Our Present Knowledge of the Chemistry of Black Powder

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ABSTRACT

Black Powder has been around for centuries and has had a profound influence on the history of the world. Over this time, a considerable amount of knowledge has been gained that not only sheds light on the chemistry of Black Powder but also on other pyrotechnic reactions. This knowledge cannot be considered complete, in spite of all the research that has taken place, and this article attempts to summarize the present understanding about Black Powder's ignition and propagation chemistry.

Keywords: Black Powder chemistry, ignition, propagation, Black Powder research

Introduction

From early times, when Black Powder came to the attention of the alchemists, researchers have wondered and speculated about its explosive power when ignited. Science has indeed come a long way since the mysticism of the alchemists and the phlogiston theory of combustion. Today our understanding of the chemistry of Black Powder's ignition and propagation is far more accurate and precise.

The speculation of bygone ages has been largely replaced with solid knowledge backed by solid data. However, there remain, to this day, areas of our knowledge about Black Powder that are sparse and even virtually non-existent. Having been around for so long, and studied so extensively, many have concluded that current knowledge about its ignition and propagation characteristics is virtually complete. This, however, is not true.

This paper attempts to summarize present knowledge of the chemistry of Black Powder. Specifically it examines the chemistry of ignition and propagation.

Problems Relating to Black Powder Research

Black Powder research has been hampered by several factors. Perhaps one of the most important of these is the waning interest in its use, with Black Powder having been replaced by other more efficient explosives and propellants. Traditionally Black Powder research (with its necessary funding) has been sponsored by the military. With declining military use came a corresponding decline in research, but not a total decline. Black Powder still has certain superior properties to the more powerful smokeless powers that have largely superseded it. For example: in military use, where Black Powder has been superseded by newer propellants, it still finds uses in fuses and as an initiator of other explosive materials. This utilization is largely due to its superior ability to produce a large percentage of hot solids after ignition. These solids are more efficient in igniting other substances than hot gases.

Some might suppose that Black Powder's use as a fuse or an igniter merits less study than its uses as explosives and propellants. This might be true from a fireworks maker's viewpoint but not from a military standpoint. Recent military research has focused on consistency in performance—a goal critical to Black Powder's role in igniting other propellants.

Another factor influencing the gathering of scientific data about Black Powder is its most important characteristic, its explosive power. To meaningfully study Black Powder's ignition and propagation characteristics, one needs to simulate its actual application as closely as possible. This means that the Black Powder usually needs to burn with explosive force. This force, unfortunately, tends to scatter the combustion components, making their collection and detection difficult. This explosive force is also dependent on its unique application. Thus far, less explosive force is generated in the tube of a fireworks mortar than in a barrel of a gun.

Lack of standardization has also hampered research. Different researchers at different times have used different methods of sampling and testing. This has resulted in "comparing apples with pears" scenarios where data has been misapplied and misinterpreted. The literature frequently refers to research that took place many years ago. And while some of this research may be very well documented, its authors and their associates are no longer available to share their insights through personal correspondence. Thus seeking clarification on many of the finer points in their research is very difficult, if not impossible. Again, this can result in "apples and pears" scenarios when recent experimental data is compared with much older data.

The Importance of Black Powder Chemistry

What is there to be gained from studying the chemistry of Black Powder ignition and propagation? To many the answer is—not much. Where their chief concern is having a powder with reasonably predictable explosive characteristics, many conclude that the study of its chemistry contributes little beyond mere academic interest. However, a lot can be gained from studying Black Powder chemistry. Here are a few reasons why such knowledge can be advantageous:

- Toxic gases may be formed when Black Powder ignites.
- Black Powder still does many unpredictable things.
- Black Powder has certain undesirable characteristics.
- Tighter control of variables is needed for critical applications.
- Knowledge of Black Powder contributes to the general pyrotechnics knowledge pool.

Parameters of this Investigation

There are many variables involved in both the production and utilization of Black Powder. Some of these variables may have a marked effect on the resulting chemical reactions when Black Powder is ignited. For the purposes of this discussion, it is assumed that the Black Powder in question has been made by a process that optimizes the incorporation of its ingredients. These ingredients are also assumed to be: potassium nitrate (KNO_3), sulfur (S) and charcoal (C) in the approximate percentages of 75, 10 and 15, respectively. Thus other Black Powder mixes with different ingredient ratios such as those used in gerbs, drivers and rockets are not examined here.

Here and elsewhere in this paper charcoal is represented merely as carbon (C). This convention is used to both simplify some of the discussions and to accurately represent the works of the various authors quoted. Many of these authors treated charcoal as pure carbon, ignoring its smaller percentages of other elements such as hydrogen and oxygen. So charcoal is represented just as carbon where deemed appropriate and as a complex of carbon and other substances where it is helpful to examine charcoal in greater detail.

Although this paper is mainly confined to the above-mentioned definition of Black Powder, it is useful to explore the properties of sulfurless Black Powder and Black Powder that substitutes sodium nitrate ($NaNO_3$) for potassium nitrate. Black Powder mixes that do not use sulfur give a clearer picture of the importance of sulfur in most Black Powder mixes. Sodium salts are similar enough chemically to potassium salts to merit serious study. In practice, sodium nitrate is used in Black Powder made for blasting applications. Thus, both sulfurless Black Powder and sodium nitrate powder form part of this discussion.

Reactions and Combustion Products

In the early 19th century, Guy-Lussac[1] proposed that the gases formed by exploding Black Powder comprised:

Carbon dioxide (CO_2)	52.6%
Carbon monoxide (CO)	5.0%
Nitrogen (N_2)	42.4%

These results were contested by Piobert[1] but the main disagreement appears to relate to gas volumes rather than content. Later research conducted by numerous other researchers shows that these conclusions concerning the types of gases produced were overly simplistic and that many other gaseous products could be formed. Notable is the extensive research done by Noble and Abel.[2] Nevertheless, these later experiments showed that the principle gases produced from exploding Black Powder are carbon dioxide and nitrogen.

Chevreuil[1] conducted experiments with Black Powder exploded in a gun barrel and also burnt in the open air. These experiments can be considered a milestone in our present understanding of Black Powder chemistry, for they showed that quite different results are obtained when Black Powder is ignited under different conditions. Later experiments by Noble and Abel[2] re-affirmed these results.

Chevreuil concluded that Black Powder exploded in the barrel of a gun reacted according to the following equation:

$$2\ KNO_3 + S + 3\ C \rightarrow K_2S + N_2 + 3\ CO_2 \quad (1)$$

Part of Chevreuil's reasoning points to the fact that this formula represents almost exactly the proportions found in Black Powder made with the 75:10:15 ratios. Substituting the atomic masses of KNO_3, S and C into the above formula gives:

KNO_3	74.8%
S	11.9%
C	13.3%

This explanation seems to have gained enough credibility in certain quarters that even more than a century later it was still accepted by some. This author has a chemistry textbook[3] dated 1936 that accepts the above theoretical explanation with the above formula modified only as follows:

$$4\ KNO_3 + S_2 + 6\ C \rightarrow 2\ K_2S + 2\ N_2 + 6\ CO_2 \quad (2)$$

Graham[1] accepted Chevreuil's view, and expanded on it by proposing that potassium sulfide (K_2S) is converted to the sulfate (K_2SO_4) when it is exposed to air.

Slower burning Black Powder, according to Chevreuil, yielded carbon and the following potassium compounds: sulfide, sulfate, carbonate (K_2CO_3), cyanide (KCN), nitrate and nitrite (KNO_2).

In 1857, Bunsen and Schischkoff published a classic paper on Black Powder research.[1,2] This research investigated the nature and proportions of the permanent gases generated when Black Powder explodes and the amount of heat generated by this transformation. From these experimental data, they deduced theoretically the temperature of explosion, the maximum pressure in a closed chamber, and the total theoretical work done on projecting a projectile. It is worth noting that these findings were theoretical in nature, as their experiments did not properly emulate the type of conditions typically found when Black Powder is exploded in a confined space. Their experiments were performed on Black Powder that was deflagrated by being allowed to fall into a heated bulb.[2]

From these observations, they concluded that the permanent gases represented only about 31%, by weight, of the powder and occupied a volume of 193 times that of the original unexploded Black Powder. Table 1 lists their results.[2]

It can be seen from Table 1 that the Black Powder used in this experiment was comprised of a slightly different formula than the commonly used ratio of 75:10:15. Here the approximate ratio is: potassium nitrate 79%, sulfur 10% and charcoal 11%. Also worth noting is their representation of charcoal as a substance comprising not only carbon, but also hydrogen and oxygen.

Berthelot[1] derived the following equation based on Bunsen and Schischkoff's investigations:

$$16\ KNO_3 + 6\ S + 13\ C \rightarrow 5\ K_2SO_4 + 2\ K_2CO_3 + K_2S + 8\ N_2 + 11\ CO_2 \quad (3)$$

Table 1. Results of the Bunsen and Schischkoff Experiments.[2]

Sample Size	Components before Ignition (in grams)		Components after Ignition (in grams)		
			Solids		
1 gram of Black Powder	KNO_3	0.7899	0.6806	K_2CO_3	0.1264
				$K_2S_2O_3$	0.0327
	S	0.0984		K_2SO_4	0.4227
				K_2S	0.0213
	Charcoal			KCNS	0.0030
	C	0.0769		KNO_3	0.0372
	H	0.0041		$(NH_4)_2CO_3$	0.0286
	O	0.0307		S	0.0014
				C	0.0073
			Gases		
			0.3138	H_2S	0.0018
				O	0.0014
				CO	0.0094
				CO_2	0.2012
				H	0.0002
				N	0.0998

He then developed the first theory about the explosion of Black Powder. Here he drew extensively on the experimental work of Bunsen and Schischkoff. Berthelot's theory assumes two limiting cases for the decomposition of Black Powder.

In Berthelot's first case, K_2CO_3 forms the chief product of decomposition and K_2SO_4 is a by-product.

In his second case, K_2SO_4 forms the chief product of decomposition and K_2CO_3 is a by-product.

In the first case, the decomposition proceeds according to the following three equations:

$$2\ KNO_3 + S + 3\ C \rightarrow K_2S + 3\ CO_2 + N_2 \quad (4)$$

$$2\ KNO_3 + S + 3\ C \rightarrow K_2CO_3 + CO_2 + CO + N_2 + S \quad (5)$$

$$2\ KNO_3 + S + 3\ C \rightarrow K_2CO_3 + 1.5\ CO_2 + 0.5\ C + S + N_2 \quad (6)$$

Berthelot further proposed that the above occurred in the ratios of 1/3 for equation 4, 1/2 for equation 5, and the remaining 1/6 for equation 6.

In the second case, the decomposition proceeds according to equations 4 and 6 above plus the following two equations:

$$2\ KNO_3 + S + 3\ C \rightarrow K_2SO_4 + 2\ CO + C + N_2 \quad (7)$$

$$2\ KNO_3 + S + 3\ C \rightarrow K_2SO_4 + CO_2 + 2\ C + N_2 \quad (8)$$

And the above are supposed to occur in the proposed ratios of 1/3 for equation 4, 1/2 for equation 6, 1/8 for equation 7, and the remaining 1/24 for equation 8.

A different conclusion was reached by Debus[1] who concluded that Black Powder burns in a two-stage process. In the first stage, oxidation occurs according to the following exothermic reaction:

$$10\ KNO_3 + 3\ S + 8\ C \rightarrow 2\ K_2CO_3 + 3\ K_2SO_4 + 6\ CO_2 + 5\ N_2 + 979\ \text{kcal}\ (4096\ \text{kJ}) \quad (9)$$

The resulting products are then reduced according to the following endothermic reactions:

$$K_2SO_4 + 2\ C \rightarrow K_2S + 2\ CO_2 + -58\ \text{kcal}\ (-242.7\ \text{kJ}) \quad (10)$$

$$CO_2 + C \rightarrow 2\,CO + -38.4 \text{ kcal } (-160.6 \text{ kJ}) \quad (11)$$

The resulting potassium sulfide may further undergo the following reactions:

$$K_2S + CO_2 + H_2O \rightarrow K_2CO_3 + H_2S \quad (12)$$

$$K_2S + CO_2 + 0.5\,O_2 \rightarrow K_2CO_3 + S \quad (13)$$

A part of the unburned potassium sulfide and sulfur gives K_2S_2.

Much later Kast[1] derived the following equation:

$$74\,KNO_3 + 30\,S + 16\,C_6H_2O \text{ (charcoal)} \rightarrow 56\,CO_2 + 14\,CO + 3\,CH_4 + 2\,H_2S + 4\,H_2 + 35\,N_2 + 19\,K_2CO_3 + 7\,K_2SO_4 + 2\,K_2S + 8\,K_2S_2O_3 + 2\,KCNS + (NH_4)_2CO_3 + C + S + 665 \text{ kcal/kg } (2782 \text{ kJ/kg}) \quad (14)$$

From the foregoing, a somewhat confusing picture emerges concerning the chemical reactions (with resulting products) that occur when Black Powder is ignited. While it is tempting to give more credibility to chemical equations derived by more recent research, due caution should be exercised here. The number of resulting variables, after ignition occurs, precludes chemical equations that will be true under all ignition conditions.

Ignition conditions vary widely in practice from high-pressure ignition that occurs in guns (of both large and small caliber) to lower pressures found in fireworks applications such as mortars, Roman candles and mines. Environmental factors such as temperature and relative humidity might also come into play. Noble and Abel[2] found so many variations in their experiments that they concluded that no value could be attached to a general chemical expression relating to the burning of Black Powder. So there is no "one true formula" for the chemical reaction that occurs when Black Powder is ignited. Thus, any formula presented should be treated as an approximation of what happens when igniting Black Powder.

Another consideration is some variation in the formula used in Black Powder manufacture. While the traditional Waltham Abbey ratio of 75:10:15 can be regarded as a standard, some variations do occur in practice. Propellant powders used by the military and in fireworks usually stick quite closely to the 75:10:15 ratio. (This is illustrated in Tables 2 and 3).

Note that in Table 2 the percentage value of potassium nitrate includes tiny percentages of impurities such as potassium sulfate and potassium chloride.

The data in Tables 2 and 3, gathered approximately a century apart, indicate that the 75:10:15 ratio has been fairly closely adhered to, especially with the more modern powders. This is not only true for Black Powder produced in Britain and the USA, but for Black Powder manufactured elsewhere as well. For example, Shimizu[5] gives an analysis of Japanese Black Powder containing 74.20% potassium nitrate, 9.62% sulfur, and 16.18% charcoal.

However, much variation exists in powders used for blasting. Here, not only do the ratios of

Table 2. Analysis of Black Powders (circa 1875).[2]

Description	Potassium Nitrate (%)	Sulfur (%)	Charcoal (%)	Water (%)
Pebble Powder	74.76	10.07	14.22	0.95
Rifle Large-grain	75.1	10.27	13.52	1.11
Rifle Fine-grain	75.18	9.93	14.09	0.80
Fine-grain	73.91	10.02	14.59	1.48
Spanish Spherical Pebble Powder	75.59	12.42	11.34	0.65
Sporting Powder	77.99	9.84	11.17	—
Austrian Cannon Powder	73.78	12.80	13.39	—
Austrian Small Arms Powder	77.15	8.63	14.27	—
Cannon Powder	74.66	12.49	12.85	—
Russian Powder	74.18	9.89	14.83	1.10

Table 3. Analysis of Black Powders (circa 1975).[4]

Description	Potassium Nitrate (%)	Sulfur (%)	Charcoal (%)	Water (%)	Ash (%)
Du Pont 3814	73.88	9.97	15.71	0.30	0.14
Du Pont 7625	73.59	10.61	14.84	0.82	0.14
CIL 1-Keg-A	73.13	10.83	14.61	0.64	0.79
CIL 1-Keg-B	73.13	10.83	14.61	0.64	0.79
GOE 76-3	74.34	10.25	14.66	0.48	0.27
Du Pont 7846	74.01	9.92	15.01	0.79	0.27
GOE 78-1	74.43	9.95	14.54	0.49	0.58
GOE 78-2	74.45	9.88	14.88	0.20	0.59
CIL 8-2-73	72.92	10.83	14.78	0.65	0.82
CIL 4-23	73.93	10.63	14.05	0.63	0.48

the three principal ingredients differ, but also it is common to find additional ingredients in such powders. Blasting powders also tend to substitute sodium nitrate for potassium nitrate and some use both oxidizers. Substitutes for charcoal are also found in some blasting powder formulas. Tables 4 and 5 show some of these variations.

Further consideration should be given to other variations in manufacture such as the degree of incorporation and the resulting density of the powder. Also, a major factor that often is not given the consideration it deserves, is the type of charcoal used.

Charcoal's Significant Influence

While little variation is found in potassium nitrate of high purity and minimal variation in sulfur, significant differences can be found in the different charcoals used in Black Powder. These differences can be largely attributed to the fact that charcoal is derived from organic

Table 4. Blasting Powder Compositions (Potassium Nitrate Based).[1]

Description	KNO_3 (%)	Sulfur (%)	Charcoal (%)	Ammonium Sulfate and Copper Sulfate (%)
Strong Blasting (French)	75	10	15	
Slow Blasting (French)	40	30	30	
No. 1 Blasting (German and Polish)	73–77	8–15	10–15	
No. 1 Bobbinite (with 2.5–3.5% paraffin) (British)	62–65	1.5–2.5	17–19.5	13–17
No. 2 Bobbinite (with 7–9% starch) (British)	63–66	1.5–2.5	18.5–20.5	

Table 5. Blasting Powder Compositions (Sodium Nitrate Based).[1]

Description	$NaNO_3$ (%)	KNO_3 instead of $NaNO_3$ (%)	Sulfur (%)	Charcoal or substitutes (%)
No. 1 Black Blasting (German)	70–75	up to 25	9–15	10–16
Blasting (American)	70–74	—	11–13	15–17
No. 3 Black Blasting (Petrolastite or Haloclastite)	71–76	up to 5	9–11	15–19 of coal-tar pitch
No. 2 Black Blasting	70–75	up to 5	9–15	10–16 of lignite

Table 6. The Effect of Carbonization Temperature on Charcoal's Chemical Composition.[1]

Carbonization Temperature (ºC)	Charcoal Color	Yield (%)	Composition of Charcoal (%)		
			C	H	O + N
280–300	brown	34	73.2	4.3	21.9
350–400	black	28–31	77–81		
1000	black	18	82.0	2.3	14.1
1250	black	18	88.1	1.4	9.3

matter, this matter being either animal or vegetable in origin. Black Powder appears to have been made exclusively with vegetable charcoal. Any possible experiments with animal charcoal are not on record, at least not in any prominent literature in the English language. And even if it could be proven that certain animal charcoals exhibited superior properties, cost and other practical considerations would preclude their use in Black Powder.

The two most influential variables in charcoal are:

- The type of material from which the charcoal is derived.
- The method used to make the charcoal.

Charcoal Varieties

Given the abundant variety of vegetable matter in existence, the potential exists to create an endless variety of charcoals. In practice, Black Powder manufacturers have focused on materials that were readily available and suitable for Black Powder manufacture. Typically, softer woods such as willow, poplar and alder have been used. Specifically the "white wood" from such sources is preferred.[1]

In willow trees alone, many different species exist throughout the world. Even within the same species of willow, variations in its wood exist due to such factors as weather, soil conditions, the age of the tree, and the part of the tree from which the wood is taken.

Research on maple charcoal has also indicated that differences in charcoal properties can exist even within batches of charcoal obtained from the same supplier.[6]

Charcoal Manufacture

Different methods of charcoal manufacture can impart different properties to the charcoal. Even variations in the same method can yield different results. For example, charcoals produced at lower temperatures retain meaningful percentages of volatiles. Higher temperatures drive these volatiles out of the charcoal. Excessively high temperatures can cause the charcoal to transition into graphite.

For centuries, charcoal used in Black Powder was made using traditional methods such as igniting a large pile of wood and then covering it with earth to exclude oxygen from the air. Typically, a kiln was used, consisting of a pile of wood covered with earth or other material. Modern variations use metal covers and are more efficient.[7] But these are still not optimal for charcoal used in Black Powder. At the end of the 18th century, an Englishman, Richard Watson, invented a new method that revolutionized charcoal manufacture.[8] This method used metal cylinders that were filled with wood and sealed prior to heating. Ballistic tests on Black Powder made with this charcoal showed an increase in range of about 60%.

Temperature Considerations

The temperature at which charcoal is made has a very large influence on the temperature at which it burns. This property of charcoal was explored by Violette in 1848.[1,8] Violette prepared charcoals in a retort, using different types of wood, and subjecting the woods to different temperatures of carbonization. Violette's work was a milestone in research on the properties of charcoal. Some of his findings are reflected in Tables 6 and 7.

Table 7. The Relationship between Carbonization Temperatures and Ignition Temperatures.[1]

Carbonization Temperature (ºC)	Ignition Temperature (ºC)
260–280	340–360
290–350	360–370
432	400 (approx.)
1000–1500	600–800

Thus, Black Powder made with charcoal carbonized at lower temperatures will ignite at lower temperatures, and it burns at lower temperatures. This could be advantageous or disadvantageous, depending on the application. Typically, blasting powders are designed to burn at lower temperatures. Highly carbonized charcoal tends to absorb moisture less readily than less carbonized charcoal. Thus, certain tradeoffs exist in charcoal made for Black Powder manufacture, and thus it is wrong to describe any charcoal as ideal.

Volatiles

Volatiles in charcoal noticeably affect the burn rate of Black Powder. Generally, it is desirable to use such charcoal rather than charcoal where the volatiles have been driven out. Sassé[6] determined that a 25% volatile content was about the optimal amount for Black Powder use. This figure came from his own research, which correlated with research done by others who are referenced in his paper.[6]

Charcoal Variations

The many variations in charcoal have influenced research by the US military. Notable is the research done by Rose[9] at the Naval Ordnance Station at Indian Head, Maryland and by Sassé at the US Army Ballistic Research Laboratory, Aberdeen Proving Ground, Maryland. Both research projects aimed at producing more uniform powders by establishing more exacting standards for charcoal. Rose's research compared charcoal made from different species of trees, while Sassé[6] focused on maple charcoal. Even within the narrower confines of Sassé's research, notable variations in properties were found between charcoal samples. One example is the variation in volatile content of between 21 and 29%. Sassé concluded that the properties could vary even between different samples in the same lot obtained from a single supplier. He suggests that these variations are due to variations in the wood used and differences in temperature in different parts of the kiln. His proposed solution to this problem is to preblend such charcoal to obtain a more predictable Black Powder.

Chemical Analysis

Charcoal should never be regarded as pure carbon, but rather as an organic hydrocarbon compound. Just as there is no one true equation for Black Powder's chemical reaction, there is no one true formula for charcoal. Again, some authors of textbooks and technical papers have erred here. The formula for charcoal depends on which charcoal it is meant to represent. Often this representation is approximate and not exact. Table 8 shows that even charcoal obtained from the same type of wood may have variations in chemical content.

The data in Table 8 is extracted from experiments conducted by Sassé[6] in trying to determine the characteristics of maple charcoal. These data demonstrate that noticeable differences in chemical composition are to be found in charcoal made with the same type of wood.

Table 8. Chemical Characteristics of Roseville Maple Charcoal.[6]

Sample	O_2 (%)	C (%)	H_2 (%)	N_2 (%)	S (%)	Ash (%)
1	12.71	78.40	3.26	0.44	0.68	5.11
2	13.10	78.40	3.24	0.35	0.01	4.90
3	14.20	75.83	3.15	0.35	0.02	6.45
4	14.14	75.41	3.24	0.34	0.02	6.85
5	16.03	76.87	3.49	0.32	0.01	3.30

These values, however, are close to the empirical formula of C_8H_4O. Sassé[10] also refers in a later paper to other empirical formulas for charcoal:

- $C_{14.57}H_{7.17}O_{1.00}$
- $C_{8.68}H_{4.96}O_{2.00}$

Charcoal Substitutes

Charcoal substitutes have been investigated by researchers seeking Black Powder with characteristics that are more predictable. Notable is the research conducted by Wise, Sassé and Holmes,[11] which was followed by research done by Weber.[12] Many different crystalline organic compounds were tested by Wise, et al., who concluded that some of these compounds showed promise as viable alternatives for charcoal. Their research, however, did not exhaustively test the properties of the powders produced, and they concluded that such tests were necessary before claims of a viable charcoal substitute could be considered conclusive.

Weber focused on a process that used phenolphthalein as a charcoal substitute, with promising results. His findings, however, were not subjected to all the test criteria outlined by Wise, et al.[11]

None of these findings has resulted in a large-scale commercially viable production process. Possibly the cost of alternate substances such as phenolphthalein is in itself prohibitive. However, there may be niche applications of these alternate formulations where cost and large-scale manufacture are not major factors.

The foregoing discussion focused on the resulting products produced when Black Powder is ignited and its ignition allowed to go to completion. While some of this discussion has involved intermediate reactions in the combustion process, it has not attempted to explain the ignition process itself (i.e., what happens when heat of sufficient intensity is applied to the powder, causing it to ignite).

The Ignition Process

The following discussion examines the ignition process itself.

Principal in importance in Black Powder ignition is its oxidizer, potassium nitrate. Here, as with other oxidizers, potassium nitrate supplies oxygen to the reaction. This oxygen, if supplied with sufficient heat, causes the two other components to burn. Given the right combination of the ratios of the ingredients and an efficient method of manufacture, the resulting Black Powder will burn very rapidly. This rapid burning makes it useful as an explosive or propellant.

While the potassium nitrate supplies most of the oxygen to the reaction, a small percentage of oxygen is contributed by the charcoal and also possibly by the atmosphere. Charcoal itself contains oxygen atoms in its chemical composition and may contain absorbed oxygen and other atmospheric gases.

Ignition Phases

Although Black Powder ignites very rapidly, its ignition can be separated into several distinct phases. The most important phase is the decomposition of the potassium nitrate, which is preceded by a pre-ignition phase. This decomposition of the potassium nitrate is essential for it to yield its important oxygen component to the process. The decomposition starts with the melting of the potassium nitrate.

Potassium nitrate melts at 334 °C. Its counterpart, sodium nitrate, used in various blasting powders, melts at 307 °C. This suggests that sodium nitrate powders ignite at lower temperatures, which indeed they do. Interestingly, a eutectic mixture of potassium nitrate and sodium nitrate melts at 220 °C.[1]

Experiments performed by Hoffmann[1] have shown, however, that the Black Powder ignition process begins at a much lower temperature. This is due to the influences of the charcoal and sulfur. An important factor here is the melting point of sulfur, which is about 115 °C. Thus at about 150 °C, molten sulfur reacts with hydrogen to form hydrogen sulfide (H_2S). This H_2S then reacts with the KNO_3 to form potassium sulfate (K_2SO_4). This reaction generates heat, causing the KNO_3 to melt. This process is often referred to as the pre-ignition process.

Sulfur's Importance

The importance of sulfur has been demonstrated in experiments performed by Hoffmann.[1] These experiments showed that sulfur did the following:

- Facilitated an increase in the quantity of gases evolved on explosion
- Reduced initial decomposition temperature and temperature at which explosion occurred
- Intensified the sensitiveness of mixtures to impact
- Counteracted the formation of carbon monoxide

The above conclusions were drawn in part from some of Hoffmann's following experimental data:

- Potassium nitrate ignited with carbon produces only K_2CO_3, but in the presence of sulfur produces CO_2, K_2SO_4 and K_2S. Thus, more gases are created by exploding Black Powder that contains sulfur than Black Powder that does not.
- A mixture of two moles of KNO_3 and three moles of carbon (charcoal with a 71% carbon content) begins to decompose at 320 °C and explodes at 357 °C, while a mixture of two moles of KNO_3 and one mole of sulfur begins to decompose at 310 °C and explodes at 450 °C. A mixture of KNO_3 with both sulfur and charcoal yields both lower decomposition and explosive temperatures as shown in an experiment where a mixture of two moles of KNO_3, one mole of sulfur and three moles of carbon begins to decompose at 290 °C and explodes at 311 °C. This latter experiment is very significant in that it shows that sulfur does not only reduce decomposition and explosion temperatures, but it greatly narrows the gap between initial decomposition and explosion temperatures.
- Sulfur increases the sensitiveness of Black Powder mixes to impact while carbon (charcoal) reduces it. This is shown by the following experimental data. A 2 kg mass dropped from 45–50 cm caused a mixture of KNO_3 and sulfur to explode while a mixture of KNO_3 and charcoal was unaffected. A mixture of KNO_3 with both sulfur and charcoal exploded when a 2 kg mass was dropped on it from a height of 70–85 cm.

Hoffmann[1] also concluded that sulfur counteracts the formation of carbon monoxide when Black Powder explodes and also has an impact on the amount of potassium cyanide (KCN) gas produced. This is because the addition of sulfur causes K_2SO_4 to be formed in addition to K_2CO_3. Thus, the amount of potential K_2CO_3 is reduced. The formation of K_2CO_3 causes both carbon monoxide and potassium cyanide to be formed as follows:

$$K_2CO_3 + 2\,C \rightarrow 2\,K + 3\,CO \qquad (15)$$

$$2\,K + 2\,C + N_2 \rightarrow 2\,KCN \qquad (16)$$

The decomposition of K_2SO_4 does not result in either carbon monoxide or potassium cyanide gases forming, as shown in the following equation:

$$K_2SO_4 + 2\,C \rightarrow K_2S + 2\,CO_2 \qquad (17)$$

The importance of sulfur in Black Powder is further emphasized by experiments in trying to find a substitute for charcoal. Such experiments were conducted by Wise, et al.[11] Their research demonstrated that sulfur has a profound effect on combustion when phenolic materials were used as charcoal substitutes. However, their experiments did reveal opposing trends when different types of phenolic materials were used. For example, quinizarin and anthraflavic acid both produced more rapid burning powders with the absence of sulfur. Other polyphenols exhibited the opposite trend but to a lesser degree. These data challenged the perceived importance of the sulfur being reduced by organic compounds and strengthened the hypothesis that the influence of sulfur is more marked in its role in the flame-spread rate after ignition occurs. Wise, et al. concluded that this hypothesis needs to be explored further using both charcoal and charcoal-substitute mixes.

Sulfurless Black Powder

No discussion about the role of sulfur in Black Powder would be complete without examining useable Black Powder that does not contain any sulfur. Here the term "useable" denotes Black Powder that performs adequately as an explosive, propellant or igniter. Probably the most famous type of sulfurless Black Powder was the so-called "Cocoa" powder, which used incompletely carbonized charcoal.[1] This charcoal, known as "Cocoa" or "Red" charcoal, was typically manufactured at a temperature of 140–175 °C. It had a carbon content of 52–54%, which is much lower than other charcoals used in Black Powder. Its major drawback was its sensitivity to friction, which easily ignited it.

A stoichiometric mixture of sulfurless Black Powder comprises 87.1% potassium nitrate and 12.9% charcoal. The decomposition occurring after ignition can be represented theoretically as follows:

$$4\,KNO_3 + 5\,C \rightarrow 2\,K_2CO_3 + 2\,N_2 + 3\,CO_2 \quad (18)$$

In practice, sulfurless Black Powder mixtures are generally not used for propellants, but rather as igniters. These have a potassium nitrate content of between 70–80% and a charcoal content of between 20–30%. Some "sulfurless" powders actually do contain a small percentage (about 2%) of sulfur, which is far below the normal percentage.

Binary Mixtures

Blackwood and Bowden[1] made extensive studies on the ignition of Black Powder and also on the following binary mixes:

- potassium nitrate + sulfur
- sulfur + charcoal
- potassium nitrate + charcoal

Amongst their findings, they concluded that ignition could take place as low as 130 ºC, depending upon the pressure to which the Black Powder was subjected. They also confirmed the importance of having charcoal with the right constituents. In their opinion, it was advantageous to remove the constituents that could be dissolved with organic solvents. This, they said, made ignition easier and gave a faster burn rate.

Blackwood and Bowden formulated the mechanism for Black Powder's ignition and subsequent burning reactions. Accordingly, sulfur reacts first with the organic substances in the charcoal:

$$S + \text{organic compounds} \rightarrow H_2S \quad (19)$$

Potassium nitrate reacts almost simultaneously with these organic compounds:

$$KNO_3 + \text{organic compounds} \rightarrow NO_2 \quad (20)$$

The following reactions may also occur:

$$2\,KNO_3 + S \rightarrow K_2SO_4 + 2\,NO \quad (21)$$

$$KNO_3 + 2\,NO \rightarrow KNO_2 + NO + NO_2 \quad (22)$$

$$H_2S + NO_2 \rightarrow H_2O + S + NO \quad (23)$$

This last reaction proceeds until all the H_2S is consumed. The remaining NO_2 then reacts with the unconsumed sulfur according to the following reaction:

$$2\,NO_2 + 2\,S \rightarrow 2\,SO_2 + N_2 \quad (24)$$

The SO_2 formed in the above reaction may then immediately react with the KNO_3 as follows:

$$2\,KNO_3 + SO_2 \rightarrow K_2SO_4 + 2\,NO_2 \quad (25)$$

Reactions 23 and 24 are endothermic while reaction 25 is strongly exothermic. Reactions 19 to 25 constitute the ignition process.

Blackwood and Bowden concluded that the chief reaction is the oxidation of charcoal by the potassium nitrate. This is when the Black Powder starts to burn.

Flame Spread Rates

The flame-spread rate of Black Powder is firstly dependent on the solid salts produced after ignition has commenced. These tiny hot pieces of solid matter are driven into the surrounding Black Powder, causing it to ignite and the flame to spread until all the powder is consumed. While the production of solid hot particles produced by different chemical reactions is an important factor in Black Powder's flame spread characteristics, other physical attributes are also important.

Many processes have been tried over the centuries to improve and control the flame-spread attributes of Black Powder. Essential to these attributes is the process of granulation or corning where the Black Powder is formed into solid grains. Recent research on the influence of physical properties on the burn rate has been done by Sassé[13] and also by White and Horst.[14] Sassé's research showed flame spread to be dependent on density, surface area and free volume. White and Horst found that grain position and the ability of grains to move was important.

Thus, the flame-spread rate of any sample of Black Powder is dependent both on the chemical reactions that take place and on the physical attributes of the powder grains.

The Influence of Moisture

Most Black Powder contains some moisture, and this property does have an effect on the powder's ignition and explosive properties. Nearly every Black Powder manufacturing process uses water, some of which remains in the powder. Black Powder may also absorb moisture from the atmosphere. There remains a certain amount of controversy as to whether a certain small percentage of moisture aids ignition. The author's own observations indicate that it might. Some have made similar claims that have been refuted by other authorities. Shimizu[5] refers to an optimal moisture content of about 1%, but this statement in itself appears based more on hearsay rather than empirical evidence from experimentation.

Where there is agreement, is the fact that moisture does have an effect and that variations in moisture content do produce variations in ignition. So, where uniformity in performance is critical, the challenge is to find a range of moisture content where performance can be regarded as sufficiently uniform and then, to control this moisture range.

One suggested range is 0.3 to 0.5%.[15] Here the challenge is to keep the moisture level above 0.3% while not allowing it to exceed 0.5%. This is far more difficult to achieve than merely aiming at a specified upper moisture limit.

The Effect of Aging

Another area of controversy is the effect of aging on Black Powder. Black Powder has shown itself to be far less susceptible to aging than many other explosives, but the question is: Does it actually (like a good wine) improve with age? And if it does improve with age, under what conditions? And why does it improve with age? One possibility is that the charcoal in the Black Powder absorbs oxygen from the atmosphere over a period of time. Some tests have, however, been done on aging Black Powder. Notable among these are the tests performed by Kosanke and Ryan[16] on US Civil War vintage Black Powder (ca. 1865). These tests showed that such powder performed very well in spite of its age.

The question of aging is a difficult one to answer as the aging process itself, by its very nature, takes a long time. A proper objective test would be to determine the properties of a batch (or batches) of Black Powder and then perform the same tests after an aging period. Practically speaking, this would be difficult to achieve.

Conclusion

Over several centuries, a considerable amount of knowledge has been gained concerning the chemistry of Black Powder. Some of this knowledge comes from extensive research done under tightly controlled laboratory conditions and supplemented with field research in practical applications. But there is still a lot that is not known. And there is still a lot to be gained from further research and experimentation.

A big challenge still is in achieving consistency in performance. Even with modernized, tightly controlled manufacturing techniques, there is still one major variable in the equation—charcoal. Perhaps one day a viable alternative to charcoal will be found, or a method to produce charcoal with very tightly controlled specifications.

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