4. Propellants and Ignition Materials

«Greek Fire»

Literature

Elgger von, Karl, Kriegsfeuerwaffen I, Page 2, ElKa
Schmidt, Rudolf, Entwicklung der Handfeuerwaffen, Schaffhausen, 1868, Page 5 ff., SmRu68
Gartz, Jochen, Vom Griechischen Feuer zum Dynamit, GaJo

Description

The Greek fire (old Greek Hygron Pyr, New Greek Igro Pyr, liquid fire) was a military weapon used in the Byzantine Empire. The name goes back to the naming of the neighboring Greek speaking Byzantines that called themselves 'East Romans'. The 'Greek fire' is often referred to as 'Roman fire' or 'Sea fire'. The fuel was based on crude oil or asphalt that rose occasionally to the surface in an area close to the Black Sea in the Byzantine Empire. It was mixed with resin from trees, sulphur, and quick lime. After the 10th century, it was also mixed with saltpeter in liquid form. For the Byzantine's fleet that ruled the oceans for a century, the 'Greek fire' was essential.

Source: www.wikipedia.com: Greek Fire

Application

With a pressurized bronze tube or with a hand pump, a burning flash was sprayed against wooden fortresses and ships. Besides the use in liquid form, the fuel was also mixed with oakum, resin covered wood or other fillers and shaped into balls. It was also filled into barrels with a burning fuse attached to it. With the help of a catapult these barrels were thrown towards the enemy. In addition, arrows with attached burning fuels were brought into action.
Source: www.wikipedia.com: Greek Fire; SmRu68, Page 2

Callinikus

Around the year 677, the 'Greek fire' which was possibly invented by the Greek Callinikus from Heliopolis, was used successfully against the occupiers of Constantinople for the first time. It was apparently, a mixture of sulphur, petroleum, resin and pitch.
Source: SmRu68, Page 2

Fig. 4 – 1

Only existing Presentation of the Greek Fire. 12th Century. Source: wiki

Black Powder

Literature

Baetz, Manuel, Schwarzpulver für Survival, Survival Buch Press, 2001, P. 19 - 50, BaMa
Bretscher, Ulrich, www.musketeer, Black Powder, 2007, BrUl
C.V.H, Schiesspulver & Feuerwaffen, Otto Spamer, 1866, Morion Reprints, P. 4 - 13, CVH
Elgger von, Karl, Kriegsfeuerwaffen I, P. 1 - 8, ElKa
Hoff, Arne, Feuerwaffen, Bd. 1, Braunschweig, 1969, P. 1, HoAr
Pope, Dudley, Feuerwaffen, Genf, 1971, P. 17 - 23, PoDu
www.wikipedia.com, Black Powder, 2007, wiki
Gartz, Jochen, Vom Greichischen Feuer zum Dynamit, GaJo

General Reference

The history of the emersion of black powder is entwined with many assumptions and myths. Still today, it is unclear where and who invented black powder. The term black powder was only introduced around 1890. It distinguished the old powder or 'thunder weed' made from charcoal, saltpeter and sulphur from the newer smokeless nitro powder or what was then called 'white powder'. The following specifications are meant as a short description of the origin of black powder. To study the matter more extensively, it is recommended to read the web page (www.musketeer.ch) of Ulrich Bretscher, Uznach, Switzerland.

Description and Use

Description

Mixture of saltpeter, charcoal and sulphur with an ignition temperature of 300 degrees Celsius, with a burning speed of 300 to 600 M/S at the temperature of 2000 degrees Celsius with a very large gas development. These values depend on the mix and the size of the grain.
Literature: BrUl, wiki

Use

Black powder was the first explosive material that was used for muzzle loaders. In following years, it was also used for the cartridges in breech loaders. It was used between the years of Ca. 1200 – 1900. Today, black powder is mainly used in pyrotechnics, particularly in fireworks.

History

China

Literature mentions often in that the Chinese already knew of black powder in 900 BC. However, this cannot be verified. Source: BrUl

Wu-Ching-Tsung Yao

In the Chinese Empire, igniters containing saltpeter were mentioned in 'Wu-Ching-Tsung Yao' of 1044. The book is however, only a copy preserved from 1550 of the Ming Dynasty. It is unclear if the notes regarding these igniters were added later.

Marcus Graecus

In the 11th century, under the pseudonym Marcus Graecus, the book 'Liber Ignum AD Comburendos Hostes' was written. Translated, it means 'The Book of Fire to Burn Enemies'. It is presumed that the book was locked up in a monastery for a long time. The oldest, still available copy is from 1250 and the newest is dated 1481. In these copies, there are several recipes for black powder containing saltpeter, charcoal and sulphur. In today's view, the original script represents the first mention of saltpeter and charcoal, unless they were added by later writers.
Literature: BrUl

Theophilus the Monk

In the 12th century, Theophilus the Monk wrote a substantial paper about the chemistry known at the time. It was called, 'Schedula Diversarum Artium'. This work showed that Theophilus had extensive knowledge about chemistry. In neither the chapter about the manufacturing of glass or in the completed book, is there any mention of saltpeter which is important in chemistry and in the process of making glass. From this, it could be derived that saltpeter as a chemical was not known. This again could mean that at that time, black powder was unknown in Europe.
Literature: BrUl

Roger Bacon

Roger Beacon 1214 – 1294 was a Franciscan monk and scholar from Illchester, England. In 1245, he was called to the University of Paris as 'Magister Regens' (Regent Master). In 1250, he entered the Franciscan Order of Oxford. The years from 1257 – 1267, he spent in exile in a French Franciscan Monastery. In the year of 1266/1267 he created the three publications, 'Opus Maius, Opus Minus and Opus Tertium', for Cardinal Guy le Gros de Foulques. In today's view, the work Opus Tertium that is still in existence includes the first European reference to a black powder mixture. The writing begins with the words, 'as is widely known…. takes seven parts saltpeter, five parts hazelnut charcoal and five parts sulphur and this makes thunder and lightening if you understand this craft'.
Literature: BrU, WiFr, Page 8

Berthold Schwarz

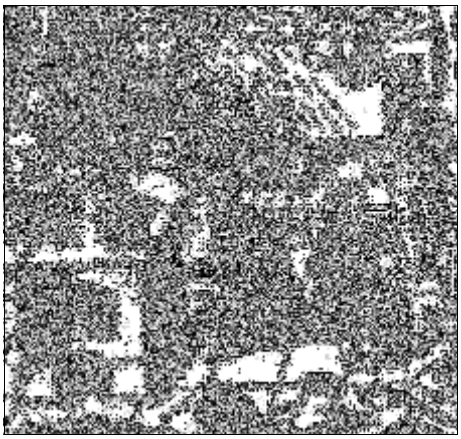
The legend of the monk Konstantin Anklitzen alias Berthold Schwarz as being the inventor of the black powder, has long been abandoned. There is no proof that there was a monk of that name and that he invented black powder.
Literature: BaMa, BrUl, PoDu

Concluding Remarks

It is still not established who invented black powder or where. According to Roger Beacon, it was known before 1267. If the later copies of the original book of Markus Graecus correspond with the original work, it could have been known already in the 9th and 11th century.

Pictures of Sulphur and Saltpeter Production

Fig. 4 – 2



Georgius Agricola
De Re Metallica Libri XII, 1556
Source: EBGF

Ca. 1550:
Sulphur Distillation

- Raw sulphur is evaporated in a vacuum.
- In a separate vessel, the sulphur gas is condensed at about 110 degrees Celsius.
- The clean liquid sulphur is poured into moulds and cooled down to solidify.

Fig. 4 – 3

Georgius Agricola
De Re Metallica Libri XII, 1556
Source: EBGF

Ca. 1556:
Cleaning of Saltpeter

- A mixture of plants containing nitrogen, liquid manure and alkaline compounds such as limestone are stored for three years.
- The collected saltpeter is washed out and the created alkaline suds are boiled.
- The created lime and magnesium saltpeter is converted to potassium nitrate by adding lye and potash.

Common Black Powder Mixes

Area and inventor	Saltpeter	Charcoal	Sulfur	Source
8th Century: Marcus Graecus	66.66	22.22	11.11	2),3)
Ca. 1252: Roger Bacon	41.2	29.4	29.4	2)
Ca. 1350: Arderne	66.66	22.2	11.1	1)
Ca. 1560: Whitehorne	50.0	33.3	16.6	1)
Ca. 1560: Belgium Studies	75.0	15.62	9.38	1)
1635: British Government	75.0	12.5	12.5	1)
1781: Bishop Watson	75.0	15.0	10.0	1)
To days Black Powder	75.0	15.0	10.0	1)

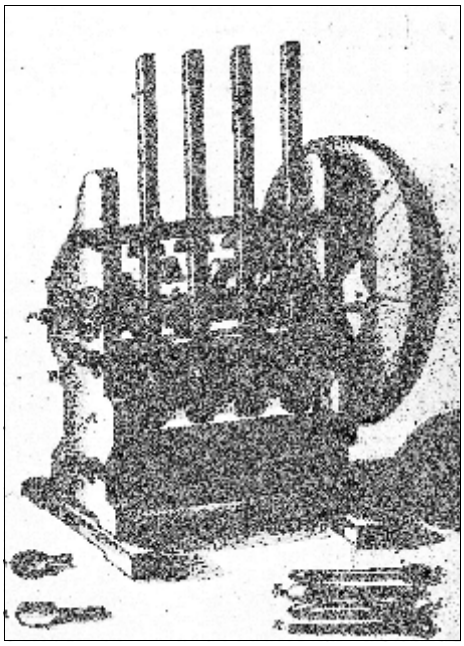
Literature: 1) BaMa, Page 23, 2) BrUl, 3) CvH, Page 4 - 13

Fig. 4 – 4

Granular Black Powder
Photo: KuPe

Black Powder Manufacturing

Fig. 4 – 5



Ca. 1620:
Hand cranked Black Powder Mill

- The wooden tappers are lifted with the cams on the driving axle
- Their own weight drops them onto the black powder lumps in the wooden barrels beneath the mill

Joseph Furtenbach, Mannhafter Kunstspiegel Augsburg, 1663
Photo: HeRo, Page 32

Fig. 4 – 6

Ca. 1650:
Sifting of the Black Powder

- With sieves shaken by hand, the black powder from the powder mill is sorted according to grain size

- After further sorting by helpers, the powder is filled into special containers

Unknown Artist
Photo: LuJa, Vol. 2, Page 411

Ca. 1660: Black Powder Manufacturing

Fig. 4 – 7

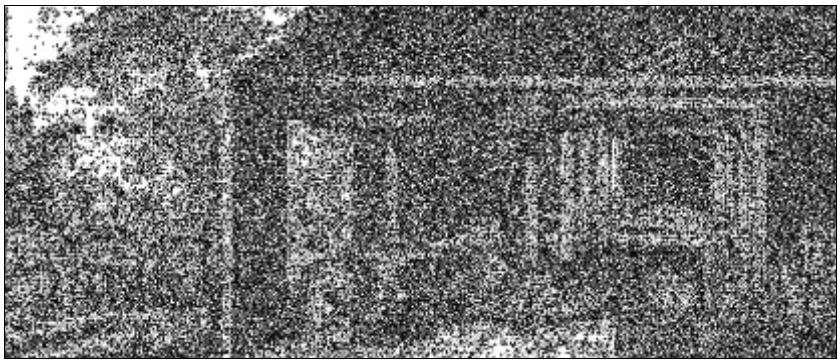


Photo: NBCH, Page 19

Ca. 1760: Warehousing of Black Powder

Fig. 4 – 8

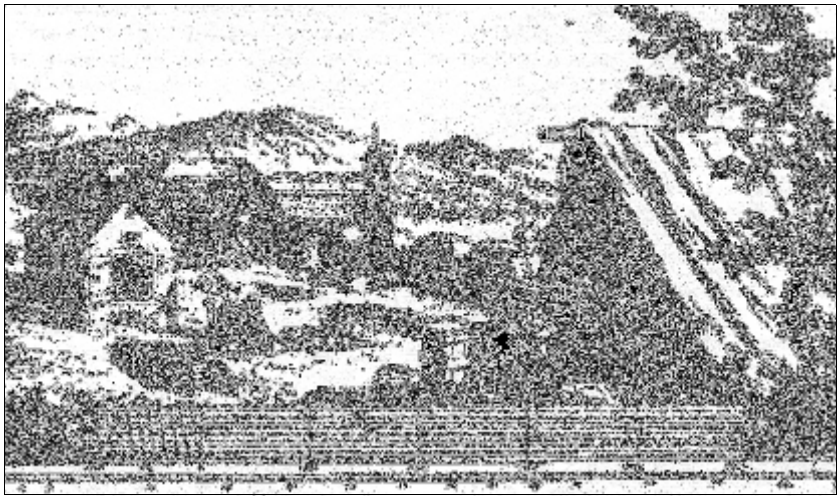


Photo: NBCH, Page 21

Ca. 1760: Ammunition Warehouse

Fig. 4 – 9

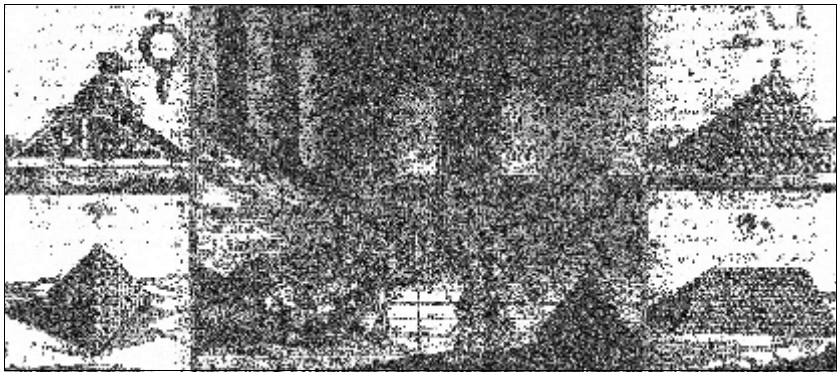


Photo: NBCH, Page 25

Priming Powder

Literature Baetz, Manuel, Schwarzpulver für Survival, Survival Buch Press, 2001, P. 23 - 25, BaMa

Properties Priming powder is either black powder with a very small grain (grain for FFFF) or no grain at all, the so-called 'flour powder'. It is used in the powder pan of muzzle loaders with flint, wheel or matchlock to ignite. It is necessary to use priming powder because the black powder propellant is difficult to ignite with sparks. For this reason, the easily ignited priming powder is used as an intermediate step. The flintlock for example, has a flint powered by a spring that strikes a steel plate. The sparks that are created, ignite the priming powder in the powder pan beneath. Through the vent in the barrel, the ignition is transferred onto the load.

«Salpotika» Shooting Powder

Literature Schmidt, Rudolf, Die Entwicklung der Handfeuerwaffen, Schaffhausen, 1868, Pages 5 ff., SmRu68
Gartz, Jochen, Vom Greichischen Feuer zum Dynamit, GaJo

Mixture In the year 1649, a shooting powder called Salpotika, containing saltpeter, camphor and sulphur was used in Simienowitz. Nothing more is known about this powder. It seems that it was never very successful.

Fuse

Literature C.V.H, Schiesspulver & Feuerwaffen, Otto Spamer, 1866, Morion Reprints, CVH
Ulrich Bretscher, www.musketeer.ch/blackpowder/lunte.html

The mention of a fuse in connection with the igniting of a firearm 'a hell machine' is thought to have been recorded for the first time in a document in 1378.

Potassium Nitrate

Lead Acetate

In those days, fuses were made from hemp rope that was saturated with a liquid solution of potassium nitrate and poisonous lead acetate. After the fuse was dipped in this solution, it was then dried. With this fuse, a steady smouldering could be achieved. This was ideal to ignite the powder in a powder pan. In those days, the fuse was a great invention to be used with firearms. Later, fuses were braided from cotton and dipped into a solution of saltpeter. The more concentrated the saltpeter solution is, the stronger and faster the smouldering of the fuse lasts.

Fig. 4 – 10

Private Collection
Photo: KuPe

Ca. 1580:
Fuse in a Matchlock

- It is an art to make a fuse that smoulders broad and slow
- The smouldering creates a strong smelling smoke that makes these fuses unsuitable for hunting
- From this comes the saying in German: "Lunte riechen" (Smell the fuse) and "die Lunte brennt, sie riecht schon" (The fuse burns, it already smells)
- Fuses were used on muskets and rifles for almost 300 years

Tinder Polypore

Literature www.natur-lexicon.com, Zunderschwamm

Characteristics Simultaneously with the matchlock, the so-called sponge snaphaunce lock was used. Compared to the matchlock, the sponge had the advantage that the smouldering occurred with barely any smoke or odour. It was easier to aim, without smoke in the air. The tinder polypore is very small and light. This allows a fast move of the cock spring to the powder pan. This results in a shorter ignition time, and lessens the possibility of pulling a shot. For target shooters, there was the small advantage that at the impact on the powder pan, the glowing tinder polypore was usually extinguished and a safe reloading of the weapon was possible. However, the tinder polypore had to be relit after every shot. For this reason, tinder polypore was mainly used for target shooting. It was also popular for hunting, because there was no odour when shooting.
The tinder polypore (fomes fomentarius) is also called wound fungus (Wundschwamm), blood fungus (Blutschwamm) or false fire fungus (Falscher Feuerschwamm). It is a fungus that grows mostly on beech and birch where it causes a white rot. It can also grow for years on dead and fallen trees. A very involved process to use the loose middle layer of the fungus for tinder was known as early as in the Neolithic period. The process involved the middle layer being soaked, cooked, rolled and then put into a saltpeter solution or urine and then dried.

Fig. 4 – 11
Tinder Polypore on Wood
Photo: KuPe

Fig. 4 – 12
Ca. 1514: Tinder Lock
Private Collection; Photo: KuPe

Firearms

For the use in firearms, it was also the middle part of the fungus that was used. It was cut out, dried and filed into the desired shape. The treatment with saltpeter or urine was not necessary if the tinder polypore was of good quality.

Iron Pyrite

History

Iron Pyrite was used to ignite the priming powder in the powder pan of wheel lock guns. When pyrite is rubbed against a rough surface, sparks are produced. The first uses of pyrite as an ignition tool, goes back most probably to the 15th century when it was used with the so-called monks gun. With the flint lock gaining popularity, the wheel lock and the use of iron pyrite with firearms slowly disappeared.

Properties

Iron Pyrite

Pyrite is a mineral with a chemical formula FeS2 and belongs to the sulphites. It is composed of iron and monovalent sulphur. It crystallizes in a cube shaped crystal system and has a hardness of 6 or 6.5.

Fools Gold

The metallic hue and its gold colour earn the pyrite the name, 'Fools Gold'. In German, Fools gold is called 'Katzengold' which is derived from the word 'Ketzer' meaning heretic. Different from real gold, pyrite is not malleable and is much harder than the precious metal. Pyrite contains small amounts of gold that can make it commercially minable.

Fig. 4 – 13

Pyrite, Fools Gold in its natural form.

Photo: KuPe

Flint

Literature

Hans Dieter Götz, Vorderlader, Page 69, GöHD
www.wikipedia.org, Flint, wiki

Importance

In the time from 1550 – 1850, flint was the most important igniter for hand and small firearms. Its quality could be the deciding factor if prey could be shot or a battle could be won. Flint was already known about in pre-historic times. Since the Iron Age, flint and firing steel are the most common archaeological finds at burial sites of different cultures. It is not known if flint and hardened steel were first used as tools to light fires or to light the powder in a firearm.

Properties

Flint, German Feuerstein, and French: Silex is an anisotropic sedimentary stone with a glass like appearance. Flint is a variety of horn stone and consists mainly of cryptocrystalline (very fine crystalline rock texture) Chalcedon (silicium dioxide). Other authors have used the generic term Silex and limit the expression 'flint' to silicate stones from chalk. Silicate stone from the Jura regions are called horn stones. Sub-microscopic inclusions of air and water give the flint a light colour (white flint), carbon colours it black. Besides Chalcedon SiO_2 modifications can be crystal graphically proven.

Findings

The Michelsberg Civilization pursued flint mining in the Dutch Rijkholt-Sint-Geertruid-Mines and at Plancher les Mines at the west slope at the Tète Ronde in the Vogeses. Various stratifications that were mined in the Stone Age were known in Germany. They are: Aachen-Lousberg, Kleinkems, County Lörrach, Schernfeld near Eichstätt, Osterberg near Pfünz, Baiersdorf near Erlangen, Abensberg-Arnhofen, Lengfeld County Kelheim. On the Island of Rügen, the flint fields between Mukran and Prora are well known and are popular places for outings. While digging for gravel in a pine forest near the village of Arnhofen by Abensberg in the 1980's, the largest flint mines in middle Europe were discovered. In this area, covered by fresh water molasses, are the foothills of the Frankish Jura. In the time of Ca.4000-3000bc, numerous (estimated approximately 20,000) mine-shafts of a depth of 6 – 8 meters were dug into the soft sand to reach the flint that lay in slabs in the Jura. Because of the characteristics of the layers, the origin from Arnhofen can be scientifically proven. Flint tools from Arnhofen were found more than 400 kilometers away in Bohemia and Westphalia.

Flint Manufacturing

The Flint used in flint locks is split and knapped from larger blocks in two sizes. The larger size has a width of approximately 22 – 30 millimeters. The smaller is approximately 12 – 22 millimeters. The lower facet is straight. On the backside of the upper facet, parallel to the lower facet, the flint has a distance of about 3 – 7 millimeters.
The front slants steeply towards the lower facet and forms a relatively sharp edge. With a leather or lead setting, the flint is clamped into the cock of the snaphaunce or flint lock. A good flint can be used to fire about 30 shots.

Fig. 4 – 14

Flints:

- Flints of various sizes from different areas.
- With a setting of leather, lead or felt, the flint is clamped into the cock.

Private Collection; Photo: KuPe

Mercury Fulminate and Percussion Caps

Literature

C.V.H, Schiesspulver & Feuerwaffen, Otto Spamer, 1866, Morion, P. 19 - 20, CVH
Lugs, Jaroslav, Handfeuerwaffen, Berlin, 1956, Vol. 1, P. 61 ff., LuJa
Gartz, Jochen, Vom Greichischen Feuer zum Dynamit, GaJo

Fulminate Gold

Potassium Chloride

Mercury Fulminate

In the year of 1608, physician and alchemist Crollius, described the so-called fulminate gold. In the year 1788, the Frenchman Claude Louis Berthollet, discovered fulminating silver. These explosives were extremely hazardous to handle and were not suitable for technical use. In the year 1796, the Englishman Edward Howard, discovered the so-called mercury fulminate. This highly combustible explosive, which could be ignited with a blow, was too dangerous to be used as a propellant. However, it was the foundation used in the progress and development of the propellant load of percussion pills and percussion caps.

Fig. 4 – 15

Mercury Fulminate

Photo: KuPe

Properties

Mercury Fulminate is mainly composed of mercury (II) fulminate $Hg_2(CNO)_2$, which is a mercury salt of the mercury fulminate. The composition of this substance is made up of white to beige crystals and is highly toxic. In a dry state, under minimal mechanical or thermal stress, it can explode and split into Hg, N_2 and CO. This split can easily result in a detonation by compacting or igniting large amounts.

Earlier, mercury fulminate was used in ignition and detonation caps. In the meantime it has been replaced by other substances (for example lead azide). It is easily soluble in hot water, ethanol and nitric acid, but not in cold water. The product is made from mercury, nitric acid and ethanol.

Use

Based on the properties of mercury fulminate, the priest Alexander Forsyth of Aberdeenshire in Scotland patented a so-called chemical lock in 1807. In this lock, a measured amount of mercury fulminate is ignited with the hammer.
In 1808 in France, Johannes Samuel Pauly was awarded the patent for the percussion lock. In the year 1845, the dentist Maynard from Washington, patented an ignition tape from paper in which measured amounts of mercury fulminate were imbedded in precisely measured lengths.

Fig. 4 – 16

Percussion Caps

- Percussion Caps of more Recent Times for Percussion Lock Rifles M 1842
- Caps from the 19th Century were often contained in a copper cup.

Private Collection; Photo: KuPe

Cellulose Nitrate

Literature C.v.H., Schiesspulver und Feuerwaffen, Leipzig, 1863, Morison, 1975, P. 14 - 17, CVH

History Cellulose Nitrate, often wrongly referred to as nitro cellulose, was discovered in 1846 by Professor Christian Friederich Schoenbein in Basel, Switzerland. Simultaneously, it was also discovered by Rudolph Christian Boettinger in Frankfurt, Germany and presented to the 'Deutscher Bund' in the year 1846 as a replacement for black powder. In the years, 1847 and 1848 in Mainz, Germany and in 1850 and 1851 in Vienna, Austria, extensive testing was performed to check the suitability of cellulose nitrate in firearms. French and British commissioned agencies carried out tests as well, but were unable to achieve satisfactory results. These testings resulted in several failures as well as tragic accidents.

Production The original method to produce cellulose nitrate was to soak cotton fibers in a mixture of concentrated nitric acid and sulphuric acid for a few minutes. It was then washed in water and then dried. Today's cellulose nitrate is made by transforming cellulose with nitric acid. The nitrogen content is regulated by the compound of the nitric acid and the reaction time. If there is a nitrogen content of more than 12.75%, it is called cellulose nitrate.
The production of cellulose nitrate was not only dangerous, but it was challenging to achieve a consistent quality. It was particularly difficult to create an invariable detonation speed that was satisfactory for the demands in the use of firearms.

Properties Cellulose nitrate explodes at a temperature of 3100 degrees Celsius. After the explosion, there is barely any residue or smoke visible to the human eye. This is the reason cellulose nitrate, is often referred to as 'smokeless powder'. These qualities make it very suitable as a propellant for firearms.

Use For reasons mentioned earlier, cellulose nitrate was not used in firearms. Today, cellulose nitrate is used in pyrotechnic for its smokeless qualities.

Fig. 4 – 17

Cellulose Nitrate in Various Sizes, Picture Source: Ku Pe