TECHNICAL NOTE

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Reduction of Specular Reflectance on Projectiles and Toolmarks by Ammonium Chloride Fuming

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ABSTRACT: A method for reducing specular reflectance from metallic surfaces in which ammonium chloride is used as a fuming reagent is described. This method has the advantage of being easily controlled, and is rapid. The deposit of ammonium chloride salt on the metallic surface is easily and effectively removed by washing.

KEYWORDS: criminalistics, toolmarks, firearms, projectiles, reflectance

Situations arise in which the specular reflectance from the surface of a projectile or a toolmark detracts from the image of the striae on the surface. Historically, this problem has been addressed by coating the surface of the bullet, toolmark, or toolmark replica with magnesium oxide smoke [1-3]. This approach is effective, but is frequently frustrating because the rate of application of the oxide is difficult to control; it is not uncommon to find that the layer of white oxide is either too thin to accomplish the desired results, or too thick, burying striae that are essential to the comparison. Additionally, after deposition, the coating is fragile and prone to chip or crack. It is not necessary that a coating be white; it is only necessary that the coating attenuate the specular reflectance from the illumination without obscuring any fine detail in the specimen.

Anyone who has worked in a chemistry laboratory has probably experienced the phenomenon that occurs when a bottle of ammonium hydroxide is opened in close proximity to a bottle of hydrochloric acid. The bilious white fumes produced are submicron sized particles of solid ammonium chloride; as described here they may be used effectively to coat a metallic surface to reduce specular reflectance. While the fumes appear white when dispersed in air, a very thin coating of these fumes on a metallic or silicone rubber surface cause the surface to appear a neutral gray.

The ammonium chloride salt may be formed directly on the surface of a bullet, toolmark, or toolmark replica. A 100 mL vacuum Ehrlenmeyer flask was plugged with a stopper that had been bored for a short section of glass tubing. A section of rubber tubing was used to connect the vacuum arm of the flask to a Pasteur pipet. Approximately 10

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mL of concentrated HCl was placed in the flask, and the central section of glass tubing connected to a gentle flow from the laboratory air source. This apparatus is depicted in Fig. 1.

The surface of the metal is lightly coated with concentrated NH_4OH by swabbing, and then fumed with the acid vapors emanating from the tip of the Pasteur pipet. The accumulation of ammonium chloride on the surface of the metal (or a silicone rubber replica of a toolmark) is sufficiently slow that the operator can control the deposition by rotating the surface, by manipulation of the Pasteur pipet as a type of "air-brush" to spray the surface, or by doing both. This does in fact result in a reduction of the reflectance of the surface, but does not mask the striation marks.

Coating with ammonium chloride does not result in a thick white layer, as with magnesium oxide. It is the position of the writers that an antireflective coating need not be white, and should not be thick. Manipulation of the ammonium chloride exposure enables the thickness of the coating to be controlled with a good degree of precision.

In the experience of the authors, it is imprudent to attempt to pre-mix the acid and base to deliver already-formed ammonium chloride salt to the surface. Attempting to do so will result in large clumps of the salt being deposited in an irregular fashion. It would also be imprudent to coat a metallic surface with acid and fume with base, since copper is very susceptible to oxidation by strong mineral acids and aluminum is even more reactive. The chemistry of the reaction of lead with HCl is not quite as straightforward, and the reaction is not nearly as fast, but lead is attacked nevertheless by strong hydrochloric acid. Lead first reacts with HCl to form a protecting layer of lead chloride:

$$Pb + 3HCl \rightarrow H(PbCl_3) + H_2$$

However, this layer of lead chloride is soluble in hot concentrated HCl [4], and therefore almost certainly slowly soluble in cold concentrated HCl. This would make coating with acid and fuming with base an undesirable sequence, as the acid may remove some of the finer striae.

Lead is virtually insoluble in NH_4OH , however [5]. Any lead that has been oxidized to the ionic form (which ordinarily would be about nil) will react with ammonium hydroxide according the following reaction:

$$Pb^{++} + 2NH_4OH \rightarrow Pb(OH)_2 + 2(NH_3) + H_2$$

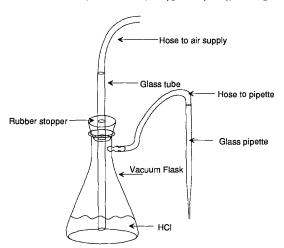


FIG. 1—The apparatus used for the production of ammonium chloride smoke.

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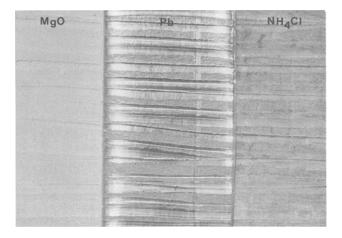


FIG. 2—Comparison of untreated striated metallic surface (in the middle) with a section coated with magnesium oxide (on the left) and a section coated with ammonium chloride (on the right).

However, the white precipitate of lead hydroxide which is formed is insoluble in the ammonium hydroxide reagent.

The white precipitate of ammonium chloride forms according to the reaction:

$$H^+Cl^- + NH_4^+OH^- \rightarrow NH_4Cl + HOH$$

As with all strong acid-strong base pair salts, ammonium chloride is soluble in water, and therefore can be easily removed from the surface upon which it has been deposited. This can be useful in situations where possible overfuming has taken place, or where another comparison must be made with the surface preferably in the uncoated state. The salt deposit is a dull white color, and with a minimum of care, the reaction is easy to control.

Figure 2 illustrates, for purposes of comparison, a toolmark test impression in lead showing the reflectance inherent in the untreated surface, together with a section of the same test mark coated with MgO and a section coated with NH_4OH .

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