

Development of Latent Fingerprints on Metallic Surfaces Using Electropolymerization Processes

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ABSTRACT: We propose a new process for developing latent fingerprints on metal items, applicable to unfired weapons made of Ergal in particular. The method is based on the presence of fatty acids that are contained in fingerprints and act as an insulator on the surface where fingerprints are to be developed. The process of polymerization occurs on the metal portions left untouched by finger contact. Hence, the developing process results as a negative pattern of the original fingerprint. The reaction consists in the electropolymerization of pyrrole and substituted porphyrins, i.e., tetra (*o*-aminophenyl) porphyrine: radical-cations are generated on superficial nucleation sites by oxidation of monomer, close to the electrode surface; subsequently, the radical species react with the neutral monomer, which begins to diffuse to the electrode. We have also studied the polymer's morphology by means of SEM and AFM, in order to find a correlation between the reagent to be used and the quality of the enhancement process. These are only preliminary results; however, they show that the suggested method is a new way to increase the rate of success in developing latent fingerprints on metal surfaces. In this regard, it may be considered complementary to other conventional procedures, due to the low costs of the instruments and reagents, and the rapidity and simplicity of the treatment.

KEYWORDS: forensic science, electropolymerization, fingerprints, pyrrole, porphyrine, ergal, weapons

Fingerprint detection is an essential way of identifying individuals. In the past ten years, however, the increasing interest in DNA PCR-based techniques, which undoubtedly has become a fundamental tool in solving crimes, has caused most of the scientific efforts to concentrate on genetic analyses rather than fingermark strategies. Yet, fingerprints may still be the only evidence available for many crimes because they are left on several surfaces, resulting in numerous chances for identification. Two main points need to be taken into consideration:

- a. fingerprints form during the intrauterine life of the fetus and remain unchanged throughout the life of each individual unless some serious injury occurs (1–3);
- b. well-established and powerful electronic databases have been developed that allow easy identification and comparison of fingerprints among millions of individuals (2).

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Based on these facts it seems more urgent than ever before to improve the existing analytical techniques for developing latent prints on metal (4–6), especially in the case of weapons, as they are so closely tied to serious and organized crimes.

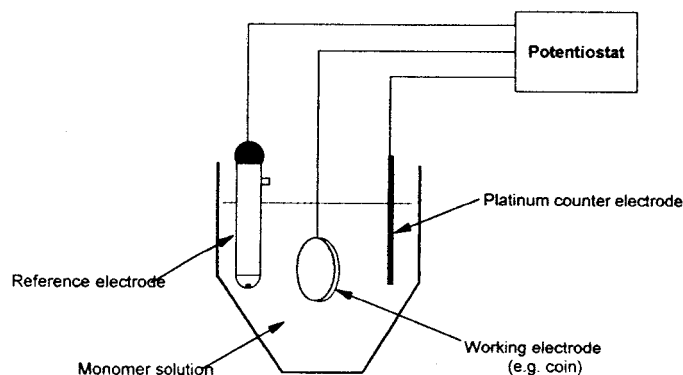
Several methods have been proposed to visualize latent prints on both fired and unfired weapons and ammunitions including: dusting (3–6); Superglue® fuming coupled with dye staining (7–15); multimetal deposition (16–18); acid and redox based etching techniques; gun blue solution followed by acidified hydrogen peroxide formulas; silver nitrate solution; and reflected ultraviolet imaging systems, i.e., RUVIS (19–23). Cyanacrylate ester is probably most commonly used in forensic laboratories worldwide for its high sensitivity; wide range of applications on nonporous surfaces; repeatability; and capability to treat evidence under controlled conditions of heat, humidity, and vacuum.

Despite their reliability, the treatments mentioned above do not seem to be always effective, especially on firearms (24). We therefore decided to start a preliminary study in order to find an alternative method that could help in solving the problem and considered a new procedure that would be easy to use, fast to develop, effective, and have low costs. In this attempt, we also thought of a method that would be specific for the fatty component of fingerprints and therefore more effective with older fingerprints.

It is well known (25–27) that electropolymerization processes on metallic surfaces are affected by the morphological characteristics of the material on which the polymeric film has grown. The mechanism of electrogeneration of pyrrole (25) and substituted porphyrins (28,29) has been widely studied on both pure metal and steels of different composition. In the present study, a preliminary voltammetric characterization of monomers was carried out on some metals, especially on pieces of finished Ergal, provided by some Italian weapon manufacturers, as this material is widely employed in the production of weapons. The results we obtained are very interesting and show that the electropolymerization process could be a new method for developing latent prints on unfired weapons, as well as on other metal surfaces such as gold, silver, iron, and different alloys, which represent interesting items potentially linked to a specific crime.

Experimental Procedures

Tetra-*o*-aminophenylporphyrin (TAPP) and the relevant metal complexes with cobalt (II) and nickel (II) ions were synthesized using the method described by Murray et al. (28). Pyrrole reagent (98%) was purchased from Aldrich (Milan, Italy), *p*-TsONa [(CH₃)C₆H₄SO₃Na] and sodium sulfate (Na₂SO₄) were purchased from Fluka-selectophore (Milan, Italy).



SCHEME 1—Schematic representation of the electrochemical cell.

Electropolymerizations were performed in a three-electrode electrochemical cell, employing the studied materials as working electrodes, a platinum counter electrode, and an Ag/AgCl/KCl 0.1 M reference electrode (Scheme 1). Experiments were conducted using a computerized Autolab PGSTAT 20 potentiostat, Ecochemie (Utrecht, The Netherlands) connected to a Metrohm 663 VA Stand, (Herisau, Switzerland).

Working electrodes of several materials were used in different shapes and dimensions: platinum, gold, silver, and Ergal alloy used in weapons. (Aluminum alloy: Zn 5.8%, Mn 2.5%, Cu 1.6%, Cr 0.3%.)

The electropolymerizations of pyrrole were accomplished using 0.3 M monomer aqueous solutions with *p*-TsONa, or H₂SO₄, or Na₂SO₄, as supporting electrolyte (1 M), and by cycling the potential between 0 and 1400 mV. Scan rates were chosen in the range of 50 to 300 mV/s. The electropolymerizations of substituted porphyrins were performed in 0.1 M HCl / 1 M KNO₃ aqueous solution containing 10⁻³ M monomer, by cycling the potential between 0 and 1200 mV, at a potential scan rate of 200 mV/s. Frequency Response Analysis measurements were performed using the same equipment employed in voltammetric studies, by a dedicated FRA software (FRA 2.5, Ecochemie, The Netherlands). Measurements were performed at 25°C on Pt electrodes in the 10 KHz to 100 mHz range at a constant potential of 600 mV.

The polymer deposit surface morphology was investigated by an Atomic Force Microscope Nanoscope IIIA (Digital Instruments, Santa Barbara, CA) operating in contact mode. Every material used as a working electrode was preliminarily polished by Alumina (0.3 mesh, BUEHLER) and carefully washed with distilled water. Coatings to be studied by means of AFM were washed by distilled water just after polymerization and stored under nitrogen until AFM measurements. They were also analyzed by X-ray Diffraction using a Philips PW 1050 instrument operating between 0° and 40°, 2θ angles.

The fingerprints were deposited on various metallic objects using a forefinger realized with a silicon mold by a dental technique. Fatty fingerprints were deposited by the same donor in all experiments. The forefinger was rubbed against the fatty areas of the face (nose, forehead, behind the ears) and then gripped on the studied metal piece. The fingerprint images were recorded with a digital camera.

Results and Discussion

Morphologic Aspects

The characteristics of substrate on which the polymeric film is grown have been found to influence the electropolymerization

processes on metallic surfaces. While electrogeneration mechanism of pyrrole (25) and substituted porphyrins (28,29) has been widely studied, no data are available from literature for the polymerization on Ergal; for this reason a preliminary voltammetric characterization of monomers on this alloy as substrate was carried out.

At the first stage, radical-cations are generated on superficial nucleation sites by oxidation of monomer, close to electrode surface; subsequently the radical species react with neutral monomer, diffusing to electrode.

If somewhat region of electrode is totally or partially isolated, there the electropolymerization process will be thwarted. With the aim to identify the morphologic discriminating factor, the fingerprint/metal borderline regions have been studied by SEM and AFM superficial techniques, after electropolymerization of both monomer employed. SEM images relevant to polypyrrole (PP) and polyTAPP are shown in Figs. 1 and 2. Zones of partial isolating, apparently arising from hydrosoluble components of deposit like aminoacids, have been also detected. The AFM study also allowed observing the "step" of the fingerprint borderline, clearly showing that the polymer grows selectively on the non-isolated metal.

On the basis of preliminary experiments with PP and PTAPP films that have been shown to enhance fingerprints, a systematic study of morphology of deposit as function of experimental parameters has been set up, with the aim of identifying possible correlations between the material morphology and the quality of enhancement. The morphology and the look of polymeric films are strongly dependent on experimental factors such as substrate material, supporting electrolyte, monomer concentration, and potential application modality (potentiodynamic or potentiostatic conditions). An AFM analysis on the three studied materials clean plates was done preliminarily, and results have been used as blanks for subsequent analyses.

The two monomers studied have been electropolymerized under potentiodynamic conditions (cyclic voltammetry), on silver, gold, and Ergal, employing H₂SO₄, *p*-TsONa, or Na₂SO₄ as supporting electrolytes for pyrrole (25) and KNO₃/HCl for porphyrin derivatives. The morphologies of the polymeric films obtained with each combination of such experimental parameters were examined by means of AFM.

For example, electropolymerization of pyrrole on silver, with *p*-TsONa as the supporting electrolyte, made films with granular structure highly rough, suggesting a columnar growth on metallic surface, as illustrated in Fig. 3. A quite different morphology was achieved with the same monomer electropolymerized on the same substrate, but with sulfuric acid as the supporting electrolyte: the structure is characterized by equally spaced vertical scales (Fig. 4), indicating that the polymer grows in two dimensions. This same relationship between structure and supporting electrolyte has also been found on other materials (Au, Ergal), thus indicating the supporting electrolyte as the main parameter on which to modulate the morphologic characteristics of coverages.

The marked dependence of polymer structure from the nature of the electrolyte is due, as previously reported (26,27), and confirmed by us from elemental analysis on films by englobing hindering anions of electrolyte into the positively charged polymer, with strong effects on morphology. Apparently, this influence results primarily from the imprinting effect of the substrate, with the differences caused by electrolytes independent of the employed material.

We explain such behavior with the difference of the steric hin-

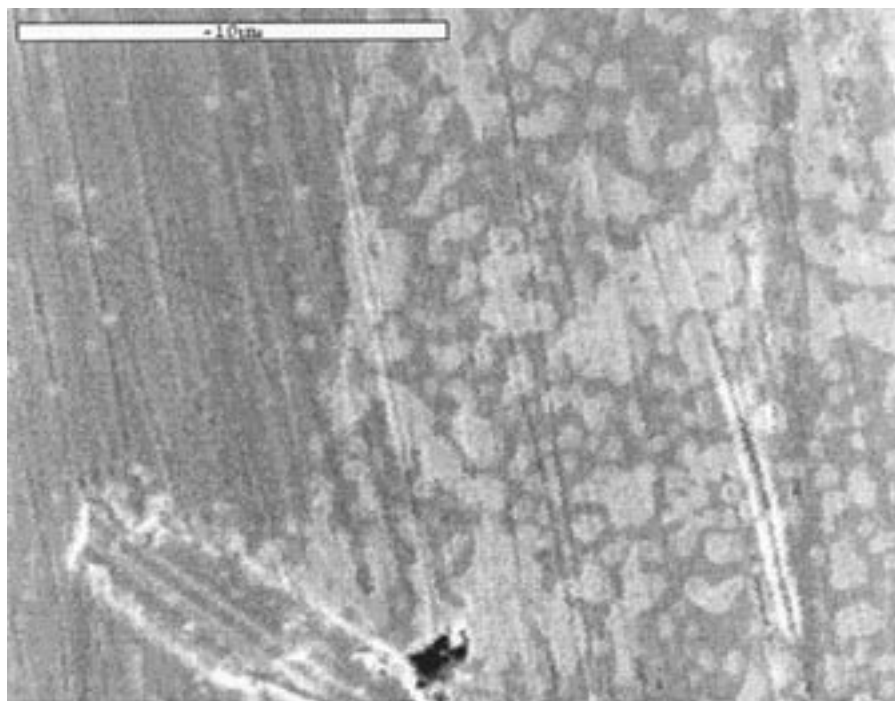


FIG. 1—SEM image of PP coating on platinum (fingerprint borderline region).

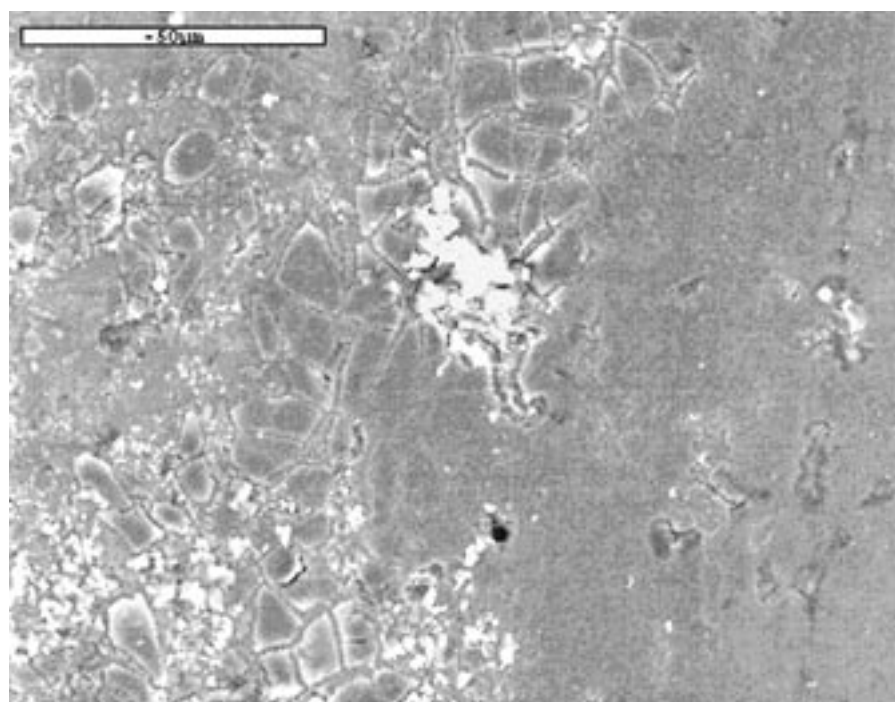


FIG. 2—SEM image of PolyNiTAPP coating on Ergal (fingerprint borderline region).

drance of two anions. Instead, the effect of acidity is noticeable in a lower oxidation potential of monomer, determined by a chemical activation of the system. In fact, pyrrole leads a spontaneous polymerization promoted by nitrogen protonation, and successive generation of carbocationic species. No correlation was noticed between acidity and morphology by means of AFM on polymeric

films obtained in the presence of sodium sulfate: a structure similar to that of coverages achieved from sulfuric acid was found. This study was useful in identifying optimal conditions of fingerprint enhancement, whose goodness is systematically referable to morphologic aspects of deposited material, especially in terms of topologic selectivity of electropolymerization process.

Application of the Method

Chemical or physical techniques used for fingerprint enhancing operate with superficial components of papillary ridges, such as proteins that disappear after a degradation, or water evaporating quickly depending on the temperature and humidity of the environment. The result of the performance is strongly affected by the storage conditions, age, and kind of deposit. On nonporous surfaces, like metals, the developing of fingerprints is difficult because the nonabsorbent surfaces do not let deposits preserve.

In order to find out the best experimental conditions, a good repeatability of the fingerprint was necessary, i.e., the fingerprints had to be impressed on a metallic surface with the same pressure and amount of lipids. Thus, we used an artificial finger, built up with dental technology, that was stained by natural secretion and pressed on different objects with controlled pressure, in a reproducible way.

Polypyrrole Film—Fingerprint legibility is affected by morphological properties of the polymer film, i.e., by the sharpness of its outline and by its roughness, determining the light reflection. As seen, these properties are in turn determined by the polymerization conditions: monomer concentration, potential scan rate, and supporting electrolyte.

To enhance the fingerprints, we used the solutions described earlier. Starting from 0.1 M solution of pyrrole, the deposition of film on fingerprints deposited on metals had only partial results with both sulfuric acid or with TsONa as supporting electrolytes, either by cyclic voltammetry or by constant potential. This concentration gave an insufficient covering, probably because the diffusion steady state conditions were reached just after a deposition of a small amount of pyrrole.

The polymer grows quickly and homogeneously on noncovered parts in a whole area of a fingerprint using concentrations higher than 0.3 M (the exposed area was about 2.5 cm²). The potentiodynamic deposition turned out to be more selective for zones free from the grease of the papillary ridges with respect to the proof done by a potentiostatic way. We obtained a maximum number of characteristic points with three scans between 0 and 1000 mV, at the scan rate of 300 mV/sec. The topologic selectivity of the deposition could also be related to a vertical growth induced by *p*-TsO⁻ resulting in higher roughness of the PP, and then with better enhancing regarding those obtained from H₂SO₄ or Na₂SO₄. The presence of hindering *p*-TsO⁻ anions into polymeric films seems to be necessary in order to obtain coverages morphologically suitable for fingerprint enhancing.

As our aim was to determine the “life-time” of fingerprints and to study the influence of temperature and humidity toward their legibility, the fingerprints have been artificially aged in desiccator with silica gel and then in an oven for different periods at different temperatures. We studied their degradation in the range of the usual conservation of the items (25 to 35°C). Using this procedure, fingerprints left on guns have been developed for different times, enhancing their characteristic points as shown in Fig. 5. The trends of identified characteristic points, as a function of aging time, obtained by employing *p*-TsONa or H₂SO₄ as the supporting electrolyte, are compared in Fig. 6.

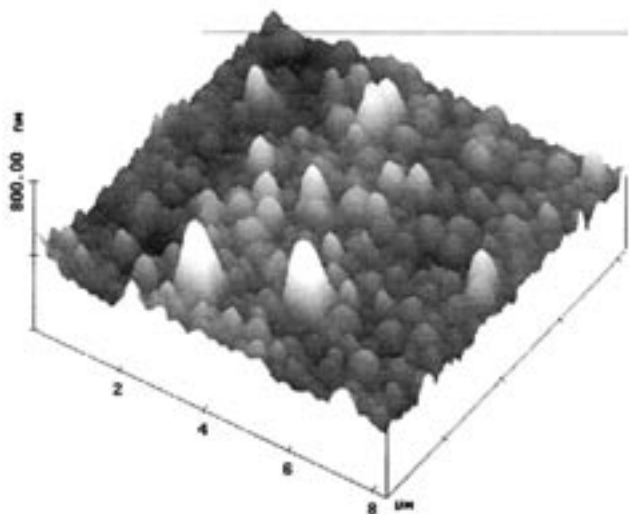


FIG. 3—AFM image of PP from *p*-TsONa.

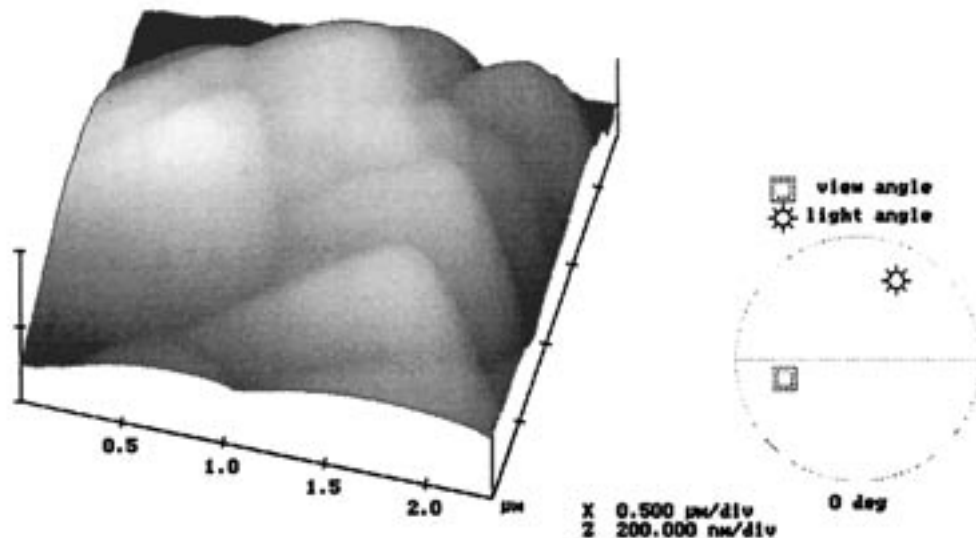


FIG. 4—AFM image of PP from H₂SO₄.

Because of the natural processes of the decay deposits, an evident decrease of characteristic points is observed after one week. After three weeks it was possible to enhance only a moderate amount of characteristic points. The better performance of TsONa, however, still holds for aged fingerprints (Fig. 6). A drastic fall of the number of characteristic points is observed if the samples are placed in an oven at 35°C for 24 h. This is likely due to quickened oxidation processes of fatty acids. In fact, because of the oxidation of fatty acids, the original fingerprint deposits progressively harden and crumble off the surface of metal.

The discussed results have been achieved by enhancing fingerprints on Ergal, steel (Fig. 7), gold (Fig. 8) and silver.

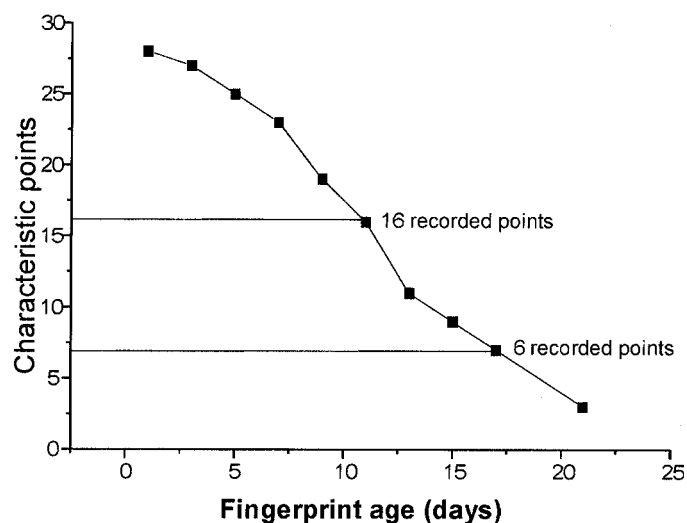


FIG. 5—Trend of found characteristic points, as function of aging time.

supporting electrolyte, the enhancing of the fingerprints had better results on gold and silver than on Ergal and steel according with their oxidation potentials: gold and silver are not oxidized at upper limits of the potential scans and their ions cannot interact with the polymer. Even on silver and gold, the TsO^- anion works better than chloride and sulfate. Also, the time and temperature effects on the decay of the fingerprints on these metals follow those on Ergal.

Polyporphyrine Film—Polymerization tests of porphyrins were also performed on Ergal, silver, gold, and platinum. Thin plates of Ergal—smoothed, polished and cleaned—were prepared for preliminary polymerization tests on this alloy. Firstly 10^{-3} M solutions of tetra(o-aminophenyl)-porphyrin in 1M HCl were em-

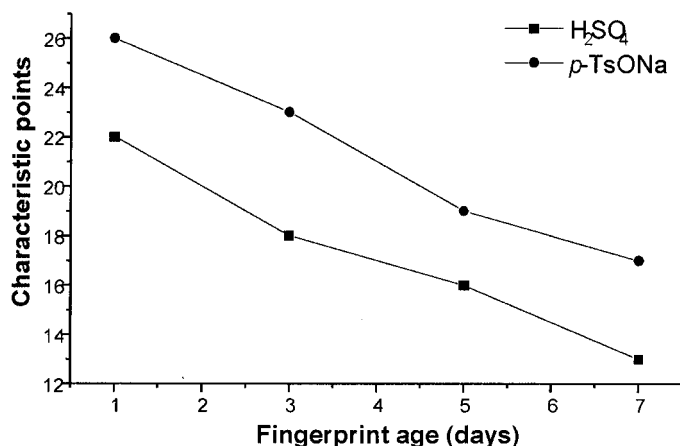


FIG. 6—Trend of found characteristic points, as function of aging time, for two different supporting electrolytes.

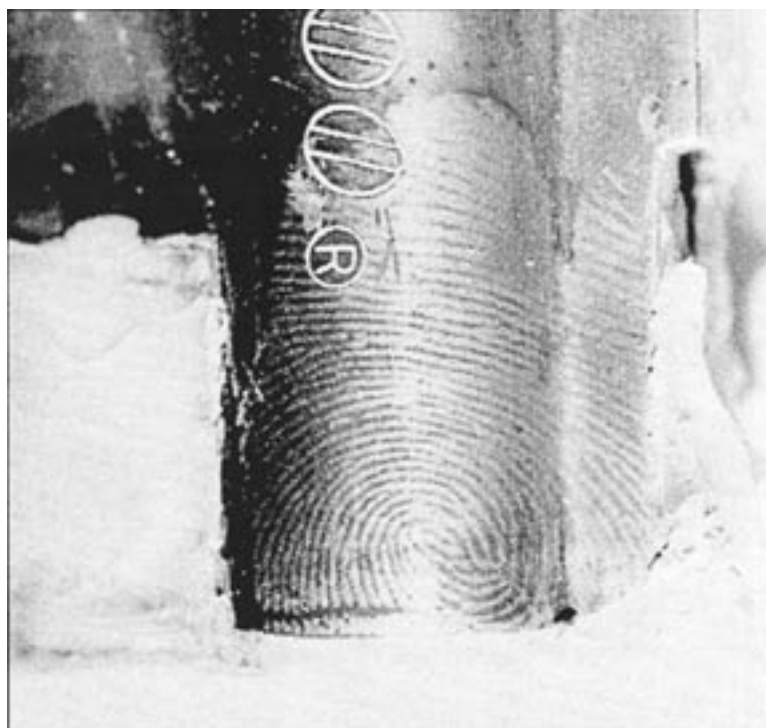


FIG. 7—Fingerprint enhancement on a Magnum 357 gun, obtained with PP, from p-TsONa solutions.

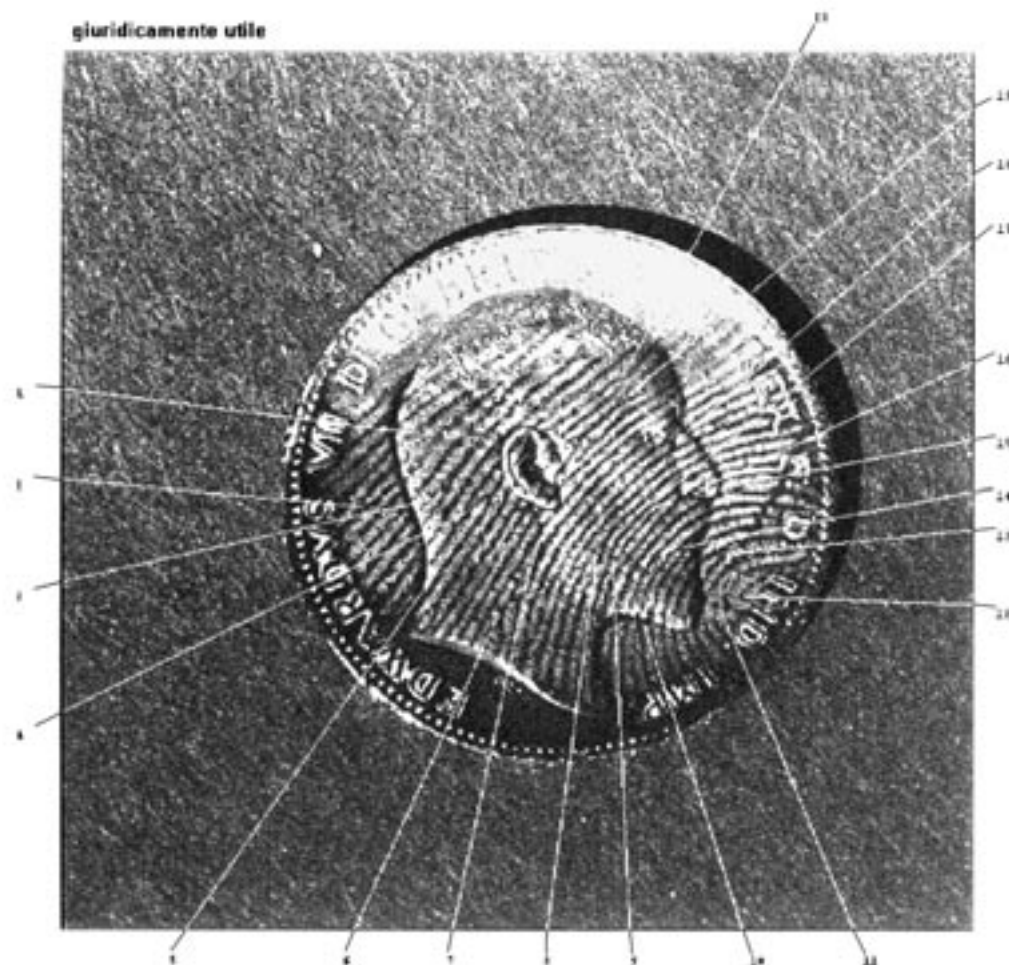


FIG. 8—Fingerprint enhancement on a gold coin, obtained with PP, from p-TsONa solutions.

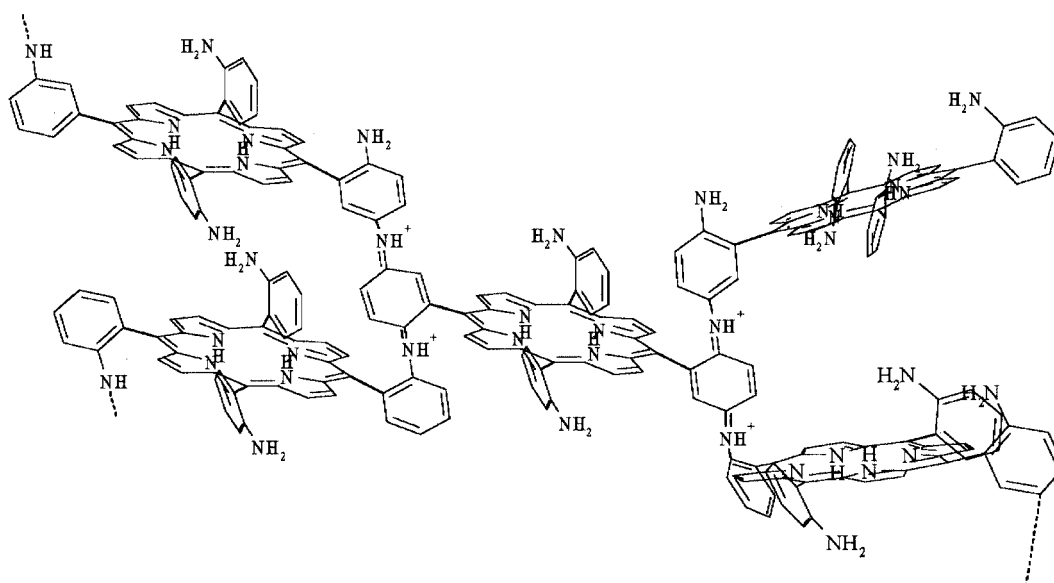


FIG. 9—Schematic representation of polyTAPP structure.

ployed. Applied potential was either kept constant at 1100 mV, or scanned between 0 and 1100 mV. These procedures gave rise to the oxidation of the alloy, likely because of the formation of chlorine that subsequently oxidizes some components of the alloy, resulting in the formation of a superficial dark mug. To avoid this

browning, we used KNO_3 1M as the supporting electrolyte, whereas HCl was kept 0.1M. In this way, we also obtained a good enhancing of the fingerprints. All enhancements on Ergal, achieved by electropolymerization of TAPP and derivatives, were obtained under the above experimental conditions. The polymer-

ization was performed by cyclic voltammetry varying the scan rates. The best topologic selectivity of the polymeric growing on the samples was achieved with two scans between 0 and 1100 mV at the rate of 250 mV/sec.

The development of fingerprints with the porphyrinic polymeric film on chromium plated metals failed because the polymer turned out to be almost transparent on the reflective surface. PolyTAPP films are instead more suitable to enhance fingerprints on silver and gold. In fact, on silver we used films obtained from polymerization of TAPP and relevant transition metal complexes (Fig. 9). The greatest limit of this technique is the weakly contrasted film. A film from NiTAPP is a pale orange color, therefore on gold it is less contrasted and the characteristic points are detected with difficulty. Fingerprints fifteen days old on gold present six characteristic points detected that, in some cases allow us to consider this proof at least useful for the investigation.

Conclusions

The present method is, to our knowledge, a new way for developing latent fingerprints on metal items (such as weapons, keys, coins, and locks) that are closely tied to serious and organized crimes. The method yielded useful results on both pure metal and Ergal alloy, the latter being widely used to produce modern weapons in Italy. The data we obtained with morphology studies confirmed the close relationship between polymer characteristic and hindrance of anion, which acts as a counterion for cationic species formed during the electropolymerization process. Fingerprint legibility depends on other morphological properties of the film, i.e., sharpness and roughness. These properties are determined by the polymerization conditions, like monomer concentration, potential scan rate, and supporting electrolyte. Low costs of the instrumentation and of the reagents, rapidity, and simplicity are the strongest attributes of the present method.

We intend to extend these experiments to fired weapons and ammunitions, and also test various kinds of items, in order to deal with most of the metallic evidence that can be found on the scene of a crime and/or during investigations.

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