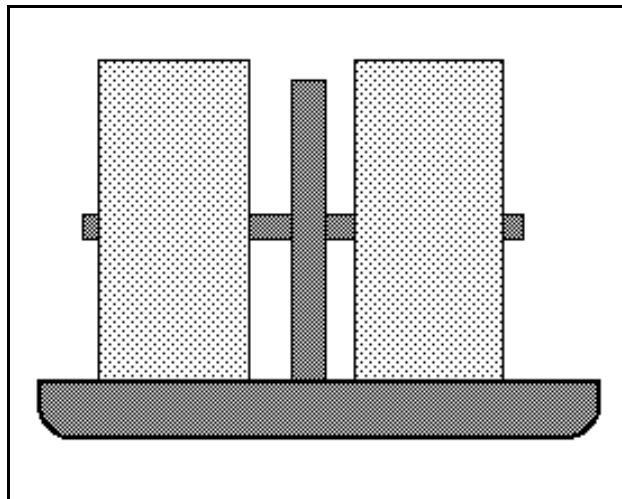


Black Powder



Black Powder Manufacturing Techniques and how Processing Variations Effects Behavior in Small Arms

William A. Knight
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A Brief History of Black Powder Production

The exact length of time in which black powder has been produced is unknown. Its use as a propellant is documented in the 14th century in both China and Europe. The use of what we know as black powder as a firearms propellant occurs in both Europe, Turkey and China within a span of about 20 years.

China.

The Chinese have been given credit for the development of black powder. Black powder was once known as "Fire Drug" in China. Saltpeter and sulfur were important pharmaceuticals and

black powder had been used to treat skin diseases, as an insecticide, desiccant and disinfectant.

The combination of saltpeter, charcoal and sulfur appeared before the end of the Tang Dynasty (618 -907).

Near the end of the Tang Dynasty small packages of gunpowder were attached to arrows.

Later, larger packages of gunpowder with ignited fuses were hurled by catapults or ballistas formerly used to hurl stones.

Hollow iron bombs filled with gunpowder appear about 1100. These were used as fragmentation bombs against leather armor and iron mail coats.

Early in the 12th century long bamboo tubes were filled with gunpowder and were used to throw sparks and flames.

By the mid-12th century pieces of metal were included with the gunpowder which were then ejected from the tube with the flames and sparks.

Bronze and iron barrels appear during the Yuan Dynasty (1271-1368). The Beijing Historical Museum houses a cast bronze cannon dated 1332.

There are of course questions on exactly how this "technology" migrated to Europe. The Arabs and Persians had learned of gunpowder in the first half of the 13th century and this has been proposed as a possible connection in the transfer of the technology.

Europe.

European tradition has it that black powder was invented in Europe by a monk named Berthold Schwarz in Freiburg, Germany. The date of this is placed around 1250 or as late as 1350. There is some question as to the accuracy of this or if such a person even existed at that time.

It is known that the development of black powder and black powder firearms occurred almost simultaneously in China, the Middle East and in Europe. The information simply following long established trade routes between these areas.

Black powder production evolved over a long period of time that reached its peak in both quantity and quality by the latter half of the 19th century. This evolutionary process included improvements in ingredient purity and methods of processing. Advances in powder-making technology lead to a greater number of applications for the product.

As a firearm propellant, black powder reached it's peak in quantities produced and product quality between 1850 and 1890. Black powder manufacturers were then faced with the introduction of other explosives and propellants that caused a decrease in demand for black powder and at the same time forced the industry to begin reducing the cost of producing black powder.

Prior to the early years of the 20th century black powder manufacturers purchased ingredients in what would best be described as a raw form. They then refined these ingredients, or prepared them, to their own specifications. The early years of the 20th century saw changes in sources of raw materials and the methods by which they were produced. In some instances the powder-maker was forced to change sources of raw materials even though it might result in a small compromise in powder quality. Powder-makers also had to change raw material sources as a means of reducing production costs.

Black powder manufacturing had always been a very labor intensive industry. The rise of labor costs in the early years of the 20th century resulted in changes in production methods to reduce the number of man-hours required to produce a pound of powder. These changes also resulted in some compromising of product quality.

Types Of Small-Arms Black Powder

During the 19th century there were 3 types of black powder in use in small-arms. Each type was specifically produced to give optimum performance in a particular caliber range or with different projectile masses. It is possible to vary the combustion characteristics of black powder to produce a powder best suited in specific applications.

Sporting powder.

Sporting powders were generally used in the smaller caliber arms. This included round-ball guns up to, and including .50 caliber. Sporting powders were, generally, low density powders with very fast burn rates. Sporting type powders continued to be used in the smaller pistol cartridges. Sporting powders were generally loaded at "one grain per caliber", or less. A sporting powder would give diminishing returns above one grain per caliber.

Rifle powder.

Rifle powders were used in round-ball guns between .52 and .54 caliber. A rifle powder gives diminishing returns at about 1.4 to 1.5 grains per caliber. Rifle powders were used in a number of rifle and pistol cartridges. A rifle powder does not burn as fast as a sporting powder.

Musket powder.

Musket powders were used in round ball guns of .58 caliber, or larger, and in guns firing elongated projectiles and in black powder cartridges .45 and larger. Musket powders gave diminishing returns at 1.6 grains per caliber.

The differences in ballistic strength between the 3 types of black powder is shown in the following data where three different brands of black powder presently on the U.S. market represent the three different types of small-arms black powder produced throughout the 19th century.

Test rifle: .50 caliber Lyman Great Plains Rifle, flintlock ignition with a 30 inch barrel.
 .490 Speer balls, .018 pillow ticking wetted with Lehigh Valley Shooting Patch Lubricant.
 Charges being 84 to 85 grains weight thrown by a calibrated volumetric measure.

Grain sizing.

Swiss #2 powder, 18 mesh to 32 mesh, loading density 1.08 g/cc.
 Goex 3f powder, 20 mesh to 50 mesh, loading density 1.05 g/cc.
 Elephant 3f powder, 20 mesh to 50 mesh, loading density 1.09 g/cc.

Velocity.

1877 fps ave., Swiss #2 powder.
 1671 fps ave., Goex 3f powder.
 1469 fps ave., Elephant 3f powder.

In this data one sees the classic difference in ballistic strength. Ideally the difference should be 10%. That is to say that a rifle type powder is 10% “stronger” than a musket type (burn rate) powder as a sporting type (burn rate) powder is 10% “stronger” than a rifle type powder.

These data show that the rifle type powder is 13.8% faster, or “stronger” than the musket type powder in this gun while the sporting type powder is 12.3% faster, or stronger, than the rifle type powder. In total, the sporting type powder is 26.1% faster, or stronger, than the musket type powder.

This data shows the difference in burn rates and how it affects velocities when grain size and grain densities are similar.

The increasingly higher velocities are of course the product of increasingly higher pressures in the bore.

There are differences, between the three types, in ingredient properties, processing methods and physical properties in the finished powder.

These data may be compared to a well known mid-19th century source of information of various types of black powder from various manufacturers.

In 1845 Capt. Alfred Mordecai of the U.S. Army Ordnance Department published his work titled, “Report Of Experiments On Gunpowder Made At Washington Arsenal, In 1843 and 1844”.

Using the .69 caliber musket barrel, a .64 caliber round ball weighing 397.5 grains, a paper wad weighing 10.8 grains and 120 grains (Troy) of various powders.

1499 fps, musket powder, du Pont.

1680 fps, rifle powder, du Pont.

1856 fps, sporting powder, du Pont.

Here we see rifle powder that is 12.1% faster than the musket powder while the sporting powder is 10.5% faster than the rifle type powder. The sporting powder being 22.6% faster than the musket powder.

1522 fps, rifle powder, Hazard Powder Company.

1648 fps, sporting powder, Hazard Powder Company.

Here we have a sporting powder that is 8.3% faster than the rifle type powder from the same manufacturer.

1606 fps, rifle powder, English manufacture.

1818 fps, sporting powder, English manufacture.

Here we have a sporting powder that is 13.2% faster than the rifle powder.

1478 fps, musket powder, French manufacture.

1735 fps, sporting powder, French manufacture.

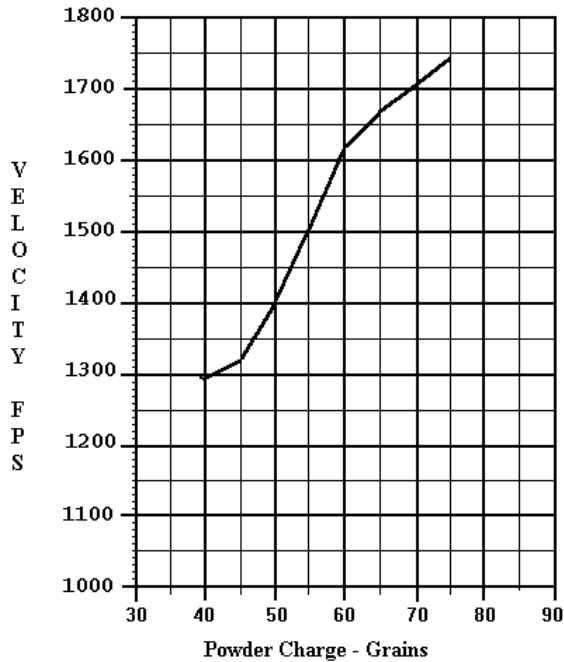
Here we have a sporting powder that is 17.4% faster than the musket powder.

To explain point of diminishing returns, powder type and charge volume.

When you work up a load in a muzzle loading firearm, using black powder, you make incremental increases in the volume, or weight, of powder charged to the bore. A point is reached

where the incremental increase in powder produces less of a velocity increase compared to previous increases. The point at which the decreased gain is noted is the point of diminishing returns. This point of diminishing returns is determined by the "expansive force" of the powder charge. The expansive force being a relationship between the volume of gases produced by the powder charge and the temperature at which the powder burns and the diameter of the bore.

Using powder charges in excess of the point of diminishing returns may cause a marked increase in bore fouling, a noticeable increase in recoil and may reduce the useful life of the barrel by increasing the rate at which the breech area metal erodes, or wears away.



Test rifle: TVM Southern Mountain rifle
 .45 caliber, 35.5" barrel with flintlock ignition.
 .440 Hornady round balls.
 .020" #40 cotton drill patching.
 Lehigh Valley Shooting Patch Lubricant.
 Elephant 3f, Date Code 25/99 Lot 054

40 grs., 1295 fps ave.
 45 grs., 1317 fps ave. (22 fps increase)
 50 grs., 1399 fps ave. (82 fps increase)
 55 grs., 1509 fps ave. (110 fps increase)
 60 grs., 1619 fps ave. (110 fps increase)
 65 grs., 1676 fps ave. (57 fps increase)
 70 grs., 1702 fps ave. (26 fps increase)
 75 grs., 1747 fps ave. (45 fps increase)

Figure 1. Point of diminishing returns graph

The line formed on the graph changes angles at 60 grains charge volume. The numerical data shows a drop in the incremental increase in velocity with incremental increases in the amount of powder charged to the bore. This drop off is the point of diminishing returns. This 60 grain charge drop off is typical with a rifle burn rate (type) powder in a .45 caliber bore.

This particle size distribution graph shows the effect of wheel-milling times on the particle size of the charcoal ingredient in black powder. Basically, longer milling time yields

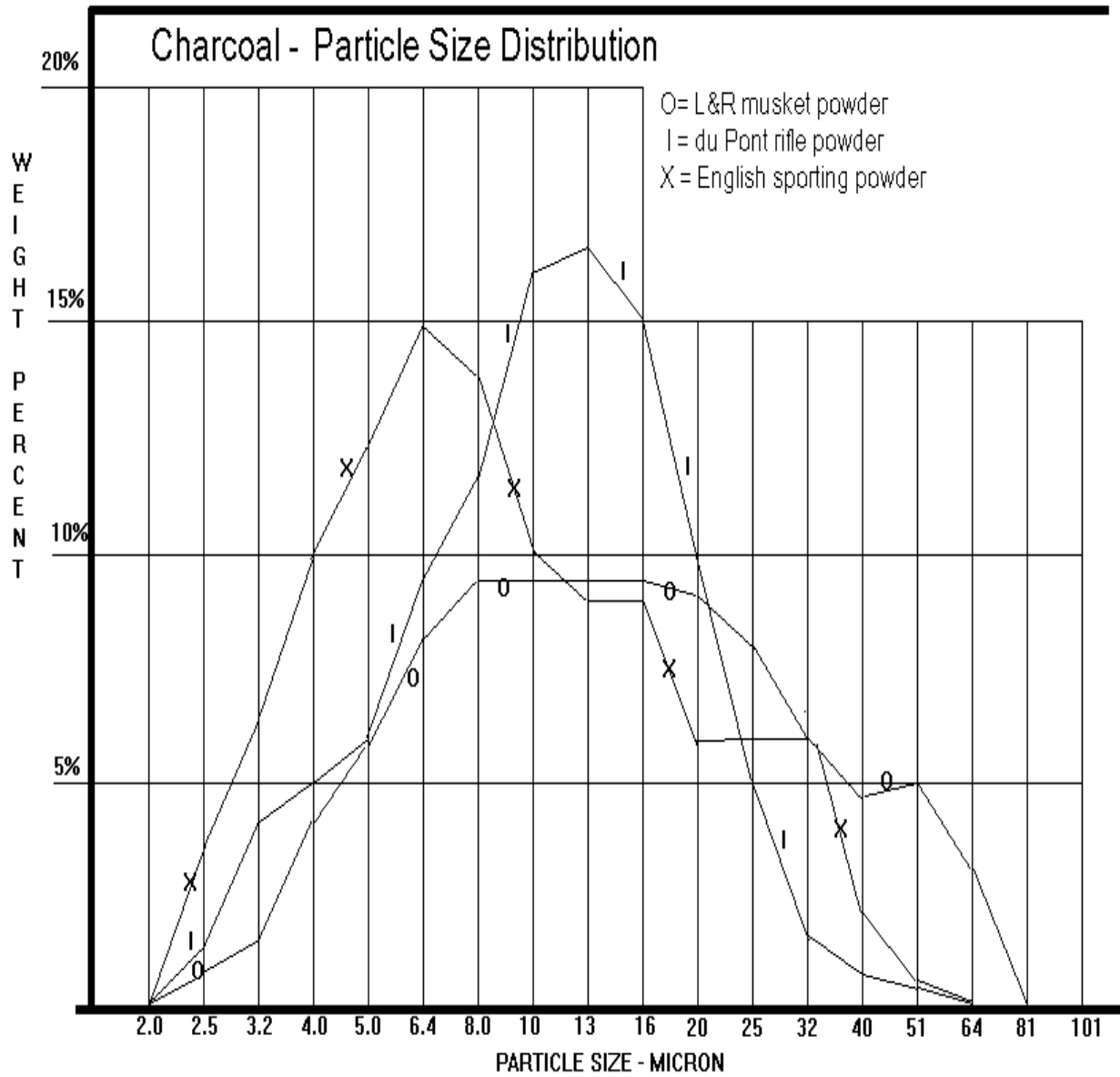


Figure 2. Powder type - charcoal particle size distribution

smaller particle sizes and therefore faster burning powder.

- Sporting powder: 65 - 75% in the 2 to 10 micron size range.
- Rifle powder: 50 - 55% in the 2 to 10 micron size range.
- Musket powder: 35 - 45% in the 2 to 10 micron size range.

Ingredients, proportions and desired properties.

Sulfur.

The sources of commercial sulfur changed several times during the past 100 years. During the first half of this century, sulfur from the Gulf Coast replaced sulfur imported from Italy. More recently, sulfur produced as a by-product of petroleum refining began to replace Gulf Coast sulfur.

Powder-makers will alter the proportion of sulfur depending on the type of powder being produced or use fractional alterations in the formula to adjust final burn rates in the powder.

Different sources of sulfur may produce changes in burn rates if a powder producer changes suppliers.

In the powder, sulfur acts as a combustion reaction rate accelerant.

During exposure to high relative humidity, powdered sulfur showed no weight gain so it does not add to the hygroscopic properties of the finished powders.

Potassium nitrate.

Potassium nitrate is used as the source of oxygen in propellant types of black powder. In discussing potassium versus sodium nitrate in black powder formulations, potassium nitrate is retained in black sporting powders and in fuse powders, where uniformity of burning and of moisture content is essential. (Rogers' Industrial Chemistry)

Over the period of the past 100 years the source of potassium nitrate has changed several times. Presently, almost all potassium nitrate is produced by reacting potassium chloride with nitric acid with chlorine gas as a by-product. Almost every country with salt deposits is in the business of producing various potassium salts, used mainly in agricultural applications.

There are a number of processes used to convert potassium chloride to potassium nitrate via nitric acid. Some processes are more efficient than others. Published purity data shows that minimum purity is 99.0% and a maximum purity of 99.9%, though some do fall below the 99.0% purity level. The process used in Israel produces a less pure product that is then given a second pass. The product from the second pass is roughly 99.9% purity potassium nitrate with chlorides less than 350 parts per million and no detectable level of sodium.

I point these differences out since residual potassium chloride in black powder is what gives the powder's combustion residue corrosive properties. Black powder that is almost entirely free of chlorides is relatively non-corrosive.

Some powder-makers specify 99.5% purity potassium nitrate while others might insist on 99.9% purity. In many respects it is more important to look at what the actual impurities consist of rather than fractional differences in amounts.

Saltpeter purity and hygroscopic behavior.

Haifa Chemical Ltd. 99.9% purity, sodium free.
Supplier "B", 99.0% purity, 0.4% sodium nitrate.

100 grain samples placed in foil trays measuring 3 inches by 4 inches.
Samples previously dried to constant weight in an oven for 4 hours at 250 Degrees F.

	Haifa Chem. <u>Increase, % weight</u>	Supplier "B" <u>Increase, % weight</u>
59% RH	0.1%	0.4%
78% RH	0.1%	0.4%
80% RH	0.3%	0.9%
83% RH	0.3%	1.9%
86% RH	0.4%	2.4%
93% RH	1.0%	8.9%
93% RH(24 hrs. Total)	1.2%	17.9%

After the initial 93% RH reading the Supplier "B" sample continued to gain in weight and the contents of the tray began to liquify.

The above data does not suggest that those levels of moisture weight increase would be found in the finished powder. The data simply shows that in a finished powder the amount of sodium nitrate present could exert an influence on the hygroscopic property of the powder out of proportion to the actual amount of sodium nitrate present.

What the data does show is that a powder prepared with the sodium-free 99.9% purity saltpeter will be more resistant to high humidity compared to a powder prepared with a saltpeter containing even small amounts of sodium nitrate

The inclusion of traces of sodium nitrate will make it difficult to exactly determine the moisture content in a finished powder since it is necessary to heat the sodium nitrate to the boiling point of water (212 F) to drive all of the water from the sodium nitrate. Heating black powder above 170 degrees F results in the volatilization of a portion of the sulfur and it is not then possible to relate weight loss as moisture loss alone.

Potassium nitrate exhibits hygroscopic behavior. Sodium nitrate exhibits deliquescent behavior. Webster's New World Dictionary defines Hygroscopic as, "absorbing moisture from the air". Deliquescence is defined as, "to become liquid by absorbing moisture from the air."

The so-called standard 75 parts of potassium nitrate is not really standard in small-arms black powder. The Swiss presently make a sporting type black powder using 78 parts of potassium nitrate in the formula. Old French and English powder makers used 76 to 77 parts of potassium nitrate in the faster burning grades of small-arms black powder. Other types, such as blasting or safety fuse, may be formulated with 70 to 72 parts of potassium nitrate.

Charcoal.

While the properties of all three ingredients are important, properties of the charcoal used to make black powder are critical to what a shooter would perceive as "quality" in a black powder.

When the formula for black powder is shown as a chemical equation the charcoal ingredient will be shown as pure carbon, or C. In actuality you would not want to make a black powder using pure carbon.

Numerous types of wood have been used to make black powder and why some are better than others has been treated as something of a mystery.

Slow-burning types of black powder may be prepared from any form of cellulose, starch or sugar. In the preparation of faster-burning types, such as a musket or rifle powder, the acceptable type of woods are reduced in number. In preparing the very fast-burning sporting type powders the acceptable woods are few in number.

Cellulose is considered to be a "high-polymer" of sugar. Sugar molecules form long chains which form the basic units of structure in the cellulose. The number of sugar units forming a unit of structure in cellulose may vary from a few thousand to over one million.

Wood "cell" structure varies considerably from one species to another. The tubular "macro-structure" of wood also varies considerably.

Different species of woods produce varying amounts of lignin which acts as a binder within the macro-structure of the wood. Starches and simple sugars are often stored within the wood's macro-structure. All of these play some part in how the wood will char, the char's final properties and how the char will behave in a black powder.

The macro-structure of the wood must be fine and somewhat delicate. Wood with a thick, or heavy, structure will be difficult to grind to the particle sizes required for faster-burning types of black powder.

Ideal charcoals based on type of powder being prepared.

Sporting: In order of preference; Glossy Buckthorn Alder, Black Alder and then White Willow.

Rifle or Musket: Alder or Willow. Maple will work, but not as well.

Blasting: almost any form of cellulose, starch or sugar. (Sugar though is most hygroscopic.)

Charcoal used in black powder is not pure carbon. The char is composed of pure carbon, partially carbonized cellulose, minerals and varying amounts of phenolic-structured liquid hydrocarbons (specifically creosote).

S. Fordham, "High Explosives" wrote that the properties of black powder depend considerably on the charcoal used. He cites 74% fixed carbon as being ideal with alder and buckthorn alder. Soft woods freed from bark give the best results.

Fordham also goes on to describe a constituent of charcoal "which can be extracted with acetone and is shown to contain carbon, hydrogen and oxygen".

In working with alder charcoal charred below 320 degrees C an acetone extraction of the char produced creosote. Wood creosote having been known as oil of creosote. An interesting observation came out of this work. Here in the U.S. the preferred woods for black powder charcoal were, in descending order, alder, willow and lastly maple. These being the preferred woods for use in small-arms powders. In the charring tests and acetone extractions the alder wood char would yield as much as 6 to 8% creosote by weight of char. Willow would yield 4 to 5%, while maple char would yield 2 to 3% creosote by weight of char.

S. Fordham describes the behavior of this acetone extractable liquid hydrocarbon during powder combustion and suggests that its presence speeds up the chemical combustion reactions within the powder. This theory was put to the test using Swiss black powder that proved to be rich in creosote. Several ounces of some Swiss #2 size powder was extracted in dry acetone. The acetone extraction had no effect upon the mechanical properties of the grains of powder. Contact with dry acetone did nothing more than remove any traces of moisture present along with the creosote. When fired in the test gun there was no difference in the velocity produced by the acetone extracted powder compared to the powder as received. That would suggest that the presence of creosote in the charcoal does not act as a combustion reaction accelerant. The comparative shooting did show that the Swiss powder noted for being a "moist-burning" (Nassbrand) powder no longer exhibited this property once the creosote was removed. The bore residue left by the sample of acetone extracted powder was dry and powdery. Not unlike any of the other brands of black powder prepared with chars that are almost totally lacking in measurable amounts of wood creosote.

Recent experiments at the S/A Pernambuco Powder Factory, in Brazil, have shown that given the same species of wood, a char produced at relatively low charring temperatures will be soft compared to the same char produced at higher temperatures. This soft char is more easily reduced in particle size in the wheel mill and will produce a faster burning powder as a result. When rubbed between the thumb and forefinger the low temperature char will give a "silky" feel while char prepared at a high temperature will feel somewhat hard and gritty.

S. Fordham mentioned, "soft woods freed from bark". Within the present black powder manufacturing industry some powders are prepared using wood with the bark removed while others use charcoal prepared with the bark still on the wood.

If one reads late 19th century sources on the subject of charcoal they will comment that powder prepared from charcoal containing charred bark will exhibit a property they called scintillation. When the powder is fired in a gun under low light conditions there will be sparks thrown from the bore when the projectile exits the muzzle.

When wood is charred with the bark on the wood the bark chars to nearly pure carbon. Pure carbon does not ignite until the temperature reaches 2000 degrees C and then burns only slowly. That portion of the charcoal that had been bark simply increases the amount of bore residue left after the powder has burned. Some of this nearly pure carbon is ejected from the bore with the gases following the exit of the projectile from the muzzle. These minute bits of carbon continue to glow after being thrown from the muzzle of the gun.

The presence of charred bark in a charcoal prepared for use in a black powder is objectionable from another point of view.

Specifications for charcoal to be used in black powder usually call for an ash content of 2.5% maximum. The ash left by charcoal being composed almost entirely of minerals that were present in the wood during charring. These are alkaline in nature and a small amount is desired in a powder to act as an anti-acid or buffering agent in the event the sulfur particles produce traces of acids with presence of small amounts of moisture. An excess of mineral content will add to the amount of fouling the powder leaves in the bore of the gun.

An excessive mineral (ash) content in a charcoal will also increase the hygroscopicity of the finished powder. Generally, the minerals that comprise the ash portion of the char will border on being deliquescent rather than being merely hygroscopic.

To look at the effect of mineral content on the hygroscopic property of charcoal two samples of imbauba wood charcoal were prepared. One portion was washed with hot water on a filter. Both the washed and "as received" samples were then dried in an oven at 250 degrees F for 3 hours, or "constant weight". Weighed portions were then spread out in a shallow layer in aluminum trays and exposed to the air at varying levels of relative humidity. Weight increases were recorded and calculated as percentage weight increase, or decrease.

	<u>"As received"</u>	<u>"Washed"</u>
49% R.H.	3.4% increase	2.9% increase
51% R.H.	4.6% increase	4.2% increase
67% R.H.	5.4% increase	5.2% increase
80% R.H.	6.2% increase	5.8% increase
89% R.H.	7.4% increase	7.4% increase

This data suggests that at low levels of relative humidity the mineral content of the charcoal will effect the hygroscopic behavior of the char but that at high levels of relative humidity the vast surface area of the ground char plays the dominate role in hygroscopic behavior.

While on the subject of the hygroscopic properties of charcoal there is another aspect that requires some explanation. Sources from the 19th century in England commented that charcoals prepared for sporting type powders were more hygroscopic than those prepared for the slower burning types of black powder. The difference between the two chars being their respective fixed carbon levels.

To look at that two samples of imbauba charcoal were prepared. The charcoal normally used has a 70 to 72% fixed carbon content. A portion of this was charred a second time to raise the fixed carbon content to 90%. These samples were then dried at 250 degrees F in an oven for 3 hours, or to constant weight. Weighed portions were then placed in aluminum foil trays and exposed to air at varying levels of relative humidity. Weight changes calculated as percentage increase or decrease.

<u>R.H. and total time</u>	<u>As received, 70% Carbon</u>	<u>90% Carbon</u>
59% R.H. - 0.5 hr.	2.5% increase	1.6% increase
59% R.H. - 1.0 hr.	3.9% increase	2.5% increase
65% R.H. - 3.0 hr.	5.9% increase	4.0% increase
70% R.H. - 4.0 hr.	6.3% increase	4.9% increase
85% R.H. - 6.0 hr.	6.9% increase	5.7% increase

These data might best be explained by comparing the hygroscopic properties of wood to the hygroscopic properties of graphitic carbon. Higher fixed carbon content simply results in a less hygroscopic char.

At this point it is necessary to broaden the scope of this section and sum up the subject of the hygroscopic behavior in a finished powder. Minimizing the hygroscopic property of a powder is important in ballistic strength and the storage life of a finished powder. Sulfur is not hygroscopic so the question of hygroscopic behavior is addressed in the purity level of the potassium nitrate used and in the properties of the charcoal used. Mineral content influence on hygroscopic behavior is addressed through the removal of the bark on the wood prior to charring. The type of powder being prepared determines the optimum fixed carbon content of the char so the degree of hygroscopic behavior relating to the fixed carbon content simply becomes a fixed property that must be dealt with in other ways. That will be covered in the section on glazing black powder.

Post-charring preparation of the charcoal.

After the charcoal has been removed from the charring vessel it is necessary to grind the charcoal to a powder prior to its use with potassium nitrate and sulfur in the wheel mills. This may be accomplished by any of several methods. In some powder plants the charcoal is run through a hammer mill. Another manufacturer may combine charcoal with sulfur and use a ball mill to grind both together at the same time. The old English and European method called for grinding the charcoal in a small wheel mill. The charcoal wheel mill usually being a 2.5 ton mill.

How well the charcoal is ground prior to being incorporated with sulfur and potassium nitrate in the large wheel mills is seen in the following data.

Test rifle: .50 caliber Lyman Trade Rifle, 28 inch barrel with percussion ignition.
 .490 Speer round balls, .020 #40 cotton drill patching, Lehigh Valley Shooting Patch Lubricant.
 #11 CCI Magnum percussion caps.
 Pact Professional Chronograph.
 80 grain charges
 1450 fps ave. velocity, control sample.
 1540 fps ave. velocity, wheel mill ground charcoal passed through a 40 mesh screen.

The only difference in the processing of these powders was that the control sample used charcoal directly from the break-down mill while the experimental sample used a finer particle size charcoal that had been passed through a 40 mesh screen to cull out the larger pieces of char.

Water.

Water is never shown as an ingredient in black powder since only trace amounts are found in the finished powder. With some powder-makers, a batch of black powder may contain as much as 10%, by weight, of water at the beginning of the wheel-milling cycle.

The purity of the water used to wet the batch of powder, during processing, is critical to the chemical stability of the powder. The use of impure water will result in a black powder lacking in chemical stability. A black powder lacking in chemical stability will lose ballistic strength and the powder grains will become weak and crumble as they lose the cohesiveness of the mass imparted by press densification. This process will occur at varying rates independent of actual storage conditions.

One 19th century English military paper stated that powder made with impure water will be weak and not store well.

At that period in time most companies manufacturing black powder would purify raw potassium nitrate imported from India. The purification process used large quantities of water. Their concern centered on the mineral content of their water source. Distilled water being used in the potassium nitrate purification process to prevent the addition of unwanted minerals to the potassium nitrate being purified.

The first point in this to be addressed will be the “and not store well” comment from the 19th century English military paper.

In the mid-1970's the U.S. military suffered several large caliber gun malfunctions that were traced to a specific lot of black powder that had been used as the intermediate primer in this large-caliber gun loadings. The Ballistic Research Laboratory at the Aberdeen Proving Ground, Maryland, began an extensive study into the problems in these large-caliber gun loadings. A portion of the results of their work was published in a paper titled, “Effect Of Black Powder Combustion On High And Low Pressure Igniter Systems”.

One of the tests run on various lots of black powder from two different suppliers is known as “Relative Quickness” or RQ. The sample of powder to be tested is placed in a pressure bomb. An ignitor device ignites the powder. The “relative quickness” is the length of time from the moment of ignition until peak pressure is reached in the bomb. This is something of a comparative test hence the use of the term “relative” quickness.

<u>Lot</u>	<u>Relative Quickness</u> (Based on CIL 7-3)
CIL 7-3	100.0
CIL 7-6	95.2
CIL 7-10	99.1
CIL 7-11	88.3
GOE 75-2	107.7
GOE 75-7	131.1
GOE 75-14	121.9
GOE 75-24	117.0
GOE 75-32	129.8
GOE 75-40	148.3
GOE 75-44	149.3
GOE 75-53	149.5
GOE 75-61	162.6

In the case of the powder known as “GOE” we see samples representing a span of production in the year 1975. Lot 75-2 would have been produced early in 1975 while Lot 75-61 would have been produced toward the end of 1975. Lot 75-2 would be almost a full year older than Lot 75-61 at the time these powder samples were being tested in 1979. Lot 75-61 being about 4 years old while Lot 75-2 was closer to 5 years in age.

The RQ data shows a clear pattern of a slowing of the ignition and combustion of the powder with increasing periods of aging.

The old concept of chemical stability in a black powder involved a slow acidification of the powder. The concept being that when you grind sulfur to a fine particle size it will form a mono-molecular layer of the oxide of sulfur on the surfaces of the particles. When combined with traces of moisture, sulfurous acid is formed. Given time, this sulfurous acid will auto-oxidize to sulfuric acid. The acid initially formed will attack the potassium nitrate. The end product of this chemical change being potassium sulfate.

I should point out that this process is usually inhibited by the presence of alkaline minerals contributed by the charcoal used in the powder. Once these minerals, acting as an anti-acid, or buffering agent, are consumed the process of chemical change becomes a typical self-accelerating reaction.

Though not stated in any technical sources, the chemical attack on the potassium nitrate ingredient liberates lower oxides of nitrogen that will then be found as nitric acid in the powder when traces of moisture are present. Any air in the powder container will also contain lower oxides of nitrogen. Both the powder and air extracted from the container will test positive in a diphenylamine spot test.

Chemical change within the powder will slow both the ignition and combustion of the powder in addition to reducing the total amount of energy a given weight of powder will produce. Loss of elemental sulfur slows the chemical reactions during powder combustion. Loss of available oxygen reduces the amount of energy released by the powder.

When black powder manufacturers purified raw saltpeter, usually imported from India, they always used distilled water in the purification process.

When a batch of black powder is “laid up” in the bed pan of a wheel mill it is necessary to wet the batch prior to starting the mill wheels in motion. The amount of water used to wet the batch is usually about 10% of the batch. Or roughly 10 pounds of water per 100 pounds of mill batch weight. During the milling time it may be necessary to add more water to compensate for evaporation, especially at low relative humidity. Another point where water might come in contact with the powder is just prior to the pressing of the powder in the powder press.

When a powder manufacturer purified saltpeter they would use “liquor” from the saltpeter refining house. This would be distilled water containing some potassium nitrate in solution.

When powder manufacturers ceased refining their saltpeter after high-purity potassium nitrate became available as an item of commerce the powder plants then used “potable” water. If it was good enough to drink it was considered good enough for use in the powder. Only a few powder manufacturers continued to use distilled water in their powder and some reserved it for use only in critical speciality powders, such as time ring fuse powder.

When a grained black powder undergoes chemical decomposition the chemical reactions involved are promoted by the presence of moisture. Chemical changes will be most noticeable on the surfaces of the grains. Chemical changes within the core portion of the grain will be less in relation to the surface since the condition (moisture) that promotes these changes is confined mainly to the surface and near surface portions of the grains.

While the military looked at chemical stability of black powder via the Relative Quickness test there are other methods useful in this.

One of the end products of chemical change in a black powder is potassium sulfate that will be found as minute crystals deposited in the areas of the grain that underwent chemical change. Potassium sulfate is only poorly soluble in water and is totally insoluble in water if some other salt is in solution with the water. This allowed the use of a somewhat novel approach in looking at the extent of chemical change in a grain, or granule, of black powder.

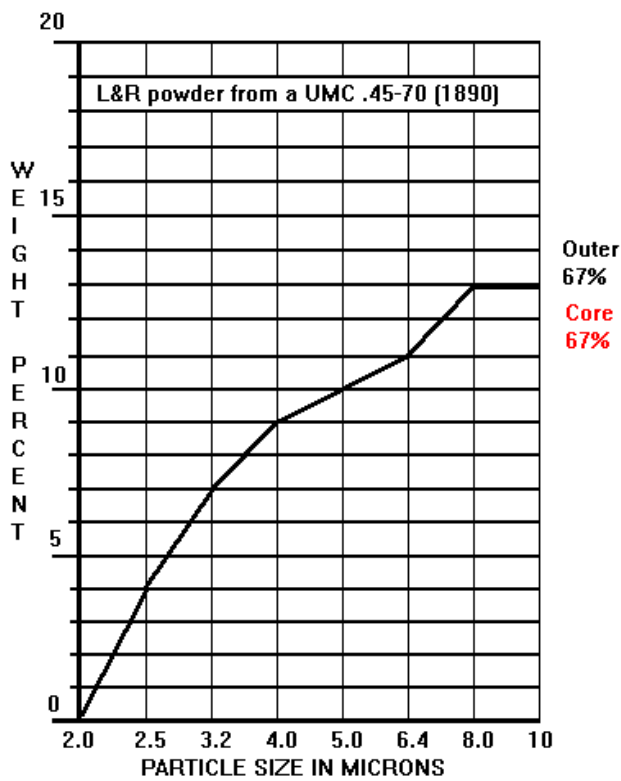


Figure 3. UMC .45-70 powder

under an optical microscope prior to running them through the Coulter Counter for actual numerical values.

Here we see a sample of black powder that was manufactured by the Laflin & Rand Powder Company. Made at a time when the company carried out their own saltpeter purification using distilled water.

The Coulter Counter scan of the near grain surface washing and the core of the grain shows no difference. This indicates that during the nearly 100 years of storage in a loaded .45-70 cartridge there was little detectable chemical change in the powder. In addition, L&R advertised that their powder was “triple refined” meaning that they refined the ingredients to a high state of purity. This was known to promote chemical stability in the black powder.

If you place a few grains of black powder in a funnel made from 200 mesh stainless steel screening you may slowly erode the grains through incremental washing with water. You may literally take the powder grains apart in layers from the surface down to what would be a central core. If you use a saline solution as the wash water any crystals of potassium sulfate will remain intact since they are insoluble in a saline solution.

The piece of test equipment used in this work was a Coulter Counter used in medical laboratories to count and size blood cells. It also proved very useful in looking at the size of the charcoal and sulfur particles in a large number of samples of black powder. The machine is to count and size any particle of matter that is not soluble in the saline solution used as an electrolyte in the testing procedure. The samples were first viewed

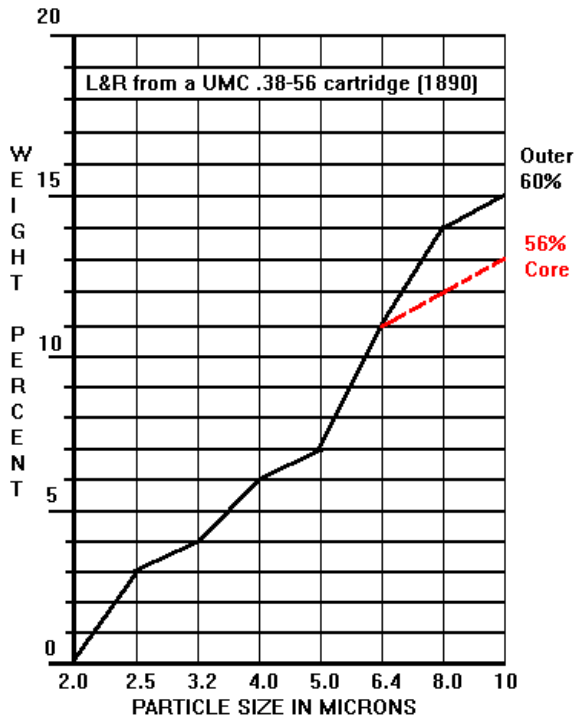


Figure 4. UMC .38-56 powder

Here is another sample of L&R powder from a .38-56 black powder cartridge loading. This data shows a small amount of change in roughly 90 years of storage in a brass cartridge.

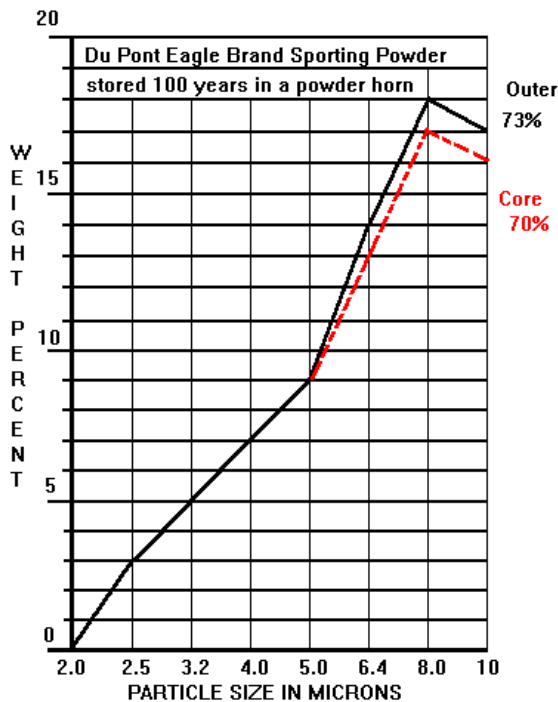


Figure 5. Du Pont Eagle Brand Sporting

This is a sample of Du Pont Eagle Brand Sporting Powder that came out of a powder horn. A tag on the horn stated that the powder dated to 1880. The horn came down to the owner from his great-grand father who shot a muzzle loading rifles until the last decade of the 19th century.

This Du Pont powder had been made at the original E. I. Du Pont De Nemours Gunpowder Manufactory on the Brandywine Creek a short distance to the North of Wilmington, Delaware. One of the plant's wheel mills was dedicated to sporting powder production and was known as the "Eagle Mill". This sample of powder was produced when Du Pont was still purifying saltpeter.

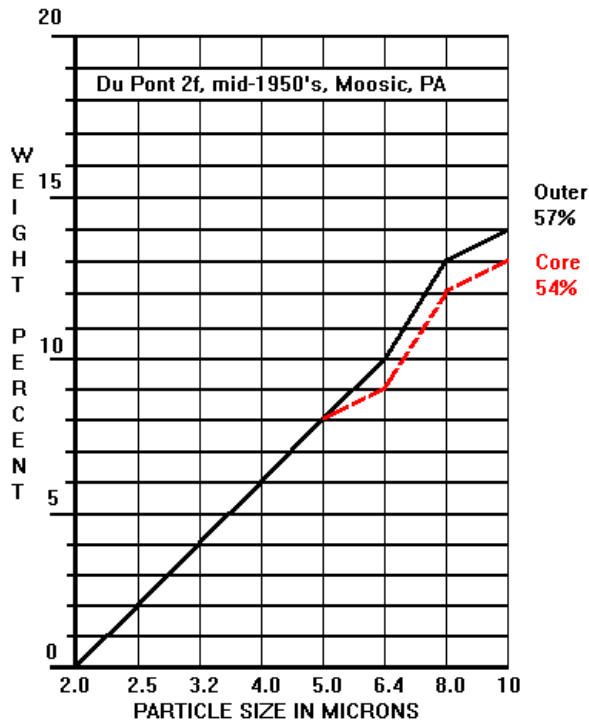


Figure 6. Du Pont - 1950's - Moosic, PA

This is a sample of Du Pont 2f Rifle powder made sometime in the mid-1950's at the Moosic, PA powder plant.

At this point in time Du Pont was using commercial potassium nitrate that did not require purification prior to its use in black powder. The plant also used commercially prepared charcoal purchased outside of the company.

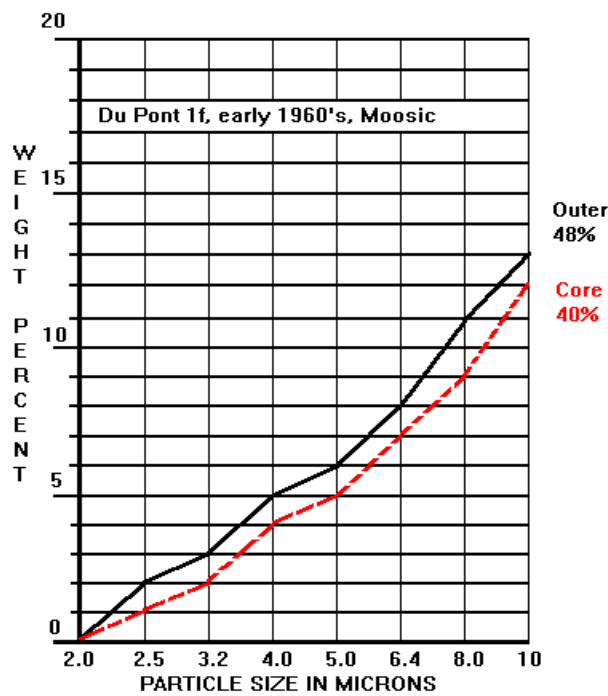


Figure 7. Du Pont - 1960's - Moosic, PA

This is a sample of Du Pont 1f Rifle powder made in the early 1960's at the Moosic, PA powder plant.

Note that we now see a noticeable difference between the outer portions of the grain and the inner core of the grain.

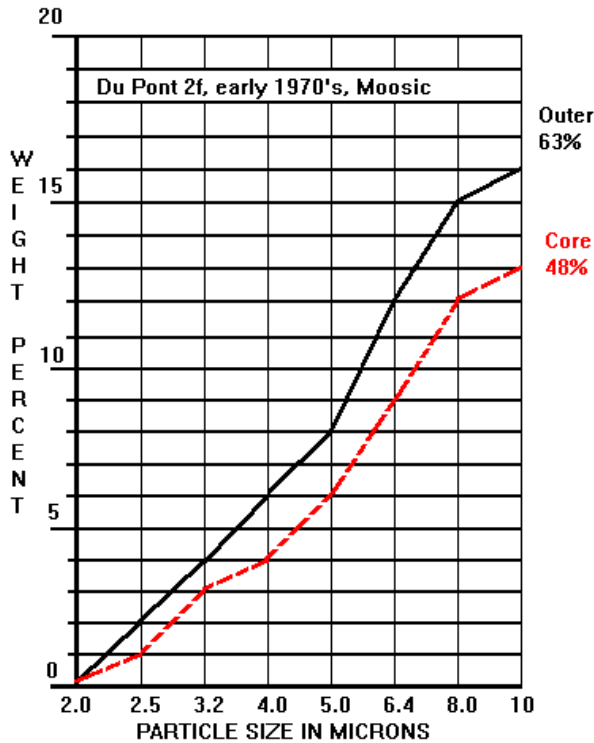


Figure 8. Du Pont - 1970's - Moosic, PA

Here we see a sample of Du Pont 2f Rifle powder produced in 1970 at the Moosic, PA powder plant.

Note the change from the previous graph (1960's) and the graph prior to that (1950's).

The difference between the outer portions of the grain and the inner core had been steadily increasing in the 3 powder samples from the Moosic, PA powder plant so far.

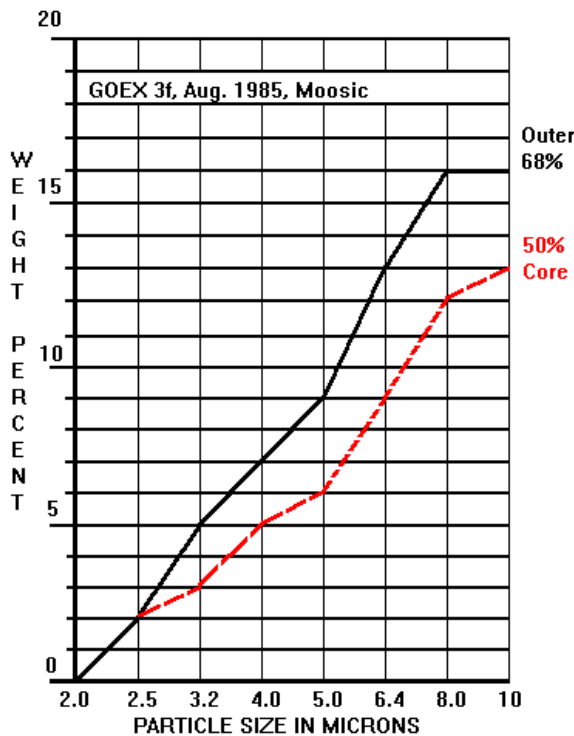


Figure 9. Aug. 1985 - Moosic, PA

In 1972 Du Pont sold their black powder business to what was then Gearhart-Owens and the company became known as Gearhart-Owens Explosives, or GOE as it appears in the Aberdeen Proving Ground work shown previously.

Within a few years the name changed to GOEX.

Here we see a sample of 3f powder made in August, 1985. The difference between the outer portions of the grain and the inner core have again increased.

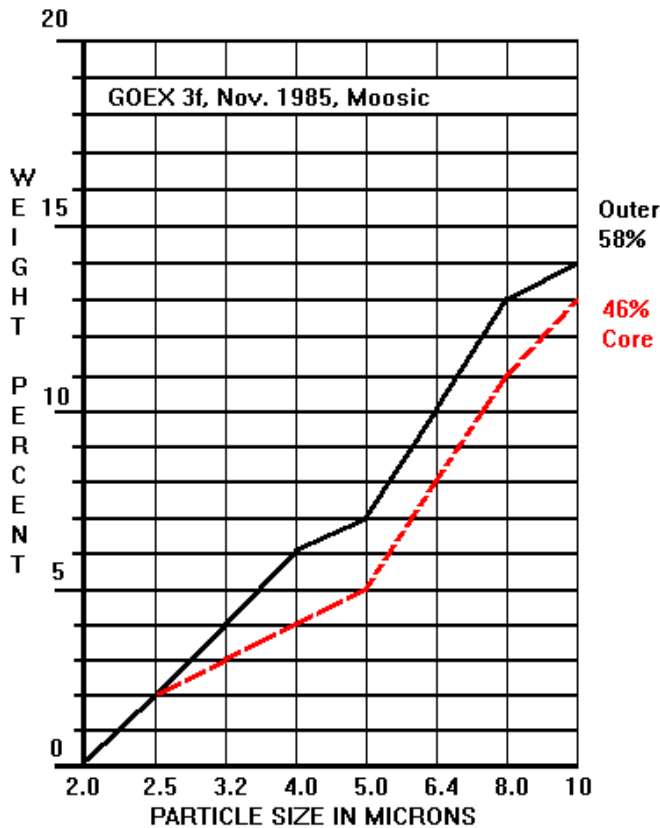


Figure 10. Nov. 1985 - Moosic, PA

To sum up the numerical data on the Moosic, Pa powder plant samples.

- 3% difference between the core and the outer portions of the grains in the 1950's sample.
- 8% difference between the core and the outer portions of the grains in the 1960's sample.
- 15% difference between the core and the outer portions of the grains in the 1970's sample.
- 18% difference between the core and the outer portions of the grains in the Aug. 1985 sample.
- 12% difference between the core and the outer portions of the grains in the Nov. 1985 sample.

If you look at the graph of the Du Pont powder made at the Moosic, PA plant in the 1950's and compare it to the graph of the powder from the same plant in the 1960's you see a very noticeable change in the extent of chemical change within the powder. That change was brought about by a change in the purity of the ground water in the area around Scranton, Pa and what constitutes the eastern end of the Pennsylvania hard coal mining area. This may be traced to a single event that occurred in 1959.

Here we have a sample of Goex 3f produced in November, 1985 or about 2 ½ months after the August sample. It is seen here that the difference between the outer portion of the grain and the inner core have decreased rather than increased.

These samples ranging from 1950's Du Pont to 1985 Goex represent a study in the effect of water purity on the chemical stability of black powder.

The Aberdeen Proving Ground Relative Quickness data looked at the chemical stability of a black powder from the view of behavior in the field. The graphs presented define one of the causes of chemical instability in black powder.

On the morning of January 22, 1959 the roof of a coal mine tunnel gave way in the Pittston Vein near Port Griffith, PA, a small town midway between Scranton, PA and Wilkes-Barre, PA. The event became known as the Knox Mine Disaster when 12 miners lost their lives by drowning. The coal mine tunnel extended under the Susquehanna River with only 6 feet of rock as a tunnel ceiling under the river bed. Roughly 2.7 million gallons of water per minute poured into the mine tunnel. That single event put an end to the deep mining of coal in that end of Pennsylvania's hard coal area. With a year or two, the water table in the area stabilized with the river level.

By the mid-1960's mine waste water seepage became a serious problem in that area. The mine waste waters are highly acidic and rich in dissolved ferrous sulfate. The state of Pennsylvania then began a program of sealing up any seepages that were allowing mine waste waters to enter local streams and rivers. This program had serious consequences in the quality of the well water in the area.

When veins of coal are removed the adjoining layers of rock will usually have large amounts of iron pyrites. Once the mine tunnels are abandoned and flooded the pyrites become "food" for bacteria. Iron fixing bacteria will remove the iron from the pyrite crystals. Sulfur oxidizing bacteria then use the elemental sulfur that was part of the pyrite. The sulfur oxidizing bacteria produce sulfuric acid as part of their biological waste. The water in the mine tunnels becomes rich in sulfuric acid and dissolved ferrous sulfate.

This process effected the quality of the ground waters over a wide area. The area had seen extensive underground coal mining for over 100 years. Extensive tunnel systems were interconnected so the water pollution created by the bacterial activity spread widely throughout the area's ground water. The Moosic, PA black powder plant sat roughly in the middle of this area.

Normally the plant used "potable" water supplied by the Moosic, PA municipal water treatment plant. That plant draws water from a small surface stream just outside of Moosic. In a visit to that stream in 1988 it was noted that the bottom of the stream has a coating of iron oxide showing that some mine waste water does enter into this stream. During periods of extreme drought the powder plant would be forced to use water from an on-site well as service water in order to reduce the demands upon the municipal system. This switching in and out of the plant's on-site well is what we see in the difference in data with the Aug. 1985 sample and the Nov. 1985 sample. The Nov. 1985 sample was produced a few weeks after a hurricane ended a drought that had started during the summer of 1984. The intensity of the drought grew until this hurricane produced 6 inches of rain over eastern Pennsylvania in one day. With surface waters again recovered to near normal levels the plant could return to the use of municipal water in the powder.

In essence it would be accurate to state that the chemical stability of the powder was relative to the amount of rainfall in the weeks prior to its production.

In looking at other brands of black powder made in other countries this relationship between water quality and chemical stability in a powder stood out. Powder plants using artesian well water usually make a powder with a high degree of chemical stability even if the water is not distilled prior to use. One plant uses water that is passed through a demineralizer. That powder also showed evidence of chemical change as viewed from the point of surface regions versus grain core. The problem was not confined to only the Moosic, PA powder plant.

How does the subject of chemical stability impact upon the shooter?

The Aberdeen Proving Ground RQ data shows that as chemical changes in the powder proceed there will be a slowing of the powder as the shooter would see the powder perform in a gun. If the same can of powder is used in the gun at a later date the shooter may note a drop in the point of impact as a result of a loss in velocity. Cans of powder that have undergone chemical change will usually be less accurate than powder that has not suffered extensive chemical change. Powder that has undergone extensive chemical change in the near surface portions of the grain will also tend to be dusty as the surfaces of the grains weaken and crumble with movement of the grains against each other during transit and use. Fine grain powder used as a lock prime in flintlocks will begin to give misfires. While the powder ignites it simply does not burn fast enough to produce a heat wave of sufficient intensity to ignite the main charge through the vent. In the extreme form the pan powder simply refuses to ignite reliably with sparks from the frizzen.

In dealing with flintlocks and lock pan powders. About 60% of the "lock time" that is perceived by the shooter is a function of the burning speed of the powder in the pan. If the powder slows down it will give longer lock times.

In dealing with main charge powder in both flintlock and percussion guns. When the powder undergoes extensive chemical change in the near surface regions of the grains the powder becomes more difficult to ignite and slower to ignite. This will lengthen what is perceived as lock time. Powders that have undergone extensive chemical change on the surfaces of the grains will give very noticeable hangfires.

Another point here. When black powder is press densified the process of pressing causes a consolidation of the mass of powder. Contacting edges of potassium nitrate crystals fuse together. This imparts a degree of mechanical strength to the mass and keeps the powder from crumbling. Since the chemical reactions in powder decomposition effect the potassium nitrate, in the minute passageways within a grain of powder, there will be a breaking of this points were crystal fusion had occurred. With continued chemical change the grains loose some of their mechanical strength and become friable and prone to crumbling. Soft grains will cause a loss in accuracy.

The following photographs of powder from the old Moosic, PA black powder plant will show this loss of grain strength.



This is a microscope photograph of grains of Du Pont rifle type powder out of the old Moosic, PA black powder plant dating to the mid-1950's. The appearance of these grains is typical for powder grains made by the Du Pont methods and machinery.

Figure 11. Moosic, PA, mid-1950's



Here we have a microscope photograph of a lot of powder out of the Moosic, PA black powder plant made in January, 1988. This sample of powder showed that grain break-up had occurred during the handling and shipping of this lot prior to its purchase by the shooter.

Figure 12. Moosic, PA - Jan., 1988



Figure 13. Moosic, PA - May, 1988

Here we see a sample of powder produced in May, 1988 in the same plant. Note that the surfaces of the powder grains no longer exhibit the flat planes of cleavage produced during the corning step in the powder-making process. The presence of the large spherical grain of powder indicates that during the glazing step the grains of powder had been shedding considerable amounts of dust which then formed spherical agglomerations as the powder tumbled in the rotating glazing drum. Some of the bits of broken grains would attach to other grains during the tumbling. As the powder grains formed a “glaze”, or skin, the attached debris was then bonded to the surfaces of the grains where they had adhered initially.

The spherical grains were nothing more than balls of loose dust that had formed a very thin glaze, or skin, during glazing. They were easily broken and simply crumbled to dust with pressure or a light impact on the surface.

These spherical grains of black powder were not uncommon in lots of powder made during periods of severe drought when the powder plant would change from Moosic municipal water to on-site well water in the powder. The less pure well water causing chemical change in the powder while it was being processed in the plant.

Based upon examination of a large number of powder samples representing roughly 35 years of plant production there were three periods of time where well water was used to produce powder. Those periods would be 1974-75, 1984-85 and again in 1987-88. These periods were periods of extreme drought with each successive drought being more intense than the previous drought. The drought of 1987-88 being the worst drought in weather record keeping history in eastern Pennsylvania. With droughts there is not sufficient rainfall to dilute ground waters polluted with acid mine waste waters. During the drought of 1987-88 the small stream that runs through the little village of Moosic, PA was colored bright orange by the iron found in that water.

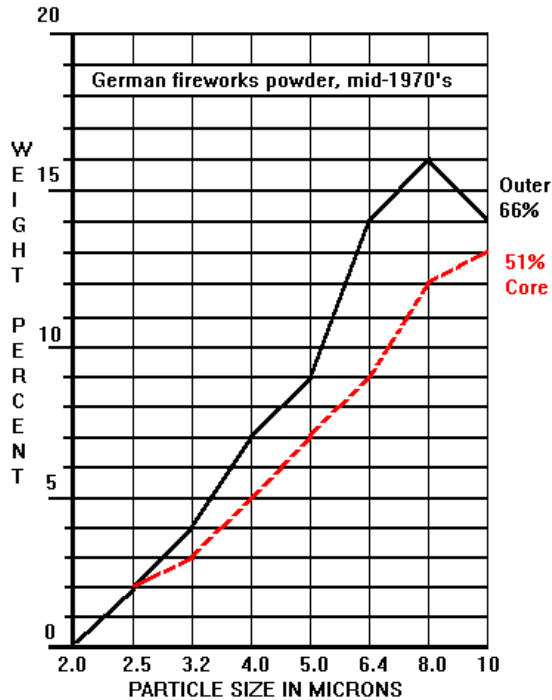


Figure 14. German powder, mid-1970's

The topic of water purity and its relationship to chemical stability in black powder is not confined to the production of black powder at the old Moosic, PA powder plant.

Here we have a graph showing the differences between the outer portions of the grain and inner core of the grain in a German-made Fireworks powder dating to the mid-1970's.

The results of the work on water purity and its effect on the chemical stability of black powder showed that no black powder is totally immune to chemical change. In looking at the powder produced by different powder plants it was clear that there were significant differences in chemical stability from one maker to the next and variations within a single maker if water purity fluctuated. The work was concentrated on powder produced at the old Moosic, PA powder plant because it was the most readily available powder. The study was also helped by the fact that the author lives about 60 miles from the plant and was able to closely follow both weather patterns and production from the plant. Local gun shops usually had lots of powder in stock within 1 to 3 months from their time of manufacture.