

CHAPTER II

BLACK POWDER

The discovery that a mixture of potassium nitrate, charcoal, and sulfur is capable of doing useful mechanical work is one of the most important chemical discoveries or inventions of all time. It is to be classed with the discovery or invention of pottery, which occurred before the remote beginning of history, and with that of the fixation of nitrogen by reason of which the ecology of the human race will be different in the future from what it has been throughout the time that is past. Three great discoveries signaled the break-up of the Middle Ages: the discovery of America, which made available new foods and drugs, new natural resources, and new land in which people might multiply, prosper, and develop new cultures; the discovery of printing, which made possible the rapid and cheap diffusion of knowledge; and the discovery of the controllable force of gunpowder, which made huge engineering achievements possible, gave access to coal and to minerals within the earth, and brought on directly, the age of iron and steel and with it the era of machines and of rapid transportation and communication. It is difficult to judge which of these three inventions has made the greatest difference to mankind.

Black powder and similar mixtures were used in incendiary compositions, and in pyrotechnic devices for amusement and for war, long before there was any thought of applying their energy usefully for the production of mechanical work. The invention of guns—and it seems to be this invention which is meant when “the discovery of gunpowder” is mentioned—did not follow immediately upon the discovery of the composition of black powder. It is possible that other applications antedated it, that black powder was used in petards for blowing down gateways, drawbridges, etc., or in simple operations of blasting, before it was used for its ballistic effect.

Berthold Schwarz

The tradition that the composition of black powder was discovered and that guns were invented about 1250 (or 1350 or even later) by Berthold Schwarz, a monk of Freiburg i. Br., in Germany, is perpetuated by a monument at that place. Constantin Anklitzen assumed the name of Berthold when he joined the Franciscan order, and was known by his confreres as *der schwarzer Berthold* because of his interest in black magic. The records of the Franciscan chapter in Freiburg were destroyed or scattered before the Reformation, and there are no contemporaneous accounts of the alleged discovery. Concerning the absence of documents, Oesper¹ says:

If he is a purely legendary inventor the answer is obvious. However, history may have taken no interest in his doings because guns were said to be execrable inventions and their employment (except against the unbelievers) was decried as destructive of manly valor and unworthy of an honorable warrior. Berthold was reputed to have compounded powder with Satan's blessing, and the clergy preached that as a co-worker of the Evil One he was a renegade to his profession and his name should be forgotten. There is a tradition that he was imprisoned by his fellow monks, and some say he made his diabolic invention while in prison. According to another legend, Berthold blew himself up while demonstrating the power of his discovery; another states that he was executed.

The lovers of fine points may argue over Berthold's existence, but it can be historically established that Freiburg in the fourteenth and fifteenth centuries was a flourishing center for the casting of cannon and the training of gunners.

Boerhaave on Black Powder

Although black powder has done immeasurable good through its civil uses, it has nevertheless been regarded as an evil discovery because of the easy and unsportsmanlike means which it provides for the destruction of life. Boerhaave, more than two centuries ago, wrote in the modern spirit on the importance of chemistry in war and condemned black powder² in a manner

¹ Oesper, *J. Chem. Education*, 16, 305-306 (1939).

² Boerhaave, "A New Method of Chemistry," etc., trans. Peter Shaw, London, 1753, Vol. I, pp. 189-191. The quoted passage corresponds to the Latin of Vol. I, pp. 99-101, of the first edition of Boerhaave's "Elementa Chemicæ," Leiden, 1732.

similar to that in which some of our latest devices of warfare have been decried in public print.

It were indeed to be wish'd that our art had been less ingenious, in contriving means destructive to mankind; we mean those instruments of war, which were unknown to the ancients, and have made such havoc among the moderns. But as men have always been bent on seeking each other's destruction by continual wars; and as force, when brought against us, can only be repelled by force; the chief support of war, must, after money, be now sought in chemistry.

Roger Bacon, as early as the twelfth century,³ had found out gunpowder, wherewith he imitated thunder and lightning; but that age was so happy as not to apply so extraordinary a discovery to the destruction of mankind. But two ages afterwards, *Barthol. Schwartz*,⁴ a German monk and chemist, happening by some accident to discover a prodigious power of expanding in some of this powder which he had made for medicinal uses, he apply'd it first in an iron barrel, and soon after to the military art, and taught it to the *Venetians*. The effect is, that the art of war has since that time turned entirely on this one chemical invention; so that the feeble boy may now kill the stoutest hero: Nor is there anything, how vast and solid soever, can withstand it. By a thorough acquaintance with the power of this powder, that intelligent *Dutch General Cohorn* quite alter'd the whole art of fighting; making such changes in the manner of fortification, that places formerly held impregnable, now want defenders. In effect, the power of gun-powder is still more to be fear'd. I tremble to mention the stupendous force of another

³ Bacon lived in the thirteenth century; we quote the passage as it is printed.

⁴ Shaw's footnote (*op. cit.*, p. 190) states:

What evidently shews the ordinary account of its invention false, is, that *Schwartz* is held to have first taught it to the *Venetians* in the year 1380; and that they first used it in the war against the *Genoese*, in a place antiently called *Fossa Caudeana*, now *Chioggia*. For we find mention of fire arms much earlier: *Peter Messius*, in his *variae lectiones*, relates that *Alphonsus XI.* king of Castile used mortars against the *Moors*, in a siege in 1348; and *Don Pedro*, bishop of *Leon*, in his chronicle, mentions the same to have been used above four hundred years ago, by the people of *Tunis*, in a sea fight against the *Moorish* king of *Sevil*. *Du Cange* adds, that there is mention made of this powder in the registers of the chambers of accounts in *France*, as early as the year 1338.

powder, prepar'd of sulfur, nitre, and burnt lees of wine;⁵ to say nothing of the well-known power of *aurum fulminans*. Some person taking a quantity of fragrant oil, chemically procured from spices, and mixing it with a liquor procured from salt-petre, discover'd a thing far more powerful than gun-powder itself; and which spontaneously kindles and

⁵This is *fulminating powder*, made, according to Ure's "Dictionary of Chemistry," first American edition, Philadelphia, 1821:

by triturating in a warm mortar, three parts by weight of nitre, two of carbonate of potash, and one of flowers of sulfur. Its effects, when fused in a ladle, and then set on fire, are very great. The whole of the melted fluid explodes with an intolerable noise, and the ladle is commonly disfigured, as if it had received a strong blow downwards.

Samuel Guthrie, Jr. (cf. *Archeion*, 13, 11 ff. [1931]), manufactured and sold in this country large quantities of a similar material. In a letter to Benjamin Silliman dated September 12, 1831 (*Am. J. Sci. Arts*, 21, 288 ff. [1832]), he says:

I send you two small phials of nitrated sulphuret of potash, or yellow powder, as it is usually called in this country. . . . I have made some hundred pounds of it, which were eagerly bought up by hunters and sportsmen for *priming* fire arms, a purpose which it answered most admirably; and, but for the happy introduction of powder for priming, which is ignited by percussion, it would long since have gone into extensive use.

With this preparation I have had much to do, and I doubt whether, in the whole circle of experimental philosophy, many cases can be found involving dangers more appalling, or more difficult to be overcome, than melting fulminating powder and saving the product, and reducing the process to a business operation. I have had with it some eight or ten tremendous explosions, and in one of them I received, full in my face and eyes, the flame of a quarter of a pound of the composition, just as it had become thoroughly melted.

The common proportions of 3 parts of nitre, 2 parts of carbonate of potash and 1 part of sulphur, gave a powder three times quicker than common black powder; but, by *melting together* 2 parts of nitre and 1 of carbonate of potash, and when the mass was cold adding to 4½ parts of it, 1 part of sulphur—equal in the 100, to 54.54 dry nitre, 27.27 dry carbonate of potash and 18.19 sulphur—a greatly superior composition was produced, burning no less than eight and one half times quicker than the best common powder. The substances were intimately ground together, and then melted to a *waxy* consistence, upon an iron plate of one inch in thickness, heated over a muffled furnace, taking care to knead the mass assiduously, and remove the plate as often as the bottom of the mass became pretty slippery.

By the previously melting together of the nitre and carbonate of potash, a more intimate union of these substances was effected than could possibly be made by mechanical means, or by the slight melting which was admissible in the after process; and by the slight melting of the whole upon a *thick* iron plate, I was able to conduct the business with facility and safety.

The melted mass, after being cold, is as hard and porous as pumice stone, and is grained with difficulty; but there is a stage when it is cooling in which it is very crumbly, and it should then be powdered upon a board, with a small wooden cylinder, and put up hot, without sorting the grains or even sifting out the flour.

burns with great fierceness, without any application of fire.⁶ I shall but just mention a fatal event which lately happen'd in *Germany*, from an experiment made with balsam of sulphur terebinthinated, and confined in a close chemical vessel, and thus exploded by fire; God grant that mortal men may not be so ingenious at their own cost, as to pervert a profitable science any longer to such horrible uses. For this reason I forbear to mention several other matters far more horrible and destructive, than any of those above rehearsed.

Greek Fire

Fire and the sword have been associated with each other from earliest times. The invention of Greek fire appears to have consisted of the addition of saltpeter to the combustible mixtures already in use, and Greek fire is thus seen as the direct ancestor both of black gunpowder and of pyrotechnic compositions.

The Byzantine historian, Theophanes the Confessor, narrates that "Constantine [Constantine IV, surnamed Pogonatus, the Bearded], being apprised of the designs of the unbelievers against Constantinople, commanded large boats equipped with cauldrons of fire (tubs or vats of fire) and fast-sailing galleys equipped with siphons." The narrative refers to events which occurred in the year 670, or possibly 672. It says for the next year: "At this time Kallinikos, an architect (engineer) from Heliopolis of Syria, came to the Byzantines and having prepared a sea fire (or marine fire) set fire to the boats of the Arabs, and burned these with their men aboard, and in this manner the Byzantines were victorious and found (discovered) the marine fire."⁷ The Moslem fleet was destroyed at Cyzicus by the use of this fire which for several centuries afterwards continued to bring victory to the Byzantines in their naval battles with the Moslems and Russians.

Leo's *Tactica*, written about A.D. 900 for the generals of the empire, tells something of the manner in which the Greek fire was to be used in combat.

⁶ Shaw's footnote (*op. cit.*, p. 191): "A drachm of compound spirit of nitre being poured on half a drachm of oil of carraway seeds *in vacuo*; the mixture immediately made a flash like gun-powder, and burst the exhausted receiver, which was a glass six inches wide, and eight inches deep."

⁷ Quoted by N. D. Cheronis, article entitled "Chemical Warfare in the Middle Ages. Kallinikos's Prepared Fire," *J. Chem. Education*, **14**, 360 (1937).

And of the last two oarsmen in the bow, let the one be the *siphonator*, and the other to cast the anchor into the sea. . . . In any case, let him have in the bow the *siphon* covered with copper, as usual, by means of which he shall shoot the *prepared fire* upon the enemy. And above such siphon (let there be) a false bottom of planks also surrounded by boards, in which the warriors shall stand to meet the on-coming foes. . . . On occasion [let there be] formations immediately to the front [without maneuvers] so, whenever there is need, to fall upon the enemy at the bow and set fire to the ships by means of the *fire of the siphons*. . . . Many very suitable contrivances were invented by the ancients and moderns, with regard to both the enemy's ships and the warriors on them—such as at that time the *prepared fire* which is ejected (thrown) by means of *siphons* with a roar and a lurid (burning) smoke and filling them [the ships] with smoke. . . . They shall use also the other method of small *siphons* thrown (i.e., directed) by hand from behind iron shields and held [by the soldiers], which are called *hand siphons* and have been recently manufactured by our state. For these can also throw (shoot) the *prepared fire* into the faces of the enemy.⁸

Leo also described the use of *strepta*, by which a liquid fire was ejected, but he seemed to have been vague upon the details of construction of the pieces and upon the force which propelled the flame, and, like the majority of the Byzantine writers, he failed to mention the secret ingredient, the saltpeter, upon which the functioning of the fires undoubtedly depended, for their flames could be directed downward as well as upward.

The Byzantines kept their secret well and for a long time, but the Moslems finally learned about it and used the fire against the Christians at the time of the Fifth Crusade. In the Sixth Crusade the army of Saint Louis in Egypt was assailed with incendiaries thrown from ballistae, with fire from tubes, and with grenades of glass and metal, thrown by hand, which scattered fire on bursting. Brock⁹ thinks that the fire from tubes operated in the manner of Roman candles. The charge, presumed to be a non-homogeneous mixture of combustible materials with saltpeter, "will, in certain proportions, if charged into a strong tube, give intermittent bursts, projecting blazing masses of the mixture to a

⁸ Cheronis, *op. cit.*, p. 362.

⁹ A. St. H. Brock, "Pyrotechnics: the History and Art of Firework Making," London, 1922, p. 15.

considerable distance. The writer has seen this effect produced in a steel mortar of 5½ inches diameter, the masses of composition being thrown a distance of upwards of a hundred yards, a considerable range in the days of close warfare." There is no reason to believe that the fire tubes were guns.

Marcus Graecus

In the celebrated book of Marcus Graecus, *Liber ignium ad comburendos hostes*,¹⁰ Greek fire and other incendiaries are described fully, as is also black powder and its use in rockets and crackers. This work was quoted by the Arabian physician, Mesue, in the ninth century, and was probably written during the eighth.

Greek fire is made as follows: take sulfur, tartar, sarcocolla, pitch, melted saltpeter, petroleum oil, and oil of gum, boil all these together, impregnate tow with the mixture, and the material is ready to be set on fire. This fire cannot be extinguished by urine, or by vinegar, or by sand. . . .

Flying fire (rockets) may be obtained in the following manner: take one part of colophony, the same of sulfur, and two parts of saltpeter. Dissolve the pulverized mixture in linseed oil, or better in oil of lamium. Finally, the mixture is placed in a reed or in a piece of wood which has been hollowed out. When it is set on fire, it will fly in whatever direction one wishes, there to set everything on fire.

Another mixture corresponds more closely to the composition of black powder. The author even specifies grapevine or willow charcoal which, with the charcoal of black alder, are still the preferred charcoals for making fuze powders and other grades where slow burning is desired.

Take one pound of pure sulfur, two pounds of grapevine or willow charcoal, and six pounds of saltpeter. Grind these three substances in a marble mortar in such manner as to reduce them to a most subtle powder. After that, the powder in desired quantity is put into an envelope for flying (a rocket) or for making thunder (a cracker). Note that the envelope for flying ought to be thin and long and well-filled with the above-described powder tightly packed, while the envelope for making thunder ought to be short and thick,

¹⁰ Book of fires for burning the enemy, reprinted in full by Hoefer, "Histoire de la chimie," second edition, Paris, 1866, Vol. 1, pp. 517-524, and discussed *ibid.*, Vol. 1, p. 300.

only half filled with powder, and tightly tied up at both ends with an iron wire. Note that a small hole ought to be made in each envelope for the introduction of the match. The match ought to be thin at both ends, thick in the middle, and filled with the above-described powder. The envelope intended to fly in the air has as many thicknesses (ply) as one pleases; that for making thunder, however, has a great many.

Toward the end of the *Liber ignium* the author gives a slightly different formula for the black powder to be used in rockets.

The composition of flying fire is threefold. The first composition may be made from saltpeter, sulfur, and linseed oil. These ground up together and packed into a reed, and lighted, will make it ascend in the air. Another flying fire may be made from saltpeter, sulfur, and grapevine or willow charcoal. These materials, mixed and introduced into a papyrus tube, and ignited, will make it fly rapidly. And note that one ought to take three times as much charcoal as sulfur and three times as much saltpeter as charcoal.

Roger Bacon

Roger Bacon appears to have been the first scholar in northern Europe who was acquainted with the use of saltpeter in incendiary and explosive mixtures. Yet the passage in which he makes specific mention of this important ingredient indicates that toy firecrackers were already in use by the children of his day. In the "Opus Majus," Sixth Part, On Experimental Science, he writes:

For malta, which is a kind of bitumen and is plentiful in this world, when cast upon an armed man burns him up. The Romans suffered severe loss of life from this in their conquests, as Pliny states in the second book of the Natural History, and as the histories attest. Similarly yellow petroleum, that is, oil springing from the rock, burns up whatever it meets if it is properly prepared. For a consuming fire is produced by this which can be extinguished with difficulty; for water cannot put it out. Certain inventions disturb the hearing to such a degree that, if they are set off suddenly at night with sufficient skill, neither city nor army can endure them. No clap of thunder could compare with such noises. Certain of these strike such terror to the sight that the coruscations of the clouds disturb it incomparably less. . . . We have an example of this in that toy of children which is made in many parts of the world, namely an instrument as

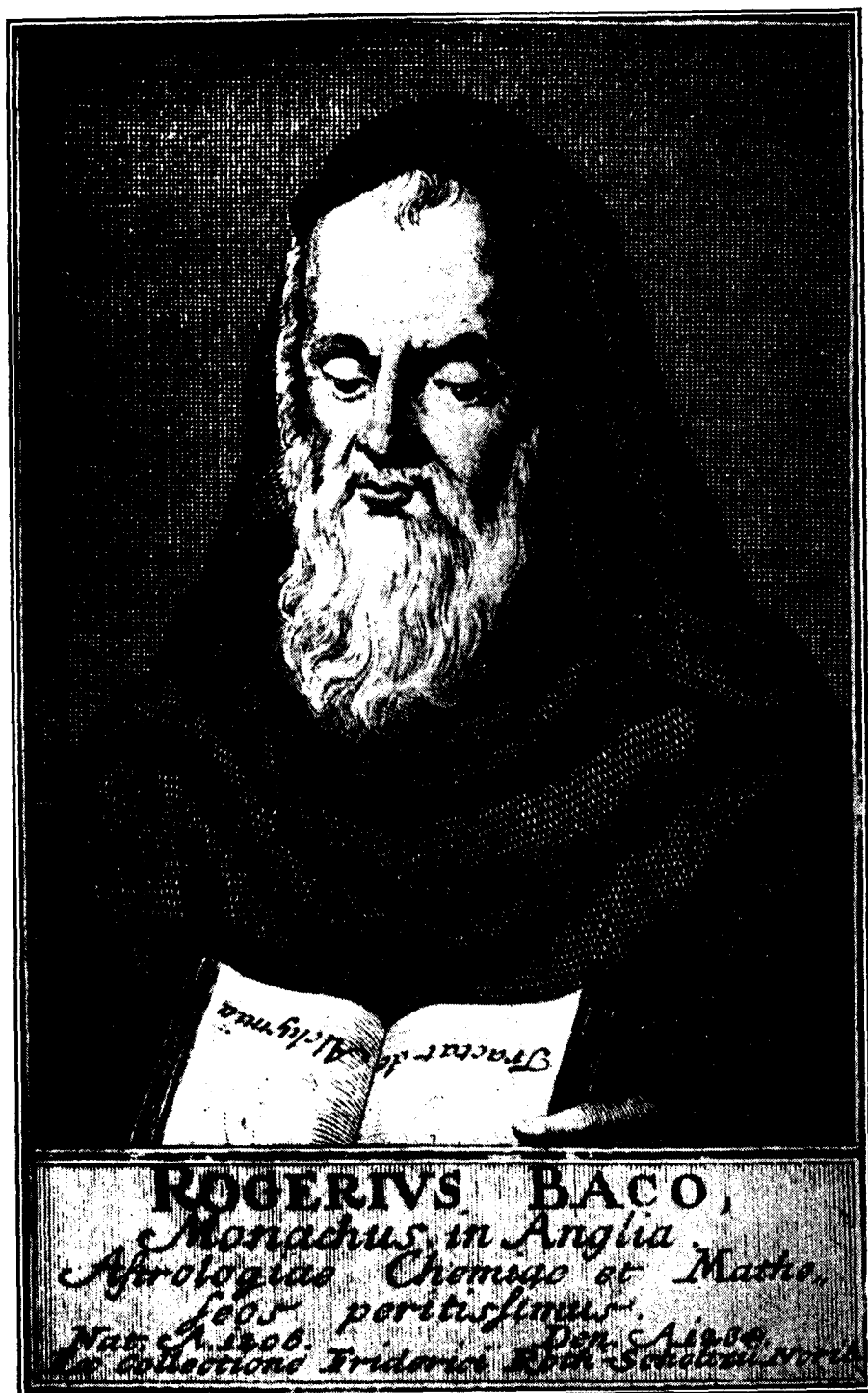


FIGURE 17. Roger Bacon (c. 1214-1292). Probably the first man in Latin Europe to publish a description of black powder. He was acquainted with rockets and firecrackers, but not with guns.

large as the human thumb. From the force of the salt called saltpeter so horrible a sound is produced at the bursting of so small a thing, namely a small piece of parchment, that we perceive it exceeds the roar of sharp thunder, and the flash exceeds the greatest brilliancy of the lightning accompanying the thunder.¹¹

A description in cypher of the composition of black powder in the treatise "De nullitate magiae"¹² which is ascribed to Roger Bacon has attracted considerable attention. Whether Bacon wrote the treatise or not, it is certain at any rate that the treatise dates from about his time and certain, too, that much of the material which it contains is to be found in the "Opus Majus." The author describes many of the wonders of nature, mechanical, optical, medicinal, etc., among them incendiary compositions and fire-crackers.

We can prepare from saltpeter and other materials an artificial fire which will burn at whatever distance we please. The same may be made from red petroleum and other things, and from amber, and naphtha, and white petroleum, and from similar materials. . . . Greek fire and many other combustibles are closely akin to these mixtures. . . . For the sound of thunder may be artificially produced in the air with greater resulting horror than if it had been produced by natural causes. A moderate amount of proper material, of the size of the thumb, will make a horrible sound and violent coruscation.

Toward the end of the treatise the author announces his intention of writing obscurely upon a secret of the greatest importance, and then proceeds to a seemingly incoherent discussion of something which he calls "the philosopher's egg." Yet a thoughtful reading between the lines shows that the author is describing the purification of "the stone of Tagus" (saltpeter), and that this material is somehow to be used in conjunction with "certain parts of burned shrubs or of willow" (charcoal) and with the "vapor of pearl" (which is evidently sulfur in the language of the medieval

¹¹ "The Opus Majus of Roger Bacon," trans. Robert Belle Burke, University of Pennsylvania Press, Philadelphia, 1928, Vol. 2, p. 629.

¹² Cf. "Roger Bacon's Letter Concerning the Marvelous Power of Art and of Nature and Concerning the Nullity of Magic," trans. Tenney L. Davis, Easton, Pennsylvania, 1922.

chemists). The often-discussed passage which contains the black powder anagram is as follows:

*Sed tamen salis petrae LVRV VO .PO VIR CAN VTRIET
sulphuris, et sic facies tonitruum et coruscationem: sic facies
artificium.*

A few lines above the anagram, the author sets down the composition of black powder in another manner. "Take then of the bones of Adam (charcoal) and of the Calx (sulfur), the same weight of each; and there are six of the Petral Stone (saltpeter) and five of the Stone of Union." The Stone of Union is either sulfur or charcoal, probably sulfur, but it doesn't matter for the context has made it evident that only three components enter into the composition. Of these, six parts of saltpeter are to be taken, five each of the other two. The little problem in algebra supplies a means of checking the solution of the anagram, and it is evident that the passage ought to be read as follows:

*Sed tamen salis petrae R. VI. PART. V. NOV. CORVLI.
ET V. sulphuris, et sic facies tonitruum et coruscationem: sic
facies artificium.*

But, however, of saltpeter take six parts, five of young willow (charcoal), and five of sulfur, and so you will make thunder and lightning, and so you will turn the trick.

The 6:5:5 formula is not a very good one for the composition of black powder for use in guns, but it probably gave a mixture which produced astonishing results in rockets and firecrackers, and it is not unlike the formulas of mixtures which are used in certain pyrotechnic pieces at the present time.

Although Roger Bacon was not acquainted with guns or with the use of black powder for accomplishing mechanical work, yet he seems to have recognized the possibilities in the mixture, for the treatise "On the Nullity of Magic" comes to an end with the statement: "Whoever will rewrite this will have a key which opens and no man shuts, and when he will shut, no man opens."¹³

¹³ Compare *Revelations*, 3: 7 and 8. "And to the angel of the church in Philadelphia write: These things saith he that is holy, he that is true, he that hath the key of David, he that openeth, and no man shutteth; and shutteth, and no man openeth; I know thy works: behold, I have set before thee an open door, and no man can shut it."

Development of Black Powder¹⁴

Guns apparently first came into use shortly after the death of Roger Bacon. A manuscript in the Asiatic Museum at Leningrad, probably compiled about 1320 by Shems ed Din Mohammed, shows tubes for shooting arrows and balls by means of powder. In the library of Christ Church, Oxford, there is a manuscript entitled "De officiis regum," written by Walter de Millemete in 1325, in which a drawing pictures a man applying a light to the touch-hole of a bottle-shaped gun for firing a dart. On February 11, 1326, the Republic of Venice ordered iron bullets and metal cannon for the defense of its castles and villages, and in 1338 cannon and powder were provided for the protection of the ports of Harfleur and l'Heure against Edward III. Cannon were used in 1342 by the Moors in the defense of Algeciras against Alphonso XI of Castile, and in 1346 by the English at the battle of Crécy.

When guns began to be used, experiments were carried out for determining the precise composition of the mixture which would produce the best effect. One notable study, made at Bruxelles about 1560, led to the selection of a mixture containing saltpeter 75 per cent, charcoal 15.62 per cent, and sulfur 9.38 per cent. A few of the formulas for black powder which have been used at various times are calculated to a percentage basis and tabulated below:

	SALTPETER	CHARCOAL	SULFUR
8th century, Marcus Graecus	66.66	22.22	11.11
8th century, Marcus Graecus	69.22	23.07	7.69
c. 1252, Roger Bacon	37.50	31.25	31.25
1350, Arderne (laboratory recipe)	66.6	22.2	11.1
1560, Whitehorne	50.0	33.3	16.6
1560, Bruxelles studies	75.0	15.62	9.38
1635, British Government contract	75.0	12.5	12.5
1781, Bishop Watson	75.0	15.0	10.0

It is a remarkable fact, and one which indicates that the improvements in black powder have been largely in the methods of manufacture, that the last three of these formulas correspond very closely to the composition of all potassium nitrate black powder for military and sporting purposes which is used today. Any considerable deviation from the 6:1:1 or 6:1.2:0.8 formulas

¹⁴ An interesting and well-documented account of the history of black powder and of other explosives may be found in Molinari and Quartieri's "Notizie sugli esplodenti in Italia," Milano, 1913.

produces a powder which burns more slowly or produces less vigorous effects, and different formulas are used for the compounding of powders for blasting and for other special purposes. In this country blasting powder is generally made from sodium nitrate.

John Bate early in the seventeenth century understood the individual functions of the three components of black powder



FIGURE 18. Gunpowder Manufacture, Lorraine, 1630. After the materials had been intimately ground together in the mortar, the mixture was moistened with water, or with a solution of camphor in brandy, or with other material, and formed into grains by rubbing through a sieve.

when he wrote: "The Saltpeter is the Soule, the Sulphur the Life, and the Coales the Body of it."¹⁵ The saltpeter supplies the oxygen for the combustion of the charcoal, but the sulfur is the life, for this inflammable element catches the first fire, communicates it throughout the mass, makes the powder quick, and gives it vivacity.

Hard, compressed grains of black powder are not porous—the sulfur appears to have colloidal properties and to fill completely

¹⁵ John Bate, "The Mysteries of Nature and Art," second edition, London, 1635, p. 95.

the spaces between the small particles of the other components—and the grains are poor conductors of heat. When they are lighted, they burn progressively from the surface. The area of the surface of an ordinary grain decreases as the burning advances, the grain becomes smaller and smaller, the rate of production of gas decreases, and the duration of the whole burning depends upon the dimension of the original grain. Large powder grains which required more time for their burning were used in the larger guns. Napoleon's army used roughly cubical grains 8 mm. thick in its smaller field guns, and cubical or lozenge-shaped grains twice as thick in some of its larger guns. Grains in the form of hexagonal prisms were used later, and the further improvement was introduced of a central hole through the grain in a direction parallel to the sides of the prism. When these single-perforated hexagonal prisms were lighted, the area of the outer surfaces decreased as the burning advanced, but the area of the inner surfaces of the holes actually increased, and a higher rate of production of gas was maintained. Such powder, used in rifled guns, gave higher velocities and greater range than had ever before been possible. Two further important improvements were made: one, the use of multiple perforations in the prismatic grain by means of which the burning surface was made actually to increase as the burning progressed, with a resultant acceleration in the rate of production of the gases; and the other, the use of the slower-burning *cocoa powder* which permitted improvements in gun design. These, however, are purely of historical interest, for smokeless powder has now entirely superseded black powder for use in guns.

If a propellant powder starts to burn slowly, the initial rise of pressure in the gun is less and the construction of the breech end of the gun need not be so strong and so heavy. If the powder later produces gas at an accelerated rate, as it will do if its burning surface is increasing, then the projectile, already moving in the barrel, is able to take up the energy of the powder gases more advantageously and a greater velocity is imparted to it. The desired result is now secured by the use of progressive-burning colloided smokeless powder. Cocoa powder was the most successful form of black powder for use in rifled guns of long range.

Cocoa powder or brown powder was made in single-perforated

hexagonal or octagonal prisms which resembled pieces of milk chocolate. A partially burned brown charcoal made from rye straw was used. This had colloidal properties and flowed under pressure, cementing the grains together, and made it possible to manufacture powders which were slow burning because they contained little sulfur or sometimes even none. The compositions of several typical cocoa powders are tabulated below:

	SALTPETER	BROWN CHARCOAL	SULFUR
England.....	79	18	3
England.....	77.4	17.6	5
Germany.....	78	19	3
Germany.....	80	20	0
France.....	78	19	3

Cocoa powder was more sensitive to friction than ordinary black powder. Samples were reported to have inflamed from shaking in a canvas bag. Cocoa powder was used in the Spanish-American war, 1898. When its use was discontinued, existing stocks were destroyed, and single grains of the powder are now generally to be seen only in museums.

Burning of Black Powder

Black powder burns to produce a white smoke. This, of course, consists of extremely small particles of solid matter held temporarily in suspension by the hot gases from the combustion. Since the weight of these solids is equal to more than half of the weight of the original powder, the superiority of smokeless powder, which produces practically no smoke and practically 100 per cent of its weight of hot gas, is immediately apparent. The products of the burning of black powder have been studied by a number of investigators, particularly by Noble and Abel,¹⁶ who showed that the burning does not correspond to any simple chemical reaction between stoichiometrical proportions of the ingredients. Their experiments with RLG powder having the percentage composition indicated below showed that this powder burned to produce (average results) 42.98 per cent of its weight of gases, 55.91 per cent solids, and 1.11 per cent water.

¹⁶ Noble and Abel, *Phil. Trans.*, 1875, 49; 1880, 203; *Mém. poudres*, 1, 193 (1882). See also Debus, *Proc. Roy. Soc.*, 30, 198 (1880).

Potassium nitrate.....	74.430
Potassium sulfate.....	0.133
Sulfur.....	10.093
Charcoal {	
Carbon.....	12.398
Hydrogen....	0.401
Oxygen.....	1.272
Ash.....	0.215
.....	14.286
Moisture.....	1.058

Their mean results from the analysis of the gaseous products (percentage by volume) and of the solid products (percentage by weight) are shown in the following tables.

Carbon dioxide.....	49.29	Potassium carbonate.....	61.03
Carbon monoxide.....	12.47	Potassium sulfate.....	15.10
Nitrogen.....	32.91	Potassium sulfide.....	14.45
Hydrogen sulfide.....	2.65	Potassium thiocyanate.....	0.22
Methane.....	0.43	Potassium nitrate.....	0.27
Hydrogen.....	2.19	Ammonium carbonate.....	0.08
		Sulfur.....	8.74
		Carbon.....	0.08

One gram of the powder in the state in which it was normally used, that is, while containing 1.058 per cent of moisture, produced 718.1 calories and 271.3 cc. of permanent gas measured at 0° and 760 mm. One gram of the completely desiccated powder gave 725.7 calories and 274.2 cc. These results indicate by calculation that the explosion of the powder produces a temperature of about 3880°.

Uses of Black Powder

Where smoke is no objection, black powder is probably the best substance that we have for communicating fire and for producing a quick hot flame, and it is for these purposes that it is now principally used in the military art. Indeed, the fact that its flame is filled with finely divided solid material makes it more efficient as an igniter for smokeless powder than smokeless powder itself. Standard black powder (made approximately in accordance with the 6:1:1 or the 6:1.2:0.8 formula) is used in *pétards*, as a base charge or expelling charge for shrapnel shells, in saluting and blank fire charges, as the bursting charge of practice shells and bombs, as a propelling charge in certain pyrotechnic pieces, and, either with or without the admixture of other substances which modify the rate of burning, in the time-train



FIGURE 19. Stamp Mill for Making Black Powder. (Courtesy National Fireworks Company and the *Boston Globe*.) This mill, which makes powder for use in the manufacture of fireworks, consists of a single block of granite in which three deep cup-shaped cavities have been cut. The stamps which operate in these cups are supplied at their lower ends with cylindrical blocks of wood, sections cut from the trunk of a hornbeam tree. These are replaced when worn out. The powder from the mill is called "meal powder" and is used as such in the manufacture of fireworks. Also it is moistened slightly with water and rubbed through sieves to form granular gunpowder for use in making rockets, Roman candles, aerial bombshells, and other artifices.

rings and in other parts of fuzes. Modified black powders, in which the proportion of the ingredients does not approximate to the standard formulas just mentioned, have been used for blasting, especially in Europe, and have been adapted to special uses in pyrotechny. Sodium nitrate powder, *ammonpulver*, and other more remote modifications are discussed later in this chapter or in the chapter on pyrotechnics.

Manufacture

During the eighteenth century, stamp mills (Figure 19) for incorporating the ingredients of black powder largely superseded the more primitive mortars operated by hand. The meal powder, or *pulverin* as the French call it, was made into gunpowder by moistening slightly and then pressing through sieves.¹⁷ The powder grains were not uniform with one another either in their composition or their density, and could not be expected to give very uniform ballistic results. The use of a heavy wheel mill for grinding and pressing the materials together, and the subsequent pressing of the material into a hard cake which is broken up into grains, represent a great advance in the art and produce hard grains which are physically and ballistically uniform.¹⁸ The operations in the manufacture of black powder as it is carried out at present are briefly as follows:

1. *Mixing* of the powdered materials is accomplished by hand or mechanical blending while they are dampened with enough water to prevent the formation of dust, or the powdered sulfur and charcoal are stirred into a saturated solution of the requisite amount of potassium nitrate at a temperature of about 130°, the hot mass is spread out on the floor to cool, and the lumps are broken up.

2. *Incorporating or Milling.* The usual wheel mill has wheels which weigh 8 or 10 tons each. It takes a charge of 300 pounds of

¹⁷ The French still make *pulverin*, for the preparation of black match and for use in pyrotechnics, by rolling the materials with balls, some of lead and some of *lignum vitae*, in a barrel of hardwood. They also sometimes use this method for mixing the ingredients before they are incorporated more thoroughly in the wheel mill.

¹⁸ The black powder wheel mill is also used for reducing (under water) deteriorated smokeless powder to a fine meal in order that it may be reworked or used in the compounding of commercial explosives, and for the intimate incorporation of such explosives as the French *schneiderite*.

the mixture. The wheels rotate for about 3 hours at a rate of about 10 turns per minute. Edge runners turn back under the tread of the wheels material which would otherwise work away from the center of the mill. Considerable heat is produced during the milling, and more water is added from time to time to replace that which is lost by evaporation in order that the material may always be moist. The "wheel cake" and "clinker" which result from the milling are broken up into small pieces for the pressing.

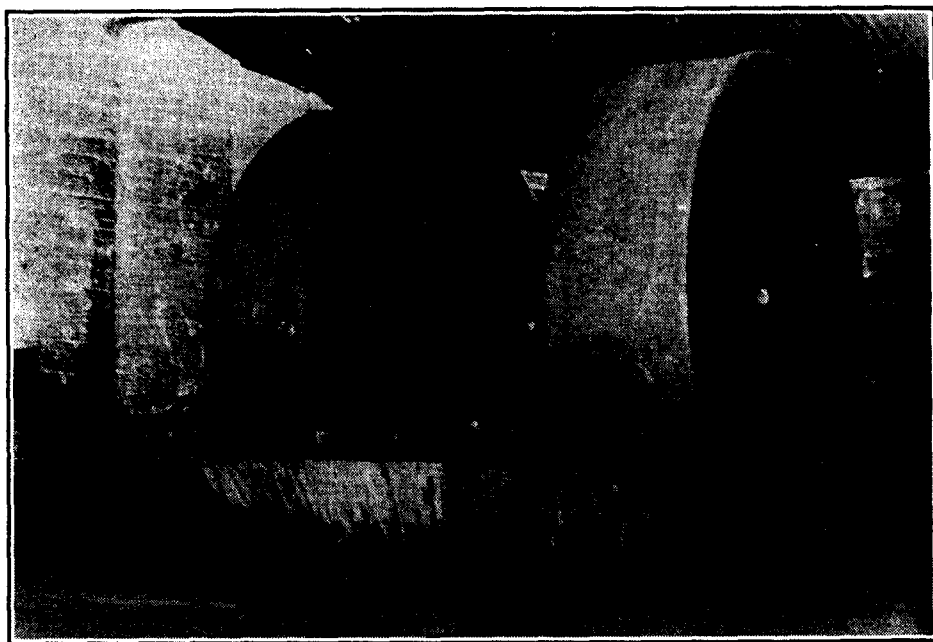


FIGURE 20. Modern Wheel Mill for Making Black Powder. (Courtesy Atlas Powder Company.) The large wheels weigh 10 tons each.

3. *Pressing* is done in a horizontal hydraulic press. Layers of powder are built up by hand between plates of aluminum, and the whole series of plates is pressed in one operation. The apparatus is so designed that fragments of powder are free to fall out at the edges of the plates, and only as much of the material remains between them as will conveniently fill the space. An effective pressure of about 1200 pounds per square inch is applied, and the resulting press cakes are about $\frac{3}{4}$ inch thick and 2 feet square.

4. *Corning or granulating* is the most dangerous of the operations in the manufacture of black powder. The corning mill is usually situated at a distance from the other buildings, is barri-

caded, and is never approached while the machinery, controlled from a distance, is in operation. The press cake is cracked or granulated between crusher rolls. Screens, shaken mechanically, separate the dust and the coarse pieces from the grains which are of the right size for use. The coarse pieces pass between other crusher rolls and over other screens, four sets of crusher rolls being used. Corning mill dust is used in fuse powder and by the makers of fireworks, who find it superior for certain purposes to other kinds of meal powder.

5. *Finishing.* The granulated powder from the corning mill is rounded or polished and made "bright" by tumbling in a revolving wooden cylinder or barrel. Sometimes it is dried at the same time by forcing a stream of warm air through the barrel. Or the polished powder is dried in wooden trays in a dry-house at 40°. If a glazed powder is desired, the glaze is usually applied before the final drying. To the polished powder, still warm from the tumbling, a small amount of graphite is added, and the tumbling is continued for a short time. Black powder of commerce usually contains about 1 or 1.5 per cent moisture. If it contains less than this, it has a tendency to take up moisture from the air; if it contains much more, its efficiency is affected.

6. *Grading.* The powder is finally rescreened and separated into the different grain sizes, C (coarse), CC, CCC, F (fine), FF or 2F, 3F, 4F, etc. The word *grade* applied to black powder, refers to the grain size, not to the quality.

Analysis¹⁹

A powdered sample for analysis may be prepared safely by grinding granulated black powder, in small portions at a time, in a porcelain mortar. The powder may be passed through a 60-mesh sieve and transferred quickly to a weighing bottle without taking up an appreciable amount of moisture.

¹⁹ A test which from ancient times has been applied to black powder is carried out by pouring a small sample onto a cold flat surface and setting fire to it. A good powder ought to burn in a flash and leave no "pearls" or residue of globules of fused salt. A solid residue indicates either that the ingredients have not been well incorporated, or that the powder at some time in its history has been wet (resulting in larger particles of saltpeter than would be present in good powder, the same result as poor incorporation), or that the powder at the time of the test contains an undue amount of moisture.

Moisture is determined by drying in a desiccator over sulfuric acid for 3 days, or by drying to constant weight at 60° or 70°, at which temperature 2 hours is usually long enough.

For determining *potassium nitrate*, the weighed sample in a Gooch crucible is washed with hot water until the washings no longer give any test for nitrate,²⁰ and the crucible with its contents is dried to constant weight at 70°. The loss of weight is equal to potassium nitrate *plus* moisture. In this determination, as in the determination of moisture, care must be taken not to dry the sample too long, for there is danger that some of the sulfur may be lost by volatilization.

Sulfur is determined as the further loss of weight on extraction with carbon disulfide in a Wiley extractor or other suitable apparatus. After the extraction, the crucible ought to be allowed to dry in the air away from flames until all the inflammable carbon disulfide has escaped. It is then dried in the oven to constancy of weight, and the residue is taken as *charcoal*. *Ash* is determined by igniting the residue in the crucible until all carbon has burned away. A high result for ash may indicate that the water extraction during the determination of potassium nitrate was not complete. The analytical results may be calculated on a moisture-free basis for a closer approximation to the formula by which the manufacturer prepared the powder.

Blasting Powder

The 6:1:1 and 6:1.2:08 formulas correspond to the quickest and most vigorous of the black-powder compositions. A slower and cheaper powder is desirable for blasting, and both these desiderata are secured by a reduction in the amount of potassium nitrate. For many years the French government has manufactured and sold three kinds of blasting or mining powder, as follows:

	SALTPETER	CHARCOAL	SULFUR
<i>Forte</i>	72	15	13
<i>Lente</i>	40	30	30
<i>Ordinaire</i>	62	18	20

In the United States a large part of all black powder for blast-

²⁰ A few drops, added to a few cubic centimeters of a solution of 1 gram of diphenylamine in 100 cc. of concentrated sulfuric acid, give a blue color if a trace of nitrate is present.

ing is made from sodium nitrate. This salt is hygroscopic, but a heavy graphite glaze produces a powder from it which is satisfactory under a variety of climatic conditions. Analyses of samples of granulated American blasting powder have shown that the compositions vary widely, sodium nitrate from 67.3 to 77.1 per cent, charcoal from 9.4 to 14.3 per cent, and sulfur from 22.9 to 8.6 per cent. Perhaps sodium nitrate 73, charcoal 11, and sulfur 16 may be taken as average values.

Pellet powders, made from sodium nitrate, are finding extensive use. These consist of cylindrical "pellets," 2 inches long, wrapped in paraffined paper cartridges, $1\frac{1}{4}$, $1\frac{3}{8}$, $1\frac{1}{2}$, $1\frac{3}{4}$, and 2 inches in diameter, which resemble cartridges of dynamite. The cartridges contain 2, 3, or 4 pellets which are perforated in the direction of their axis with a $\frac{3}{8}$ -inch hole for the insertion of a squib or fuse for firing.

Ammonpulver

Propellant powder made from ammonium nitrate is about as powerful as smokeless powder and has long had a limited use for military purposes, particularly in Germany and Austria. The Austrian army used Ammonpulver, among others, during the first World War, and it is possible that the powder is now, or may be at any time, in use.

Gäns of Hamburg in 1885 patented²¹ a powder which contained no sulfur and was made from 40 to 45 per cent potassium nitrate, 35 to 38 per cent ammonium nitrate, and 14 to 22 per cent charcoal. This soon came into use under the name of *Amidpulver*, and was later improved by decreasing the proportion of potassium nitrate. A typical improved Amidpulver, made from potassium nitrate 14 per cent, ammonium nitrate 37 per cent, and charcoal 49 per cent, gives a flashless discharge when fired in a gun and only a moderate amount of smoke. Ammonpulver which contains no potassium nitrate—in a typical example ammonium nitrate 85 per cent and charcoal 15 per cent, or a similar mixture containing in addition a small amount of aromatic nitro compound—is flashless and gives at most only a thin bluish-gray smoke which disappears rapidly. Rusch²² has published data

²¹ Ger. Pat. 37,631.

²² *Seewesen*, January, 1909, cited by Escales, "Ammonsalpetersprengstoffe," Leipzig, 1909, p. 217.

which show that the temperature of the gases from the burning of ammonpolver (ammonium nitrate 80 to 90 per cent, charcoal 20 to 10 per cent) is below 900° , and that the ballistic effect is approximately equal to that of ballistite containing one-third of its weight of nitroglycerin.

Ammonpolver has the advantages of being cheap, powerful, flashless, and smokeless. It is insensitive to shock and to friction, and is more difficult to ignite than black powder. In use it requires a strong igniter charge. It burns rapidly, and in gunnery is used in the form of single-perforated cylindrical grains usually of a diameter nearly equal to that of the space within the cartridge. It has the disadvantages that it is extremely hygroscopic and that it will not tolerate wide changes of temperature without injury. The charges must be enclosed in cartridges which are effectively sealed against the ingress of moisture from the air. Ammonium nitrate has a transition point at 32.1° . If Ammonpolver is warmed above this temperature, the ammonium nitrate which it contains undergoes a change of crystalline state; this results in the crumbling of the large powder grains and consequent high pressures and, perhaps, bursting of the gun if the charge is fired. At the present time Ammonpolver appears to be the only modification of black powder which has interesting possibilities as a military propellant.

Other Related Propellant Explosives

Guanidine nitrate powders have not been exploited, but the present availability of guanidine derivatives from the cyanamide industry suggests possibilities. The salt is stable and non-hygroscopic, and is a flashless explosive—cooler indeed than ammonium nitrate. Escales²³ cites a German patent to Gäns²⁴ for a blasting powder made from potassium nitrate 40 to 60 per cent, guanidine nitrate 48 to 24 per cent, and charcoal 12 to 16 per cent.

Two other powders, now no longer used, are mentioned here as historically interesting examples of propellants made up in accordance with the same principle as black powder, namely, the principle of mixing an oxidizing salt with a combustible material.

Raschig's white blasting powder was made by dissolving 65 parts of sodium nitrate and 35 parts of sodium cresol sulfonate

²³ Escales, *op. cit.*, p. 225.

²⁴ Ger. Pat. 54,429.

together in water, running the solution in a thin stream onto a rotating and heated steel drum whereby the water was evaporated, and scraping the finished powder off from the other side of the drum. It was cheap, and easy and safe to make, but was hygroscopic. For use in mining, it was sold in waterproof paper cartridges.

Poudre Brugère was made by grinding together 54 parts of ammonium picrate and 46 parts of potassium nitrate in a black powder wheel mill, and pressing and granulating, etc., as in the manufacture of black powder. The hard grains were stable and non-hygroscopic. The powder was used at one time in military weapons. It was more powerful than black powder and gave less smoke.