

Black powder manufacture

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As part of the session on particles this paper concerns a thousand year old product named variously as powder, black powder or gun powder (The black powder designation occurring in the 19th century when other gun powders were created.) Black powder is a physically combined mixture of four ingredients. These are classically potassium nitrate, sulphur, charcoal and water. Because a powder is black in color, it is not necessarily the chemical black powder. Other powders, as we know them today, are single or double based nitrated hydrocarbons.

The largest and most sophisticated black powder plant ever built anytime, anywhere, is about 30 miles south of Philadelphia just outside Wilmington Delaware. It was the basis of the Dupont Company, which, now a little over two hundred years after the founding has emerged as one of the world's largest chemical companies. Dupont sold the last of its black powder plants in 1972 to Gerhart Owen which is now GOEX. Part of the first Dupont plant survives as the Hagley museum which has associated with it a library containing the best historical collection of explosive related materials in existence.

Although the product has been known for about a thousand years, the dates being somewhat disputed, accurate knowledge of its burning is only about one hundred and fifty years old. Black powder burns or technically deflagrates. (as opposed to detonates which is a considerably faster reaction) Since black powder has various applications from blasting, to shooting pistols to firing cannons its utility is a factor of controlling the deflagration. To put it simply, gas generation needs to be factored by time to create the ideal burn. In blasting one needs to heave or shatter. In shooting the time of the burn is factored by the diameter of the barrel and the length. To get a continuous push (called a progressive burn) the burn needs to be complete while the projectile is in the barrel. Since barrels vary in length from about an inch for a derringer to several feet for a piece of artillery the needs are considerably different.

There are two ways to control the burn. The first and oldest was to vary the proportion of the ingredients. The other and more sophisticated is by varying the physical means of creating the powder grains. Grain is a rather loose term which encompasses the tiny particles of the early serpentine powder to the large pressed pieces of prismatic or pellet powders. There are two basic ways to control the mechanical process. The first is to simply vary the size of the grain, and the second is length of time of each manufacturing process or the nature of it. Time is tricky because after a point continuing a mechanical process has no benefit, but carrying it out to the ultimate benefit is not economical in some cases (as in cheap blasting powders).

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To continue, we will consider the four ingredients first, and then we will discuss the evolution of the mechanical processes and the ramifications of each to the burning reaction.

The major ingredient is potassium nitrate which is about three quarters of the mixture. Its purity is critical. While other nitrates have been substituted such as sodium nitrate for cheap blasting powders and ammonium nitrate, potassium nitrate is the material of choice. It is the least hygroscopic (does not as readily absorb atmospheric moisture). Because the process of extracting nitrate historically required the leaching and refining of waste materials, the early powders may well have had some calcium or sodium nitrate. This was solved by running a liquor of nitrate solution through potash. Purity was important for two reasons. The first is that anything else does not properly participate in the burn and the second, materials such as chlorides remain in the solid residue and degrade the weapons. Fortunately the process for making potassium nitrate today is not the long arduous and stinky process of old. However, issues of fertilizer grade nitrates versus reagent grade nitrates occasionally arise. Occasionally the fertilizers may contain chlorides in small amounts. The ability to artificially produce potassium nitrate is about 150 years old, but there was immediate switch to it for about a half century.

The second ingredient is sulfur or brimstone. Getting pure sulfur is relatively easy with a sublimation reaction. Simply one drives it to a gaseous state and then condenses the gas. Since sulfur is an element, it is relatively simple. It combusts with extremely noxious odors and causes great distress in the gastric tracts it ingested.

The most complex issue is the charcoal. The structure of the charcoal is determined by the wood from which it is distilled. Usually it is about 70% carbon, and the more porous the maze, the better. Classically willow, alder and hazel have been the woods of choice while the hard woods prove considerably less satisfactory, Small amounts of creosote in the charcoal produce a superior *moist* burning powder. The trace amount of ash kept the powder slightly alkaline making stable grains. The carbon takes place in the burning reaction but the reaction is a bit complicated. Carbon dioxide is about 49 %, carbon monoxide is about twelve and a half percent of the gaseous products while solid products include potassium carbonate(61%) , potassium thiocyanate (.2%) / pure carbon (.8%) and ammonium carbonate (.8%). Since wood is a hydrocarbon, there is some methane, hydrogen sulfide and pure hydrogen released as gases

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and the previously mentioned ammonium carbonate solid residue. Originally the charcoal was produced by controlled burning of mounds of wood, usually taking a couple weeks. Around the turn of the 19th century the process of distilling the wood in large iron vessels was introduced to powder making, and by the turn of the 20th century the use of superheated steam was in use to substitute for the fires under the vessels. Dupont also collected the tars and pyrolignous acids in long collection tubes for resale and internal use. The distillation was more accurate and did not have the hazard to the burners of becoming part of the burn by accidentally falling into the smoldering mound.

Water is the final ingredient – usually neglected. It is by weight about ½ of 1 percent of the final product and has a dual role of binder producing a stable grain, and reduces the explosion hazard during manufacture. Water purity was recognized as a factor in the 19th century by W.W. Greener in his famous scholarly tract The Gun and Its development (London 1835 ...first edition of about 9). More recent work at Aberdeen Proving ground and at the decontamination of the California Powder Works site has pinpointed and used the presence of micro-organisms as the cause of some powder degradation.

Another material associated with black powder is graphite. This is usually added in the glazing process. A myth in powder making is that graphite coating of the grains makes the grains less hygroscopic while in fact it makes it look better and pour better. It was initially (introduced in the early 19th century) the favorite of the African trade in which a 6 ¼ pound keg of powder was a trading unit for a slave. Not all powders were coated with graphite and it does not appear to contribute to the burning reaction at all.

Although varying the composition of the powder, most particularly the amount of nitrate, appears in the early literature as the means of controlling the burning reaction, the means of mechanically producing the powder is the real key to control. The process evolved as new procedures were invented and modified.

The early powders were called serpentine powder. The ingredients were measured out, pounded together in a mortar and pestle, and then used. This was usually done at the site of use since serpentine powder did not transport well. Serpentine powder was generally fairly weak powder because the particles were tiny. While generally the smaller grains tend to burn faster there comes a point when the particles are so small that they retard the burn rate. This is because with the larger particles the fire does not have to ignite each grain sequentially but may pass through the space between grains. With serpentine powder or powders of a granulation above 4F the particles physically block the passage of the fire and each needs ignited before the next can combust.

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The basic process of combining the ingredients is called incorporation. Originally it was done with a mortar and pestle. As early as 1607 there is evidence that an edge mill (roll mill) was known to be used. Other means were tried such as heating the nitrate and pouring in the other ingredients, mixing with shear rolls, and using a jet mill. The first tended to blow up frequently, the second made some rather wretched blasting powder and the jet mill proved unsatisfactory. Interestingly the jet mill was a Scandinavian invention used in a fire proof powder plant which blew up and was not rebuilt. The U.S. government then built an experimental plant in Indiana using the jet mill which could only make fuse powder and was subsequently mothballed.

Essentially only the mortar and pestle and later the edge mill – using two cast iron wheels over a cast iron bed plate - were satisfactory. This is because mechanically these two means shear an air surface off the ingredient's particles, placing them in direct contact which aids combustion. The length of time that the process takes place is also critical. When the large 10 ton cast iron wheels were used, it was found that four hours was optimum. Less time and the powder was weaker because the work was incomplete; more time would produce no additional benefit as the work was complete. Also critical was the amount of water added. Too little water and the mills would "dust" and tend to blow up. Too much water and the wheels would form "clinkers". These solid chunks would cause a wheel to rise up, driving the other wheel through the bed of powder and hitting the cast iron bed plate. Often this would cause an explosion also.

The powder was then dried to remove most of the water which had been previously added. This process evolved. It was originally done in ovens resembling the beehive ovens used in cooking. A fire was built in the oven and then removed when the oven was hot. The powder was then put in the oven and dried by the heat. Powder was also dried on large outdoor tables. Later gloom stoves were invented and rooks were built with stoves. The room was heated by the stove and then the fire was put out. The powder was then placed in trays in the heater room to dry. Finally the rooms were heated from the outside by either fire places or steam.

In the later nineteenth century the whole drying process changed when the glazing process (discussed later) and the drying process were combined in large barrels. At first the drying was done by "frictioning" in which the tumbling of the grains in the barrel produced heat. When the barrel reached the 12 o'clock position the door or bung opened and the moisture escaped. Later hollow trunnions (bearings) were introduced and air or steam could be shot into the barrel. The air dried the powder and a short shot of steam helped the graphite to stick to the grains.

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Historically the first quantum leap in powder making occurred around 1440. This was graining or corning. Moist powder was forced through sieves producing larger grains of powder. This was a huge improvement because the power of the powder increased as the burn rate increased. With the grains the fire did not have to ignite tiny particles sequentially but could pass between grains igniting grains further down the charge. By varying the size of the grain the burn rate could be controlled with the larger grains being slower to combust than the smaller grains. Also equally as important, powder grains were transportable. Obviously this transformed warfare – ships became floating gun platforms and while sieges continued other forms of land battles were possible. The era of the knight in armor faded (although the long bow was also instrumental).

After the powder press was common in the early 19th century the graining process changed. Instead of forcing powder through sieves, cakes of powder were broken up by roller grinders and the grains sorted by size in sieved reel type machine called bolters. The roller grinder was invented by William Congreve who also invented the rocket alluded to in the national anthem... rockets red glare. Controlling the size of the grain controls the ease of combustion and the speed of combustion.

Beginning in the mid-nineteenth century super sized chunks of powders were produced for use in large artillery and blasting. This was mostly the work of Rodman aided by Lamot duPont. Prismatic powders which were hexagon pressed pieces of powder with holes in the center to aid ignition used in artillery. Pellet powders, used in blasting, were cylindrical pressed chunks of powder. In both cases the objective was to slow the generation of gases during combustion.

The next procedure added the process was glazing (about 1660). This takes place after the graining. Not all powders were glazed. Powder sold as rough powder (mostly blasting) and molded powders (prismatic and pellet powders) were not glazed. Essentially the grained powder is tumbled in barrels. Glazing simulated the rigors of transportation. The grains were smoothed and rounded. The inferior grains were destroyed and the resulting dust was removed and recycled. Glazed powders were best for applications some distance from the point of manufacture. This was especially critical in nautical applications because if the powder was shaken it might degrade to smaller grains and the burning characteristics change.

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The big change in the glazing process occurred in the later part of the nineteenth century when small barrels were replaced with large barrels and drying was combined with glazing. It was discovered that glazing changed the nature of the grains. If the glazing were done for some time, the nitrate would move to the surface of the grain. This seems to aid the combustion. The industry term is called a *hard glaze*.

The final mechanical process to be invented was pressing. It was started in England in the mid eighteenth century but seems not to be common until the beginning of the nineteenth century. For example E.I. DuPont did not know of it when he worked with Louvosier, but knew of it when he returned to America in the very beginning of the nineteenth century. Pressing occurs after incorporation. It makes the powder more dense making it be able to produce more gas per unit volume. The process underwent only one change which began in the middle of the nineteenth century. A hand powered mechanical press was replaced by a powered press. The earlier presses were screw presses and the later presses were hydraulic. There is a press box in which the powder is pressed. To make manageable sized pressings there are separator plates held initially in place by finger boards. These are a comb affair with teeth about two inches apart. When the powder is shoveled into the press box with the separator plates, the finger boards are removed and the powder is compacted. The plate pressures used to be about 3000 pounds per square inch, but current practice is a bit less. After pressing the powder is in the form of slabs resembling slate.

These slabs are initially broken up into chunks by a grinder which consists of two bronze rollers with teeth. After it is made into chunks it is subsequently made into grains by roller grinders. These have between three and four sets of opposed rollers.. Some powders (prismatic and pellet) are pressed into their final form and not further reduced.

The big effect the pressing process had was to reduce the volume of powder to get the same effect.

A final step was added around the beginning of the nineteenth century. The French called it the *revolutionary* process which became *pulverizing*. Initially the three ingredients were combined in rotating barrels with heavy metal balls before incorporating. These mills were called dust mills and had a bad habit of disappearing. After the Civil war the American practice was to combine the charcoal and the sulfur only in the barrels. Without the nitrate the hazard of explosion was significantly reduced.

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When the powder was complete it was sent to a pack house where the dust created by the glazing was removed by a bolter – to be recycled -and the result put in kegs, cans or papers.

Dupont did experiment with a cardboard type keg called a pulp keg around the turn of the 20th century.. These were less than satisfactory having a tendency to collapse when stacked, and when the “fire proof” building in which they were made burned down , the effort was suspended.

How dangerous is making black powder? In the nineteenth century this was relative. Being a farmer (dying of an accident or tetanus) , railroad brakeman (being crushed before the invention of the Westinghouse air brakes) or hatter (dying of mercury poisoning) was far more dangerous. The most likely explosion to occur was in the incorporation process. Usually these happened at start up or shut down. Since the rolling mills were run by remote control, the loss of life was minimal. Also since the powder was not confined the explosion was not particularly violent. The other mills were considerably more dangerous because there was a larger quantity of more refined powder in a confined area. Since powder was made in a series of separate buildings, the risks were confined, however major losses did occur. The worst explosion at Hagley occurred in 1890. Over one hundred TONS of powder went up. The shock wave hit New York City. Trees a quarter mile from ground zero were blown over.

There were architectural considerations in making powder mills. These usually consisted of making buildings with heavy three walls and a light fourth wall and roof to channel an explosion, or building all walls and roof very light to minimize the amount of debris flying about. Later in the nineteenth century barriers were erected with wooden walls filled with dirt. These were called Rapauno barriers and were designed to stop flying debris. As with auto wrecks, many of the explosions were alcohol related.

Today there is one black powder maker in the United States and several in the world. Interestingly the general quality of powder and the knowledge of its making has declined world wide. There is no plant in the world as sophisticated as Hagley was in the early 1900's. It could make the blasting powders, the sporting powders, the military powders, the prismatic powders, the pellet powders and the semi-smokeless powders. Maybe this suggests that progress is not linear but a series of undulations.