Forensic Characterization of the Painted Lubricant Coating on Barnes XLC Coated X-Bullets

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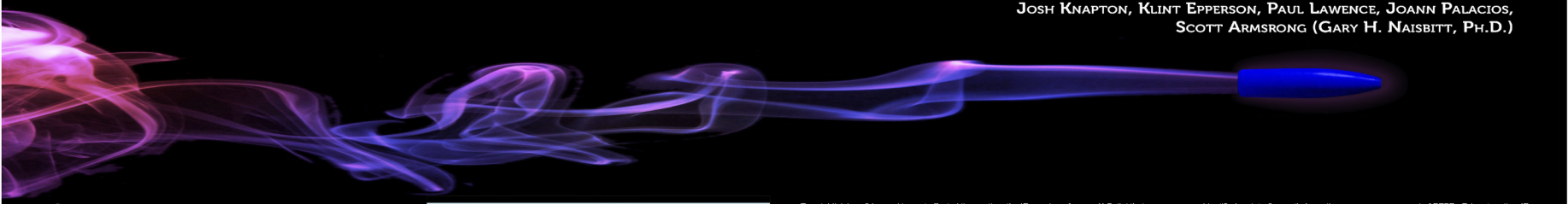


Abstract

Barnes XLC Coated X-Bullets are made for the ammunition reloading enthusiast. The solid copper bullets are distinguished by their blue coating that acts as a lubricant to improve ballistic performance. Microscopic examination showed it to be a sprayed-on single layer coating similar to automotive paint finishes. A diamond anvil and infrared (IR) microscope were used to determine the IR spectrum that will be used for forensic identification, and part of this spectrum identified polytetrafluoroethylene (PTFE) as one of the chemical components. The overall chemical composition was determined by pyrolysis that was used to breakdown the solid matrix of the coating followed by gas chromatography mass spectrometry to separate and identify the components. This information will be added to the ballistics and paint knowledge bases for forensic identification.

Introduction

Forensic examinations compare an unknown piece of evidence from the crime scene to a similar object of known origin. Both objects are subjected to the same tests under identical conditions and if found to be the same are said to "Match". Objects of known origin are called "Reference Materials" and together form a knowledge base to which new information is continually being added. The objective of this project was to characterize the blue paint on Barnes XLC Coated-X Bullets. These data will be added to the knowledge base used by firearms and trace examiners for use as a reference standard to identify these bullets found at crime scenes.

Materials and Methods

Barnes XLC Coated X- Bullets were obtained from commercial suppliers in 22, 30 '06, and 308 calibers. A relationship with the manufacturer or retailers for product promotion, monetary gain or other support for this work does not exist.
An eXtreme EPP2000 UV/Vis fiber optic spectrometer, fiber optic cable and SpectraWiz, spectrometer software v.4.2a were obtained from StellarNet Inc, Tampa, Florida 33626, www.StellarNet-Inc.com, and the microscope C-mount to fiber optic cable adaptor was purchased from Ocean Optics, Dunedin, Florida. Leica EZ4D, S6 stereo microscopes and Leica Application Suite Software version 2.4.0 R1 (Build:978) LAS EZ version 1.1were from Leica Microsystems Limited, Switzerland. Nicolet 6700 Infrared Spectrometer, Centaurus Infrared Microscope and OMNIC operating software, Thermo Fisher Scientific Inc, Waltham, MA. The diamond anvil sampler holder was obtained from High Pressure Optics, Tucson, Arizona. Pyrolysis was performed with a CDS Analytical 5250 Pyrolysis Autosampler, Oxford, PA. Agilent 6890N gas chromatograph and an Agilent 5975 mass spectrometer from Agilent Technologies, Santa Clara, CA. American Standard Testing Methods for paint analysis and forensic paint examination guidelines from the Scientific Working Group on Materials Analysis (SWGMAT), "Forensic Paint Analysis and Comparison Guidelines", Forensic Science Communications (1) were followed.

Results

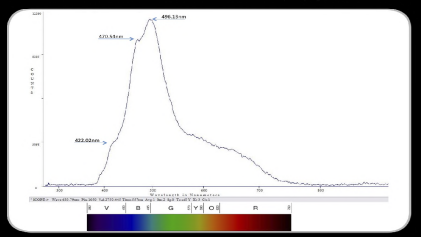
Thickness

Coating thickness was determined by scoring a line through the coating from the tip of the bullet to the tail. Turning the bullet so the exposed edge of the coating was perpendicular to the angle of view, the thickness was photographed with a Leica EZ4 stereo microscope set at 36x optical magnification. The image was photographed using Leica LAS EZ software and the photograph was enlarged digitally until pixilation started to degrade the image. Copper marked the bottom of the coating while a change of hue and focus marked the top. A total of fifty-six measurements were taken and statistically evaluated in Table 1. The average thickness of the coating was 29.6 micrometers with a variation of 14.88 micrometers. At the microscopic level the copper bullets are pitted, and the surface of the painted coating has an orange peel texture. These two factors are the major contribution to thickness variation.

Mean:	29.68643
Standard Error:	0.501217
Median:	29.79
Mode:	31.3
Standard Deviation:	3.750768
Sample Variance:	14.06826
Range:	14.88
Minimum:	23.47
Maximum:	38.35
Sum:	1662.44
Count:	56

Color Analysis

The color spectrum in Figure 2 was determined with a Leica S6 stereo microscope equipped with a eXtreme EPP2000 spectrometer. The visual spectrum lies between the color violet (400 nm) and deep red (750nm) with blue lying between 450nm and 495nm. The reflectance spectrum of the blue coating shows the major peak at 496.13nm with shoulders at 470.54nm and 422.02nm. The shape of the spectrum with its peaks and shoulders at these wavelengths is a result of the chemical formulation and is a scientific means of specifying color in courts of law.

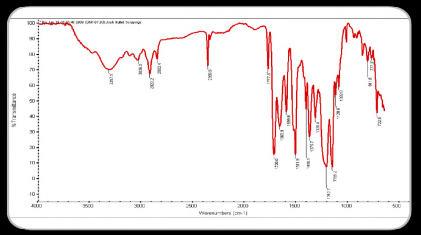


Infrared Analysis--Theory

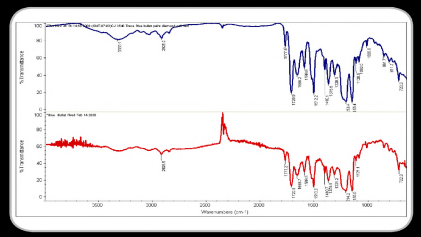
The atoms in molecules are able to vibrate side-to-side and up and down as though they are connected by springs. The magnitude of movement depends upon the amount of energy that is available and the type of bond linking an atom to its neighbor. Each combination of atoms and the type of bond linking them together has a unique energy. When a material is irradiated with a broad band of infrared light, portions of that energy are absorbed by the bonds in the molecule. The resulting spectrum, presented as a percent transmittance, can be interpreted to identify the chemical composition of the material.

Infrared Standard Reference Spectrum

An IR spectrum for a single chemical is specific for that chemical alone. However, if the sample has more than a single chemical component the IR spectrum is the combined total of individual spectra from each component. Paint coatings are a mixture of chemicals all of which are present in the infrared (IR) spectrum. Samples from unfired factory bullets were prepared in a High Pressure Optics diamond anvil compression cell for analysis. The IR spectrum of the factory bullet was determined with a Nicolet 6700 IR spectrometer and a Centaurus IR microscope with a MCT detector cooled with liquid nitrogen. The resulting spectrum seen in Figure 3A is the spectrum of the factory bullet and referred to as the Barnes XLC Coated-X Bullet Standard Reference Spectrum (X-Bullet SRS).



To establish how firing and impact affected the coating, the IR spectrum from an X-Bullet that had been fired and recovered was determined as before. The infrared spectrum of the fire bullet is presented in Figure 4B and compared to the spectrum of the X-Bullet SRS in Figure 3A. By comparing the wavenumbers of the corresponding peaks and overlaying the two spectra no significant differences are noted indicating that no chemical changes occurred during firing. Therefore X-Bullet SRS can be used in forensic examination as a standard of comparison to identify a matching bullet found at a crime scene as a Barnes XLC Coated-X Bullet.



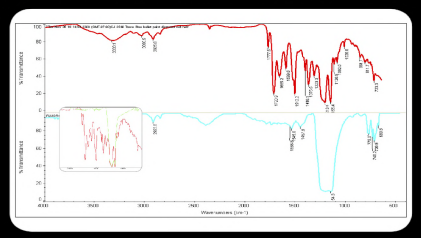
Chemical Analysis

Infrared

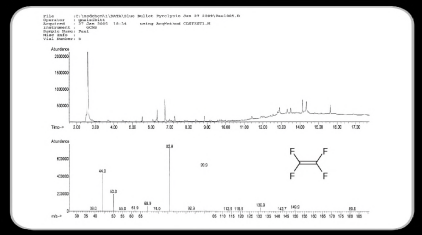
Realizing that the coating is a mixture of chemicals a rational approach is to look for anticipated components. Because the purpose of the coating is to lubricate the barrel to allow the bullet to pass with higher muzzle velocity and less wear, polytetrafluoroethylene (PTFE). Dupont trade name Teflon, is an obvious guess. Nicolet OMNIC software was used to retrieve a fluorocarbon spectrum from the HR Aldrich Polymers Library and the Stack Spectra and Peak functions to compare the two spectra in Figure 5A. Peaks at 1215 cm^{-1} and 1150 cm^{-1} in the X-Bullet SRS match corresponding peaks in the PTFE spectrum in the HR Aldrich Polymers library. Overlaying the spectra in Figure 5B shows the closeness of the match. No other chemical components were identified by this means.

Pyrolysis - Gas Chromatography - Mass Spectrometry (Pyr-GC-MS)

Although gas chromatography-mass spectrometry is a powerful technique for chemical separation and molecular identification, because of their size, paint polymers cannot be directly analyzed. Pyrolysis is a sample preparation technique that uses heat to break the polymeric bonds allowing the degradation products to be analyzed by GC-MS.



The coating was pyrolyzed with a CDS Analytical 5250 Pyrolysis Autosampler at 750°C for 20 seconds and analyzed with an Agilent 6890N gas chromatograph and an Agilent 5975 mass spectrometer using a 30 meter x 250 um HP5 column with a helium flow rate of 1 milliliter per minute. Inlet temperature was set at 280°C, the oven temperature program started at 40°C, increased 20°C per minute to 250°C and held at that temperature for 5 minutes, and the mass spectrometer transfer line was set at 250°C. The second peak in the pyrogram in Figure 6A with the retention time of 2.594 minutes and its corresponding mass spectrum in Figure 6B was identified as tetrafluoroethylene, the monomer component of PTFE. Taken together IR analysis and Pyr-GC-MS are orthogonal techniques that measure different physical properties but converge on the same conclusion that PTFE is present.



Discussion

Trace samples are typically not obvious to the unaided eye and are often only visible under a microscope. In this study the average size of any single sample was about one third of the area of the head of a common straight pin used by seamstresses to hold cloth together while sewing. Samples needed to be collected, manipulated and mounted under constant view of a stereo microscope. The only exception was color determination in which the whole bullet was examined under 10x stereoscopic magnification.

The first benefit of this study was to establish a Standard Reference Spectrum for Barnes XLC Coated-X Bullets. The coating on the conical forward portion of the bullet does not change when the bullet is fired because this area of the bullet is not exposed to the high pressures, heat, and friction present at the back and sides of the bullet; and, because the petals protect the coating at the front of the bullet during impact. Therefore, during forensic comparison examinations X-Bullet SRS spectrum can be used in place of an original factory bullet as a comparison standard for either a fired or unfired bullet. Forensically, this is a "class match" that eliminates all other bullets that do not have this coating. However, a class match will not conclusively associate the suspect bullet with an individual weapon.

The second goal of this study was to determine the chemical composition of the coating. Because the designed purpose of the coating was to reduce friction confirming the presence of PTFE was not a surprise. The suggested presence of 2-Propenoic acid, 3-(4-methoxyphenyl)-,2-ethylhexylester was not expected but plausible. The commercial names for this compound are Parsol MCX, Parsol MCX, Beclovent inhaler, Escalol 557 and Neo heliopan AV and it is used as an ultraviolet ray absorbent to protect against UV light damage to outdoor surfaces.

Other components that frequently appeared include acrylic acids, aromatic esters, and fatty acid drying oils. Determining how these or other possible components combine to form the binder, dye or pigment is currently being investigated.

References

1. Scientific Working Group on Materials Analysis (SWGMAT), "Forensic Paint Analysis and Comparison Guidelines". In: *Forensic Science Communications*, Federal Bureau of Investigation, July1999, Volume 1, Number 2, May 2000 Revision.
2. Max M. Houck, Editor "Mute Witness: Trace Evidence Analsis", Academic Press, 2001, ISBN 0-12356760-2.

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