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Burning Rate and Grain Size of Component Materials of Pyrotechnic Mixtures

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ABSTRACT

It has been generally believed that the finer the grain size, the faster the burning when we select the component materials of a pyrotechnic mixture. It is not always true because a small explosion occurred in the past when we tested a smoke mixture, although it contained a dye of very coarse grains.

The purpose of this paper is to make clear the general mechanism of the burning rate of pyrotechnic mixtures on the standpoint of the grain size of component materials of pyrotechnic mixtures.

Experiments on burning rate were carried out with four types of mixtures changing the grain size of the component materials:

(a) base mixtures of oxidizer (conventional materials as potassium chlorate, potassium perchlorate or ammonium perchlorate) and fuel (accroides resin),

(b) mixtures of the base and an inert material (clay),

(c) mixtures of the base and a semi-inert material (barium nitrate),

(d) mixtures of an explosive of synthesized simple substance (potassium picrate) and an inert material (clay).

All the materials except potassium picrate were sieved to obtain grains of six class sizes.

With decreasing the grain size of the component materials, some mixtures increased and some decreased the burning rate. In other cases there were grain sizes which gave the smallest burning rate: the burning rate at first decreased and then increased. In general, the burning reaction seemed to be stabilized as the grain size decreased. These effects will help the designing of pyrotechnic mixtures for various purposes.

I. Introduction

The objective of this work was to find possibly the general law of the relation between the burning rate and grain size of component materials of pyrotechnic mixtures.

As a representative case, four types of mixture were experimentally examined:

(a) base mixtures of oxidizer and fuel,

(b) mixtures of the base and an inert material,

(c) mixtures of the base and a semi-inert material,

(d) mixtures of an explosive of simple synthesized substance and an inert material.

II. Experimental

2.1. Materials and classification of their grain size

As the oxidizers three conventional substances, potassium chlorate from Nippon Soda Co., potassium perchlorate from Nippon Carlit Co. and ammonium perchlorate from Kanto Kagaku Co. were used. As the fuel accroides resin[1] was used due to its wide use in firework field**.** It was obtained through Daiichi Yakuhin Kogyo Co. As the inert material a kind of clay of Kanto loam was used. As the semi-inert material barium nitrate, which is not easily decomposed at ordinary flame temperatures (1500–2200 °C), from Barite Industry Co. was used. As the explosive potassium picrate was synthesized with picric acid (a reagent) and potassium carbonate by the author.[2]

For the classification of grain sizes of the materials six types of sieve were used:

14 mesh with openings of 1.40 mm, used in our work room,

20 mesh with openings of 0.77 mm, used in our work room,

32 mesh with openings of 0.495 mm, standard,

48 mesh with openings of 0.295 mm, standard,

65 mesh with openings of 0.208 mm, standard,

150 mesh with openings of 0.104 mm, standard.

2.2. Preparation of samples

The oxidizers or the semi-oxidizer in powdered state were once dissolved in hot water and recrystallized by cooling slowly to obtain possibly large crystals. The crystals were roughly ground in a porcelain mortar and sieved using the sieves above mentioned. The grains of each material were classified as it is seen in Figure 1.

For example, G3 means the grains that passed the 32 mesh sieve and did not pass the 48 mesh sieve.

The fuel, accroides resin, in powdered state was once melted in a 120 °C oven to a black mass. Then it was ground and sieved as it was with the oxidizers.

The inert material, clay, was prepared by crushing well dried clods of the clay by a hammer and ground in the mortar to proper grain sizes, which were classified by the same way as before.

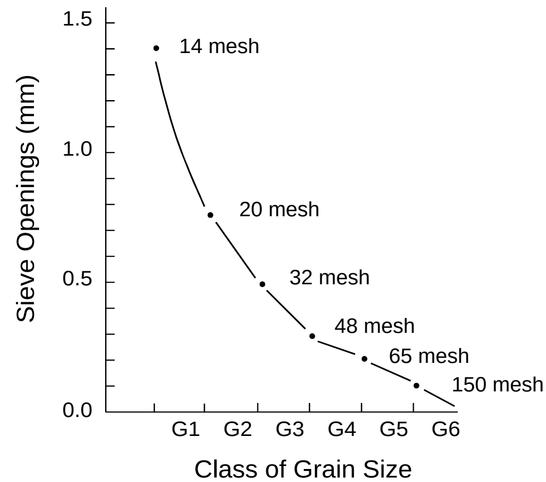

Figure 1. Classification of grain sizes.

Base mixtures to see the effect of the grain sizes were prepared with 36 types as shown in the matrix 1 (below) for each oxidizer. Each element is denoted by three letters: the first G means the “grain”, the second letter means the grain class of the accroides resin and the third, that of the oxidizer. For example, G23 means a mixture of the accroides resin of the second class grain size and the oxidizer of the third class. The weight ratio of the oxidizer and accroides resin was 80/20, the value of which was common to all element mixtures.

Fifteen grams of each element mixture without binding material was put into a Kraft tube of 27 mm inside diameter, 50 mm long and having a wall thickness of 1 mm in a split mold with three segments. It was pressed under a pressure of 2.8 ton/cm^2 for five seconds using a press. For ignition a small quantity of a fine magnesium powder was placed on the one end surface adding a small piece of black match (Figure 2).

Matrix 1:

G11	G12	G13	G14	G15	G16
G21	G22	G23	G24	G25	G26
G31	G32	G33	G34	G35	G36
G41	G42	G43	G44	G45	G46
G51	G52	G53	G54	G55	G56
G61	G62	G63	G64	G65	G66

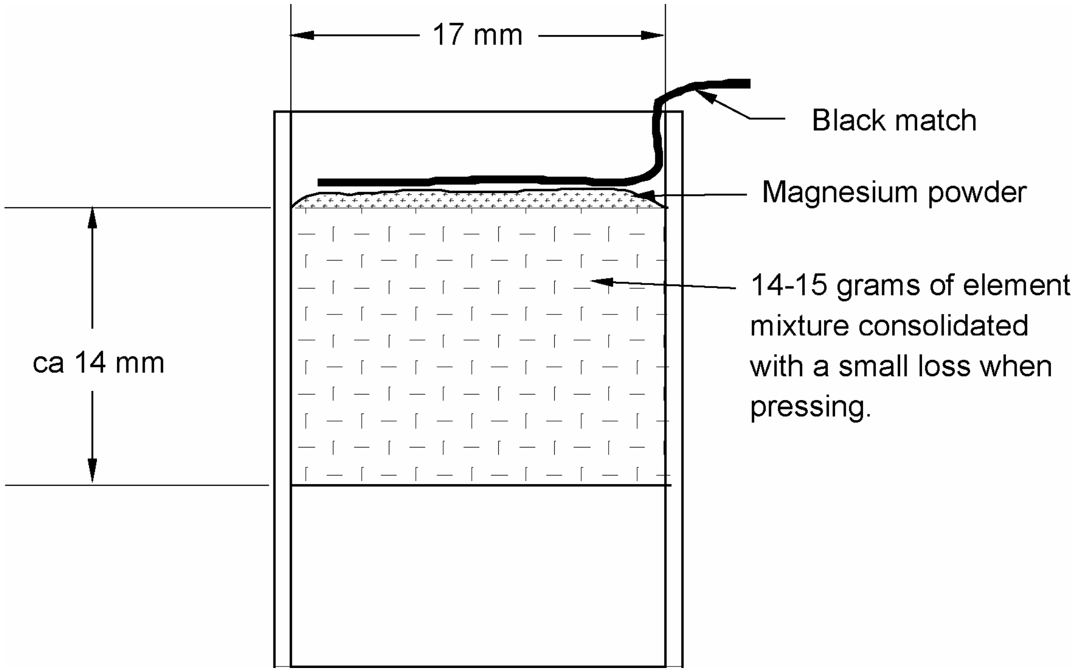

Figure 2. Sample for burning test.

Mixtures of the base and the inert material, clay, were prepared with 18 types as shown in the Matrix 2 for each oxidizer. As the base the element mixture G66 was used (Matrix 2). Each element is denoted by 7 letters: the first G66 means the element mixture in the former matrix of the base in the foregoing page (matrix 1), the next two letters, 1C to 6C, mean the class of grain size of the clay and the next figures, 10 to 30, mean the weight percentage in each element mixture. For example, G66-4C20 means a mixture of 20% clay of 4th class of grain size and 80% G66 element mixture. The G66 is a mixture of the smallest grain size of both the oxidizer and fuel. Mixtures of the base and the semi-inert material, barium nitrate, were prepared in the same way as the Matrix 2 (Matrix 3). In the Matrix 3 the symbol B means barium nitrate in place of C in the Matrix 2. Other symbols are the same as those of the Matrix 2.

Matrix 2:		
G66-1C10	G66-1C20	G66-1C30
G66-2C10	G66-2C20	G66-2C30
G66-3C10	G66-3C20	G66-3C30
G66-4C10	G66-4C20	G66-4C30
G66-5C10	G66-5C20	G66-5C30
G66-6C10	G66-6C20	G66-6C30

Matrix 3:		
G66-1B10	G66-1B20	G66-1B30
G66-2B10	G66-2B20	G66-2B30
G66-3B10	G66-3B20	G66-3B30
G66-4B10	G66-4B20	G66-4B30
G66-5B10	G66-5B20	G66-5B30
G66-6B10	G66-6B20	G66-6B30

The element mixtures without binding material were consolidated by the same method as those of the Matrix 1 as the samples to use for the burning test.

The explosive of simple substance, potassium picrate, was mixed with the clay of six size classes of grains. The weight ratio of the picrate to the clay was 90/10. Two grams of each element mixture were pressed into a stainless steel tube of 11 mm inside diameter, 60 mm long and having a wall thickness of 1 mm.

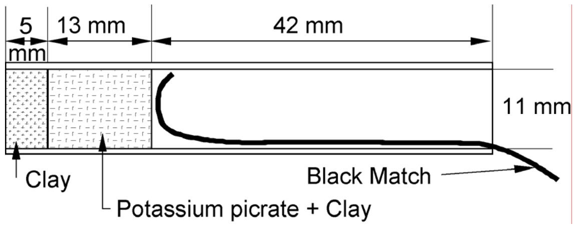

Figure 3. Sample of burning test of potassium picrate mixture.

Matrix 4:

PP-1C	PP-2C	PP-3C	PP-4C	PP-5C	PP-6C

2.3. Burning test and the result

The number of the sample for each matrix element was one. The samples were placed in the open air and the burning times were measured by stop watch. The results are shown with following matrixes (1)–(10) and Figures 4–13.

2.3.1. Burning rate in mm/s with the mixtures of oxidizer and accroides resin following the Matrix 1

(1) Potassium chlorate and accroides resin

0.77	0.74	0.78	1.09	0.80	1.04
0.79	1.07	0.93	0.84	0.99	1.17
1.16	1.10	1.08	1.09	1.12	1.06
1.05	1.16	1.22	1.45	1.42	1.71
1.23	1.24	1.37	1.61	1.61	1.97
1.18	1.19	1.59	1.68	1.43	1.67

(2) Potassium perchlorate and accroides resin

0.17	0.59	0.71	0.66	0.82	0.76
0.85	0.75	0.80	0.87	0.65	0.93
0.79	0.85	0.87	0.86	0.92	1.18
0.84	0.85	0.95	1.07	1.28	1.09
0.79	0.90	1.00	1.15	1.29	1.33
0.87	0.99	—	1.04	1.11	1.19

(3) Ammonium perchlorate and accroides resin

0.54	0.50	0.46	0.50	0.56	0.52
0.56	0.61	0.60	0.61	0.60	0.67
0.50	0.62	0.65	0.76	0.73	0.87
0.63	0.60	0.77	0.84	0.88	0.94
0.63	0.68	0.80	0.94	1.02	1.14
0.69	0.81	0.88	1.03	1.15	—

2.3.2. *Burning rate in mm/s with the mixtures of the base G66 and the inert material, clay. The data obtained are arranged following the Matrix 2.*

(4) $KClO_3$ base		
1.10	1.29	0.87
1.01	0.93	0.66
1.00	1.02	0.81
1.08	0.98	0.97
1.31	1.23	1.12
1.38	1.61	1.97

(5) $KClO_4$ base		
1.07	0.82	0.88
0.96	0.85	0.65
1.04	0.88	0.87
1.00	0.74	0.57
1.14	0.72	0.57
1.06	1.27	0.99

(6) NH_4ClO_4 base		
1.25	1.02	0.92
1.22	1.01	0.87
1.06	1.01	0.87
1.11	1.09	0.81
1.55?	0.99	0.93
1.28	1.14	1.14

2.3.3. *Burning rate in mm/s with the mixtures of the base G66 and the semi-inert material, barium nitrate. The data are arranged following the Matrix 3.*

(7) $KClO_3$ base		
1.24	0.98	0.79
1.09	1.03	0.78
1.17	0.98	0.78
1.17	0.92	0.85
1.17	1.04	0.89
1.18	1.08	1.10

(8) $KClO_4$ base		
1.01	0.86	0.65
1.00	0.88	0.72
0.94	0.92	0.75
0.96	0.89	0.79
0.94	0.93	0.86
1.06	1.12	0.88

(9) NH_4ClO_4 base		
1.19	0.94	1.03
1.24	1.03	0.93
1.19	1.06	1.02
1.11	1.01	0.87
1.14	0.84	0.72
1.09	0.85	0.58

With the element mixtures, G66-6B20, G66-4B30, G66-5B30 and G66-6B30 of NH_4ClO_4 base a flame of very deep green was produced.

2.3.4. *Burning rate in mm/s with the explosive of simple substance, potassium picrate, mixed with 10% inert material, clay. The data are arranged following the Matrix 4.*

(10) 5.42 4.28 4.19 3.94 3.16 4.33

A whistling noise was produced from each element mixture. It seemed the tone of the whistle increased as the grain size of the clay decreased.

2.3.5. *Graphical expression of the results*

All of the results which are expressed by matrixes from (1) to (10) are further graphically expressed by the following figures.

With Figures 4, 5 and 6, which concern the mixtures of oxidizer and fuel, the left curves are mainly to see the effect of the grain sizes of fuel, accroides resin, and the right of the effect of oxidizer. With Figures 7–12, which concern the mixtures of the base G66 and the inert material, clay, or semi-inert material, barium nitrate; the left curves are mainly to see the effect of the grain sizes of the inert or semi-inert material, and the right the effect of the mixing ratios of the material to the base mixture G66. Figure 13 shows the effect of the grain sizes of the inert material, clay, when ten percentages of clay were mixed to potassium picrate. (1)–(10) show the corresponding matrix number.

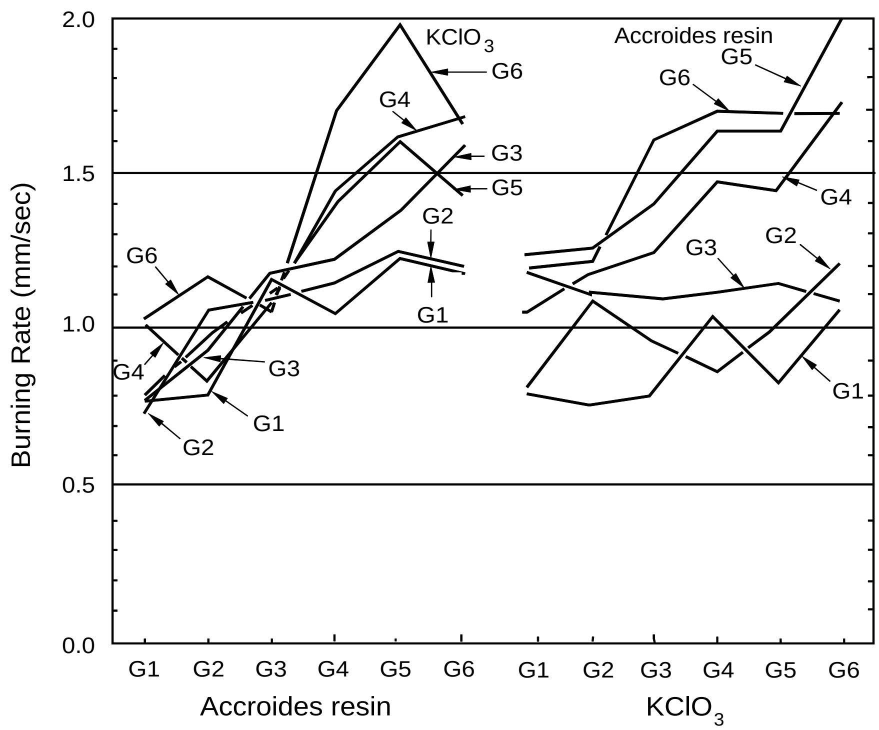

Figure 4. Potassium chlorate and accroides resin, (1).

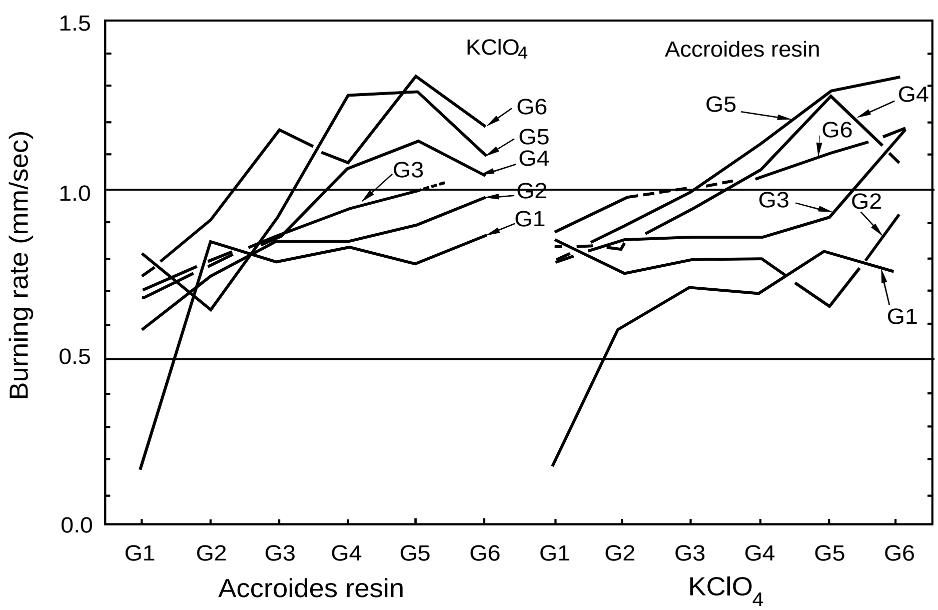

Figure 5. Potassium perchlorate and accroides resin, (2).

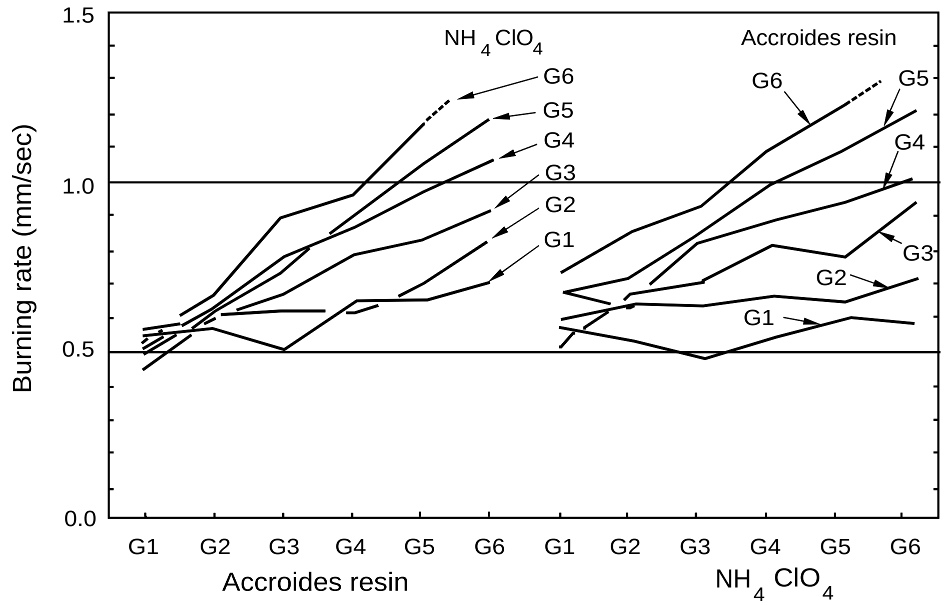

Figure 6. Ammonium perchlorate and accroides resin, (3).

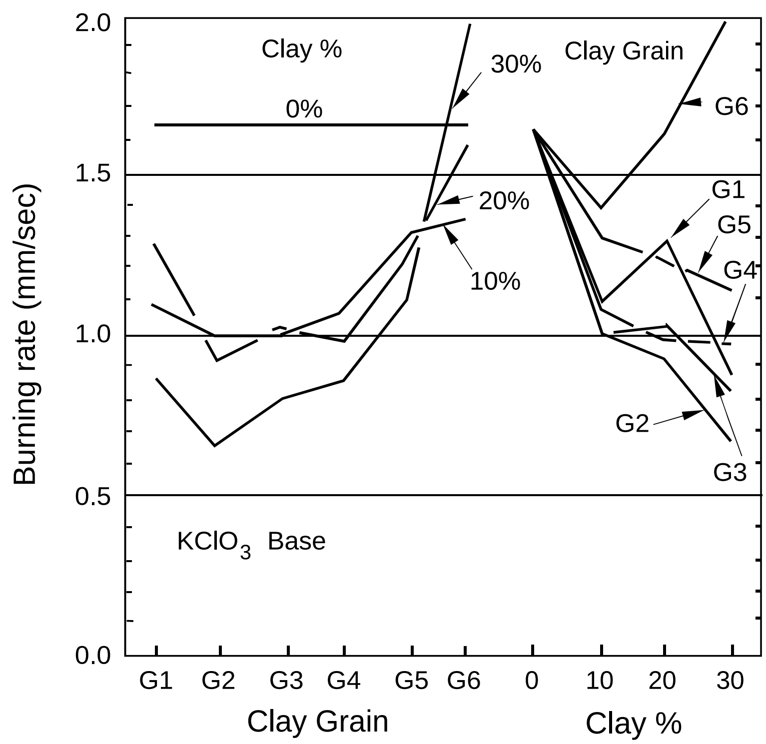

Figure 7. Potassium chlorate base G66 and clay, (4).

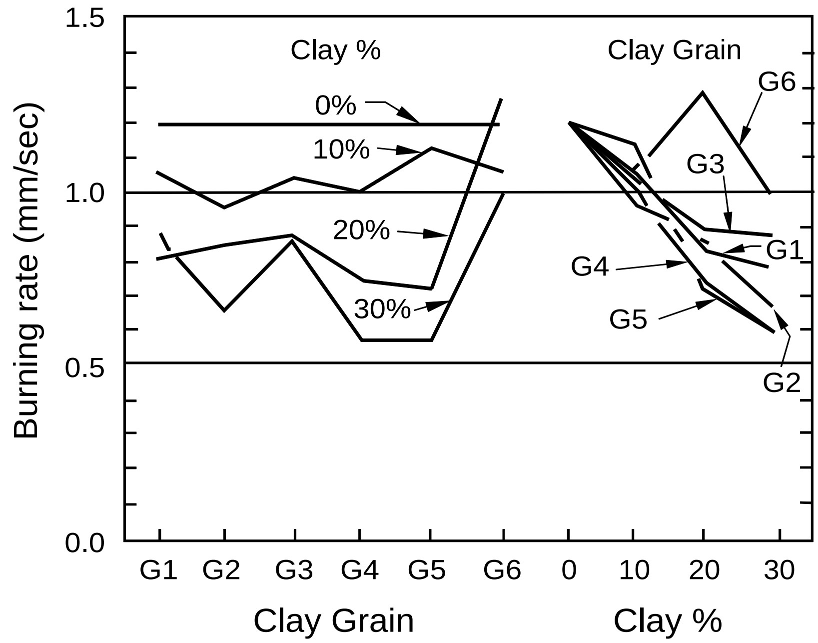

Figure 8. Potassium perchlorate base G66 and clay, (5).

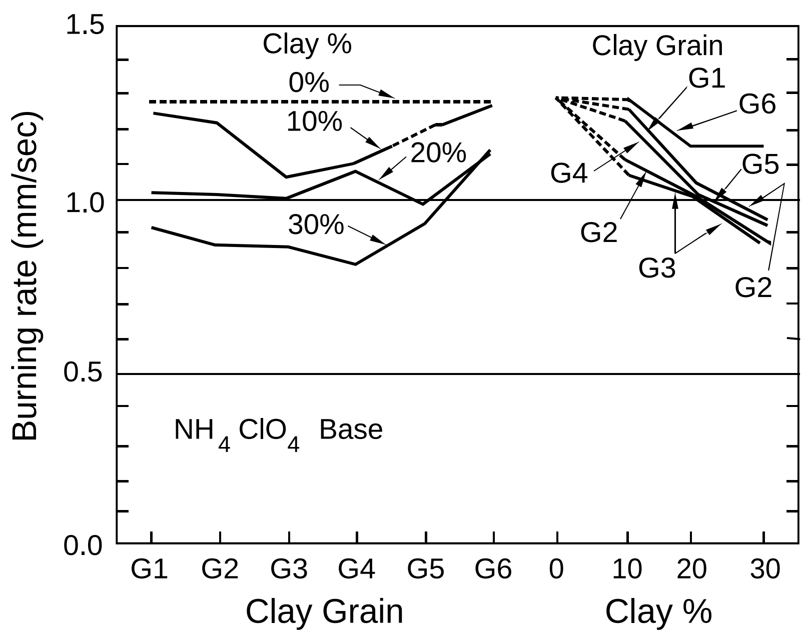

Figure 9. Ammonium perchlorate base G66 and Clay, (6).

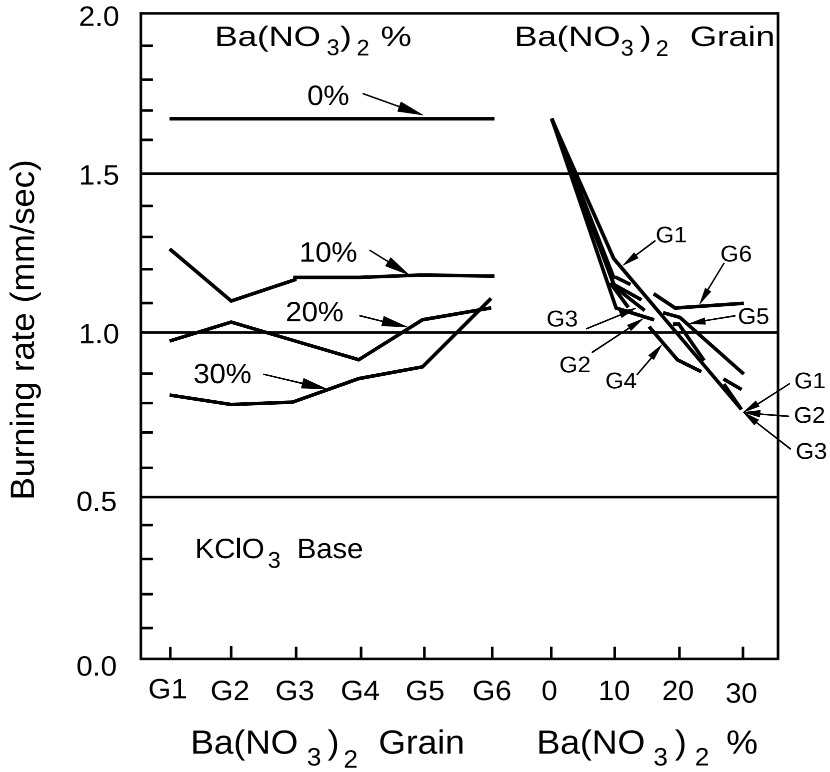

Figure 10. Potassium chlorate base G66 and barium nitrate, (7).

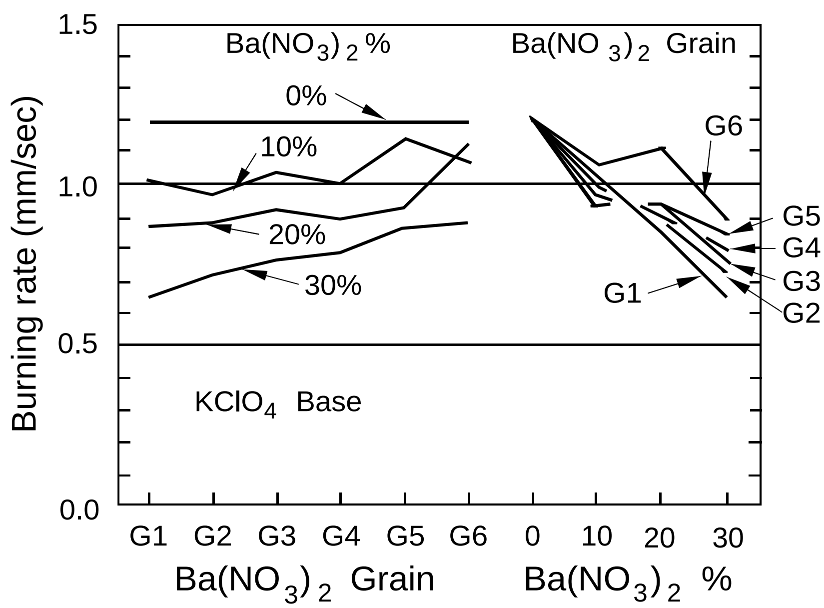

Figure 11. Potassium perchlorate base G66 and barium nitrate, (8).

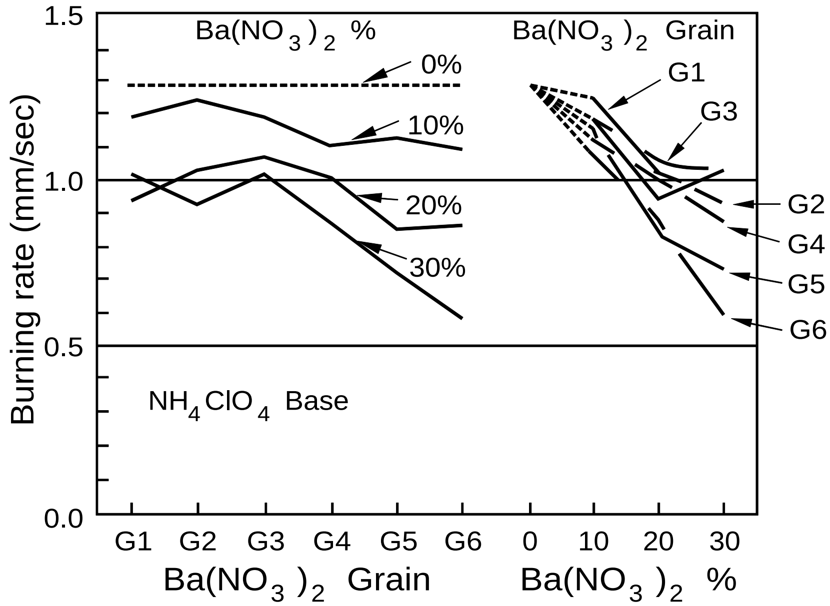

Figure 12. Ammonium perchlorate base G66 and barium nitrate, (9).

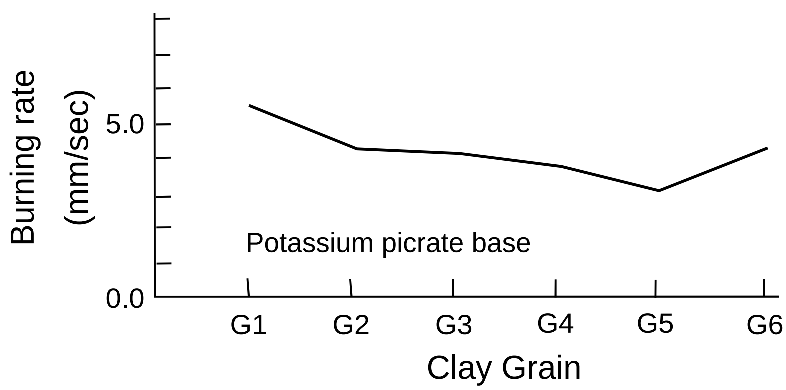

Figure 13. Potassium picrate base and clay, (10).

III. Discussion and Conclusion

(1) The Mixtures of Oxidizer and Fuel, Accroides Resin

This is the most general and fundamental case of burning. With ammonium perchlorate base the mixtures most smoothly burned with steadily increasing the burning rate as the grain size of the oxidizer or fuel decreased (Figure 6 or Matrix (3)). The large grain sizes, G1 or G2, of the fuel had almost no effect on the burning rate. The burning rate with G6 of the fuel was twice as large as that with G1. With the grain sizes of ammonium perchlorate the same effects as those of the fuel were observed.

In the case of potassium chlorate or perchlorate base of the effects were somewhat different from those of the above case. (Figures 4, 5 or Matrices (1), (2)). The fuel grain sizes G1 or G2 gave unstable burning effects as it is seen with the zigzag curves in the right side of Figure 4 or 5 nearly irrespective of grain size of the oxidizer. It should be remembered the mixture which gave the largest burning rate was not G66, but G56.

(2) The Mixtures of the Base Mixture G66 and Inert Material, Clay

The G66 mixture, a mixture of smallest grains of the oxidizer and fuel, was selected due to its highest burning stability to see the effect of the inert material. The clay was selected as the inert material due to its low reactivity when burning with a mixture of no magnesium.

The burning rate generally decreased as the percentage of the inert material increased. There were grain sizes of the inert material, clay, which gave minimum burning rate for each mixture: G2 for the potassium chlorate base, G4 or G5 for the potassium perchlorate base and G4 for the ammonium perchlorate base. Such a tendency very clearly appeared with the chlorate base. (Figures 7–9 or Matrixes (4)–(6))

It should be remembered the burning rate increased as the percentage of the clay increased when the minimum grain size G6 was used, especially with the chlorate base. The burning rate of the mixture, G66-6C30, exceeded that of G66 which contained no clay. Such a positive effect certainly came from the fact that even an inert material takes part in some chemical reaction at high temperatures when its grains are very fine.

(3) The Mixtures of the Base Mixture G66 and Semi-Inert Material, Barium Nitrate

Barium nitrate has an oxidizing power, but is not easily dissociated by heating.

The burning rate of the mixtures of this type decreased as the percentages of the barium nitrate increased. On the other hand, the burning rate increased as the grain size of the barium nitrate decreased with the potassium chlorate or perchlorate base. However, with the ammonium perchlorate base it went reversely, i.e., the rate decreased with decreasing the grain size of the barium nitrate. This was a notable effect of the ammonium perchlorate base. When the grain size of the barium nitrate was 5G or 6G with 20–30% content, a very deep green flame was produced. It might be due to some different burning reaction from others which was caused by the small size grains.

(4) The Mixtures of a Simple Explosive, Potassium Picrate, and an Inert Material, Clay

Ten percentages of the clay decreased the burning rate as the grain size of the clay decreased. However, the rate increased at last with the grain size G6. The smallest grains of the clay gave the highest tone of the whistling sound.

References

1) R. Lancaster, *Fireworks, Principles and Practice*, 2^{nd} ed., 1992, p 43.

2) *ibid*., p 277.