

Study on the Reaction Mechanism of Black Powder and Its Applications

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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.

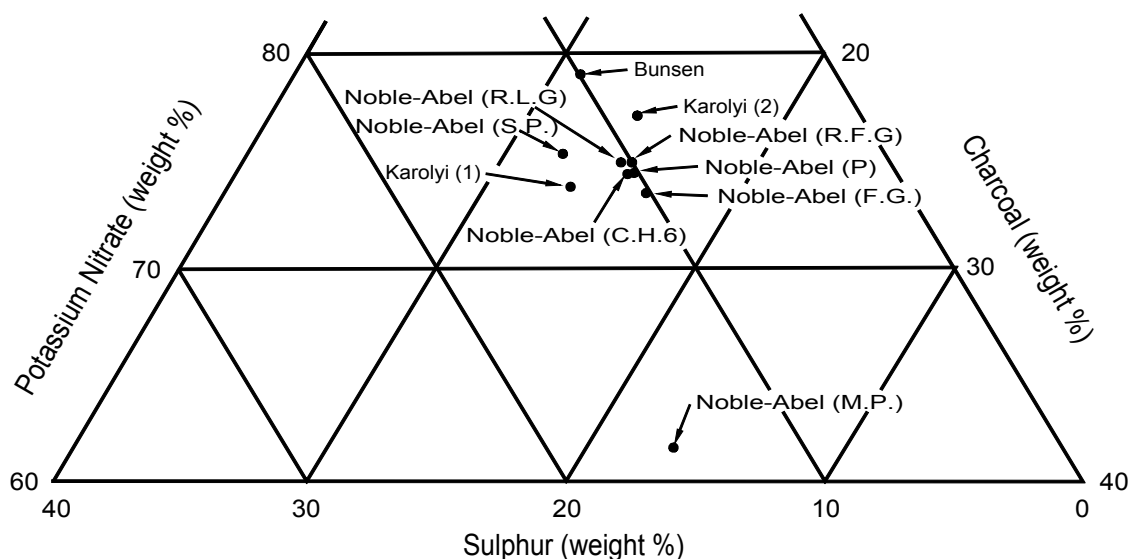


Figure 1. Test powder used by Bunsen, Karolyi and Noble-Abel^[1,2,3].

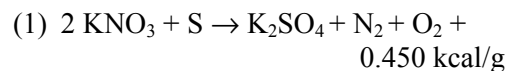
Symbols:

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		

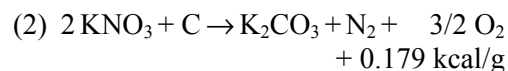
Figure 2 illustrates the results of the testing. The symbols on the curves represent the primary products. There were others, such as $K_2S_2O_3$, $(NH_4)_4H_2(CO_3)_3$ or $KSCN$, but in very small quantities. When the curve for total percentage of ash by weight is compared to the curve for the gases, 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:



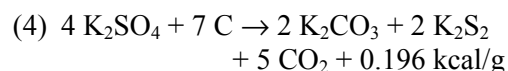
When the sulfur is used up, the charcoal is then oxidized by the potassium nitrate:



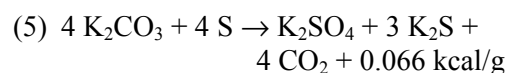
The oxygen from reactions (1) and (2) oxidizes the charcoal:



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



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



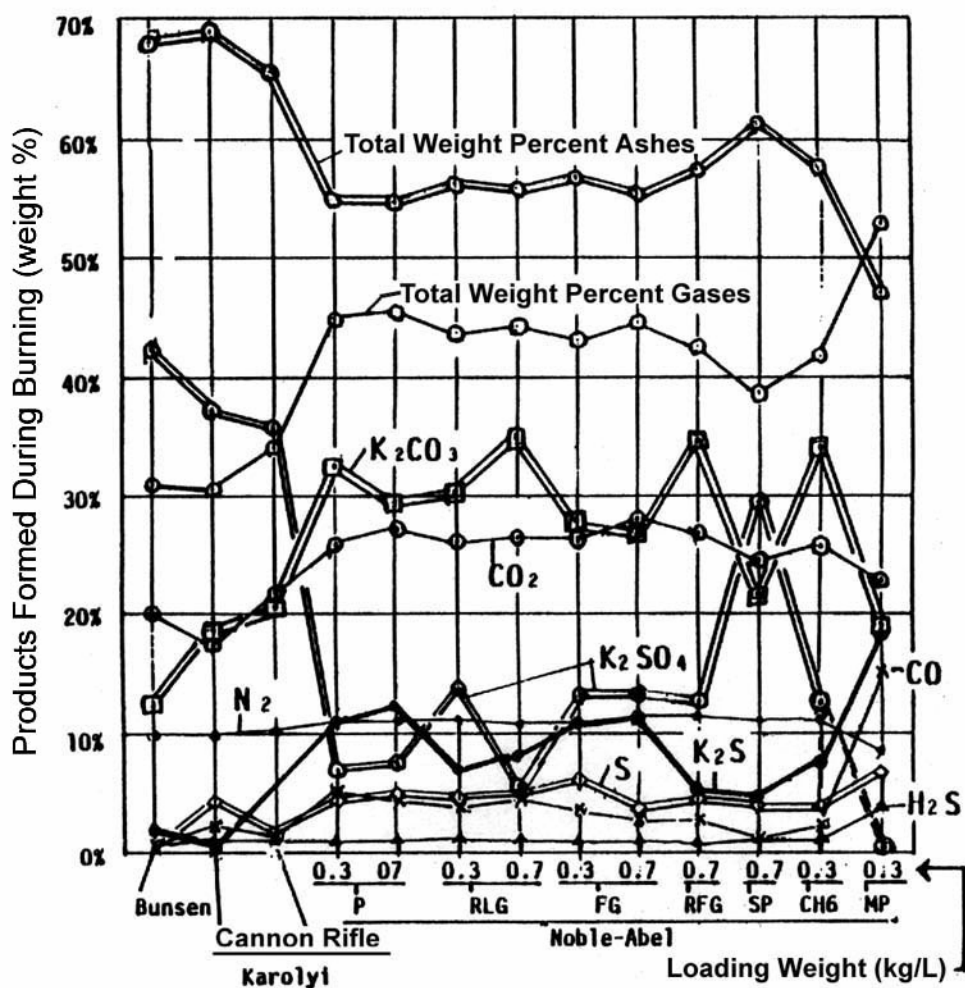
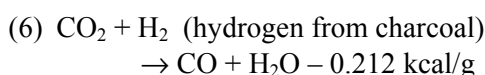
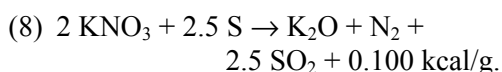
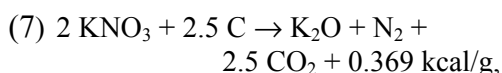


Figure 2. Primary products on burning of the test powder by Bunsen, Karolyi and Noble-Abel.

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.

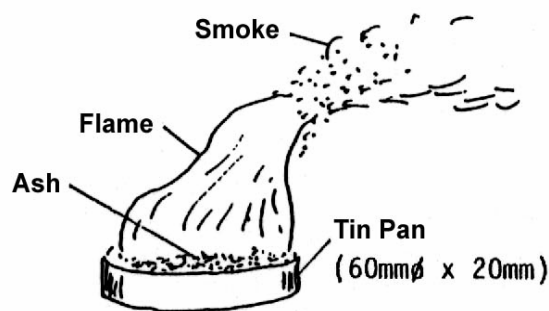


Figure 3. Burning phenomenon of test mixture in air.

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.

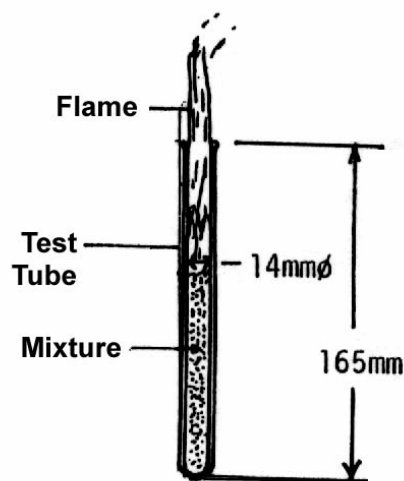


Figure 4. Method for collecting ashes.

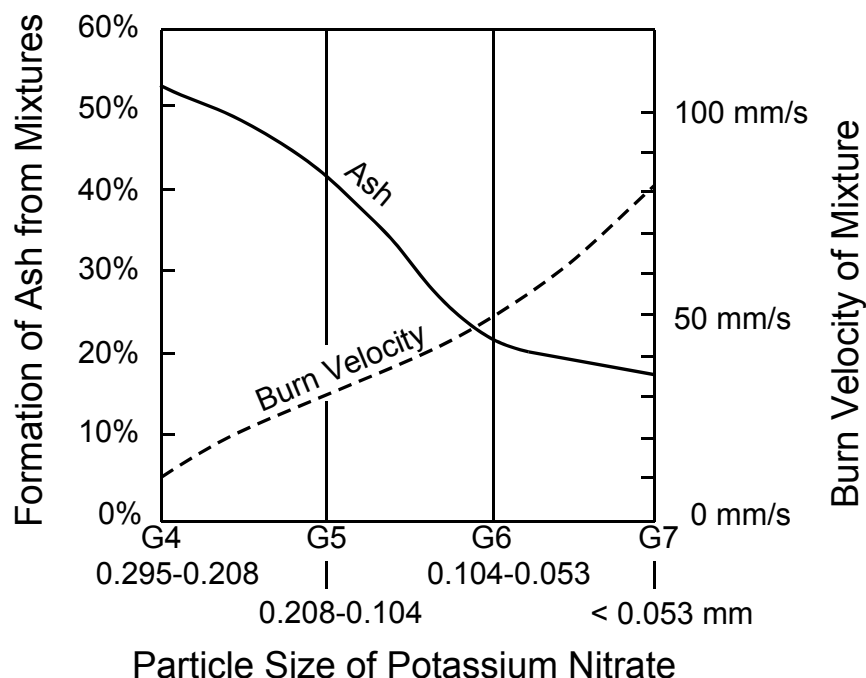


Figure 5. Burn effects with particle sizes of potassium nitrate I: Burn velocity and amount of ash produced.

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

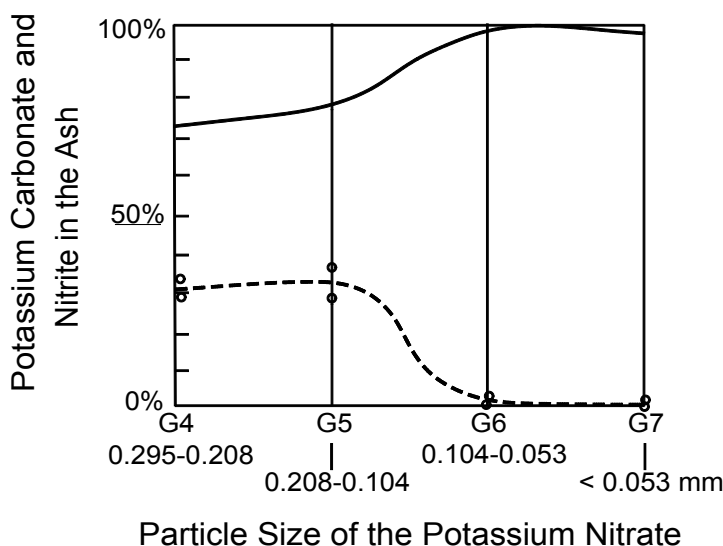


Figure 6. Burn effects with particle sizes of potassium nitrate II: Potassium carbonate and potassium nitrite content in the ash.

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!).

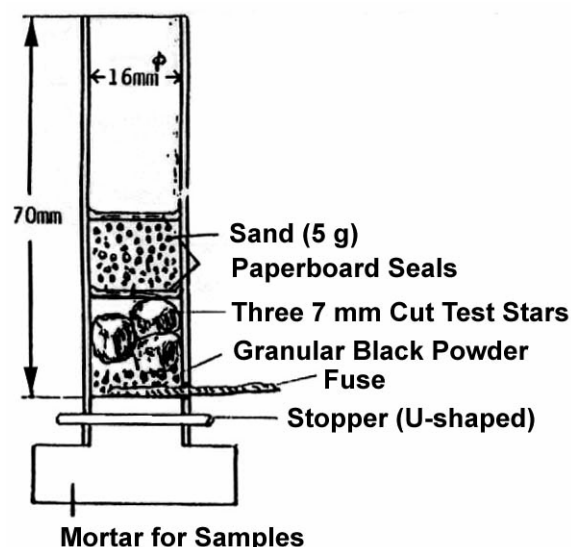


Figure 7. Assembly for ignition tests for test stars.

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.

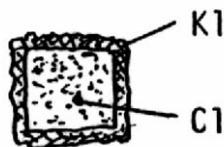


Figure 8. Star C1 coated with a mixture K1.

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	×	1	×
2	3	3	2	2	3	1
3	3	3	2	2	1	1
4	2	3	3	×	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	×	1*	2*
2	1	1	×	3*	3*
3	2	2	×	3*	2*
4	1	2	×	2*	×
5	1	1	×	3*	3
Star C3	Number of Ignitions				
1	1	3	×	3*	1
2	3	2?	1	2*	2
3	3	2?	2	3*	2
4	3	3	×	2*	2
5	3	2	2	1*	2

References

- 1) Pogg. *Annalen*, cii (1857) p 325.
- 2) *Ann. d. Chmie*, cix (1858) p 53 and 325.
- 3) Sir Andrew Noble, *Artillery and Explosives*, London (1906) p 101–384; *Trans. Roy. Soc.* (1875) 1879.
- 4) N. Yamaga and T. Denawa, *Kaheigaku-kaishi* (1940) p 435.
- 5) T. Shimizu, *Feuerwerk* (1976) p 67.