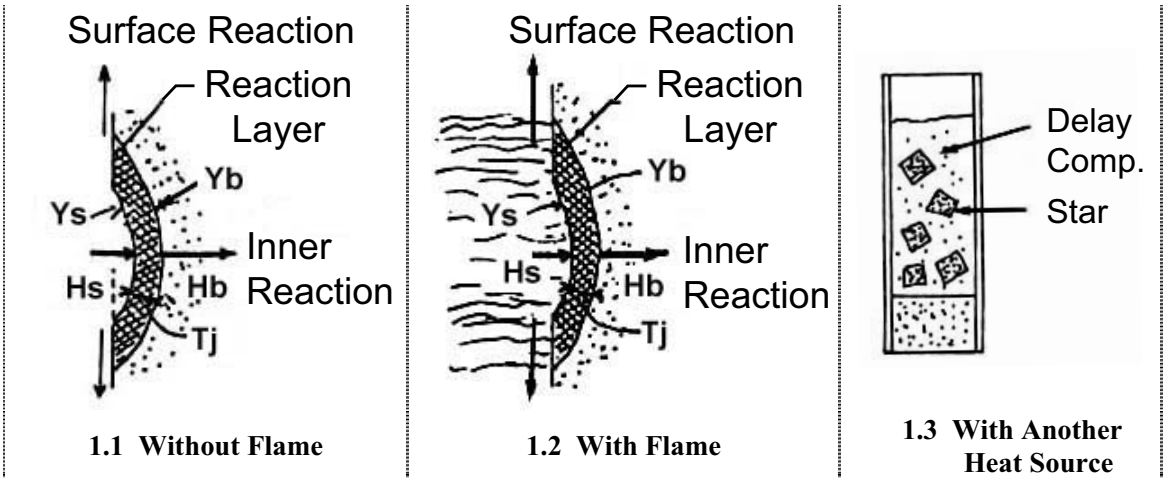
There are three types of reactions: smoldering, burning and detonation. In addition, there are several interesting variations like sparking, flashing [strobing] and pyrotechnic whistling. These phenomena fall between smoldering and burning or between burning and explosion and should be referred to as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



1.1 Without Flame **1.2 With Flame** **1.3 With Another Heat Source**

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).

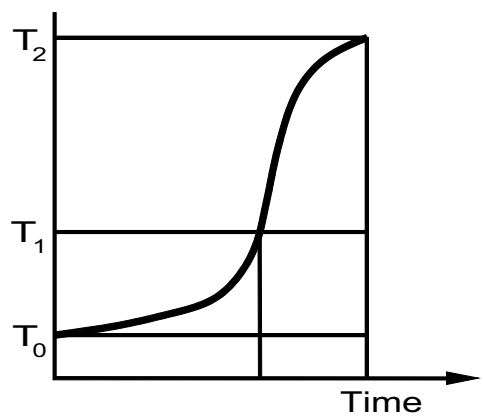


Figure 2. Reaction temperature at a given point inside the reaction layer as a function of time.

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.

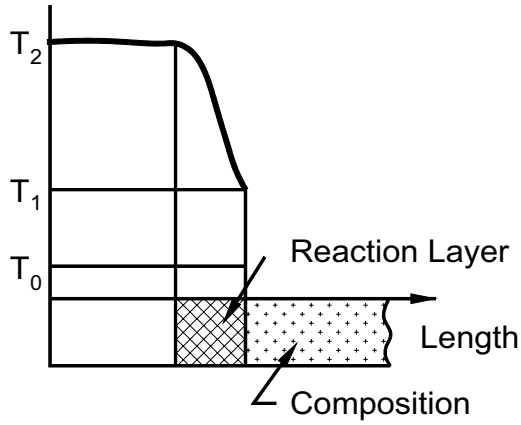


Figure 3. Temperatures inside the reaction layer at a given point in time.

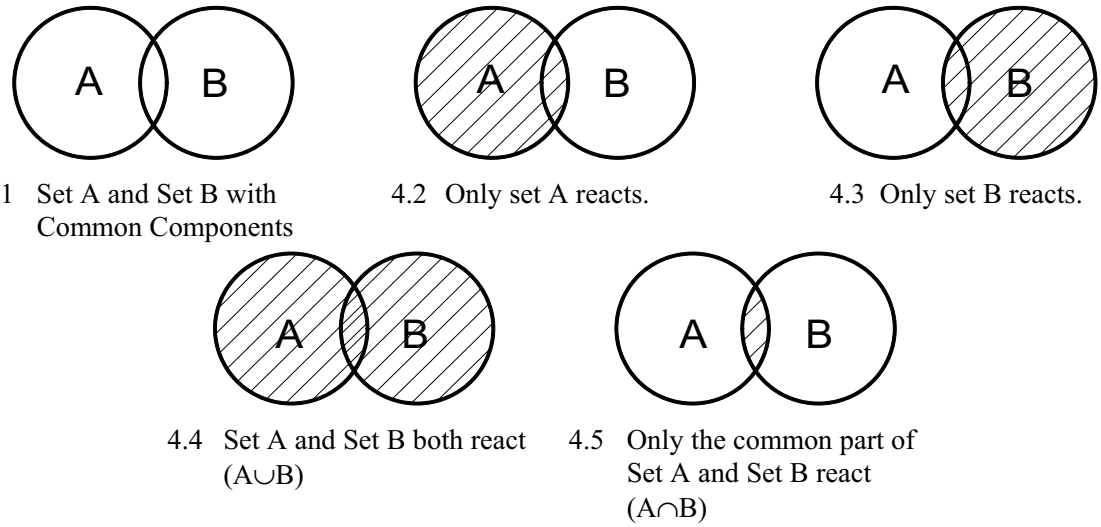
The surface reaction is a function of the surface conditions and the surroundings of the charge. As a rule, it progresses faster than the inner reaction.[2]

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

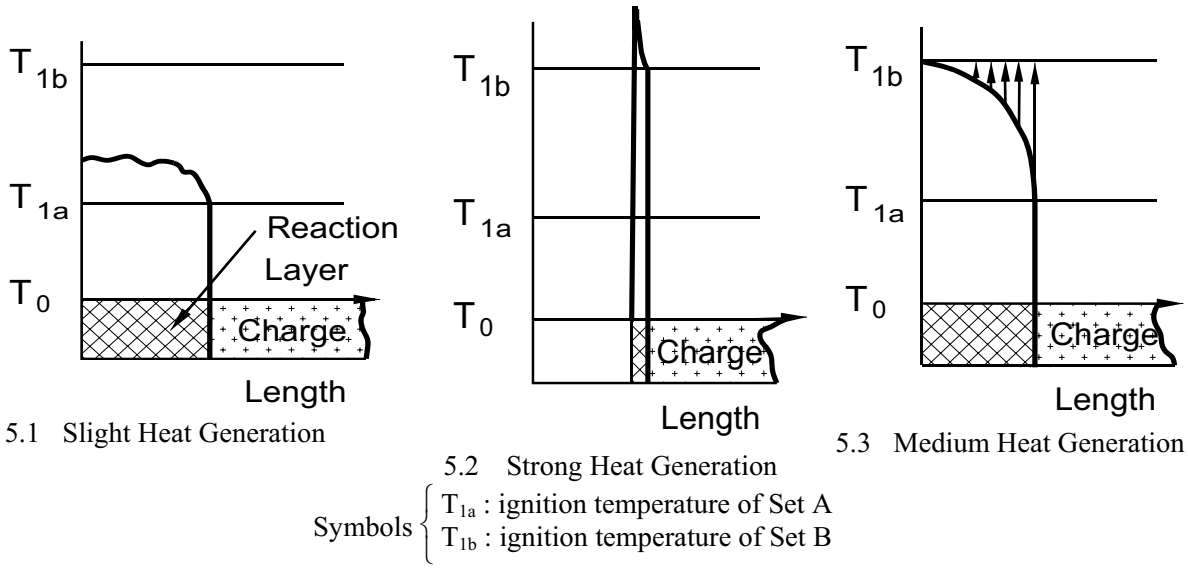
4.2 Only set A reacts.

4.3 Only set B reacts.

4.4 Set A and Set B both react (A∪B)

4.5 Only the common part of Set A and Set B react (A∩B)

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

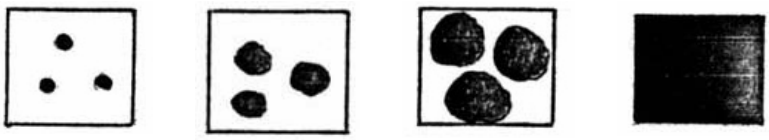


5.1 Slight Heat Generation

5.2 Strong Heat Generation

5.3 Medium Heat Generation

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



1. 2. 3. 4.

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

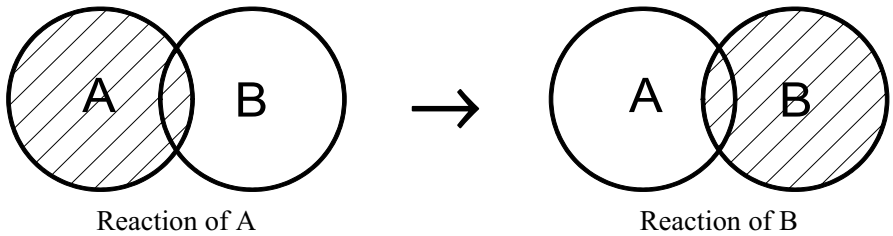


Figure 7. Two-phase reaction.

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∪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).

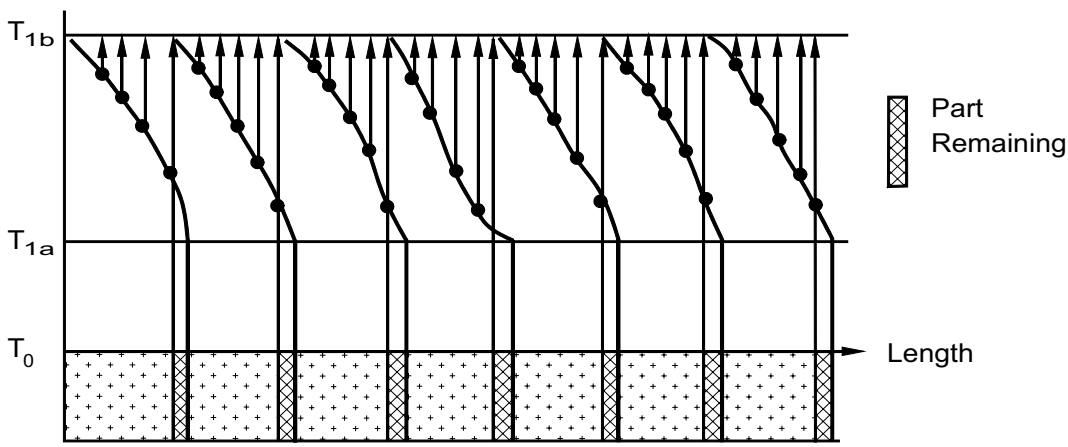


Figure 8. Repetition of two-phase reaction.

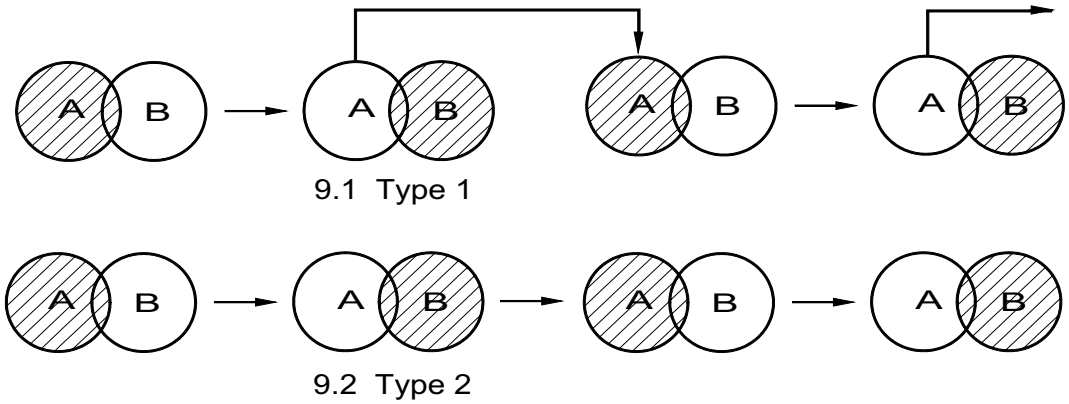


Figure 9. Flashing (strobe) reactions.

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.

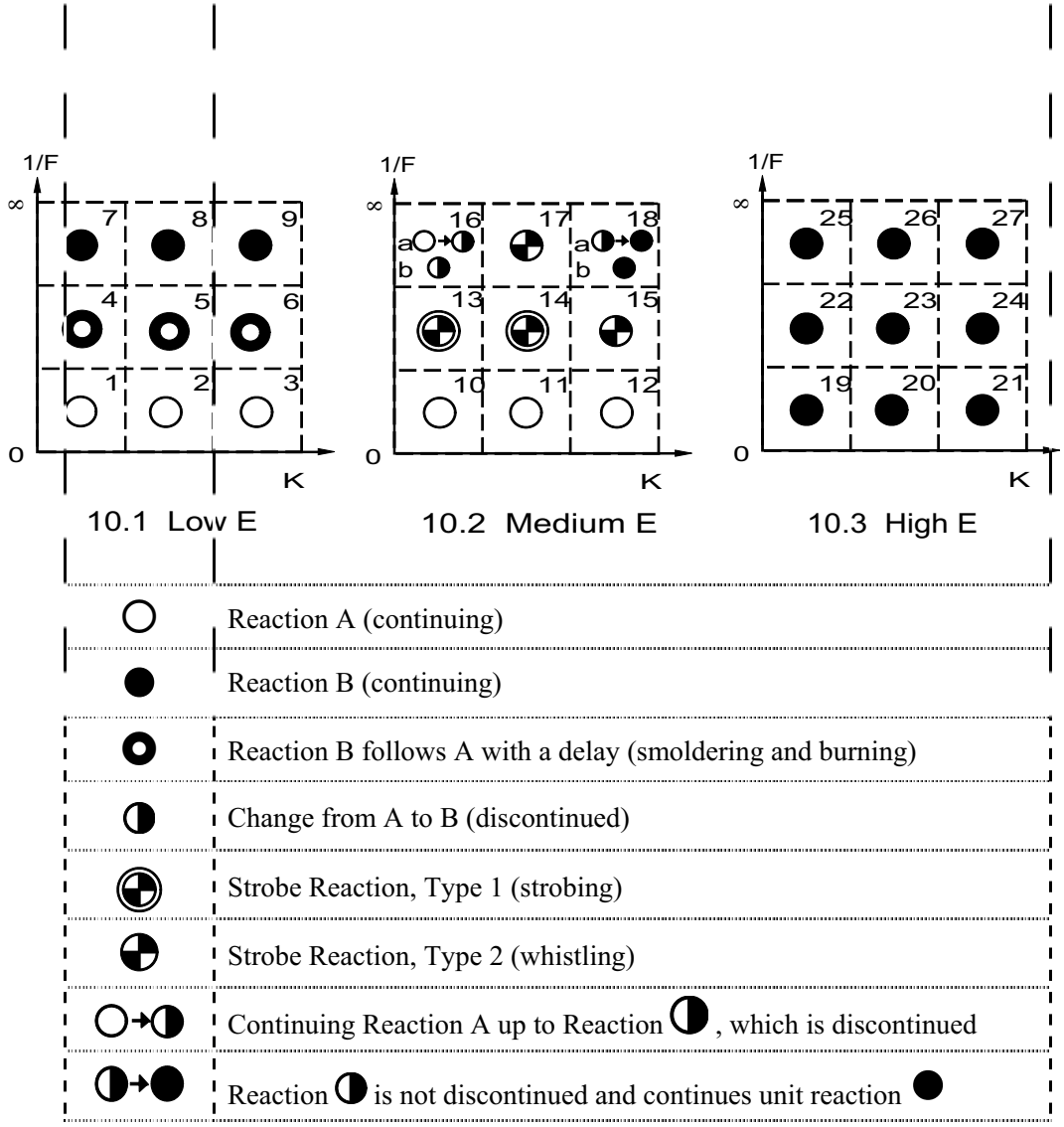


Figure 10. Possible reactions in compositions with two ignition temperatures.

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.

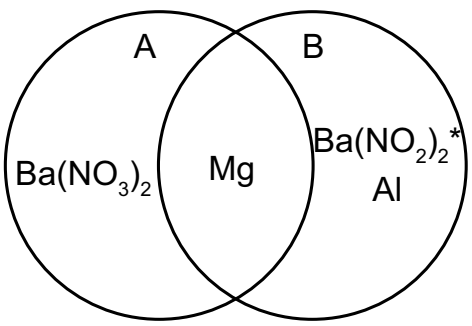


Figure 11. Two-phase reaction of a charge consisting of $Ba(NO_3)_2$ and magnalium.

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

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

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 5º. 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 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.

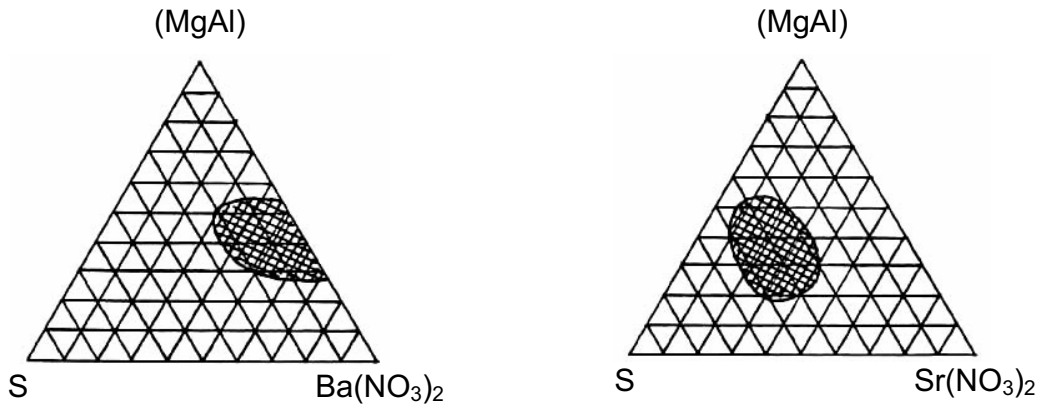
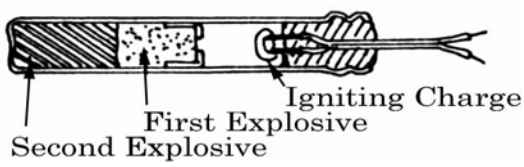


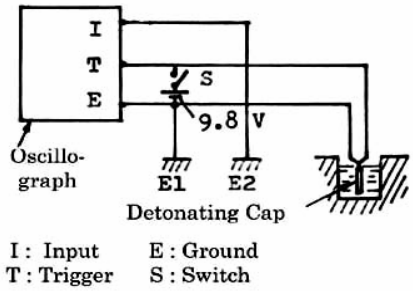
Figure 13. Effective area of two-phase reactions for tri-component mixtures.

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).

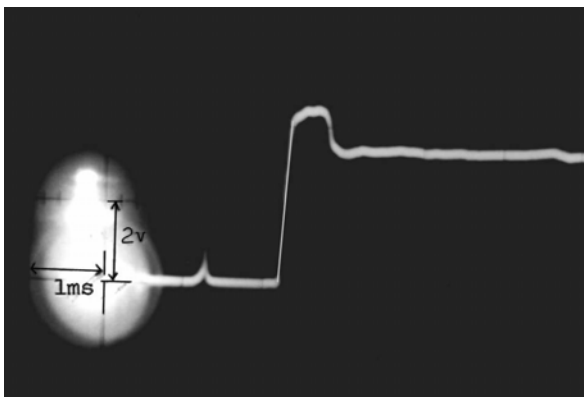
Based on the aluminum spectrum observed, we suspect a two-phase reaction here, as shown in Figure 15.3. In set A, KCl*, which is formed during the reaction of $KClO_4$ with Al, will promote decomposition of the $KClO_4$.[6] Over the course of the reaction, the quantity of KCl increases in set A and it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



14.1 Detonating Cap.



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

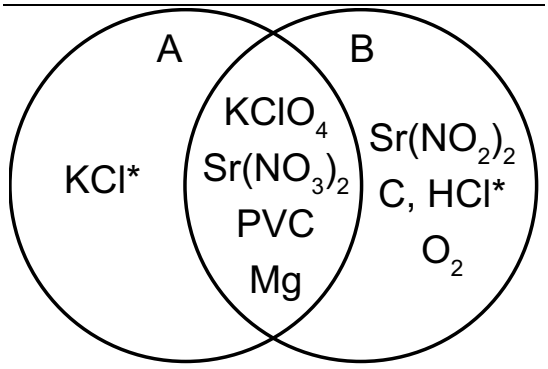
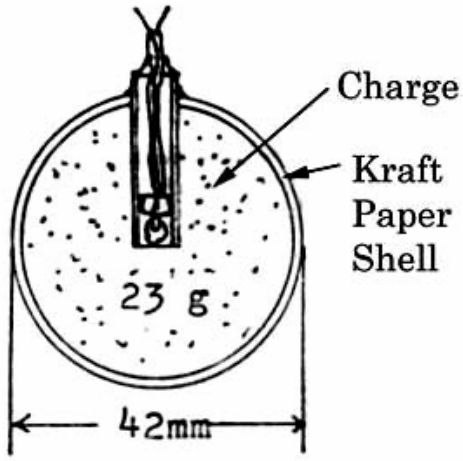
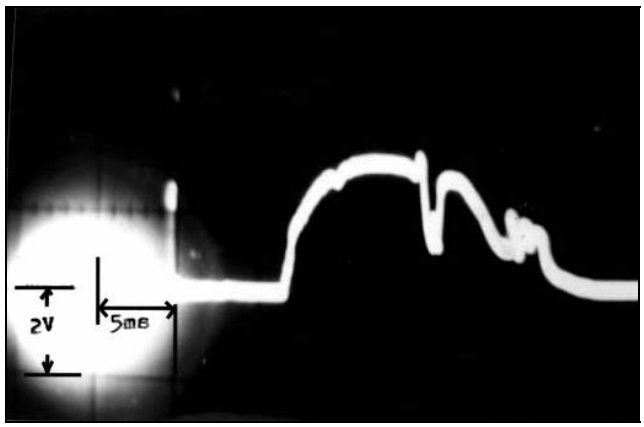


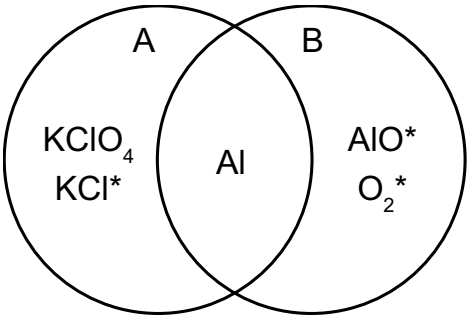
Figure 16. Sets involved in the two-phase reaction of a composition used for a flare.



15.1 Sample of a salute charge.



15.2 Electrical-voltage differential between sample piece and ground.



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

Figure 15. Measuring the delay for an explosive composition.

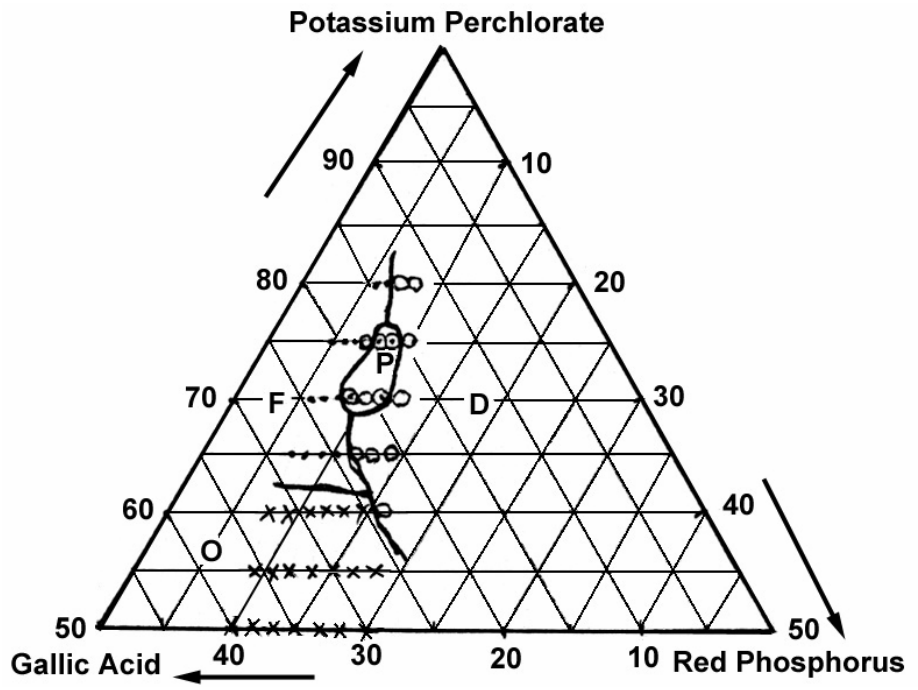


Figure 17. Whistling using A_1 ($KClO_4$, gallic acid, red phosphorus).

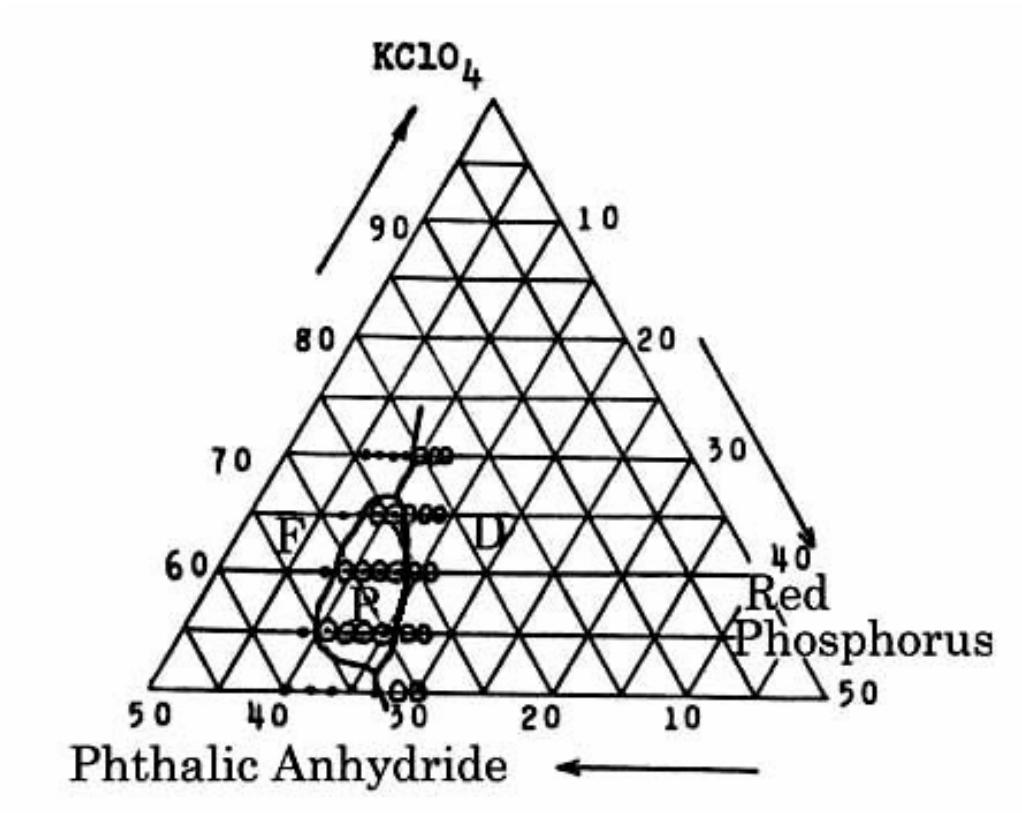


Figure 18. Whistling using A_2 ($KClO_4$, phthalic anhydride, red phosphorus).

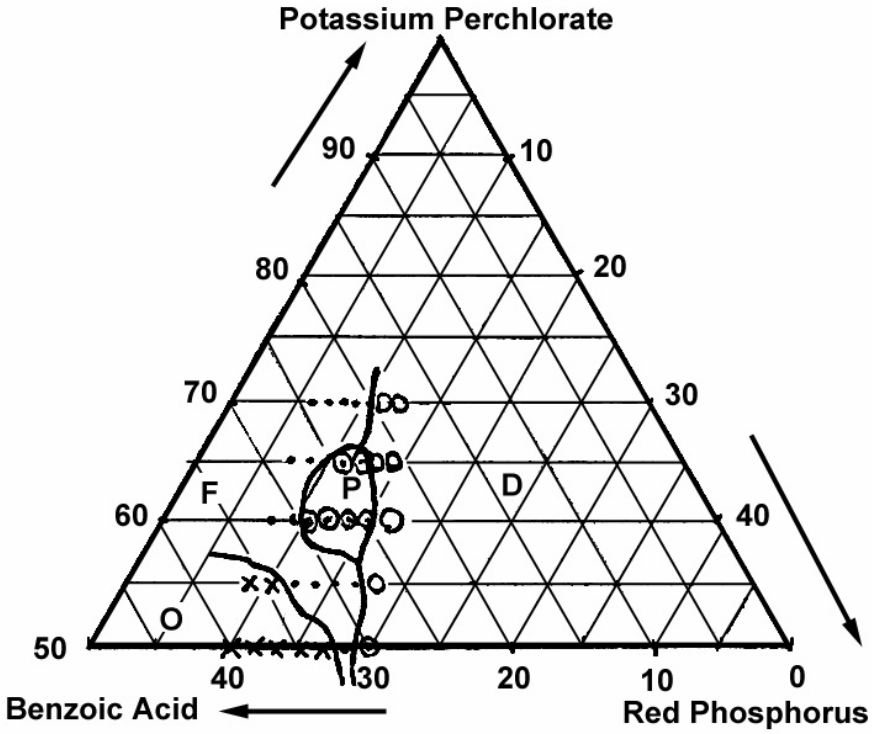


Figure 19. Whistling using A_3 ($KClO_4$, benzoic acid, red phosphorus).

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/cm^2, 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).

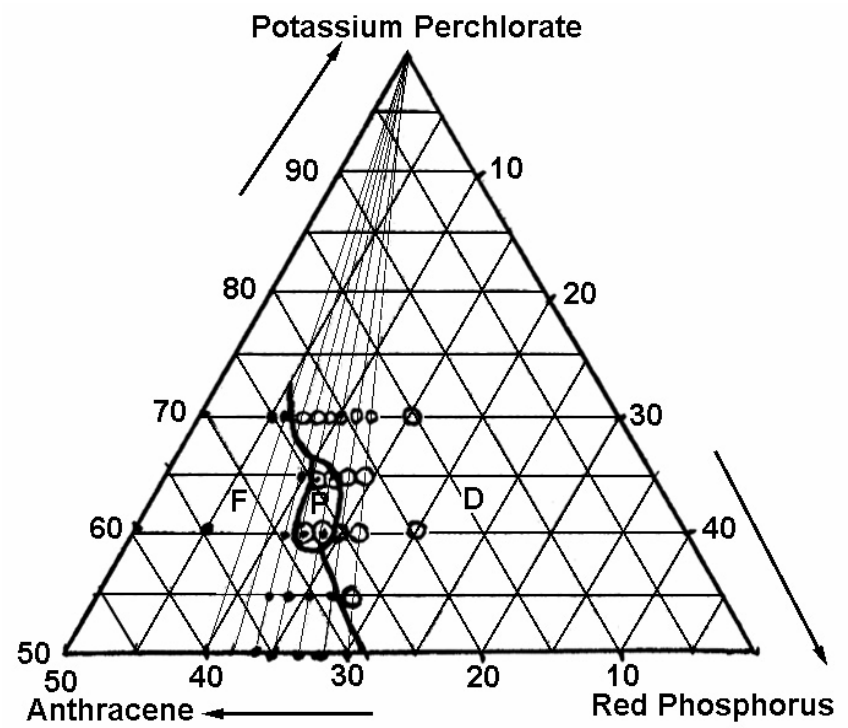


Figure 20. Whistling using A_4 ($KClO_4$, anthracene, red phosphorus).

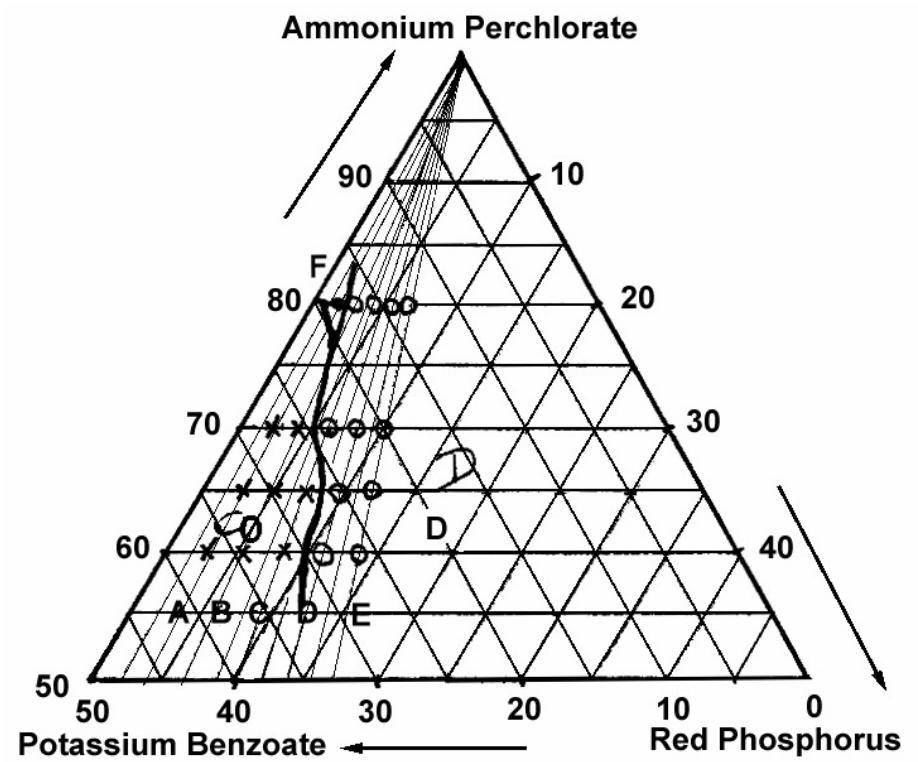


Figure 21. Whistling using A_5 (NH_4ClO_4, potassium benzoate, red phosphorus).

Table 1. Two-Component Mixtures.

A↓ \ B→	Potassium picrate	Gallic acid	Potassium benzoate
$KClO_3$	0/100**: D	75/25, 70/30: P	75/25, 70/30, 65/35: P
$KClO_4$	40/60: P*	75/25: F	80/20, 75/25, 70/30, 65/35, 60/40**: P
KNO_3	5/95**, 10/90**, 15/85**, 20/80**, 25/75**, 30/70, 35/65, 40/60, 45/55, 50/50: P	75/25: F	70/30: F
NH_4ClO_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 NH_4ClO_4, 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 NH_4ClO_4, potassium benzoate and red phosphorus does not result in whistling. Table 1 also shows that there is no whistling when NH_4ClO_4 is used.

In a mixture of KNO_3 and potassium picrate, KNO_3 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 K_2O*, the latter of which comes from KNO_3, suppresses reaction B, while KCl* promotes the decomposition of $KClO_4$. 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-

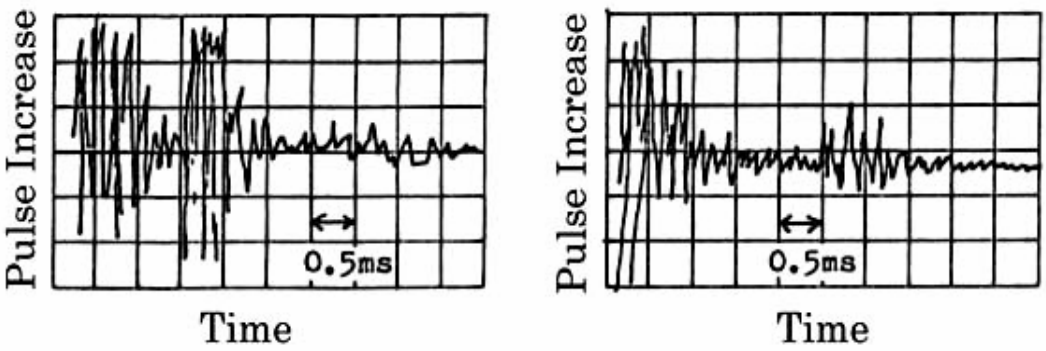


Figure 22. Oscillograms prepared by M. Kusakabe and N. Ishikawa[9] showing the effects produced by a pulse sample containing picric acid.

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 A_5 (70% $KClO_4$, 30% potassium benzoate), A_6 (75% $KClO_3$, 25% gallic acid) and A_7 (37% KNO_3, 63% potassium picrate).

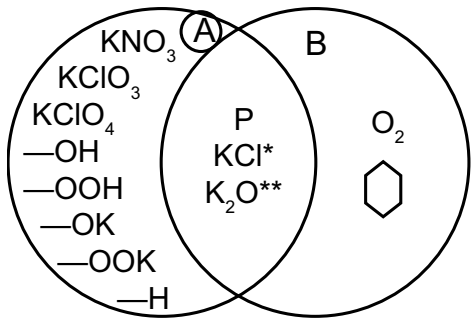


Figure 23. Probable sets involved in oscillating reactions of whistling compositions.

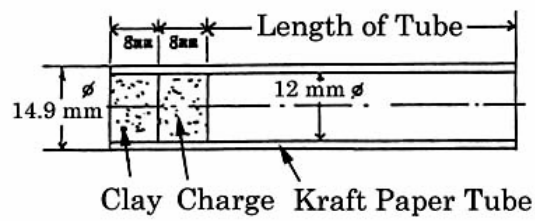


Figure 24. Sample piece.

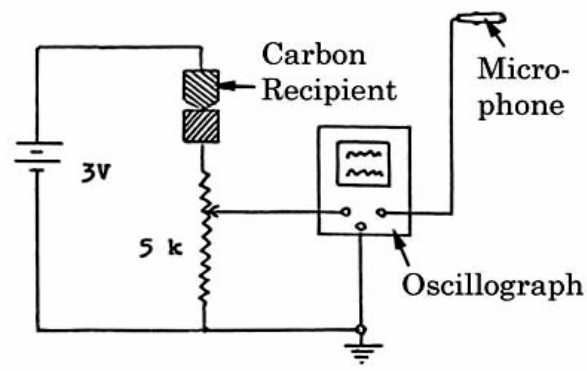


Figure 25. Assembly for measuring thrust waves and sound waves.

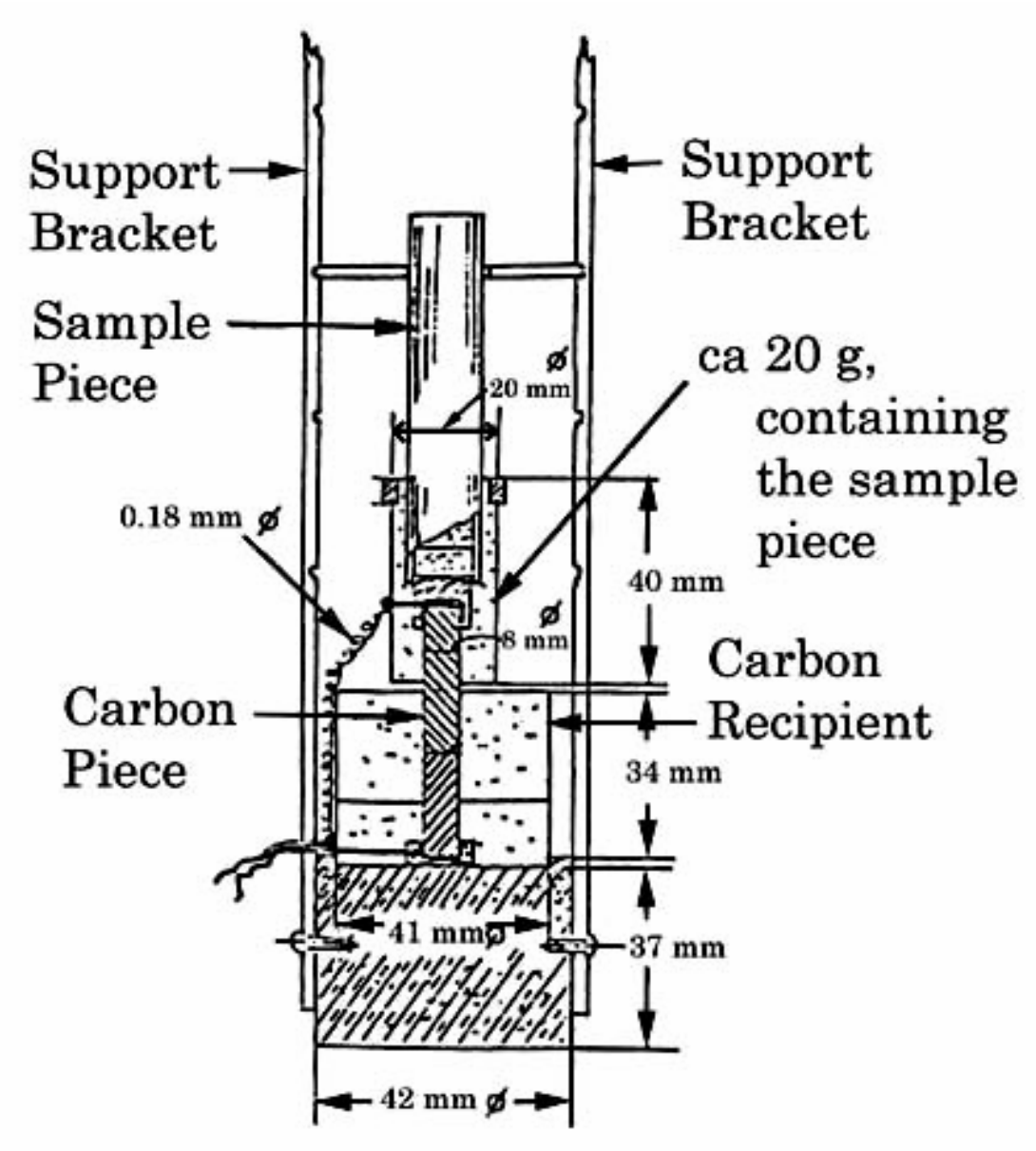


Figure 26. Assembly for measuring thrust waves.

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.

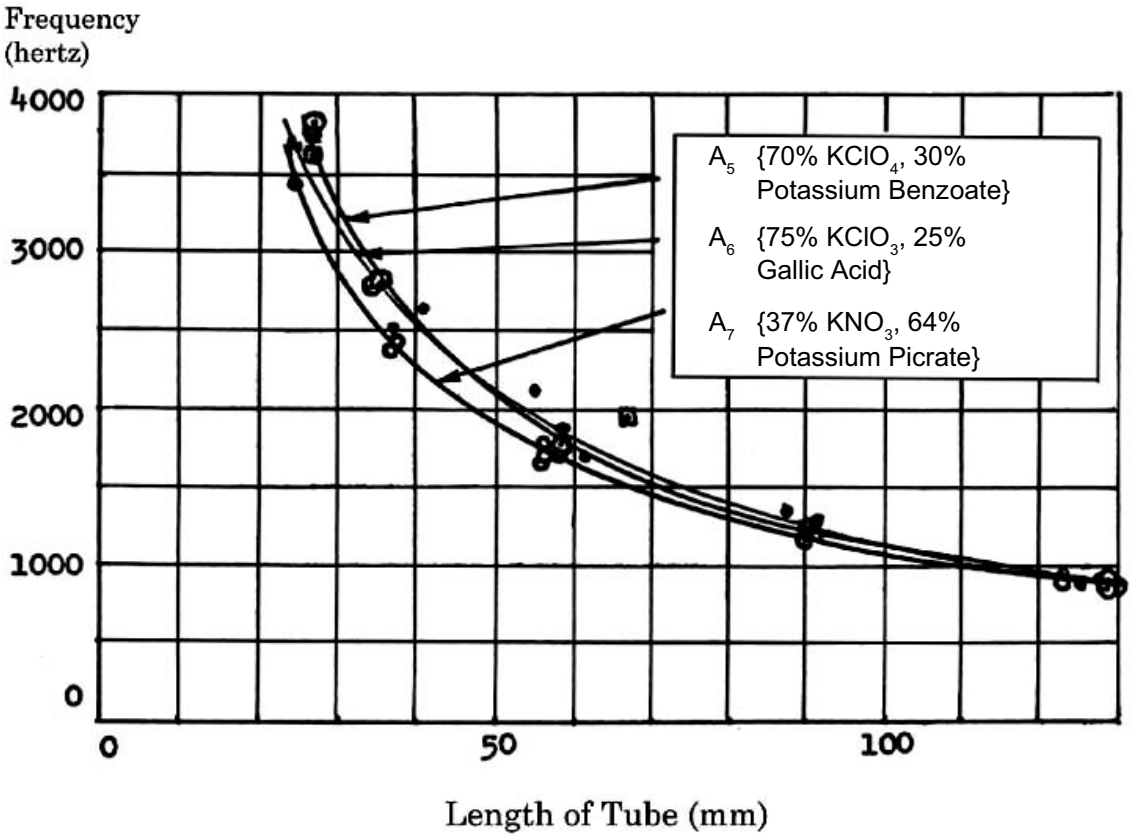


Figure 27. Frequency of the sound as a function of the length of the tube.

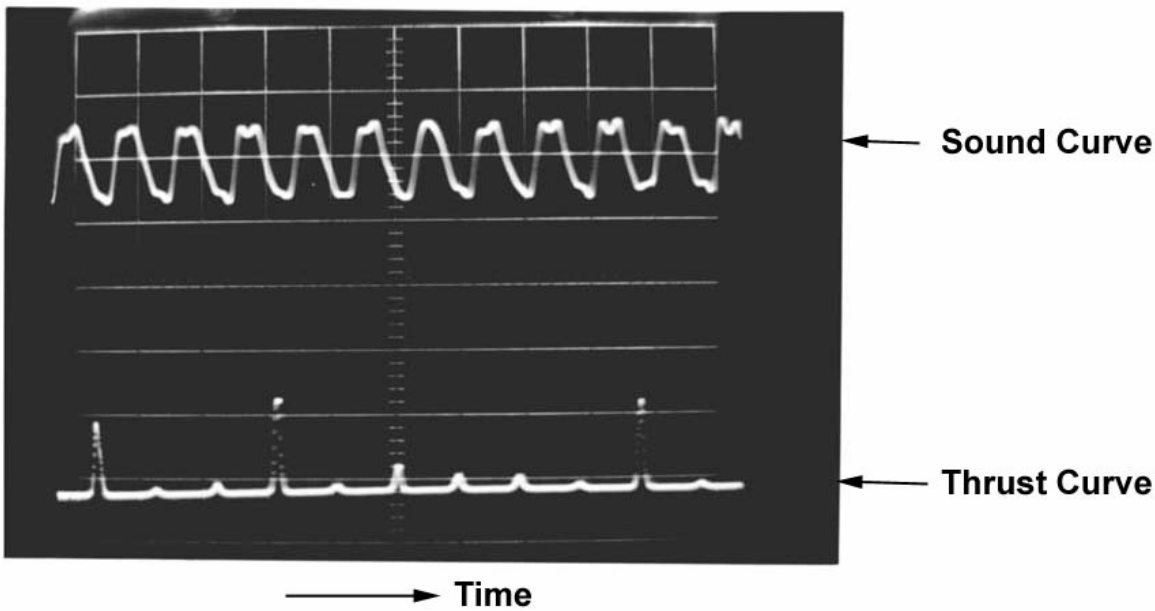


Figure 28. Effects of sound waves (top) and thrust waves (bottom); composition A_6: length of tube = 56 mm; horizontal section = 0.5 ms; vertical section = 1 V (top) and 0.2 V (bottom).

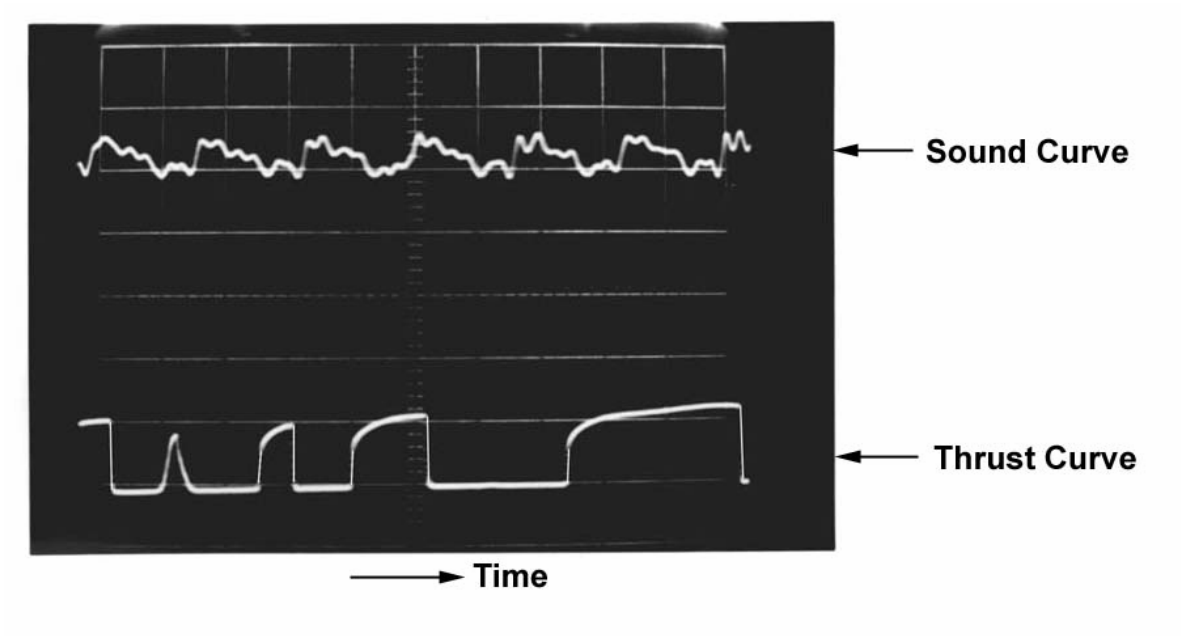


Figure 29. Effects of sound waves (top) and thrust waves (bottom); composition A_7: length of tube = 91 mm; horizontal section = 0.5 ms; vertical section = 1 V (top) and 0.2 V (bottom).

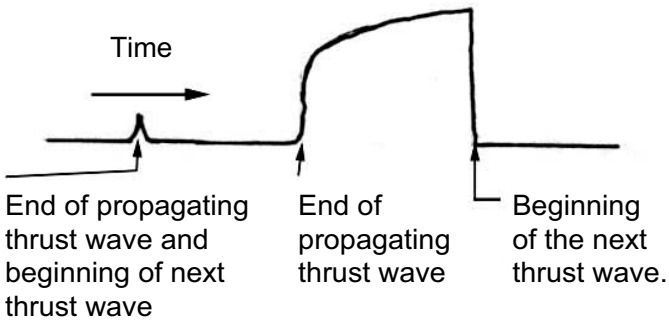


Figure 30. Significance of thrust curves.

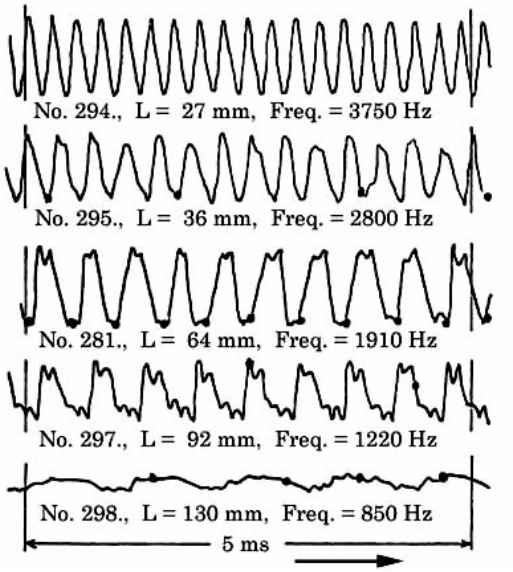


Figure 31. Sound curve of A_5; L = length of tube; Freq. = periodic number of waves.

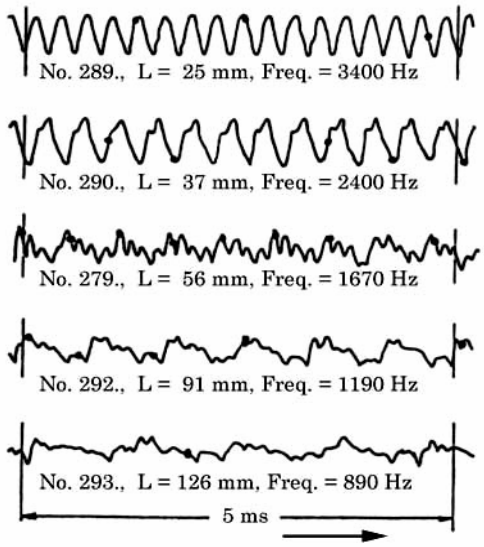


Figure 33. Sound curve of A_7.

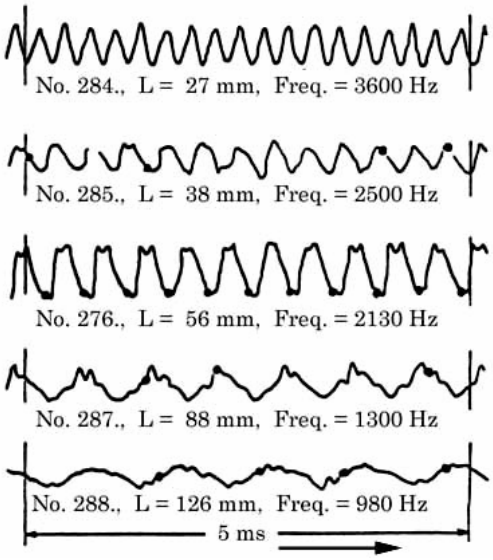


Figure 32. Sound curve of A_6.

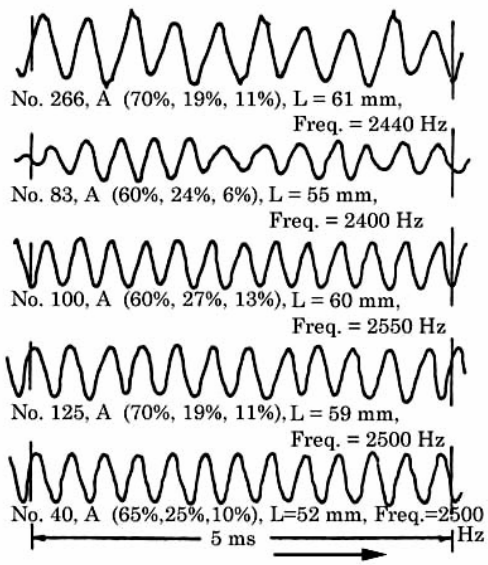


Figure 34. Sound curve of A_1, A_2, A_3 and A_4 (See Figures 17, 18, 19 and 20).

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.

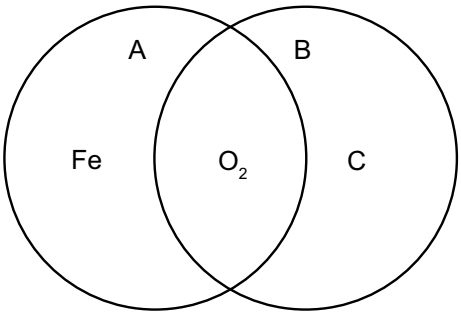


Figure 35. The principal reaction involved in the sparking of iron.

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

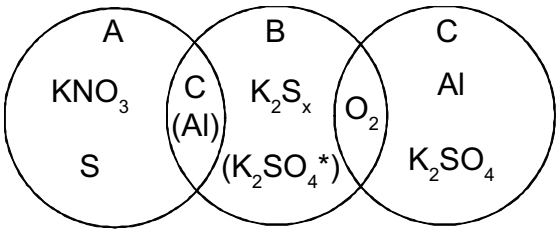


Figure 36. Three-phase reaction. (*) indicates that the substance is not involved in the reaction.

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.

Literature

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.
4) T. Shimizu, "Studies on Microstars" *Pyrotechnica* X (1982).
5) T. Shimizu, "Detection of Explosion in under Water Blasting from Electrical Noises", *J. Ind. Exp. Society, Japan*, Vol. 39, No. 1 (1978) p. 30.
6) H. Osada, Y. Hara, N. Nakajima and H. Nakamura, "Thermal Decomposition of Potassium Perchlorate", *J. Ind. Exp. Society, Japan*, Vol. 28, No. 6 (1967) p. 479.
7) T. Shimizu, "Studies on Strobe Light Pyrotechnic compositions", *Pyrotechnica* VIII (1982) p. 5.
Robert G. Cardwell, "Strobe Light Pyrotechnic Compositions: A Review of Their Development and Use", *Pyrotechnica* V (1979) p. 6.
8) W.R. Maxwell, "Pyrotechnic Whistles", *4th Symposium on Combustion*. [Ed. Note: This article was reprinted in *Journal of Pyrotechnics* No. 4 (1996) p. 37.]
9) M. Kusakabe and N. Ishikawa, "Initiation of Explosion by Drop Hammer Machine", *J. Ind. Exp. Society, Japan*, Vol. 24, No. 6 (1963) p. 318.