TECHNICAL NOTE

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Restoration Tactics for Seriously Corroded Cu and Cu-Alloy Firearms Evidence*

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ABSTRACT: A cleaning procedure for seriously weathered or corroded bullets and cartridge casings was developed and implemented for evidence specimens from a multiple homicide. The restoration protocol entailed successive treatments with increasingly aggressive chemical solvents and cleaning solutions while monitoring the progress of the method by optical microscopy. Treatment of worst-case, Cu-alloy jacketed bullets and casings resulted in reconditioned specimens that subsequently underwent successful firearms examinations.

KEYWORDS: forensic science, evidence cleaning techniques, metal restoration, solvent treatments, firearms examination

An execution-style, triple homicide occurred in a rural California town several years ago. The crime scene, along with bullets recovered from the victims, resulted in approximately two dozen items of firearms evidence. These specimens included a variety of bullet fragments, .38 caliber hollow-point bullets, jacketed 9-mm bullets, 9-mm casings, and unfired 9-mm cartridges. The weapons used to fire the crime-scene bullets were never recovered.

However, the ensuing investigation ultimately identified potential suspects and led to a residence that they had occupied near the time of the homicides. Upon executing a search warrant for the premises, investigators found a number of expended .22, .38, and 9-mm casings scattered around the grounds of the house. Further, they identified a large palm tree that appeared to have been used for target practice. A work crew dug up the tree, its lower portion was cut into five 4-ft segments, and the sections were transported to the emergency room of a local medical facility. There, computed axial tomography (a CAT scanner) was used to locate a number of .22 and 9-mm bullets embedded in the tree.

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* Names of commercial manufacturers are provided for identification only, and their inclusion does not imply endorsement by the Forensic Science Center, LLNL, or the U.S. government.

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The question was whether any of the residence bullets or casings could be matched to evidence from the crime scene (Fig. 1). Unfortunately, the residence specimens had been exposed to their ambient environments for an estimated two years or so and were in extremely poor condition. The casings were very weathered and were caked with mud and other debris (Fig. 2), while the bullets from the palm tree were exceedingly corroded and had strands of plant fiber strongly bound to them (Fig. 3). Any underlying striae were completely obscured, and practical firearms comparisons were impossible.

In order to functionally compare crime-scene specimens with those from the residence, the latter required chemical treatment to remove or reduce extensive corrosion and miscellaneous debris adhering to their surfaces. Any wiping or scrubbing tactics were expressly avoided to minimize the risk of obliterating minute or fragile individual characteristics. The cleaning procedure that was developed was such that the underlying striae remained viable for forensic analysis via comparison microscopy.

Materials and Methods

The casings to be examined were "cartridge brass," of nominal composition 70% Cu, 30% Zn, while elemental analysis of the bullets indicated that they were jacketed with Alloy 210 or gilding metal (~95% Cu, 5% Zn). The cleaning procedures developed were therefore optimized for Cu alloys.

The metal protocols were evolved using well-corroded, but non-evidentiary, exemplars of cartridge brass and oxidized Cu for method development. An attempt was made to utilize appropriate industrial cleaning techniques, or adaptations thereof, to remove the specific corrosion and debris deposited on the evidence. In general, these methods entail solvent degreasing and hot alkaline and/or acidic cleaning steps, interspersed with water washes (1). Ultrasonic enhancement is necessary when the surface debris or corrosion products are sufficiently thick to warrant use of the technique.

The effects of the various cleaning agents and experimental parameters were followed at each step of the procedure by optical microscopy and scanning electron microscopy (SEM). The SEM, in particular, allowed a close assessment of any pitting or other damage to underlying striae by the cleaning protocols. These results indicated that even the most aggressive chemical treatment utilized for this work could be adequately controlled (by limiting the time

FIG. 1—*Representative 9-mm bullet and cartridge casing from the homicide scene (original microscope magnification ~6×).*

of exposure and solution temperature) such that damage to the underlying metal surface occurred only at dimensions < 100 nm. This scale is well below the resolution of the usual operational magnification employed by firearms examiners using bullet-comparison microscopes.

The present approach deviated from a standard practice of initially implementing a strong, hot, degreasing solution (1). The decision was made to remove debris from the evidence in a gentle and very controllable fashion, and the developed cleaning procedure consequently entailed the stepwise implementation of increasingly aggressive chemical solvents and solutions. These included water, methanol, trichloroethylene (TCE), acetone, dimethylsulfoxide (DMSO), an alkaline cleaning solution, and an acidic cleaning solution. After evaluation of the effectiveness of the various solvents, solutions, temperatures, and exposure times on the 9-mm palm tree bullet shown in Fig. 3, a seriously corroded but representative specimen of the evidentiary items, the following protocol was implemented for the various bullets and cartridge casings seized at the residence.

- The bullet or casing was first immersed in ultrapure, 18-MΩ deionized water (Millipore milli-Q water) in a glass beaker. The mQ water had been heated to ~75°C, and the specimen was either balanced on its base at the bottom of the beaker (bullet) or suspended in the liquid by a coiled, stainless-steel wire extending into its interior (casing). Ultrasonic agitation then occurred for 2 min, typically resulting in ejected particulates from the specimen and a brown, cloudy appearance imparted to the water.
- After the mQ treatment, a casing was dried and immersed in reagent-grade, light-stabilized TCE at room temperature. Ultrasonication was then conducted for 2 min, usually resulting in a pale yellow color imparted to the solvent. For the bullet specimens from the palm tree, however, the extensive, adhered organic debris dictated a more lengthy TCE treatment. Those samples were dried and then soaked in hot (~75°C) TCE for several hours, but without sonication.
- The specimen was then sonicated in HPLC-grade acetone for 2 min.
- A specimen was next treated with an alkaline cleaning solution heated to ~50°C. This solution consisted of an aqueous mixture of 10% (by weight) sodium metasilicate and 10% ethylene

FIG. 2—*Side view and end view of representative 9-mm casing recovered from the yard of the suspects' residence (original magnifications ~5× and ~8×, respectively).*

FIG. 3—*Representative 9-mm bullet removed from the residence palm tree. Heavy corrosion and fragments of plant material strongly adhered to the surface (original magnification ~7×).*

glycol monobutyl ether, at pH ~12.5, with ultrasonication performed in this fluid for 2 min. [Commercial cleaners, such as Haviland Products' SWISH formulation, can be quite satisfactory for this step after dilution with water.]

- The final chemical regime was one or more exposures to a sulfuric acid-based cleaning solution, inhibited with thiourea, at ambient temperature. The composition of this medium was 3% concentrated sulfuric acid, 5% thiourea, and 0.1% sodium lauryl sulfate, with pH ~1.5. For the significantly corroded palm tree bullets, specimens were sonicated in this solution for times on the order of 1 min; for the less-eroded casings, however, quick contact times of 2–5 s, without sonication, were typical. In both instances, the extent of the remaining corrosion, as well as any substrate metal damage, was evaluated with a stereomicroscope after each immersion. A decision on whether to repeat the step was based on this assessment.
- Finally, to arrest any further chemical attack, the specimen was sonicated for 2 min in two rinses of room-temperature mQ water.

Verification of the conservation of individual striae by the overall chemical treatment was demonstrated by firing four 9-mm standard rounds from a control handgun at the Sacramento Department of Justice forensic lab. Both the bullets and the casings from two of these firings were cleaned by the developed procedure. Comparisons of the cleaned specimens with the untreated ones by an experienced DOJ firearms examiner subsequently showed that the individual striae were still present and that conclusive matches could be made.

Results and Discussion

The appropriate exposure time of a specimen in each cleaning solution is optimally determined on an individual basis for a given application. For this questioned evidence, minimal times and ultrasonic agitation were important. Of particular consequence was the careful control of the exposure time in Step 5, as samples can be over-etched by the acidic thiourea if prolonged beyond the removal of surficial contamination. However, the acidic solution can also be diluted as necessary and satisfactory results obtained.

For the palm tree bullets, the complete protocol was successful in loosening miscellaneous debris and dissolving the corrosion to expose the underlying Cu-Zn jacket (see Fig. 4). However, optical microscopy revealed that any fine striae or other characteristic markings had been effectively obliterated by the years of organometallic reactions within the interior of the tree.

All but one of the 9-mm casings found on the grounds of the residence were cartridge brass (the other was Ni-plated brass). The qualitative improvement in the external appearance of these casings as a result of the cleaning treatments was extremely good (Fig. 5), and forensic comparisons of firing-pin, breach-face, ejector, and extractor striae with those of the crime-scene 9-mm casings became possible. The result was positive matches of four residence casings with the crime-scene specimens.

Prior reports of firearms- and bullet-restoration techniques have included abrasive methods and ultrasonic cleaning systems with aqueous detergents (2,3). The present cleaning procedure was compared to a method published by Booker, which utilized an aqueous solution of 5% oleic acid and 5% concentrated ammonium hydroxide at 80°C (4). Booker's protocol, as presented, was a one-step process and a final cleaning step for Cu alloys. It was therefore

FIG. 4—*Bullet in Fig. 3 after cleaning procedure (same magnification and orientation as Fig. 3).*

FIG. 5—*Casing in Fig. 2 after cleaning procedure (same magnifications).*

compared to Step 5 of the present procedure and evaluated as a possible replacement.

Booker's solution performed adequately on exemplar materials related to this investigation, but we qualitatively assessed it to be less desirable than the present method. As a multiphase system at room temperature, it is necessary to heat and thoroughly mix Booker solution before it can be effectively used, and the reported cleaning conditions varied from several minutes to many hours at 80°C. Booker solution immersion times that were equivalent to 30 s of the room-temperature acidic thiourea treatment were determined to be on the order of 0.25 to 2 h.

It is also important to completely immerse brass objects in the Booker medium because a green-black layer of Cu complex(es) forms on brass at the liquid-air interface (such reactions are typical of most ammonia-based Cu-alloy cleaners). In addition, once cleaned in Booker's solution, specimens retain a coating of oleic acid that must subsequently be removed if further processing is required.

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