

# Speculation on The Effect of Gunshot or Explosive Residue on Silk

## Introduction

This paper was originally presented on November 3, 1989 as an informal lecture at a one day working session on Weighted Silk Research at the Conservation Analytical Laboratory (now the Smithsonian Center for Materials Research and Education). The discussion centered around the effects of gunpowder (explosives) residue on historic silk flags used on battlefields. This lecture was intended to provide background material and speculation on effects of this phenomenon.

## Black Powder and Its Residues

Black powder was introduced into Western Europe around the 13th century and was used in military applications from the 14th century. It was the universally used explosive until about 1870 being in part replaced by nitroglycerin and/or nitrocellulose in various forms. Black powder is still used in large quantities even today.

Other propellants and explosives were developed in the 19th century, cellulose nitrate (guncotton) was introduced by Schultze in 1864 and dynamite (nitroglycerin based) by Nobel in 1867.

Black powder is a mechanical mixture of potassium nitrate, charcoal and sulfur. There are many formulas for this mixture but in general they fall into the following weight ranges:

potassium nitrate	70 - 80%
sulfur	5 - 18%
charcoal	9 - 19%

Sodium nitrate was used in some formulations as an explosive in mining.

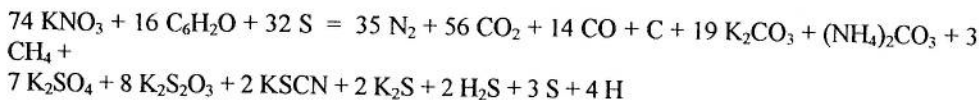
By the mid-19th century the "ideal" composition was potassium nitrate, 74.9%, sulfur, 11.8%, and charcoal, 13.3% [Watts, 1875]. The volume of gas produced by this mixture was 296 times that of the unexploded powder. British Government powder in the early 19th century was composed of potassium nitrate, 75%, sulfur, 10%, and charcoal, 15% [Braddock, 1832].

Black powder was used in propelling projectiles from both small arms and cannons and mortars. It was used as well in rockets, handgrenades and in bombs.

On detonation the black powder mixture produces about 45% gaseous products with the remainder as solids in the barrel of the weapon or as particulates in the air. The bulk of the gases are carbon dioxide, carbon monoxide and nitrogen with some hydrogen, methane, water and hydrogen sulfide as minor constituents. It should be noted that charcoal may contain substantial constituents other than carbon. For all varieties of black powder, the largest volume of gas produced is carbon dioxide, followed by nitrogen and then by carbon monoxide.

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A complicated and impressive empirical formula for ignition of black powder is given in the Kirk-Othmer Encyclopedia of Chemical Technology:



The principal solid constituents of black powder residue are:

potassium sulfate	ammonium carbonate
potassium carbonate	carbon
potassium sulfide	
potassium thiocyanate	
potassium thiosulfate	

with some unconverted potassium nitrate, sulfur and charcoal. With moisture and time these residues may be converted to other compounds.

Large amounts of black powder were often used in 19th century combat. In the Napoleonic Wars, at the siege of Ciudad Rodrigo (Jan. 1812) cannons and mortars consumed 74,978 pounds of powder in less than 31 hours. Similarly at Badajos an enormous 228,830 pounds of powder were used. At the first and second sieges of San Sebastian 502,110 pounds of powder were consumed [Schoffern, 1854]. Battlefields were often clouded with these gunpowder particulates which weighed thousands of pounds.

## Metal/Metal Ions from Projectiles

Historically lead has been the metal used in projectiles from small arms while iron and steel were used in larger weapons such as artillery and mortars. Copper, nickel, and steel covered lead projectiles are also known. Oxidation of many of these metals along with moisture or liquid water can lead to discoloration at best and decomposition of the fibers at worst.

Heavy metal salts have been used in percussion caps and cartridge primers since the 19th century. Some of the compounds used were:

- antimony sulfide
- barium nitrate
- barium carbonate
- barium peroxide
- calcium silicide
- copper sulfocyanide
- lead sulfocyanide
- lead trinitrorescorinate
- mercury fulminate
- silicon dioxide (as glass)

Early primers also contained potassium chlorate which on detonation produced potassium chloride. The potassium chloride was determined to be a serious source of corrosion in rifle barrels. Other primer constituents were nitrated organics such as picric acid, trinitrotoluene (TNT), gums, and nitrated guanidine compounds. Brass is an integral part of many primers and particles

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of brass are sometimes associated with primer residues. Brass is also commonly found as cartridge cases and brass particles are often ejected from modern autoloading weapons.

## Methods of Deposition

Two principal modes of depositing gunshot residues on flags would seem likely.

First, the particles could attach themselves either directly from the force of the weapon's discharge (under 3 ft or so from small arms) or through gravity and wind currents from the atmosphere. Of course, projectiles going through the flag will also leave some residues. Anyone handling the flag with residues on their hands may also transfer that residue to the flag as well. Deposited salts can pick up water with time and attack the fibers or dyes. High humidity or cleaning may activate particles long after deposition.

Second, dissolution or mechanical transfer of gunshot chemical species by rain may affect the condition of the flag. Large amounts of particulates in the air over battlefields has been postulated as the cause of rain following battle. Rain would dissolve or force to earth many particles formed by gunshot and attack the flag with solutions of salts.

## Chemical Reactions

Certain reaction products from gun powders can react with moisture and oxygen in the environment to produce further reactive species. For example, nitrogen oxides and moisture can produce nitric and nitrous acids. Thiosulfate ion can react in an acid environment to produce sulfur or other sulfur oxides. Moisture or water complicates the issue further.

Reaction products known to attack silks:

- nitrous and nitric acids
- sulfate ion
- hydroxide ion (alkali medium)
- formaldehyde
- heavy metal ions (lead, mercury, copper etc.)

Reaction products which can react with dyes:

- nitrous and nitric acids
- sulfur dioxide, sulfurous acid
- formaldehyde
- potassium salts, nitrate, thiocyanate, sulfide, nitrite etc.

## Examination of Flags

Non-destructive evaluation of residues on textiles can be done in several ways. Infrared imaging will show many types of residues and x-ray photography can also show many of the denser residues. Visual examination at 5X to 50X can disclose most residues but will certainly be quite tedious on an object the size of a flag. There are also several wet chemical techniques which are probably not suitable for historic objects. The forensic literature contains a considerable number of papers on the subject of gunshot residues (see Journal of Forensic Sciences, Forensic Science International, etc).



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