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Investigation of effective forensic cleaning methods for bullet and cartridge case samples

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INVESTIGATION OF EFFECTIVE FORENSIC CLEANING METHODS FOR
BULLET AND CARTRIDGE CASE SAMPLES

by

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INVESTIGATION OF EFFECTIVE FORENSIC CLEANING METHODS FOR
BULLET AND CARTRIDGE CASE SAMPLES

CASSIE MARIE SHUHERK

ABSTRACT

Bullet and cartridge case evidence may potentially link weapons and crimes through the comparison of toolmark patterns. This analysis relies on the clarity of the toolmarks and the ability of the examiner to identify patterns on the evidence. These patterns may be distorted by debris such as soil, blood, cyanoacrylate, and construction materials. Despite the potential importance of bullet and cartridge case evidence, few investigations of proper cleaning methods have been conducted. The present study was designed to examine the effects of various cleaning solutions and application methods on copper and brass bullets and cartridge cases. Additionally, this research investigated the efficacy of these cleaning protocols on the common evidence contaminants blood and cyanoacrylate.

No cleaning method was found to be universally effective on both contaminant types and nondestructive to the metal surface. Ultrasonication was the most efficient application method employed when used in conjunction with an appropriate cleaning solution. Acetone proved to be safe and successful at removing heavy cyanoacrylate deposits from brass cartridge cases without damaging the metal. Although sulfuric acid removed most of the cyanoacrylate from the brass cartridge case, ultrasonication of the fumed cartridge cases in sulfuric acid caused the nickel-plated primer caps to turn black. Additionally, etching occurred when sulfuric acid was allowed to dry on the cartridge
case surface. Citric acid, salt-flour-vinegar paste, Tergazyme®, and water did not effectively remove the cyanoacrylate from the cartridge cases, but the solutions were safe to use on the brass and sometimes resulted in a shinier surface.

Regardless of the cleaning method employed, the bloodstained bullets retained most or all of the underlying brown tarnish. Ultrasonication with sulfuric acid was successful at removing some blood-initiated tarnishing; however, the removal of residues was not complete, making it difficult to visualize the full striation pattern. Citric Acid, Tergazyme®, and water proved to be safe to use on the copper bullets and capable of removing loose debris, but the cleaning solutions did not effectively remove the brown tarnish.

Flitz® Instant Brass and Copper Tarnish Remover caused damage to both sample types by causing etching to occur on the metal surface. Additionally, the Flitz® tarnish remover caused the brass cartridge cases to turn black over time. The use of the Sunshine Polishing Cloths left light scratches on the surface of the samples, demonstrating they are not suitable for cleaning toolmark evidence.
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<tr>
<td>ATF</td>
<td>Bureau of Alcohol, Tobacco, Firearms, and Explosives</td>
</tr>
<tr>
<td>C</td>
<td>Celsius</td>
</tr>
<tr>
<td>°</td>
<td>Degree</td>
</tr>
<tr>
<td>FMJ</td>
<td>Full Metal Jacket</td>
</tr>
<tr>
<td>G</td>
<td>Gram</td>
</tr>
<tr>
<td>GSR</td>
<td>Gunshot Residue</td>
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<tr>
<td>µL</td>
<td>Microliter</td>
</tr>
<tr>
<td>mL</td>
<td>Milliliter</td>
</tr>
<tr>
<td>Mm</td>
<td>Millimeter</td>
</tr>
<tr>
<td>NIBIN</td>
<td>National Integrated Ballistic Information Network</td>
</tr>
<tr>
<td>TMJ</td>
<td>Total Metal Jacket</td>
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1. INTRODUCTION

Discharging a firearm creates an abundance of evidence that can be useful to a criminal investigation. Approximate distance between suspect and victim may be extrapolated from wound patterns. Identifying a person who recently fired a weapon may be accomplished by detecting gunshot residue (GSR). Relative locations of the victim and assailant may be ascertained by studying trajectories and intermediate objects\(^1\). Bullets and cartridge cases are particularly helpful in associating a firearm with a victim or even another crime.

The movements of a cartridge, from loading to firing, leave characteristic toolmarks on both the bullet and cartridge case. A toolmark is an impression left on the surface of an object through contact with a harder object. Toolmarks, like most evidence, can be divided into class and individual characteristics\(^2\). Class characteristics are those common to a general assembly, often caused by manufacturing processes. In firearm evidence, the brand of ammunition or the number of lands and grooves of a firearm barrel are examples of class characteristics. Individual characteristics are unique qualities that can be traced to a single source. These traits are often the result of dirt, damage, or wear\(^2\). The toolmarks on bullets and cartridge cases can be individualized to a specific firearm, just as fingerprints can be individualized to a person.

Like fingerprints, some toolmarks on firearm evidence are recorded and stored in searchable databases. The National Integrated Ballistic Information Network (NIBIN) is a Bureau of Alcohol, Tobacco, Firearms, and Explosives (ATF) managed program that connects local ballistic databases to a national network. These databases are collections
of high quality digital images of bullet and casing evidence, which are used to connect evidence to crimes or confiscated weapons\textsuperscript{3,4}. The images are analyzed by a computer algorithm that analyzes toolmarks within a particular region of interest. These regions are then compared against the database in order to identify similar patterns. The result of this analysis and comparison is a correlation score between two items. As the resolution of the digital images increases, minute details on the evidence have a greater impact on search results\textsuperscript{4}. Stains, debris, and corrosion may interfere with the digital image capture of toolmarks. It is, therefore, of great importance to determine the most effective means of evidence cleaning and preparation.

1.1 Cartridge Construction, Manufacturing and Use

In order to effectively prepare a bullet or cartridge case for analysis, it is important to understand the manufacturing process and the nature of the component metals. The modern small arms cartridge is comprised of four fundamental components: cartridge case, primer, propellant, and projectile\textsuperscript{5,6} (Figure 1). Each component has a specific purpose and design. The cartridge case (casing) houses the primer, propellant, and projectile. The percussion-sensitive primer is used to ignite the propellant, which then burns, creating hot gases and increasing the pressure within the casing. This pressure causes the casing to expand, releasing the projectile, which is pushed down the barrel of the weapon. This research uses centerfire cartridges; therefore the following descriptions focus on this type of ammunition.
Casings must be strong enough to contain and direct the explosive forces of the propellant, yet flexible enough to not crack under the extreme heat and pressure. Steel, aluminum, and nickel-plated copper are used to make casings; however, brass is the most common material. The industry standard for ammunition brass is approximately 70% copper and 30% zinc. The most common manufacturing process starts with a brass sheet formed into a cup using the mechanical force of a tool and die. The cup is then sequentially drawn with a tool and die to have longer, thinner walls. Each lengthening step is followed by a wash and annealing phase. During the annealing process, the brass is heated to eliminate the stresses caused by the mechanical forces. After the casing is drawn to the proper length and wall thickness, the rim, primer pocket, and head stamp are formed. Final stages of casing manufacture involve trimming excess material and washing away any contaminants. Once the casing is completed, the primer and propellant are added, and the projectile, in this case a bullet, is seated.
Bullets come in a wide variety of shapes and forms, each with a specific purpose. Despite the different types of bullets available, the same general manufacturing techniques are used. Historically, bullets were made of shaped lead. As propellants became more powerful, these lead balls and bullets were no longer adequate, as they would deform under the pressure. Jackets, commonly made of a copper alloy, are used to cover the soft lead core. The copper alloy used for jackets is comprised of copper and zinc in either a 95:5 or 90:10 ratio. There are three general classes of jackets: full metal jacket (FMJ), semi-jacketed, and total metal jacket (TMJ) (Figure 2). An FMJ covers all but the base of the lead core and can have either a flat or round nose shape. There are two general classes of FMJ construction. Solid nose FMJ bullets have cores composed entirely of lead, which impart a high penetrating power. These bullets are frequently used at shooting ranges because they are cheaper to produce. Expanding FMJ bullets are constructed with a softer material in the nose, which expands on impact, decreasing the penetrating power of the bullet. Lower penetration is used for home security and law enforcement because the expansion will stop the bullet from exiting the target and potentially hitting a bystander. A semi-jacketed bullet has an enclosed base and an area of exposed lead in the nose, which allows expansion on impact. A TMJ completely encapsulates the lead core. Jackets are formed in a manner similar to casings: a copper cup is formed and processed using mechanical forces. When the completed bullet is seated into the casing, a sealant or adhesive is frequently used to ensure a tight fit.
Figure 2. Comparison of bullet jackets. (1) Full metal jacket; (2) Total metal jacket; (3) Semi-jacketed bullet.

Primers are generally composed of lead styphnate, barium nitrate, antimony sulfide, as well as other binders and friction materials\textsuperscript{5,10}. These chemicals are contained in a primer cup, which is covered with copper and may be nickel-plated for corrosion resistance\textsuperscript{8}. This cup is seated into the head end of a casing and sealed into place. When the primer is struck by the firing pin of a firearm, the shock-sensitive primer chemicals react which ignites the powder. The rapid burning of the powder creates an abundance of gases that expel the bullet\textsuperscript{11}.

Nitrocellulose and Nitroglycerine are the explosive components of modern propellants\textsuperscript{5}. These substances can be used individually, in a single-base form, or together as a double-base\textsuperscript{5,6,10}. Stabilizers, retardants, and other additives are used to control the reactivity, muzzle flash, and burn time of the powder\textsuperscript{10}. Since the propellant only burns on the surface, the burning rate of the powder is further controlled by the size and shape of the grains loaded into the cartridge\textsuperscript{6}. These parameters are set by the manufacturing process. The nitrocellulose and/or nitroglycerine are dissolved in ether and alcohol, and then formed into either balls or long cords, which are further cut into...
The final product is loaded into the casing, between the primer cup and the projectile.

An assembled cartridge is ready to be loaded into a firearm and fired. Every movement of the casing and bullet in the process of firing potentially leaves an identifiable toolmark. When a cartridge is loaded from a magazine into the chamber of a firearm, characteristic striations may be left on the casing by the front edge of the magazine. Striated impressions are left near the nose of the bullet as it slides against the loading ramp. In the chamber, the extractor may leave an impression on the head of the casing and striations on the rim. When the firearm is fired, the firing pin hits the primer, leaving an impression. The primer ignites the propellant, creating a buildup of heat and gas. The pressure causes the casing to expand against the walls of the chamber, sealing the chamber and releasing the bullet. With only one direction to go, the pressurized gases push the bullet down the barrel of the firearm. Running the length of the inner surface of a rifled barrel are raised and lowered surfaces called lands and grooves. These features leave striations on the bullet as it travels. The number, width, depth, and direction of the lands and grooves are class characteristics. Fouling and imperfections can cause the surfaces of the lands to leave unique striation patterns on the bullets. After the bullet has left the casing, the casing will move backward. The head may strike the breech face, leaving an impression on the primer cap and/or the cartridge case head. As the extractor guides the casing rearward, the casing may still be slightly expanded, pressing against the chamber walls. Imperfections in the chamber can cause striations on the casing as it moves against the wall. The ejector can cause a distinct impression on or near the edge
of the casing head as the two make contact. When the casing is ejected, it may not be fully clear of the ejector port, which often leaves toolmark impressions on the top of the casing.$^{5,8}$

Brass and copper are the primary materials used for the construction of small arms ammunition because the properties of these metals meet the demands of casings and bullets. Copper is hard enough to protect the soft lead core, yet soft enough to accept the rifling of a barrel. Rifling is an important characteristic of modern firearms, as it provides ballistic stability to a projectile by causing it to spin.$^6$ Brass is used for casings because it is hard, yet flexible. A vital role of a casing is to expand and seal the chamber of a firearm in order to direct the force of the burning propellant toward the projectile and down the barrel. However, the casing must also contract so that it can be readily extracted from the chamber without breaking. Not only is brass capable of these size changes, but it is resilient enough that used casings can be reloaded and fired again; the brass is strong enough to withstand multiple firing events. Both brass and copper are capable of being cold-worked. Mechanical forces are used to form the metal without the use of heat, which leads to a cheaper manufacturing process and a stronger resulting metal. The repeated process of applying mechanical force and heat rearranges the atomic structure of the metal, imparting upon it the desired physical properties.$^{12}$ Brass and copper are also used in a variety of industries because of their corrosion resistance. This property ensures the longevity of the metal under various environmental conditions, including the extreme conditions encountered by firearm evidence.
1.2 Sources of Toolmark Distortion on Bullets and Cartridge Cases

A potential threat to firearm evidence is corrosion, which is the formation of an oxide layer on the surface of a metal. Brass and copper will naturally corrode in the presence of air and moisture\textsuperscript{13}. Further corrosion occurs with the addition of heat or pollutants such as oxidizing acids, heavy metal salts, sulfur, and ammonia\textsuperscript{14}. Both metals will form a thin oxide layer that drastically slows corrosion and protects the underlying metal. The process of forming this protective layer is called passivation\textsuperscript{13,15}. Copper corrodes in a stepwise manner: cuprous oxide (Cu\textsubscript{2}O) forms first and is then transitioned to cupric oxide (CuO). This transition is the rate-limiting process of corrosion\textsuperscript{16}. Brass undergoes a specific form of corrosion called dezincification. In this process, the zinc is selectively corroded, forming an even greater protective layer over the copper. Despite this protective quality, corrosion causes discoloration, which may interfere with forensic examination.

Body fluids are likely contaminants of bullets involved in a homicide or a shooting with an injury. Decomposition has been shown to adversely affect the surface of projectiles by causing stains and corrosion, the extent of which is related to the amount of time the metal is exposed to the decomposition environment\textsuperscript{17}. Blood may contribute to these adverse surface effects. Forensic investigators use presumptive tests for blood that rely on the peroxidase-like activity of hemoglobin to catalyze the oxidation of a given color-changing compound\textsuperscript{18}. Perhaps in a similar manner, hemoglobin catalyzes the oxidation of the metal jacket of a bullet.
Despite limited success, attempts are still made to recover latent fingerprints from casings\textsuperscript{19,20}. Cyanoacrylate (superglue) fuming is one of the most common and successful techniques currently used for latent print development\textsuperscript{21}. When heated, cyanoacrylate turns into a vapor. This vapor adheres to the fingerprint residue present on evidence\textsuperscript{22}. Although a useable latent print may not develop, the cyanoacrylate will remain on any residue, potentially distorting a toolmark.

1.3 Current Cleaning Methods

Although there is not a standard protocol for cleaning bullet and casing evidence, many forensic laboratories use similar cleaning methods. Ammunition evidence is cleaned with a soap and water solution, while a 10\% bleach solution is used to disinfect the evidence. Alcohols, acids, jewelry cleaners, brushes, swabs, and ultrasonication are used for more robust cleaning\textsuperscript{23-27}. Many of these methods were originally developed for other purposes, such as historical preservation and circuit board manufacture\textsuperscript{28-32}. Few published studies have directly examined the effects of cleaning techniques on forensic bullet and casing analysis\textsuperscript{3,34}.

Protocols must be established to not only clean the evidence, but preserve it, as well. The condition of evidence is important during examination and courtroom presentation. Evidence may be pristine during examination; however, improper handling and storage may result in tarnish or corrosion. Heavily tarnished evidence could cause a jury to question the reliability of the expert if the jury is incapable of seeing what the
examiner once saw. Additionally, evidence must be available for re-examination by an expert of their choosing should opposing counsel be granted access by the court.

Despite the obvious need for research, few studies that directly test the efficacy of cleaning solutions on firearm evidence have been published. The present study aims to investigate potential cleaning solutions and application methods by examining their microscopic effects on the surface of metal casings and bullets. It is hypothesized that ultrasonication will provide the safest and most complete method of cleaning because it uses higher energy to remove debris than simply agitation, yet its contactless nature is believed to be less abrasive than swabbing. It is also believed that there may not be a single, ideal cleaning solution for all firearm evidence; rather, a cleaning solution and method must be chosen based upon the form of debris and staining present.
2. MATERIALS AND METHODS

2.1 Bloodstain Deposition

A total of six test fired bullets were used to determine the parameters adequate for replicating surface discoloration caused by exposure to blood. Table 1 provides a breakdown of the bullet types. Three bullets were placed on their sides in a glass dish and held on the top rack of a ThermoElectron (Waltham, Massachusetts) oven preheated to 150 degrees Celsius (°C) in order to replicate the temperature of a fired weapon. Mimicking the thermal environment was considered to be important because it is possible that temperature influences the rate of corrosion when bullets are exposed to body fluids, such as blood. The heat produced by firing a firearm is affected by several factors, including bullet weight and the size and shape of propellant. Although the gases within the casing can reach temperatures of 2800°C, 9 mm bullets in flight have been measured around 150°C\(^5\). Extreme heat can cause metal to corrode, however, it has been shown that casings heated up to 400°C produced no visible corrosion\(^35\). Thus, a temperature of 150°C to simulate the temperature of being fired, while not causing visible corrosion, was used.

After 30 minutes the bullets were removed and placed in a room temperature glass bowl. The remaining three bullets were placed on their sides in a plastic petri dish. Frozen human whole blood with sodium heparin was thawed at room temperature and then vortexed to homogenize. Enough blood was added to the petri dish and glass bowl to cover the lower half of the bullets. The bullets remained in the blood for one hour, after which they were transferred to clean petri dishes and allowed to dry for one hour in
a fume hood. Once dried, the bullets were photographed with a Nikon D7100 DSLR camera (Tokyo, Japan), and the petri dishes were taped closed. The samples were photographed at 24, 48, and 120 hour intervals. At the final interval, cotton swabs moistened with water were used to clean a portion of the blood-covered bullets in order to reveal any underlying staining.

Table 1. Breakdown of bullets used in stain replication tests.

<table>
<thead>
<tr>
<th>Bullet Number</th>
<th>Bullet Type</th>
<th>Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Semi-Jacketed (expanded)</td>
<td>Not Heated</td>
</tr>
<tr>
<td>2</td>
<td>Semi-Jacketed</td>
<td>Heated</td>
</tr>
<tr>
<td>3</td>
<td>TMJ</td>
<td>Not Heated</td>
</tr>
<tr>
<td>4</td>
<td>TMJ</td>
<td>Heated</td>
</tr>
<tr>
<td>5</td>
<td>FMJ</td>
<td>Not Heated</td>
</tr>
<tr>
<td>6</td>
<td>FMJ</td>
<td>Heated</td>
</tr>
</tbody>
</table>

2.2 Ultrasonication Time Trials

Five TMJ bullets were labeled by scratching a number onto the nose using a metal probe and then photographed with a SPOT Idea 1.3 MP camera (Sterling Heights, Michigan) mounted on a Nikon SMZ1000 stereomicroscope (Tokyo, Japan). The samples were heated in a glass bowl in an oven at 150°C for 30 minutes, and then transferred to a room temperature glass bowl. Frozen whole human blood was thawed for one hour at room temperature, vortexed to homogenize, and added to the samples to completely cover them. After four hours, the bullets were removed from the blood and placed in separate petri dishes overnight. Approximately 24 hours later, bullets 1, 2, and 3 were placed into 50 mL centrifuge tubes that were filled with enough water to cover the bullets completely. The tubes were suspended in a Branson 1510 ultrasonicator.
(Danbury, Connecticut) using a polystyrene foam boat. Bullet 4 was placed in a beaker, covered with water, and gently swirled manually. Bullet 5 remained stationary in a beaker of water. Three test intervals were used: 10, 30, and 60 seconds. Between each interval, the bullets were removed from the water, placed on their bases on a paper towel, and allowed to dry. After they dried, each bullet was photographed using the stereomicroscope.

2.3 Surface Integrity

2.3.1 Cleaning Solutions

The same solution preparation was used for each experiment. Acetone and sulfuric acid were used undiluted (ACROS Organics, Geel, Belgium). The citric acid was prepared by dissolving 5.0 g of citric acid (ACROS Organics, Geel, Belgium) in water to 100 mL. Flitz® Instant Brass and Copper Tarnish Remover (Waterford, Wisconsin) was used, which required no preparation. Tergazyme® is a protease detergent produced by Alconox Incorporated (White Plains, New York). Following the manufacturer’s instructions, a 1% solution was prepared in water. Sunshine Polishing Cloths (Japan) were used and required no preparation. The salt-flour-vinegar paste was prepared by first mixing equal parts salt and flour together, then adding an equal amount of white vinegar to the dry mixture. Common household brands were used to make the paste. Table 2 provides a summary of the cleaning solutions.
Table 2. Summary of cleaning solutions.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Preparation</th>
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<tbody>
<tr>
<td>Acetone</td>
<td>Undiluted</td>
</tr>
<tr>
<td>Citric Acid</td>
<td>5% solution in water</td>
</tr>
<tr>
<td>Sulfuric Acid</td>
<td>Undiluted</td>
</tr>
<tr>
<td>Tarnish Remover</td>
<td>No preparation required</td>
</tr>
<tr>
<td>Tarnish Cloth</td>
<td>No preparation required</td>
</tr>
<tr>
<td>Tergazyme®</td>
<td>1% solution in water</td>
</tr>
<tr>
<td>Salt-Flour-Vinegar</td>
<td>Equal parts mixed</td>
</tr>
</tbody>
</table>

2.3.2 Samples

A combination of unfired bullets, unfired casings, and fired casings were used to study the effects of different cleaning solutions and application methods on the metal surfaces. The unfired FMJ bullets and unfired casings used were Union Metallic Cartridge Company, Remington Arms (Lonoke, Arkansas) 45 Auto 230 grain cartridges. Speer Lawman Ammunition (Lewiston, Idaho) 40 Smith & Wesson 180 grain TMJ unfired bullets and fired casings were also used. The bullets were removed from the casings using an inertia bullet puller. The set intended for the soak-swab-wipe test (refer to section 2.3.5) was comprised of unfired TMJ, unfired FMJ bullets, and unfired casings. The ultrasonication set was comprised of unfired TMJ bullets, unfired FMJ bullets, and fired casings. Although it is unlikely that ultrasonication could detonate a primer, previously fired casings were used as a precautionary measure. All tests were performed in triplicate.
2.3.3 Labeling

Each bullet nose was labeled with a sample number and cleaning solution used. Casings were labeled with hash marks around the open mouth end. The samples slated for the soak-swab-wipe test were divided into thirds (Figure 3); the bullets were divided into approximately 5 millimeter (mm) sections, and the casings were divided into approximately 7 mm sections. Ultrasonication samples and tarnish cloth samples were not divided. Each section of the soak-swab-wipe samples and each ultrasonication sample were photographed with the stereomicroscope.

![Diagram of bullet and casing sections]

**Figure 3. Areas of the bullets and casings subjected to different cleaning techniques.** Each sample was divided into separate zones by scratching a line onto the surface using a metal probe.

2.3.4 Tarnish Cloth

Each sample was held between the thumb and index finger. The sample was rubbed against the stationary cloth, which was lying flat on the table. Each wipe was approximately one inch. Four strokes back and forth over the same one inch area comprised one set of wipes. Each sample was wiped in four sets, for a total of 16 one-inch swipes.
2.3.5 Soak-Swab-Wipe

Water, acetone, citric acid, Tergazyme®, salt-flour-vinegar, and sulfuric acid were used to test the effects of soaking, swabbing, and wiping on the sample surface. A Kimwipe® (Roswell, Georgia) was folded into eighths, moistened by pipetting approximately 100 μL of solution onto the folded corner, and used to wipe the sample ten times around approximately half the circumference of the wipe zone. The caustic nature of sulfuric acid caused the Kimwipe® to rapidly dehydrate and disintegrate. Wiping sulfuric acid with a Kimwipe® was therefore abandoned, and only the soak and swab methods were used with sulfuric acid. Immediately following the wiping, a cotton swab was moistened by dipping it directly into the solution. The samples were each swabbed with ten strokes around approximately half the circumference of the swab zone. The sample was then placed on its base in a glass bowl, and the solution was carefully poured down the side of the bowl until the level reached the first hash mark on the sample. The
samples were tilted slightly to release any air bubbles trapped underneath. The samples remained in the soaking solution for two minutes, after which they were removed and placed upright on a paper towel. After an additional three minutes, the samples were rinsed and placed on a new paper towel to dry.

According to the manufacturer’s recommendations, the tarnish remover was to be applied for no more than one minute. A strong warning against allowing the solution to dry was also included on the label. To accommodate these instructions, the tarnish remover was swabbed then soaked for only one minute. After the minute, the samples were immediately rinsed.

2.3.6 Ultrasonication

Samples were ultrasonicated in individual 50 mL centrifuge tubes. Each sample was placed into a tube and covered with approximately 15 mL of cleaning solution. The samples were suspended in the ultrasonicator bath and sonicated for one minute. Then, they were immediately dropped into a 500 mL beaker of water, removed and rinsed under running water, and then placed on a paper towel to dry. Due to the paste consistency of the salt-flour-vinegar solution, it was not used for ultrasonication.

2.3.7 The Effects of Drying

Unfired FMJ bullets and fired brass casings were used in triplicate to study the effects of allowing the cleaning solutions to dry on the surface of the samples. The cleaning solutions studied were citric acid, acetone, sulfuric acid, tarnish remover, and
water. The samples were first labeled and photographed. For each solution, the samples were placed on their sides in a glass bowl. Solution was added until the sample was approximately half submerged. Using a disposable pipette, five drops of the cleaning solution were applied to the top of each sample. After resting for ten minutes, the samples were rinsed, allowed to air dry on a paper towel, and then photographed.

2.4 Contaminated Evidence

2.4.1 Samples

Seventy-two Remington (Lonoke, Arkansas) 9mm FMJ cartridges were fired from a Smith & Wesson model 469 semiautomatic pistol (Springfield, Massachusetts) into a water tank. The casings were caught in netting as they were being fired. Three different magazines were used and the firearm was not cleaned or allowed to cool during the process. Gloves were not worn while loading the magazines. The collection took place over a two day period: 22 bullets were fired on day one, and 50 bullets were fired on day two. One control bullet and casing from each day was set aside, and then the separate days were pooled.

2.4.2 Cyanoacrylate Fuming

2.4.2.1 Fingerprint Deposition

Fingerprint residue was intentionally applied to the fired casings before fuming by using a protocol similar to previous studies\textsuperscript{34,36-38}. The subject first washed her hands with soapy water, and then wore nitrile exam gloves for 20 minutes to stimulate sweat
production. Before depositing the fingerprint residue onto the casings, the subject rubbed her fingers together. Deposition was first made by pressing the subject’s thumb on the primer end of each casing, rotating 90° then pressing again. Pressure was applied to this deposition in an attempt to leave residue in the firing pin and breech face impressions. After the thumb prints were deposited, the subject again rubbed her fingers together, then picked up each casing by placing the thumb and forefinger on opposite sides of the casing. Using the opposite thumb and forefinger, the subject grasped the casing on the plane perpendicular to the first. After approximately every ten casings, the subject rubbed her fingers along her hairline in order to ensure the presence of residue.

2.4.2.2 Fuming

Cyanoacrylate fuming took place in a portable fuming chamber (Safariland Products, Jacksonville, Florida) using a Fume-a-Wand (Safariland Products, Jacksonville, Florida). The chamber did not have an airtight seal, which allowed the fumes to escape. To minimize fume loss, the chamber was held closed manually from the top edge and bottom right corner. All cyanoacrylate fuming took place in a fume hood. The casings were fumed using one of three protocols. For the heavy deposition, the casing was held with plastic tweezers and rotated directly in front of the fuming wand, using a cyanoacrylate cartridge and the high heat setting. For the medium deposition, the casings were hung in the fuming chamber for five minutes, using a cyanoacrylate cartridge and high heat setting. The light deposition protocol required the casings to be hung for five minutes in the fuming chamber, and used a smaller glue pellet in the fuming wand, set at
medium heat. Replicates of five were used in the cleaning solutions, while triplicates were used for the water control. Each test set contained one heavy, two medium, and two light cyanoacrylate deposition casings. The control group contained one of each category of deposition. The casings were numbered and photographed after being fumed, then photographed again after being cleaned.

2.4.2.3 Cleaning Protocols

The casings were swabbed ten times on one side and ten times around the head using cotton swabs dipped directly into the cleaning solution. The samples were immediately rinsed and allowed to dry on a paper towel. Acetone, Tergazyme®, citric acid, and water were used for this test.

Casings were gently agitated using a Barnstead Thermolyne RotoMix Type 50800 orbital shaker (Dubuque, Iowa). The casings were placed into 50 mL beakers filled with approximately 20 mL of the cleaning solution, and agitated at the lowest setting for one minute. The samples were immediately dropped into a 500 mL beaker of water, then rinsed under running water and allowed to dry on a paper towel. Water, acetone, citric acid, sulfuric acid, and Tergazyme® were used to clean the casings on the orbital shaker. A set of casings was cleaned using the salt-flour-vinegar mixture in a similar manner; however, they were not placed on the shaker. Since this mixture is a paste, the casings were simply coated with the paste and allowed to rest for one minute before being rinsed.
The casings were ultrasonicated using the protocol described in section 2.3.6. The solutions used for this set of tests included water, sulfuric acid, citric acid, acetone, and Tergazyme®.

2.4.3 Blood Exposure

2.4.3.1 Application of Blood

Sixty-eight bullets were divided among five 400 mL glass beakers and placed into an oven preheated to 150°C. Two additional bullets were placed into the oven in a separate glass bowl. All bullets remained in the oven for 30 minutes. Bovine whole blood with EDTA (Pel-Freez Biologicals, Rogers, Arkansas) was removed from the refrigerator 15 minutes prior to use. After being removed from the oven, the bullets were quickly placed into six room temperature 250 mL glass beakers. The bovine blood was vortexed and poured over the bullets until they were covered. The beakers were then placed on a heating block set at 35°C for four hours. Several samples were removed from the blood and visually examined to determine if surface discoloration had occurred. The blood appeared to run off the bullets, leaving no apparent stains after four hours. The beakers were then removed from the heating block and placed in a fume hood at room temperature overnight. In order to control the amount of evaporation, the beakers were covered with Parafilm®, and four small holes were poked into each cover. After approximately 20 hours, the bullets were removed from the blood and arbitrarily separated into plastic petri dishes in 14 sets of four and three sets of three samples. The samples air-dried for one hour before the dishes were covered and stored at room
temperature. After three days in dark storage, the samples were labeled, photographed, cleaned, and then photographed again.

2.4.3.2 Cleaning Protocols

Using cotton swabs dipped directly into the cleaning solution, one land impression on each bullet was swabbed. Bullets labeled 1 and 2 were swabbed ten times each. Bullets labeled with a 3 were swabbed 30 times, and bullets labeled with a 4 were swabbed 40 times. The samples were immediately rinsed and allowed to dry on a paper towel. Acetone, Tergazyme®, citric acid, sulfuric acid, and water were used for this test.

The bullets were agitated using the same protocol as the casings. Water, acetone, citric acid, sulfuric acid, tarnish remover, and Tergazyme® were used to clean the bullets on the orbital shaker. After being agitated and rinsed, bullets 2 and 4 in each set were swabbed with a clean dry cotton swab in an attempt to remove even more debris and staining. A set of bullets was cleaned using the salt-flour-vinegar mixture with the same protocol as the casings.

The bullets were ultrasonicated using the protocol previously described. The solutions used for this set of tests included water, sulfuric acid, citric acid, acetone, tarnish remover and Tergazyme®.
3. RESULTS

3.1 Successful Bloodstain Deposition

The initial protocol of exposing the samples to blood for only one hour did not cause any reddish brown tarnish to form on either the heated or non-heated bullets. Once the samples dried, some of the blood simply flaked away, leaving the underlying metal undisturbed. The remaining flakes of dried blood were easily wiped away with a cotton swab, even after five days. Due to the lack of successful staining, the protocol was changed to a four hour exposure to blood. This revision resulted in bullets that had less red flaky blood residue clinging to them, while retaining more brown tarnish on the surface of the metal.

3.2 Ultrasonication Time Trials

These tests used the revised stain replication protocol. Ultrasonication removed more of the loose, red residue than swirling or soaking in water, and exposed the shiny orange underlying metal. Although more red blood residue was removed with each increasing time interval, a previous study suggests that ultrasonication of five minutes or more can damage forensic evidence\(^3\). The 60-second interval is below this threshold, and was, therefore, used throughout the remaining experiments in the present study. Swirling the bullet in water produced results similar to ultrasonication, but the patches where the residue was removed were dull, rather than shiny. Soaking in water removed a minimal amount of the reddish residue. The degree of removal was independent of the time spent soaking.
3.3 Cleaning Solutions

3.3.1 Acetone

Regardless of application method and sample type, acetone did not appear to have an effect on the surface of the metal. No visible change occurred when acetone was allowed to dry on the metal surface. A greater amount of the cartridge assembly adhesive remained on the TMJ bullets than on the FMJ bullets after being pulled with the inertia bullet puller. Swabbing, soaking, and ultrasonication with acetone removed some of these heavy adhesive deposits. Cyanoacrylate residues were nearly completely removed with acetone, regardless of the application method. In contrast, the brownish surface tarnish caused by the blood remained visually unaffected.

3.3.2 Citric Acid

The metal of the TMJ samples remained visibly unaffected by citric acid when soaked, swabbed, wiped, or ultrasonicated. The adhesive did not appear affected by the acid.

Although swabbing and wiping had no obvious effects on the FMJ samples, soaking and ultrasonication removed oxidation deposits, which left a shiny, smooth surface. Allowing the citric acid to dry on the bullets had no detrimental effects. Swabbing the blood-exposed bullets with citric acid 30-40 times left a patchy shiny surface, but the remaining brown stains still distorted most of the toolmark impressions. The water rinse removed the loosely adhering blood from the swabbed samples. Agitating the blood-exposed samples resulted in small patches of shiny metal in which
faint toolmark impressions were visible. Two distinct layers of staining were apparent on the agitated samples (Figure 5). Larger patches of metal were uncovered with ultrasonication. Approximately 2 of the 5 land impressions on each bullet were cleaned well enough to identify striations, although the patterns were incomplete. The striations across the full width of the land impression were not visible.

![Image](image_url)

**Figure 5. View of layered result of citric acid agitation on Bullet 2.** (A) Blood residue that adhered to the surface of the bullet; (B) Layer of brown staining; (C) Cleaned metal.

The patchy results of the agitation and ultrasonication treatments cannot be wholly attributed to the citric acid. Comparison of before and after photographs of the citric acid test samples and the water control samples show that the action of agitating and ultrasonicating was responsible for removing the crusty and flaky residues (Figure 6). Although the citric acid was able to clean the metal exposed when agitation or ultrasonication removed the flaky blood material, it was not able to remove any of the brown tarnish from the metal surface.
The metal casings were only affected when soaked or ultrasonicated in citric acid, which left them shiny. Stains that were present before soaking or ultrasonicating were still present after cleaning. Swabbing, wiping, and drying did not result in visible changes to the surface of the non-fumed casings. Agitating the fumed casings removed some of the lighter cyanoacrylate deposits, while heavier deposits were partially removed by ultrasonication. Swabbing with citric acid removed some of superglue from the head stamps of the casings (Figure 7), but not the walls. It is possible this is due to a greater amount of pressure that could be exerted on the flat surface of the head, whereas on the curved walls, it was difficult to direct the force of the swab.
3.3.3 Sulfuric Acid

Sulfuric acid etched the soak and swab zones of the TMJ samples. This etching, visible as a slightly roughened surface, is associated with the removal of the outer protective oxidation layer\textsuperscript{28}. Ultrasonication removed the adhesive; however, the resulting surface had an appearance similar to water spots on glass with light surface etching.

Swabbing FMJ samples with sulfuric acid resulted in a light etching of the surface. Allowing the acid to dry on the bullets caused the surface to appear cracked. A pre-existing scratch present on one sample tarnished to a green color when the sulfuric acid dried (Figure 8). The soak and ultrasonication samples became shiny; however, around the base of the bullets, a ring of cloudy tarnish formed. The acid reacted with the cotton swab, producing a thick yellowy substance, which could not be used to swab the bullets. Agitating and sonicating caused the blood residue to turn a grey color, which was easily wiped away with a swab. The underlying metal had visible striations.
however, the removal of the grey and reddish brown residues was not complete, making it difficult to visualize the full patterns.

Figure 8. Tarnished scratch on FMJ. The exposed metal of the scratch was tarnished by allowing sulfuric acid to dry on the surface. (A) Area of the scratch not exposed to the drying sulfuric acid; (B) Area that has been affected by the drying acid.

Allowing sulfuric acid to dry on casings etched the surface, causing it to appear cloudy. Soaking the casings caused the metal to become shiny; however, on one sample a line at the top edge of the soak zone was deeply etched into the metal (Figure 9). Evidence of a shallow line was visible before the casing was exposed to sulfuric acid. Surface disruption such as this, where the protective layer of oxidation has been compromised, is more susceptible to the damaging effects of sulfuric acid, explaining why the line became more heavily etched than the surrounding area. Ultrasonication in sulfuric acid did not appear to damage the surface or remove any previously present stains. After ultrasonication, the casings were shiny, implying the removal of the oxidation layer. It was concluded that casings should be fully immersed in sulfuric acid in order to avoid damaging effects of drying. Agitating removed almost all the
cyanoacrylate without damaging the surface of the samples. Similarly, ultrasonication removed nearly all of the glue, but reacted with the nickel-plated primer cup, causing it to turn black.

Figure 9. Sulfuric acid etched casing. (A) The deeply etched line highlighted in red box; (B) View of etched line at 40x magnification.

3.3.4 Salt-Flour-Vinegar

The salt-flour-vinegar mixture had very little effect on the samples. The TMJ bullets were not visibly affected, and only some oxidation was removed from the FMJ samples, causing them to appear shiny. The loose blood residue was removed from the bloodstained samples. However, this could be a result of rinsing with water, rather than the action of the mixture. No striations became apparent after cleaning the bloodstained bullets with the salt-flour-vinegar mixture. Casings, like FMJ bullets, became shiny when cleaned, but the oxidation removal was not consistent and appeared spotty. Cyanoacrylate did not appear to be removed by this mixture.
3.3.5 Tarnish Remover

The tarnish remover had immediate effects on each sample type. The TMJ bullet became shiny, but the tarnish remover had no effect on the adhesive. The outer layer of oxidation was removed from the FMJ bullets using every application method, but it was determined that allowing the tarnish remover to dry on the bullets etched the surface. Swabbing, agitating, and sonicating removed the bloodstains in patches. The underlying metal of the agitated samples appeared etched, while the ultrasonication yielded visible, but incomplete, striation patterns in 1 of 5 land impressions. Although the casings immediately became clear and shiny, two weeks after being cleaned, the soaked and swabbed areas of the samples turned black (Figure 10). Both total immersion and allowing the tarnish remover to dry on the casings heavily etched the surface. Due to these adverse effects, the tarnish remover was not used for the cyanoacrylate cleaning tests.

![Figure 10. Illustrations of effects of tarnish remover on casings after two weeks.](image)

(A) Immediately after cleaning with tarnish remover. The light areas represent the swab and soak zones where the darker gold colored protective tarnish layer has been removed; (B) Two weeks after cleaning with tarnish remover. The light areas seen in (A) have become dark with corrosion.

3.3.6 Tergazyme®

Overall, the Tergazyme® removed loose debris from the surface of the samples, without affecting the metal. The TMJ adhesive appeared unaffected. After the initial
swabbing of the fumed casings, no cyanoacrylate appeared to be removed. Two fumed casings were used to determine if additional swabbing would affect the cyanoacrylate; however, only very light removal resulted. Swabbing and agitating the bloodstained bullets removed the flaky remnants of dried blood, while ultrasonication removed enough residue to create shiny patches. In approximately 1 of 5 land impressions on each of the bloodstained bullets, incomplete striation patterns became visible after being cleaned with Tergazyme®.

3.3.7 Tarnish Cloth

The tarnish cloth made the surface of each metal smooth and shiny by removing oxidation. Any surface markings that were present before being wiped with the cloth remained visible after wiping; however, very faint scratches were also produced (Figure 11). Although these scratches were quite fine, it is possible that too much pressure or wiping could cause deeper scratches. For this reason, the tarnish cloth was not used in any other experiment.

![Figure 11. Image of scratches produced by tarnish cloth.](image)

(A) View of TMJ bullet cleaned with a tarnish cloth; (B) Green rectangle enlarged to show the scratches.
3.3.8 Water

Water served as a control because it does not readily damage the protective tarnish layer that naturally forms on brass and copper, and therefore, cannot reach exposed metal. In each test, the water did not visibly affect the surface of the metal. Only loose surface debris was removed when water was used to clean the samples.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Effects on Surface Integrity</th>
<th>Drying Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>No visible effects to metal surface.</td>
<td>No visible effects.</td>
</tr>
<tr>
<td>Citric Acid</td>
<td>Agitation and ultrasonication removed oxidation, leaving a shiny surface.</td>
<td>No visible effects.</td>
</tr>
<tr>
<td>Sulfuric Acid</td>
<td>Light surface etching in swabbed areas of all samples.</td>
<td>Damaging effects on both sample types.</td>
</tr>
<tr>
<td>Salt-Flour-Vinegar</td>
<td>Left an inconsistently shiny surface.</td>
<td>Not used in this experiment.</td>
</tr>
<tr>
<td>Flitz® Tarnish Remover</td>
<td>Left a shiny surface on bullets, but casings turned black after two weeks.</td>
<td>Damaging effects on both sample types.</td>
</tr>
<tr>
<td>Tergzyme®</td>
<td>No visible effects on metal surface.</td>
<td>Not used in this experiment.</td>
</tr>
<tr>
<td>Tarnish Cloth</td>
<td>Left light scratches on the surface.</td>
<td>Not used in this experiment.</td>
</tr>
<tr>
<td>Water</td>
<td>No visible effects.</td>
<td>No visible effects.</td>
</tr>
</tbody>
</table>
Table 4. Summary of effects on fumed casings and blood-exposed bullets.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Cyanoacrylate (Casings)</th>
<th>Brown Tarnish and Flaky Blood (Bullets)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>Removed nearly all superglue, regardless of method, with no visible effects on the metal.</td>
<td>No visible effects on flaky blood, tarnish, or metal surface. Striations not visible.</td>
</tr>
<tr>
<td>Citric Acid</td>
<td>Did not remove glue from walls, but removed light deposits from head.</td>
<td>Agitating and sonicating removed flaky blood, but brown tarnish remained. Limited striations became visible.</td>
</tr>
<tr>
<td>Sulfuric Acid</td>
<td>Removed most of the cyanoacrylate, but the primer caps turned black when ultrasonicated.</td>
<td>The blood residue was easily swabbed away after sonicating or agitating. The brown tarnish was only partially removed. Limited striations became visible.</td>
</tr>
<tr>
<td>Salt-Flour-Vinegar</td>
<td>No visible effects to metal or cyanoacrylate.</td>
<td>No visible effects on metal, flaky blood, or tarnish.</td>
</tr>
<tr>
<td>Flitz®️ Tarnish Remover</td>
<td>Not used for this experiment due to damaging effects.</td>
<td>Where flaky blood was removed, the surface became shiny, but lightly etched. No effect on brown tarnish.</td>
</tr>
<tr>
<td>Tergzyme®️</td>
<td>Light cyanoacrylate deposits removed with much scrubbing.</td>
<td>Enough flaky blood removed to identify limited striations, but tarnish was unaffected. The metal surface was not visibly affected.</td>
</tr>
<tr>
<td>Water</td>
<td>No visible effects.</td>
<td>Only very loose flaky blood removed.</td>
</tr>
</tbody>
</table>
4. DISCUSSION

4.1 Bullet and Casing Sample Selection

Research performed on copper and brass often utilizes thin pieces of metal called plates. Plates provide a more controllable platform for experimentation. Fingerprint studies often use brass plates because the pressure of print deposition on a flat surface is more uniform than would be possible on the round exterior of a casing. Additionally, a consistent surface preparation is possible on flat samples.

The present study used both fired and unfired bullets and casings, rather than metal plates. The aim of this research was to examine the behavior of actual bullets and casings, not just the metals from which they are made, when exposed to various cleaning solutions and techniques. This is important because the different treatments of the metals and the extreme environments through which they pass could potentially affect the physical structure and behavior of the metal. The manufacturing of casings and bullet jackets is intended to strengthen the metal without making it brittle. This is accomplished through rearranging the atomic structure of the metal. Foreign material and GSR from the barrel of the weapon may affect the performance of a cleaning solution by interfering with the chemical reaction with the metal. Additionally, the heat produced when a firearm is fired potentially affects the surface of the metal. A simple copper or brass plate does not have the same stress history as firearm evidence. Even the rounded shape of the bullets and casings may contribute to cleaning efficiency, as noted in the results of using citric acid to swab the cyanoacrylate from the casings.
Different types of bullets were intentionally used in several of the experiments. The primary goal was to determine if the cleaning solutions would have an adverse reaction with exposed lead. If so, this reaction would be visible in the FMJ bullets, but not the TMJ samples. Furthermore, lead is a component of GSR that is often encountered on recovered evidence and may interfere with toolmark analysis. It could, therefore, be beneficial for the cleaning solution to dissolve the lighter lead deposits. A stronger adhesive was present on the TMJ bullets as compared to the FMJ bullets. The removal of this adhesive provided another way to test the performance of each cleaning solution. Overall, observing a lack of reaction between the solutions and the lead permitted further testing to be performed on only one type of bullet, the FMJ samples.

4.2 Bloodstain Deposition

It has been shown that decomposition has adverse effects on the surface of recovered bullets\(^\text{17}\). It is not known exactly what causes the corrosion and scaling of the metal. The environment created by a decomposing organism is a complex mixture of chemicals, body fluids, bacteria, and insect activity. Compounding the difficulty in understanding what creates these harsh conditions are the microenvironments generated by microorganisms\(^\text{31}\). Blood may be a contributor to the corrosive nature of decomposition. Time is required for corrosion to occur, which is why multiple time intervals were tested in this study. The initial one hour parameter was intended to be a conservative approach in order to not create too much corrosion on the bullets. It became clear that one hour was not long enough to create the brownish stains on the metal.
surface. Four hours yielded a reddish-brown layer adhering to the surface; however, even these stains were relatively simple to remove. The final test of 20 hours in blood resulted in dark brown stains that were not easy to wipe away (Figure 12). These brown stains were assumed to be the staining associated with exposure to blood.

![Figure 12. Appearance of bloodstained bullets.](image)

(A) Four bullets heated and exposed to blood for 20 hours. The brown staining is visible around the nose of the bullets, and dark flaky blood residue is present; (B) Two control bullets exposed only to heat of 150°C for 30 minutes; (C) Two control bullets not exposed to heat or blood.

### 4.3 Application Methods

Several application methods were tested in order to determine which was most effective and whether any method damaged the surface. Swabbing is frequently used in forensic laboratories\textsuperscript{23-27}, but no published studies could be located that demonstrate swabs do not scratch the surface of bullets or casings. The present study supported the current use of swabs by demonstrating the non-abrasive nature of the cotton tip. The samples were allowed to soak in solution in order to determine whether the metal surface was affected by a chemical reaction alone, or by the method used for application. In addition to dislodging surface adherents, ultrasonication also works through a process
called cavitation, in which bubbles form on the surface of the sample. The microenvironment created by these bubbles exacerbates any underlying disarray within the metal’s structure, causing pitting and etching with prolonged exposure\textsuperscript{3,34}. Although one study found that ultrasonication had detrimental effects on both jacketed and non-jacketed bullets, the minimum time interval used was five minutes of ultrasonication\textsuperscript{3}. After five minutes, there was no visual difference; however, the NIBIN correlation score based on the quality of the toolmark was lower\textsuperscript{3}. Some forensic protocols recommend the use of ultrasonication for heavy debris and scaling, but only in 5-15 second intervals\textsuperscript{24,26}. The present study used a one-minute interval as a compromise, which resulted in no visible changes to the surface.

### 4.4 Cleaning Solutions

Acetone is a degreaser commonly used to remove cyanoacrylate\textsuperscript{29,40-42}. Although a previous study of fingerprint corrosion used acetone to remove fingerprint residue\textsuperscript{34}, it was recently shown that soap and water is more effective\textsuperscript{37}. Compared to other available degreasers, such as dichloromethane, acetone is safer and less environmentally toxic\textsuperscript{43,44}. It is a reliable chemical for the removal of superglue; however, it had no effect on the bloodstained bullets.

The citric acid had a minimal effect on each of the categories tested. Found in metal polishes\textsuperscript{45}, citric acid is used to remove tarnish from brass\textsuperscript{30}. Citric acid is used as a less harsh alternative in the passivation of some metals\textsuperscript{15}. In order to manufacture a smooth, uniform surface, the metal must first be cleaned. One suggested cleaning
technique for copper uses hydrogen peroxide ($\text{H}_2\text{O}_2$) and citric acid. The $\text{H}_2\text{O}_2$ removes heavy corrosion residues, while the citric acid induces the growth of a thin layer of protective oxide\textsuperscript{46}. The need for a separate cleaning agent is supported by the results of the present study. The citric acid alone was incapable of removing any debris or tarnish from the surface.

It was originally concluded from the results of the soak test that sulfuric acid damages the FMJs and should not be used as a cleaning solution; however, similar etched patterns near the bases of the ultrasonicated FMJ samples were observed. It was first hypothesized that these patterns were caused by water that pooled around the bases of the FMJ bullets when they were placed upright to dry. Closer comparison of the soaked and ultrasonicated bullets suggested two different causes of tarnishing (Figure 13). The soaked bullets appeared etched while the ultrasonicated bullets looked as if they had water spots. It is believed that the ultrasonicated bullets were subject to the pooling water theory: it is possible that the prolonged exposure to water immediately after being subjected to sulfuric acid increased the rate of corrosion\textsuperscript{13,17}. The etching on the soaked samples is believed to be a result of the sulfuric acid drying on the surface.

![Figure 13. Comparison of sulfuric acid effects on bases of FMJ samples. (A) Etched edge of the soak zone; (B) White-staining that appears similar to water spots on a sonicated sample.](image-url)
Using sulfuric acid to clean the bloodstained bullets produced interesting results. The sulfuric acid first caused the brownish material to become grey-white in color. This material was relatively simple to swab off the bullets, although rinsing with water did not remove the residue. The pyrolytic nature of sulfuric acid appears to have catalyzed the dehydration of the organic compounds within the bloodstains\(^4\) (Figure 14).

![Figure 14. Effects of sulfuric acid on blood-exposed bullets.](image)

Figure 14. Effects of sulfuric acid on blood-exposed bullets. (A) Blood-exposed bullets before cleaning; (B) Same blood exposed bullets after sonication. The bullet on the left was swabbed, while the bullet on the right remains covered by the grey residue.

Another curious reaction with sulfuric acid occurred on the fumed casings that were ultrasonicated. As expected, the sulfuric acid removed most of the cyanoacrylate from the casings without causing damage to the brass. The primer caps, on the other hand, became discolored and almost black (Figure 15). This darkening of the primer caps occurred on the fumed casings that were ultrasonicated, but not the fumed casings that were rocked in sulfuric acid. It was therefore concluded that the ultrasonication influenced this reaction. Unlike the casings, the primer caps are nickel-plated. Samples used for the ultrasonicated surface integrity tests also had nickel-plated primer caps, yet did not turn black. It is possible that a GSR contaminant was present on the sample and
created a harsher environment for ultrasonication. Casings used in all of the ultrasonication tests had been fired, but the separate tests used different brands of ammunition. Propellant formulations may differ between the two brands, causing different chemical contaminants to be present as residue within the casings. The nickel plating itself may be the source of the difference. Like many metals, an alloy of nickel is frequently used because it further enhances the corrosion resistance of the pure metal. The constituents of the alloy may differ between the two primer caps, which could cause the difference in behavior when ultrasonicated in sulfuric acid. Since this blackening phenomenon was only observed on the ultrasonicated fumed casings, an interaction between the cyanoacrylate and the nickel plating in the sulfuric acid environment could have occurred. Further testing is necessary to determine what caused the primer caps to turn black.

Figure 15. Effects of sulfuric acid on primer caps. (A) A Speer Lawman casing used in the Surface Integrity experiment that was exposed to sonication in sulfuric acid. Note the silver color of the primer cap; (B) The primer cap of a cyanoacrylate fumed Remington casing that was sonicated in sulfuric acid turned black.
Although tarnish removers are manufactured specifically to clean brass and copper, caution is still necessary when using these substances. These solutions utilize a variety of active ingredients such as organic acids, surfactants, and salts\textsuperscript{48,49,50}. Some products are meant to be stronger than others and are more prone to damaging the surface of the metal on a microscopic level. Quartz is often included as an abrasive to buff the surface. Too much pressure or wiping with an abrasive could unintentionally damage the metal, rather than simply remove the oxidation. The tarnish remover used in this project had obvious damaging effects; however, other products use different combinations of ingredients. It is possible that another tarnish remover formulation may perform better than the product used in this experiment.

4.5 Forensic Examinations and Imaging Technology

Bullet examinations focus on comparing striations within the land engraved areas\textsuperscript{51}. A bullet will make contact with the lands of a firearm barrel as it travels, but contact with the grooves is not guaranteed. Depending upon the depth of the grooves and the hardness of the jacket metal, the jacket may not deform enough to contact the bases of the grooves; therefore, striations within land impressions are examined. Using at least two test fired bullets, the examiner will identify regions of matching striation patterns. Every bullet fired from the same firearm does not present the exact same complete striation patterns. The purpose of the multiple test fire bullets is to identify the areas of similar characteristics that are consistently reproduced on corresponding lands of other
bullets fired from the weapon. These regions of similarity are then compared to the
unknown sample in an attempt to align the patterns and determine common source\textsuperscript{51,52}.

Casing analysis relies primarily on the breech face and firing pin impressions, although other impressions can be useful\textsuperscript{5,8}. The shape and surface pattern of breech face impressions are used in the comparison of known and unknown samples. Firing pin impressions have a relatively consistent shape, size, and depth. Wear will cause distinct patterns within both the breech face and firing pin impressions, which provides important class and individual characteristics\textsuperscript{51,53}. Examiners focus on breech face and firing pin impressions because these occur when a firearm is fired, whereas other impressions may occur simply from cycling a cartridge through the action of a firearm without firing.

Different theories for evaluating the results of these comparisons have evolved over time. The oldest established theory is the pattern matching theory, which is qualitative based. Another theory that tries to incorporate a higher degree of objectivity is the Consecutive Line Theory, which is quantitative based. This theory simply defines the number of necessary matching striations based on observed trends of known matching and non-matching bullets\textsuperscript{5}. The permutation theory has been applied to striation analysis and remains popular among analytical software designers. Simply stated, the number of permutations is the number of different ways a given set of striations can be organized. As the number of striations increases, the number of possible combinations increases, as well; therefore, a greater percentage of matching striations within a large set will have more weight\textsuperscript{5,51}. The fundamental difficulty with forensic bullet and cartridge case examinations is the subjective nature of the conclusions. The forensic examiner is
responsible for determining which regions on the evidence provide sufficient toolmarks for comparison. There is no quantitative requirement for the toolmarks within these regions.

Advancing technology has attempted to replace the subjective examination with an objective digital analysis. Image collection relies on various techniques, from cameras to lasers\textsuperscript{51-55}. These systems can capture detail beyond what the human eye can see. Measuring the size, shape, and depth of each striated line, as well as the contour of a firing pin impression is becoming an attainable analysis\textsuperscript{54}. Analytical software uses various algorithms to dissect the images by focusing on different aspects such as wavelength of the image pixel, impression features, area, or depth, to create correlation scores between two samples\textsuperscript{51,53,55}. Since these scores are based on what the imaging system can collect, sample preparation is vital. Perhaps someday these systems will be able to quickly scan the atomic structure of a pattern to measure the disruption of the metal surface. Despite the advances of technology, computer analysis of bullets and casings only provides a correlation score. It is still the responsibility of the examiner to compare the samples and form a final opinion.

4.6 Future Considerations

Additional research is needed to determine ideal cleaning protocols for forensic laboratories. Different solutions, as well as combinations of solutions, and disinfectants such as bleach should be studied. Disinfectants, important for the safety of the forensic examiner, are known to be damaging to the surface of brass and copper\textsuperscript{33} yet are currently
used by some laboratories prior to the examination of bullet and casing evidence. Further investigation should also take place regarding the effects of varying the temperature at which the cleaning takes place. Chemical reaction rates are frequently influenced by temperature; heating or cooling a solution or ultrasonication may change the way the metals or contaminants react.
5. CONCLUSIONS

Overall, there is not a single universally effective protocol for preparing bullets and casings for forensic examination. Ultrasonication is a safe and efficient method for heavy blood residue removal that outperformed soaking and swirling, but the findings of one publication suggest that ultrasonication be limited to less than five minutes. The act of swabbing alone does not affect the integrity of the metal surface and swabbing is an appropriate method for applying cleaning solutions; however, flaky blood residue and brown tarnish were not effectively removed by swabbing. In some circumstances, the solution used for cleaning matters more than the method.

Acetone worked very well at removing cyanoacrylate residue regardless of how it was applied, but did not effectively remove the flaky bloodstains or brown tarnish. Additionally, the metal surfaces were unaffected by acetone. Citric acid was effective at removing the flaky blood residue, which exposed limited striation patterns; however, the brown tarnish and cyanoacrylate were not visibly affected. Flitz® Instant Brass and Copper Tarnish Remover caused damage to the metal surface of both sample types, did not remove the brown tarnish on the bullets, and caused the casings to turn black about two weeks after cleaning. Alternative tarnish removers should only be used if they have been previously validated on test ammunition that is the same brand as the evidence. Tergazyme® detergent is useful for cleaning non-corroded evidence because it does not visibly affect the metal, however, it does not remove persistent tarnish, corrosion, or cyanoacrylate. Sulfuric acid removed the thick blood residue as well as the brown tarnish, although the caustic nature of sulfuric acid caused light surface etching in
swabbed areas and damage to the metal surface when the acid was allowed to dry. Additionally, sulfuric acid effectively removed the cyanoacrylate from the casings, but caused the primer caps to turn black when ultrasonicated. It is recommended that if sulfuric acid is used to clean bullets or casings, special care must be taken to minimize exposure time and ensure that the evidence is immediately rinsed thoroughly to prevent damage. The salt-flour-vinegar paste did not visibly affect the cyanoacrylate, flaky blood residue, or brown tarnish. The tarnish cloth created faint scratches on the surface of the metals, and was therefore not used in subsequent testing. Water did not affect the metal surface, cyanoacrylate, or brown tarnish. Only very loose flaky blood residue was removed by water.

Based on the results of this study, forensic laboratories should incorporate ultrasonication into their firearms evidence cleaning procedures. Acetone is recommended for cleaning cartridge cases that have been exposed to superglue fuming. Citric acid or Tergazyme® are suggested as non-destructive cleaning solutions for bloodstained bullets, however these did not effectively remove tarnish discoloration.
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