Speculation on the Effects of Gunshot or Explosive Residues on Historic Silk Flags

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ABSTRACT

Historic battle flags and uniforms are collected by museums, and many have significance as icons representative of their owners as well as historic context. The effects of battle, both mechanical and chemical, have an impact on the projected lifetimes of these objects in museums. Modern air quality, as well as the type of display, is important. Pyrotechnic displays using Black Powder can also produce considerable amounts of particulates and gases and, if near museums, may be a significant source of damage to a museum's collection.

Keywords: gunshot residue, explosive residue, silk flag, Black Powder

Introduction

This paper was presented in November of 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 on the possible effects of gunpowder (explosives) residue on historic silk flags, primarily those from 18th and 19th century battlefields. Silk flags of this type are often found in a highly deteriorated condition, from both mechanical and chemical damage. This lecture was intended to provide background material and speculation on the effects of this hostile chemical environment on the eventual stability of these flags.

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: nitrocellulose (guncotton) introduced as the first successful smokeless powder 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.

British Government powder in the early 19th century was composed of potassium nitrate, 75%, sulfur, 10%, and charcoal, 15%.[1] By the mid-19th century the "ideal" composition was potassium nitrate, 74.9%, sulfur, 11.8%, and charcoal, 13.3%.[2] The volume of gas produced by this mixture was 296 times that of the unexploded powder.

Black Powder was used in propelling projectiles from small arms, cannons, and mortars. It was used as well in rockets, in hand grenades, and in other types of bombs.

After ignition, Black Powder mixtures produce 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 might 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.

A complicated and impressive empirical equation for describing the combustion products of Black Powder is given in the *Encyclopedia of Chemical Technology*:[3]

$$
\begin{aligned}
&74\ KNO_3 + 16\ C_6H_2O + 32\ S \rightarrow \\
&\quad 35\ N_2 + 56\ CO_2 + 14\ CO + C + \\
&\quad 19\ K_2CO_3 + (NH_4)_2CO_3 + 3\ CH_4 + \\
&\quad 7\ K_2SO_4 + 8\ K_2S_2O_3 + 2\ KSCN + \\
&\quad 2\ K_2S + 2\ H_2S + 3\ S + 4\ H_2
\end{aligned}
$$

The formula is a general one and the specific products may change depending upon the powder's composition and impurities as well as temperature and moisture.

The solid residues after Black Powder ignition are often found to be:

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

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 (34080 kg) of powder in less than 31 hours. Similarly at Badajos an enormous 228,830 pounds (104000 kg) of powder were used. At the first and second sieges of San Sebastian 502,110 pounds (228232 kg) of powder were consumed.[4] Battlefields were often clouded with these gunpowder particulates whose weight totaled thousands of pounds.

Metal or 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. Projectile residues are often found on fabrics. Oxidation of many of these metals along with water vapor or liquid water can lead to discoloration at best and decomposition of the fibers at worst. Metals will often catalyze the hydrolysis and sometimes the oxidation of proteins such as silk.

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

antimony sulfide
barium nitrate
barium carbonate
barium peroxide
calcium silicide
copper thiocyanate
lead thiocyanate
lead trinitroresorcinate
mercury fulminate
quartz
glass

Early primers also contained potassium chlorate, which—on detonation—produced potassium chloride. 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. Since primer compounds are only a small proportion of gunshot residues, their effect would probably be small on flags or historic textiles. Brass is an integral part of many primers, and particles of brass are sometimes associated with primer residues. Brass is a common component of cartridge cases and brass particles are often ejected from modern auto loading 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 (1 m) or so from small arms) or through gravity and wind currents in the atmosphere. Of course, projectiles going through a flag will generally leave some residues. People handling the flag with residues on their hands may also transfer that residue to the flag as well. Deposited materials can pick up water with time and attack both the fibers and dyes. High humidity or cleaning may reactivate particles dormant 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 have been postulated as the cause of rain following battle. Rain would dissolve, or force to earth, many particles or gases formed by gunshot, and solutions of these salts would chemically attack fabrics and dyes.

Chemical Reactions

Certain reaction products from gunpowders 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 sulfur oxides. Reactions with water vapor or liquid water complicate the issue further. Attempts to clean a silk flag with water may dissolve particulates and increase the possibility and extent of damage.

Hydrolysis is an important reaction in the degradation of silk. Any compound that will alter the pH significantly or catalyze the hydrolysis reaction is dangerous to the silk.[5] Black Powder reaction products and their derivatives that are known to attack silks include:

- nitrous and nitric acids (from reaction of nitrogen oxides with water)
- sulfate ion
- hydroxide ion (alkali medium from carbonate solutions)
- formaldehyde
- heavy metal ions (lead, mercury, copper, etc.)

Most dyes are susceptible to color changes with changes in pH, and some will regain their original color when the pH is changed back. Others have labile chromophoric groups that will react with acids or bases to change color or become colorless, irreversibly. Reaction products from Black Powder that can react with dyes include:

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

Examination of Flags

Non-destructive evaluation of residues on textiles can be conducted in several ways. Infrared imaging can disclose many types of residues and x-ray photography can also locate many of the denser residues. Visual examination at 5× to 50× 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.[6]

Conclusion

In addition to the obvious mechanical effects in war, chemical damage occurred from the active particulate debris and gases produced on the battlefield. Without proper stabilization and storage this residual debris continues its slow decomposition of the silk flags. Improper cleaning can accelerate the damage by activating residues with water (moisture).

Pyrotechnic displays, although only infrequent events, can also produce considerable amounts of similar particulates and gases. If conducted near museums, these may be a significant source of damage to a museum's collection. The effects of nearby fireworks displays can be reduced by closing air intakes (if this is not possible, filters can be added) until the particulates and gases have dissipated.

References

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6) See, for example, *Journal of Forensic Sciences*, *Forensic Science International*, etc. Also, S. S. Krishnan, “Detection of Gunshot Residue: Present Status”, *Forensic Science Handbook*, R. Saferstein, Ed., Regents/Prentice Hall, Englewood Cliffs, NJ (1982) pp 572–591.