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Development of Latent Fingerprints on Unfired Cartridges by Palladium Deposition: A Surface Study

ABSTRACT: Visualized fingerprints on unfired brass cartridge cases developed by a novel method of palladium deposition were examined by Auger electron spectroscopy (AES), scanning electron microscopy (SEM), and electron probe microscopy (EPMA). In spite of the strong contrast of colors between the ridges and the valleys of the developed images, which suggests a selective coating of palladium on the valleys, palladium was found to deposit onto both valleys and ridges. Lumps of organic material were scattered mostly along the ridges. The study suggests a model for the deposition of metals on brass cartridges on which sebaceous fingerprints were impressed.
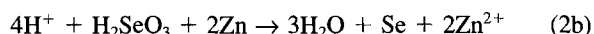
KEYWORDS: forensic science, latent fingerprints, unfired cartridge cases, palladium deposition, Auger electron spectroscopy, scanning electron microscopy, electron probe microscopy

Numerous methods have been developed for the visualization of latent fingerprints on metallic surfaces (1–3) and are occasionally used in police identification and forensic laboratories. For example, ammoniacal solution of silver nitrate and gun-blue are frequently used (4) as a means of visualizing latent fingerprints on unfired brass cartridge cases. In both methods, developed images on brass cartridges show the valleys as black lines whereas the ridges as golden brass-colored lines. These methods exploit the differences between the properties of the sebaceous material that forms the ridges of the fingerprint and the intact metallic surface in the valleys. Both reagents react with the metallic surface beneath the fingerprint (valleys being the main source), and not with the organic components of the ridges. The process of development with silver salt involves a redox reaction. Silver ions oxidize the more reactive metal, i.e., zinc (and probably some of the copper), causing metallic silver to precipitate on the brass surface (eq. 1).

$$4Ag^+ + Zn/Cu \rightarrow Ag + Cu^{2+} + Zn^{2+}(mostly) \qquad (1)$$
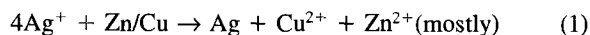
On the other hand, gun-blue development, i.e., deposition of copper-selenide films, is a rather complicated process (eq. 2a–2c) which has been studied by electrochemical techniques (5,6). The composition of the resulting deposit depends primarily on the driving force of reduction and the electrolyte composition. The redox potential of zinc will result in the formation of CuSe. Copper(II) and selenium(IV) are reduced independently and react further to give copper selenide phases. Nevertheless, the co-deposition of copper is required to make the reduction of Se(IV) into Se(0) possible.

$$Cu^{2+} + Zn \rightarrow Cu + Zn^{2+} \qquad (2a)$$

$$4H^+ + H_2SeO_3 + 2Zn \rightarrow 3H_2O + Se + 2Zn^{2+} \qquad (2b)$$

$$Se + Cu \rightarrow CuSe_{(black)} \qquad (2c)$$

The images obtained with ammoniacal silver salt or gun-blue solution show coarse black lines. In order to obtain better images of latent sebaceous fingerprints on brass cases, a novel method of deposition of palladium was developed by us (7). The method is based on palladium deposition from aqueous chloro palladate solutions and results in excellent images.

We report here on the surface analysis of Pd developed images of fingerprints on brass-28Zn cartridge cases.[2] Latent fingerprints were visualized as a result of a chemical process in which Pd was deposited. The analysis was performed by three surface techniques: Auger electron spectroscopy (AES), scanning electron microscopy (SEM) and electron probe microanalysis (EPMA). SEM imaging of latent fingerprints on gold plate (8,9), as well as of fingerprints developed by small particle reagents (MoS_2) (10), physical developer (silver electroless coating) (11) and by aluminum powder (12), have been previously reported; however, as far as we know no fingerprint image has been depth-analyzed using AES. Our principal findings show that three layers are formed as a consequence of Pd deposition and although the ridges and the valleys of the images appear quite different to the naked eye, they are chemically similar.

Experimental

Palladium dichloride and dipotassium hexachloropalladate were purchased from Aldrich. Brass 5.56 mm caliber bullets (series 83) for M16 were produced by Israel Military Industries (IMI). Surface analysis and compositional depth profiles of ridges and valleys of the developed images were obtained using a Perkin-Elmer PHI, model 590 Scanning Auger Microscope. Back-scattered electron micrographs of the developed images were obtained by the electron probe microanalyzer JEOL JAX 8600 Superprobe. X-ray microanalysis was obtained using the electron probe microanalyzer with its energy dispersive X-ray analyzer (EDS).

Brass-28Zn 5.56 mm cartridges for M16 rifle were disassembled.

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[2]Brass-28Zn is brass which consists of 28% Zn and 72% copper.

The cartridge cases were cleaned by immersion in an acetone bath for 20–30 s, and then wiped with a paper tissue. The cleaning procedure was repeated until the wiping tissue paper remained clean (4 to 5 times). It is worth mentioning that latent fingerprints can be also visualized without this pretreatment procedures: however, the developed fingerprints on these cartridges are usually of lower quality. To obtain a sebaceous fingerprint, the tip of the finger was rubbed on the face near the nose and the contaminated fingertip was gently pressed and rolled on the surface of the cartridge case. The location of the print was marked by a notch before the prints were applied. The latent fingerprints and the developed images were examined with a magnification lens (×5) equipped with a fluorescent lamp; a white screen and a desk-lamp were added for stronger illumination.
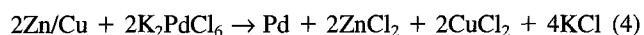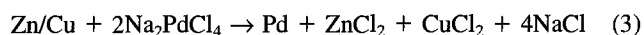
A solution of 0.1 M disodium tetrachloropalladate in 0.9 M aqueous sodium chloride was prepared in the following way: 0.88 g palladium chloride was added into a solution of 2.925 g of sodium chloride in 50 mL triply distilled water (TDW). The mixture was shaken until all the $PdCl_2$ dissolved. On the other hand, the solubility of dipotassium hexachloropalladate in water is relatively low (below 0.1 M) (13). Thus, a concentrated solution of dipotassium hexachloropalladate was prepared by dissolution of 993.4 mg dipotassium hexachloropalladate in 25 mL triply distilled water. Visualization of latent fingerprints was obtained by immersion of the impressed cases in each of the aqueous solutions for 40 s followed by shortly rinsing them in TDW.

A few experiments were performed using a combined iodine/palladium procedure. This was accomplished as follows: one or two crystals of iodine were placed in a closed jar, forming iodine vapor. The printed case was left in the iodine vapors for 1 min and immersed in a solution of 1 M $K_2S_2O_5$ for 30 seconds to remove the excess of the iodine. Then it was briefly washed in a TDW bath and immersed in a solution of 0.1 M Na_2PdCl_4 for 30 s after which it was carefully rinsed with TDW. The iodine was used to etch the cartridge metal in order to sensitize it for the Pd deposition.

Results and Discussion

Figure 1(A–B) shows two latent fingerprint images after developed in aqueous solutions of $PdCl_4^{2-}$ and $PdCl_6^{2-}$. Clear and highly contrasted images are formed employing both solutions. The valleys are covered with a metallic dark color whereas the ridges remain golden-brass. The unimpressed area of the cartridge cases, where no fingerprint was applied, became dark though unhomogeneously colored. A saturated solution of K_2PdCl_6 gave slightly better results than the solution of Na_2PdCl_4, however, since the latter is less stable than the former (13), it is less recommended for development. Varying the concentrations of palladium reagents and time of immersion showed that the best images were obtained upon immersion a brass cartridge into an aqueous 0.1 M sodium tetrachloropalladate solution for 40 s.

The reaction is a displacement process that involves the oxidation of zinc and to a less extent copper and the simultaneous deposition of palladium (eq. 3–4)

$$Zn/Cu + 2Na_2PdCl_4 \rightarrow Pd + ZnCl_2 + CuCl_2 + 4NaCl \quad (3)$$

$$2Zn/Cu + 2K_2PdCl_6 \rightarrow Pd + 2ZnCl_2 + 2CuCl_2 + 4KCl \quad (4)$$

Visualization of the fingerprints was further improved by adding an etching step before the development process. Exposure to iodine

vapors prior to the development with sodium tetrachloropalladate gave superb images, as is shown also (Fig. 1C). By this method the unimpressed area of the cartridge cases became homogeneously dark colored.

The appearance of the developed images, which consist of dark valleys and golden ridges, suggests that the sebaceous coat of the ridges efficiently covers the underlying brass and prevents its reaction with palladium ions. Since the organic deposit is transparent, it does not change the golden brass-color of the ridges. On the other hand, the exposed brass of the valleys reacts with the palladium ions, and hence, results in the coating of the valleys by dark metallic palladium. However, AES analysis of the surface of an I_2/Pd developed image reveals that the situation is more complex, and that the organic coating plays a much subtler role in the development process.

Figure 2(A–C) shows AES depth profiles of 20 by 20 μm^2 areas located on a ridge, a valley and on a spot outside the fingerprint area, respectively. Notice that the abscissa is presented by a time scale that can be converted into depth by knowing the sputtering rate. The latter appears on the figures and is a mean value obtained by digging through layers of a standard reference of Ta_2O_5 on Ta. It can be seen that the three profiles can be divided into three sections. The uppermost layer (beneath the surface) is approximately 300–600 Å deep while the middle layer is ca. 800–1600 Å. Under this layer is a third layer that extends into the bulk. The latter is exclusively made of copper and zinc (Cu/Zn = 72.38/27.62% atomic ratio).

The Surface

The compositional analyses of the surfaces of ridges, valleys and the unimpressed region are shown in Fig. 3(A–C). The results are summarized in Table 1. AES surface microanalyses are confined to a very thin surface layer, which is about 3 atom layers (about 5 nm) thick (14). The surface layer is mostly composed of carbon although its percentage is lower in unimpressed areas as compared with the fingerprint regions. Clearly, the source of carbon in the unimpressed and valley areas is the environment. However, the higher content of carbon in the valleys as compared with the unimpressed area (Table 1) suggests that this organic layer diffuses from the ridges and deposits in the valleys as well. It can also be seen that the ratio between Cu/Zn decreases in the following order: ridges>valleys>unimpressed region. This is somewhat strange, since based on thermodynamic considerations we would anticipate that zinc would preferentially react with the palladium complex than copper. Nevertheless, it is possible, vide-infra, that zinc is indeed preferentially oxidized, however, it forms ZnO that does not dissolve very fast under the experimental conditions. Therefore, the decrease in the Cu/Zn ratio under the parts, which were not covered by the fingerprint, does indicate that the reaction of palladium ions with the surface is faster on the more exposed surface. In fact, the Cu/Zn surface ratio on ridges is very similar to the bulk. Interestingly, the atomic Pd % on the surface is very low and varies between 0.6% on the unimpressed region to 0.3 and 0.2% on valleys and ridges, respectively.

A rough estimate of the thickness of the organic coating can be obtained from the depth profiles. However, AES depth profiles give only qualitative information. This is because the surfaces of both valleys and ridges are nonhomogeneous, the bombardment possibly induces diffusion of zinc toward the surface (15) and also due to the fact that the sputtering rate indicated in Fig. 2(A–C) is a mean value obtained by digging through layers of a standard
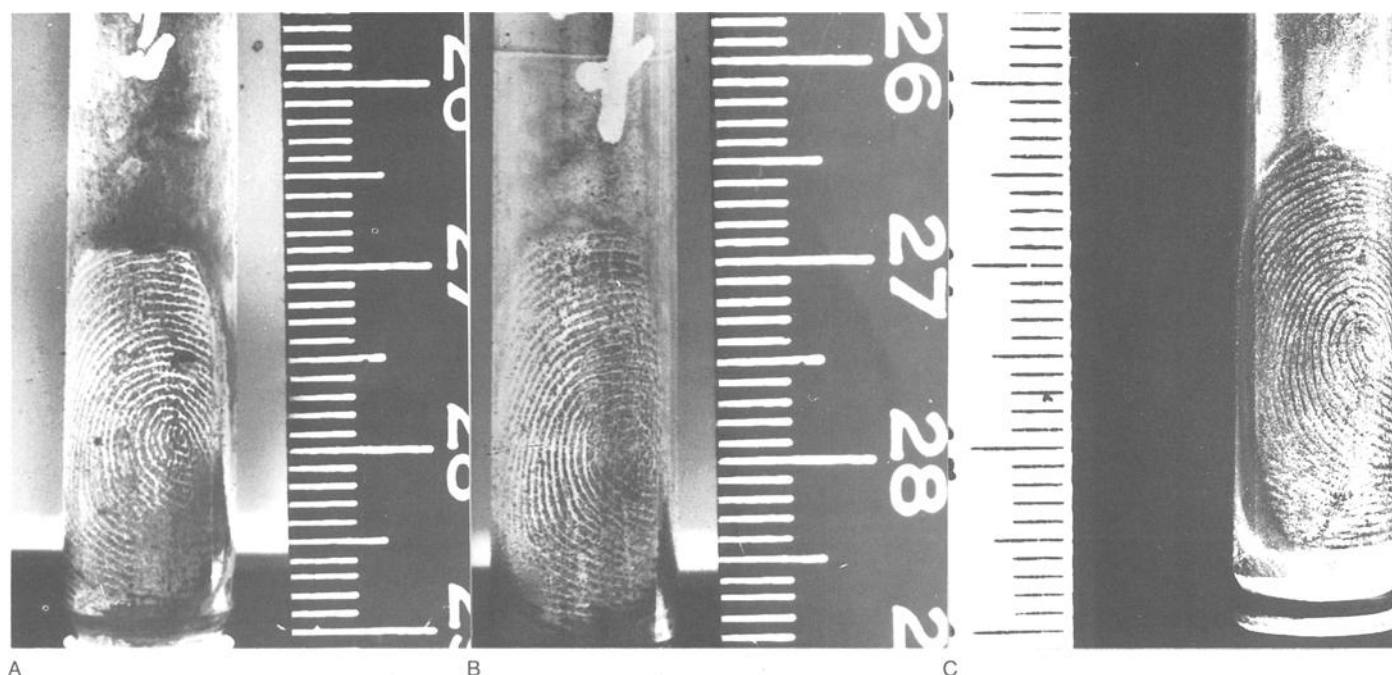
FIG. 1—*Images of sebaceous fingerprints on a brass 5.56 mm cartridge case of M16 developed in: (from left to right) A- an aqueous solution of 0.1 M disodium tetrachloropalladate; B- a saturated aqueous solution of dipotassium hexachoropalladate. C- The impressed case was exposed to iodine vapors, the iodides and the excess of the iodine were removed and the fingerprint was then developed in an aqueous solution of 0.1 M disodium tetrachloropalladate.*

reference and not through the actual materials. Figure 2(A–C) also show that organic material covers the whole cartridge case surface. The layer on the unimpressed area is thin, similar in thickness with the organic layer measured on a clean cartridge case. It is conceivable that the layer consists of environmental contamination. The organic layer on both ridge and valley are thicker as can also be seen from SEM images (Fig. 4). Clear differences can be seen between the ridges and the valleys. Relatively large organic lumps (as analyzed by EDS) are scattered along the ridges, whereas along the valleys smaller lumps are thinly scattered. Notice also that there is no clear evidence for Pd deposits which should appear as very bright white spots. The valleys are brighter indicating the presence of heavier elements. Therefore, it is not likely that the slight difference in the composition of the surface regions is responsible for the clear contrast of the fingerprint that is observed on the cartridge case. EPMA (penetrating depth of ca. 1 μm) of two spots one located in ridges while the other in valleys supports also these findings. Namely, it does not result in a significant difference between the levels of Pd (4.51 atomic % in ridges and 5.65 atomic % of Pd in valleys) in ridges and valleys. The composition of the cartridge changes dramatically as a function of the depth.

The Upper Layer (0–1 Min of Sputter Etching)

The uppermost layers (beneath the organic layer) consist of primarily carbon, oxygen and copper on ridges and valleys and oxygen and zinc in the unimpressed region (Figs. 2(A–C)). This layer is very thin in both ridge and valley regions and hardly separated from the middle layer underneath, while it is much thicker and clearly separated from the next layer in the unimpressed region. The relatively thick zinc-oxygen layer in the unimpressed region reflects the segregation of the zinc and the fact that the exposed area of the cartridge reacts faster than the other parts under the fingerprint. The accumulation of ZnO is the result of

the dezincification of the middle layer and it indicates that under the experimental conditions ZnO does not dissolve fast enough.

The Middle Layer (1–7 Min of Sputter Etching in the Fingerprint and 2–13 Outside)

The middle layer is rich with copper and palladium in areas outside the fingerprint. The stochiometric ratio between Cu and Pd is close to one in the center of the layer which suggests the formation of a Cu/Pd alloy. This is also supported by the fact that the lines representing the atomic % of these metals run parallel across the layer maintaining an almost constant Cu/Pd ratio.

It is worth noticing the changes in the Zn/Cu ratio in this layer as compared with the bulk and the upper layer. The Zn/Cu ratio in the original brass and obviously also in the bulk equals 0.38. As mentioned above, zinc is more easily oxidized and as the replacement reaction proceeds the brass cartridge undergoes a dezincification process. Brasses are known for their dealloying properties (16–22). Immersion of brasses containing more than 15 at. % Zn (23) in aqueous electrolyte solutions causes zinc to diffuse from the bulk and dissolve into the solution upon oxidation. The dezincification rate depends on the nature of the electrolytes (24) and it leaves an adherent porous layer of copper (19,25). In principle, only superficial thin coatings are produced upon immersion-plating since the deposition stops as soon as the entire surface of the metal is coated (26). However, because of the diffusion of Zn and the dezincification process, immersion plating of cartridge brass in palladate solution yields thicker layers of Pd.

EPMA X-ray microanalysis also shows that substantial amounts of zinc dissolved off the cartridge cases during the palladium treatment. EPMA determines the content of the metals on the brass cartridge surface within a thickness of about 1 μm. While the initial atomic ratio of an untreated case is Zn/Cu = 0.38, this ratio is reduced to 0.30–0.36 and 0.2–0.32 in ridges and valleys,
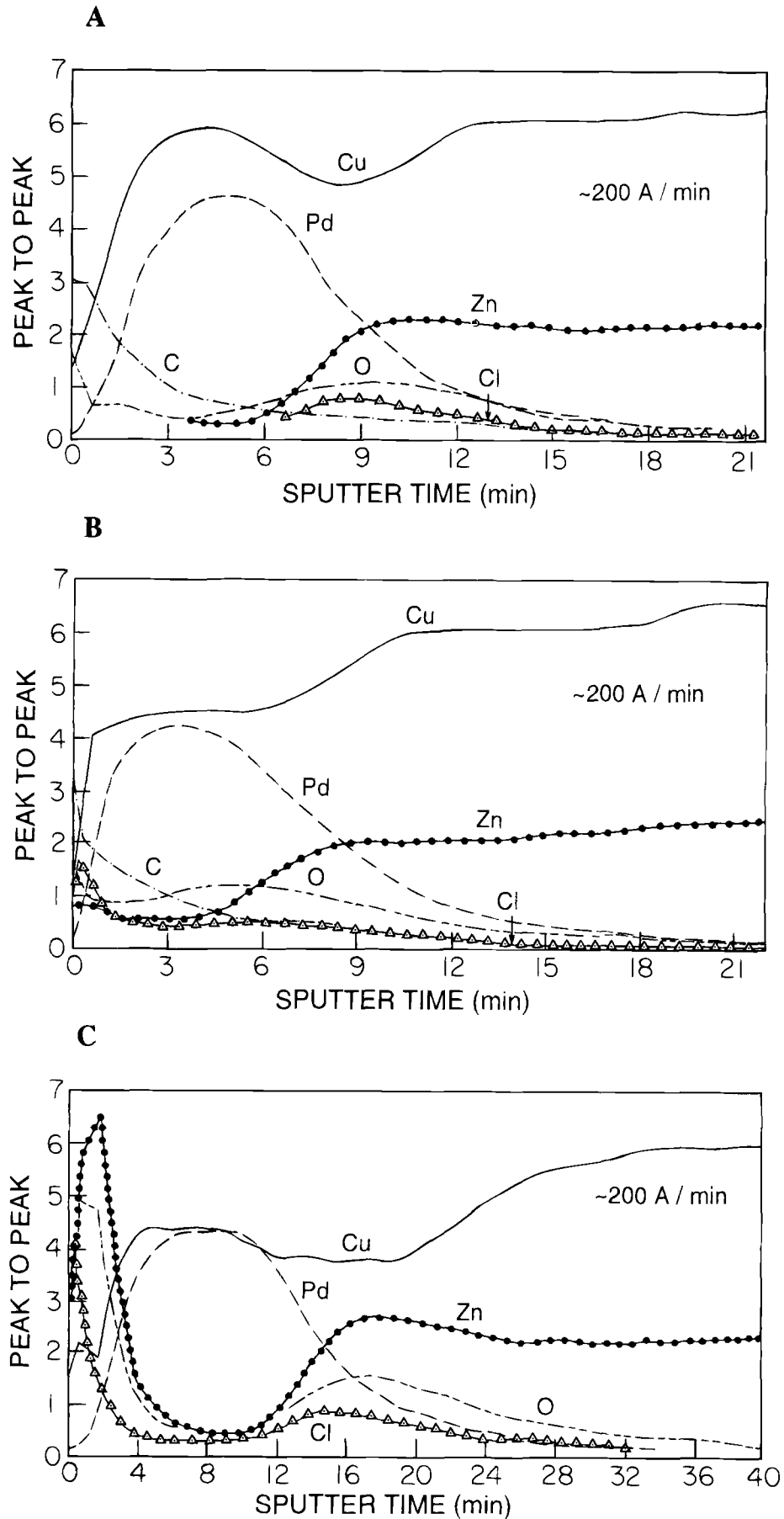
FIG. 2—(*top to bottom*) *Auger electron depth profiles measured at different locations on a brass 5.56 mm cartridge case of M16 on which a sebaceous fingerprint was impressed. The images were developed by the combined iodine-palladium process. A- profile of a ridge; B- profile of a valley; C- profile outside the fingerprint.*
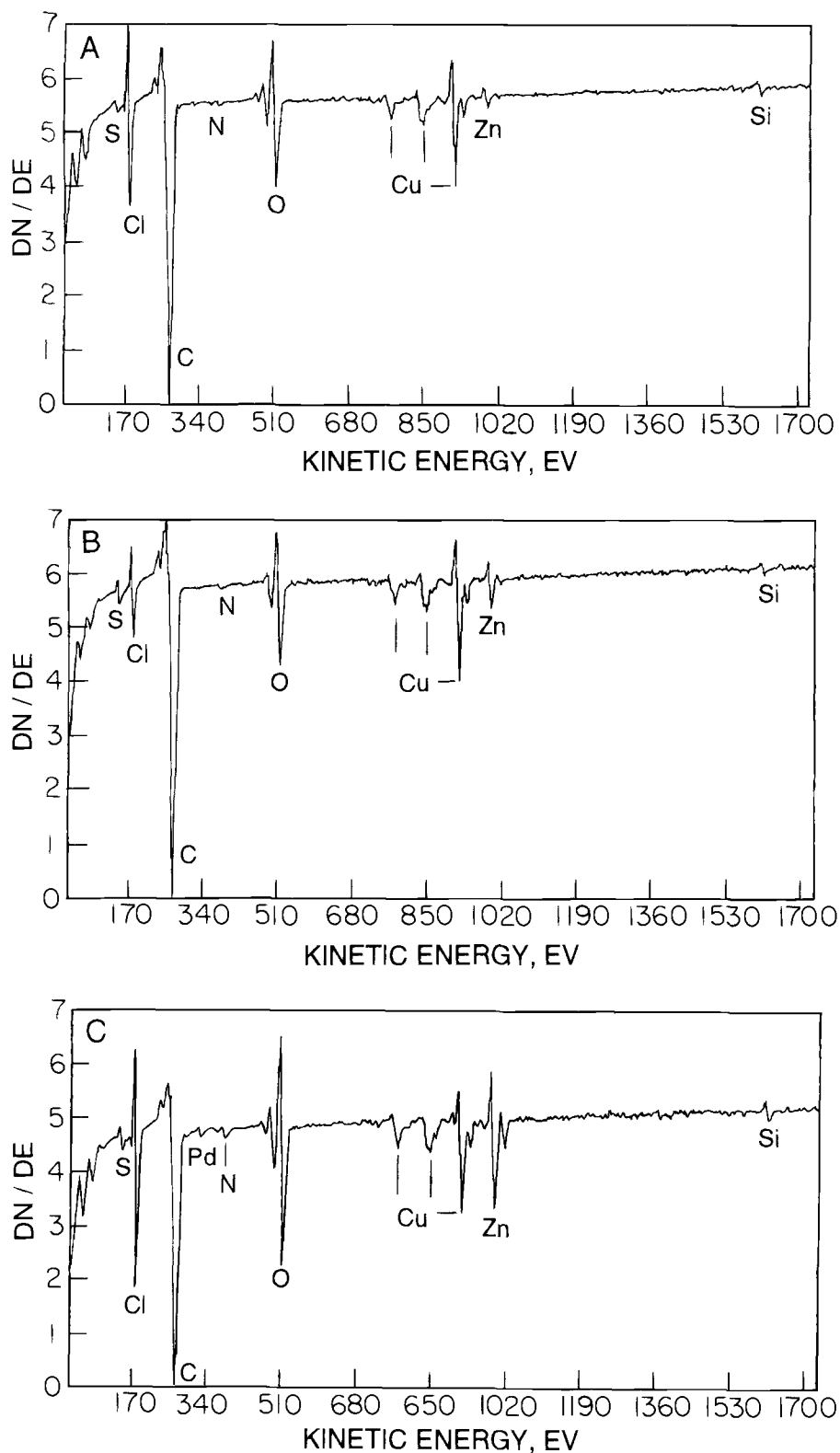
FIG. 3—*Auger electron spectra measured on a surface of a brass 5.56 mm cartridge case of M16 on which a sebaceous fingerprint was impressed. The images were developed by the combined iodine-palladium process. A- spectrum of a ridge area; B- spectrum of a valley area; C- spectrum of a location outside of the fingerprint.*

TABLE 1—*Auger surface analysis of a ridge and a valley of a iodine/ palladium fingerprint image and of the area free of fingerprint on the brass cartridge case.*

Atomic Composition	Ridge Surface	Valley Surface	Unimpressed Surface
Cu	8.9	9.1	7.5
Zn	3.1	6.0	16.9
C	64.5	65.9	42.1
Pd	0.2	0.3	0.6
O	12.3	11.1	14.9
Cl	7.0	3.9	13.4

respectively, upon Pd treatment, indicating that zinc is depleted more from brass underneath the valleys than ridges. The Pd/Cu is pretty thick in particular in unimpressed regions. The ratio Pd/Cu rises to a maximum then falls down. The maxima of the atomic ratios Pd/Cu are 0.7, 0.8, and 0.88 in the ridge, valleys and unimpressed region, respectively. It is possible that the different Pd/Cu ratios are responsible for the visual difference between the ridges and the valleys.

We do not know the structure (or the structures) of the Pd/Cu layer and its mechanism of formation. Nevertheless, since palladate is a strong oxidant that is capable of oxidizing both zinc or copper, two mechanisms can be suggested: (i) only the less noble metal, i.e., zinc, is oxidized and dissolved into the solution while the copper remains on the surface (27). (ii) Zinc and the copper are both oxidized but copper is subsequently redeposited after reaching a critical concentration (28). Both mechanisms supply the copper atoms that build with the palladium atoms the Pd/Cu layer.

The Deepest Layer (7–13 Min of Sputter Etching Inside the Fingerprint and 13–28 Min Outside)

There is a significant change in the elemental composition on going from the middle layer to the bulk. The profiles of regions beneath ridges and valleys show a gradual change from the Cu/Pd alloy to the bulk. Namely, the Pd content diminishes whereas the zinc and copper level increase. It can be seen that Pd is found as deep as 3000 Å in these areas. On the other hand, the change

FIG. 4—*A Scanning Electron micrograph of a palladium developed sebaceous fingerprint on a brass 5.56 mm cartridge case of M16. The fingerprint was developed by the combined iodine-palladium process.*

in elemental composition in areas which were unimpressed goes through an increase in the oxygen as well as chloride content before bulk composition is reached. Moreover, Pd can be found in these areas as deep as 5600 Å. The origin of the chloride is unclear although it is possible that it originates from the natural oxide layer that covers pristine cartridges prior to treatment. Indeed, similar layers are found in surface analysis of untreated cartridges.

In conclusion, the application of high resolution surface analysis techniques to study the elemental composition of immersion-plated latent sebaceous fingerprints on brass cartridges provides significant information on the process. The visualization of latent fingerprints cannot be explained by a simple approach in which the surface beneath the ridges is protected and does not react with the reductant. Palladium analysis by EPMA, SEM and AES indicates that the levels of Pd in ridges and valleys do not differ significantly. Therefore, this study suggests, that at least for the case of palladium deposition, visualization of the fingerprint is a result of the composition of layers that extend a few thousand Ångstroms beneath the surface. Our further studies, in which the same approach has been implemented for visualization of latent fingerprints on fired cartridges, indicate that this method is not satisfactory enough, and other approaches might provide the ultimate solution to this challenge. Interestingly, Saunders (29) has recently shown that the gentle treatment of a fired cartridges by superglue followed by gun-blue treatment partially visualized latent fingerprints on fired cases. On the other hand, Bensteh et al. (30) reported that only certain revolvers and the SLR rifle yielded identifiable ridge detail as a result of vacuum cyanoacrylate (with fluorescent staining) and gun blue treatments. Evidently, further research and interdiscipline approaches must be taken in order to eventually visualize fingerprints on fired cartridges.

Acknowledgment

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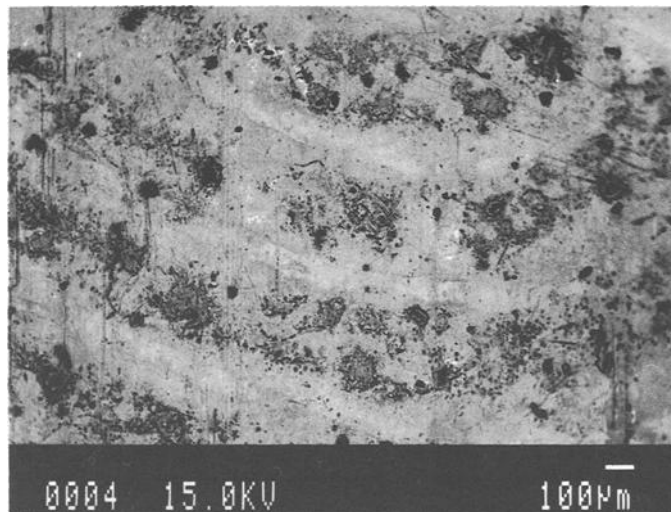
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