

Visualization of Latent Fingerprints by Aqueous Electrolytes: New Developments

Kulvir Singh* , Om Prakash Jasuca**

Abstract: Aqueous electrolytes have recently been introduced as a new chemical technique for development of latent fingerprints on various surfaces. The electrolyte solution was prepared based on the electronegativity series of the elements. The application methods such as immersion, spray, drop and gel (based) methods were applied, and the latent fingerprints were found to develop in few minutes and were permanent in nature on metal surfaces. The study was further extended to develop an aqueous electrolyte reagent (AER) which could develop latent fingerprints on different types of porous, semi-porous and non-porous surfaces. The surface independency and permanent nature of the developed fingerprints were the main advantages of this technique.

* Prof. Dr., Punjabi University, Patiala India, Corresponding author, Punjabi University, Department of Forensic Science, Patiala. India. E-mail: opjasuca@gmail.com

** Dr., RIMT University, Mandi Gobind garh, India

1. Development of Aqueous electrolytes:

An electrolyte forms charged ions when dissolved in water (polar solvent) hence termed as aqueous electrolyte such as acids, bases and inorganic salts (Silberberg, 2003). The aqueous electrolytes were introduced for detection of latent fingerprints when an enthusiastic researcher accidentally found the etched fingerprints on metal pieces which were left unintentionally in the beaker of acidic waste solution. This triggered prying leads to first report on the application of aqueous electrolytes for the development of latent fingerprints. The aqueous electrolytes as sulfuric acid and sodium hydroxide were prepared in series dilutions at different pH values and tested on metal, glass and plastic surfaces containing pre-deposited latents (Jasuja,2011, pp.215-222). The technique had shown promising developments with some inadequacies such as complexity in solution preparation and application process accompanying perilous treatment of strong acids and alkalis.

Soon after, the inorganic salts were proposed as an alternative to acids and alkali based on the electronegativity of the elements (Jasuja,2015,pp.122-136). The metathesis reactions and film formation were suggested as the possible reaction mechanism behind the development of fingerprints. The time and hazard involved in the former study were lowered to a greater extent and the technique showed quick and better development as represented in table 1. However, prerequisite of different electrolytes for different metal types had rendered the technique less feasible.

Table 1: The results of fingerprint development on different metals treated with different inorganic salts (Jasuja 2015).

Metal type	Inorganic salt	Optimum concentration (% _{w/v}) of salt	Optimum temperature (°C)	Time of development (minute/s)
Steel	Calcium Chloride	6	40	5
Aluminum	Calcium Chloride	6	40	5
Zinc	Stannous Chloride	0.25	35	1
Copper	Sodium Cobaltinitrite	2	35	1
Brass	Sodium Hydrogen Carbonate	8	55	5
Fired Cartridge Cases	Sodium Hydrogen Carbonate	8	55	5

2. Development of aqueous electrolyte reagent (AER):

The surface dependency was a constant obstacle for fingermark development techniques and further study aimed to resolve the existing issue. On advancing the previous studies the following points were intended for investigation:

1. The new reagent should be surface independent.
2. The reagent should be reactive to diverse surfaces and fingermark composition.
3. The reagent should be stable over time.
4. The reagent should be non-flammable and safe to handle.
5. The reagent should be economical.
6. The reagent should be easy to prepare excluding the need of sophisticated instrumentation.
7. The reagent should be compatible with the established fingerprint development techniques.

2.1 Preparation and Optimization of AER:

Further study was initiated with the above-mentioned aims and completed through rigorous study of the electronegativity series of elements. The materials used in the study have been explained elsewhere (Jasuja,2019,pp. 33-52). Many combinations of electrolytes, based on their electronegative values, were tested for the development of latents on diverse surfaces and most effective mixture of electrolytes was subsequently optimized as briefed in table 2. The concentration of each electrolyte and effect of temperature of solution were correspondingly studied and optimized. Four electrolytes had been selected to prepare a mixture of electrolytes containing the four most reactive halogens as counter ions (chloride ions, fluoride ions, bromide ions, permanganate ions) in the selected inorganic salts (calcium chloride, sodium fluoride, sodium bromide, potassium permanganate).

Table 2: Electrolyte combinations for formulation and optimization of AER.

Combination	Inference
1g of stannous chloride in 25 mL of distilled water + 1g of zinc chloride in 25 mL of distilled water = 50 mL of final electrolytes solution (precipitate formed)	No development on any surface
1g of stannous chloride in 25 mL of distilled water + 1 g nickel chloride in 25 mL of distilled water + 1 g copper chloride in 25 mL of distilled water + 1g aluminum chloride in 25 mL of distilled water = 100 mL of final electrolytes solution (no precipitate formed).	No development on any surface
1 g of potassium permanganate in 25 mL of distilled water + 1 g calcium chloride in 25 mL of distilled water = 50 mL of final electrolytes solution (no precipitate formed).	Development occurred on metal surfaces but not on paper, glass and plastic surfaces
1 g of potassium permanganate in 25 mL of distilled water + 1 g calcium chloride in 25 mL of distilled water + 1 g of sodium fluoride = 75 mL of final electrolytes solution (precipitate formed)	Development occurred on most of the mentioned surfaces but development was less prominent on non-metal surfaces
1 g of potassium permanganate in 25 mL of distilled water + 1 g calcium chloride in 25 mL of distilled water + 1 g of sodium fluoride + 1 g sodium bromide = 100 mL of final electrolytes solution (precipitate formed as discussed above). (Sodium fluoride was added last to the mixture)	Inconsistent development observed on all mentioned surfaces
8 g calcium chloride in 10 mL of distilled water + 4 g potassium permanganate in 35 mL of distilled water + 6 g sodium bromide in 10 mL of distilled water + 6 g sodium fluoride in 45 mL of distilled water = 100 mL final volume of the aqueous electrolytes mixture solution.	Consistent high quality development of latent fingerprints was observed

2.1.1 Chemical characteristics of AER:

The individual role of each electrolyte can be summed up as follow: the aqueous electrolyte calcium chloride forms calcium ions and chloride ions. The Ca^{2+} ions can form insoluble carbonate and sulphate salts and can bond to form water insoluble complexes with the fatty acids and amino acids by bidentate chelation (Bourne,1982). Whereas Cl^- ions depassivate the metal surfaces (Charnig,1982). According to the chemisorptions theory, the chloride ions can abolish the passi-

vity of metals because the chloride ions have low energy of activation potential for chemisorptions. Therefore, chloride ion can easily pierce the oxide film and causes corrosion of the metal surfaces (Osipow,1962). Likewise, potassium permanganate electrolyte is a strong oxidizing agent and forms potassium ions as well as permanganate ions ($[\text{MnO}_4^-]$). The sodium bromide and sodium fluoride electrolytes provide the most reactive ions of bromide (Br^-) and fluoride (F^-) which subsequently produced a highly reactive ion rich solution. Strikingly, aqueous electrolytes calcium chloride and sodium fluoride reacts to form white precipitates of calcium fluoride as shown in the equation below.



These white precipitates of calcium fluoride are simultaneously stained by permanganate ions in the solution (Jasuja, 2019, pp.33-52).

The individual electrolytes were not able to develop the latent fingermarks on diverse surfaces might be due to the different chemical properties of the surfaces. For instance, metal surfaces are lustrous and non-porous, plastic is a polymer, paper is a porous surface mainly made of cellulose fibers and glass is mixture of silica and other substances. Therefore, to counter the surface problem, the mixtures of electrolyte solutions were prepared which obviously have different chemical properties than the parent electrolytes and would be tested on diverse surfaces for the development of fingermarks. Many electrolyte(s) combinations were tested and the one which had shown best development on different surfaces was optimized. This mixture was named as aqueous electrolyte reagent (AER).

3. Mechanism of Development:

AER is a charged ion-rich solution including precipitates and other oxidizing agents. There is a continuous collisions and stochastic movements of the ions within the solution in different directions with different velocities and vibrate at their positions. These vibrations produce enough amounts of energy that permit the charged species to jump to another positions if space is available in solution (Koryta, 1993). Therefore, in AER, mixture of electrolytes of different electronegativity values were dissolved in small amount of distilled water, causing near-saturation. The densely placed ionic species produced much amount of charge (energy) due to stochastic movements and vibrations. The excess charge due to excess ions, electrons and dipoles produce the electric field. This region of excess charge is called electrical double layer where entire charge concentrates in the form of a diffuse layer. Similarly, when a substrate (which acts as a nucleation site) immersed in the reagent the charged ionic species adsorbed on the surface electrostatically as a thin film.

The main composition of AER includes ionic species and precipitates enclosed by other ionic parts. The different surfaces have different chemical and physical properties as discussed before therefore, reaction of AER can be expected to be different in nature for different surface type. For example, AER tarnished the stainless steel and nickel surfaces which means some sort of oxide film must have been formed. However, on brass surface the tarnishing effect was less prominent. On zinc metal, etching of the surface had been observed. The reagent strongly stained the polyvinyl chloride (plastic polymer) and paper surfaces but a transparent (may be oxide) film had been observed on silica rich surfaces. The present context restricts the complete possible explanations but it could safely be expressed that the technique is surface independent because it directly interacts with the fingerprint deposits. It had been confirmed by SEM-EDS analysis that differential accumulation of charged species occurred between the fingerprint residue and the background surface possibly due to the different chemical nature of both. A fingerprint is a complex matrix containing charged biomolecules, ions, fatty acids, xenobiotic materials, etc. and can attract more ionic species as compared to the background surface. This differential accumulation had been confirmed through SEM-EDS, wherein more weight and atomic percentage of elements on the fingerprint deposits was measured against the background surface (Atkins,2006) . For instance, SEM-EDS analysis of developed fingerprints on stainless-steel surface had revealed the AER composition concentrate more (such as calcium form calcium chloride/calcium fluoride, oxygen and manganese from permanganate ions, fluorine from sodium fluoride/calcium fluoride precipitates) on fingerprint's ridge deposit area as represented in the table 3 in case of stainless steel surface (Jasuja,2019, pp. 33-52).

3.1 Method of Development:

Four methods of development (immersion, spray, drop, gel) had been tested for the application of AER. The test sample was immersed in or sprayed with the reagent. In drop method the surface was placed horizontally and reagent was added dropwise until it covered the whole suspected area. The gel method was particularly prepared for vertically oriented fixed surfaces such as metal door/window bars, etc. Silica gel G was mixed with the reagent and applied on the vertical oriented surfaces. The gel adhered to the surface and developed the fingerprints. The 55 g of silica gel was mixed in 100 mL of AER. Out of four method immersion and gel methods had shown the promising consistent results. While the remaining methods showed inconsistent results.

Table 3: SEM-EDS elemental data of a developed fingerprint on a stainless steel surface (Jasuja,2019)

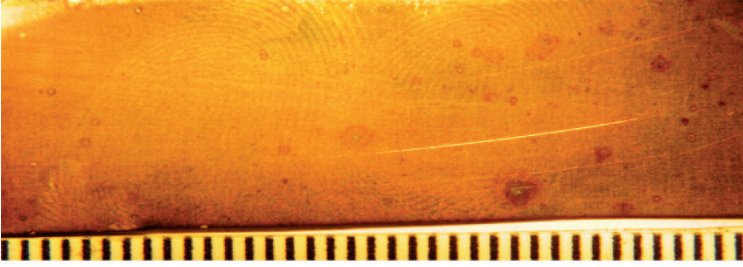
Fingerprint's ridge area			Background area		
Element	Weight %	Atomic %	Element	Weight %	Atomic %
C	2.91	33.93	Cr	0.47	21.76
O	3.80	33.26	Mn	0.42	18.56
F	3.82	28.16	Fe	1.38	59.68
Ca	0.30	1.06	Total	2.27	
Mn	0.39	0.98			
Fe	1.04	2.62			
Total	12.26				

3.2 Effect of temperature on AER:

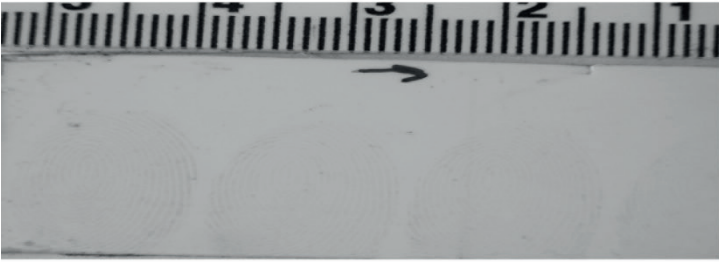
Temperature increases the reaction rate [9]. Likewise, AER was found to develop latent fingerprints in short time when heated between 50 to 55°C however, overheating overly tarnished the surface. This might be because of excessive adsorption of ions and damaged the developed fingerprint (Jasuja,2019, pp. 33-52).

3.3 Development of depletion series of latent fingerprints:

The sensitivity of AER has been tested using depletion series of fingerprints. The depletion series was obtained from volunteers on non-porous (steel, plastic, glass), semi-porous (varnished magazine paper) and porous (A4 paper sheet) surfaces. It has been observed that on steel surface the reagent responded up to 20th sequential mark. In case of plastic, magazine paper, and glass, the reagent responded up to 4th, 11th and 13th sequential fingerprint respectively (Figure 1). However, A4 paper did not show any development of depletion series of the fingerprints.



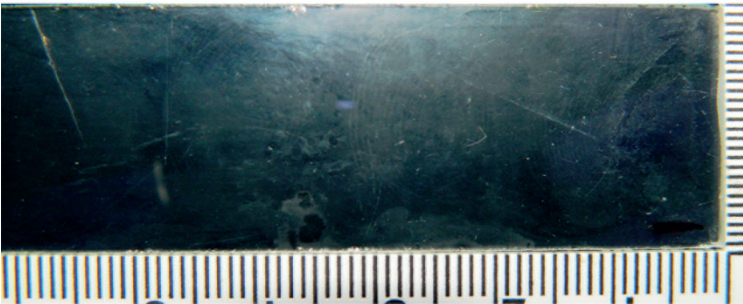
19th (left) and 20th (right) sequential fingerprints



1 to 4th sequential fingerprints



6th to 11th sequential fingerprints



10th to 13th sequential fingerprints

Figure 1: Series of latent fingerprints

3.4 Effect of water submersion on the development of fingermarks:

The effectiveness of AER for water submerged surfaces has been tested by keeping the stainless steel and glass surfaces in plastic containers containing tap (pH ~7.2) and sewage (pH ~7.5) water for seven days and for one month after the deposition of (natural) latent fingermarks. The sewage water was collected from the inlet (untreated sewage water) of water treatment plant at Punjabi University Patiala. The container was covered with plastic sheet to minimize the water loss through evaporation during the study. The results showed medium high quality of developed fingermarks in case of tap water submerged surfaces; while medium low quality has been observed in sewage water submerged surfaces. The fingermarks found developed with different qualities for glass and stainless steel surfaces in case of tap water submersion, as evident from figure 2. However, immersion in sewage water affected the quality of developed latent fingermarks on both the surfaces and the glass surface did not show any development in case of 30 days immersion time period (Figure 2).

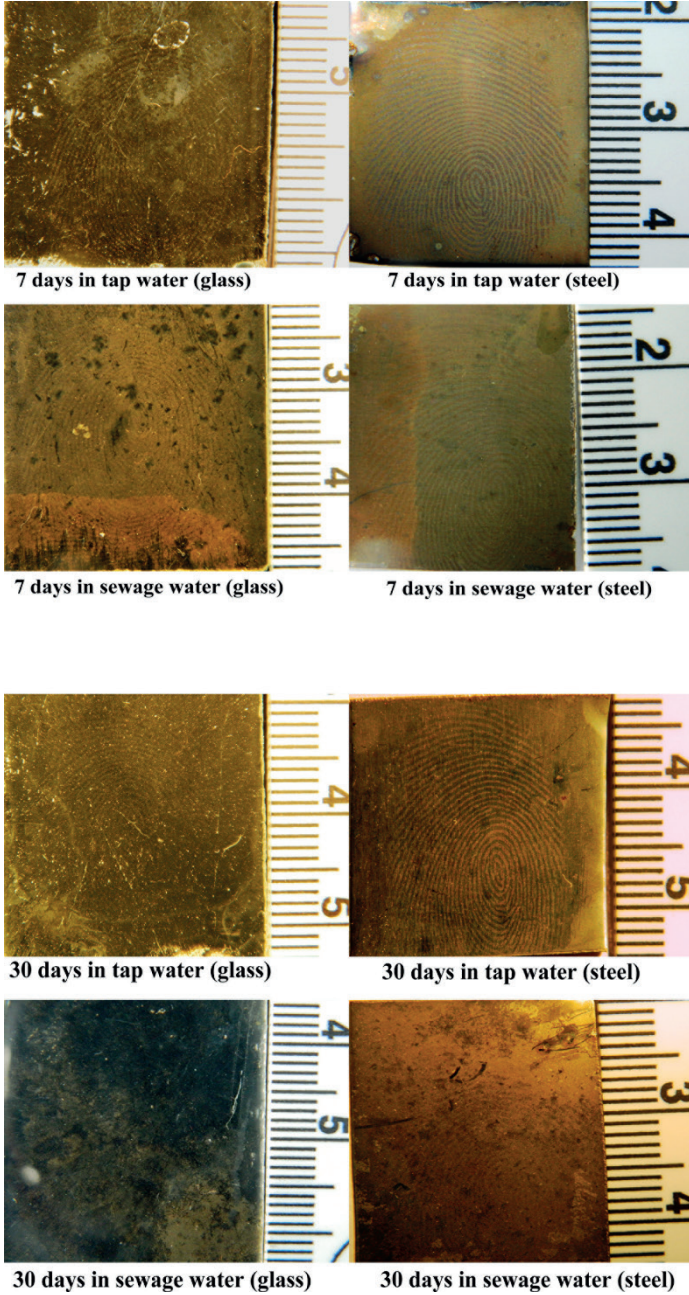


Figure 2: The fingerprints found developed with different qualities for glass and stainless steel surfaces in case of tap water submersion

3.5. The Use of AER in Sequence with Other Techniques:

Sometimes one method of fingerprint development might be failed on crime exhibits, and then the expert considered second most-relevant technique for the development of latent fingerprints. In that case if the first used technique is found to be incompatible with the subsequent used technique then the important piece of evidence would be destroyed. Therefore, AER was tested in sequence with conventional methods such as powdering, small particle reagent, cyanoacrylate and ninhydrin, as per the standard formulation (Bowman 2004). The stainless steel, aluminium and paper surfaces were used in the subsequent processing study as follow:

In pre-treatment process, the surface bearing latent fingerprints was first developed with the AER and then treated in sequence with the other techniques individually. It has been found that in sequence treatment with other techniques the developed fingerprints did not show any further enhancement.

In post-treatment process, the surfaces bearing latent fingerprints were first developed with other mentioned techniques and then treated in sequence with the AER method individually. It has been observed that post-treatment with AER did not show any effect on the performance of other techniques. However, surface background staining has been observed in the developed fingerprints. But besides the background staining, the fingerprint still hold its unique characteristics which could easily be identified (Figure 3).

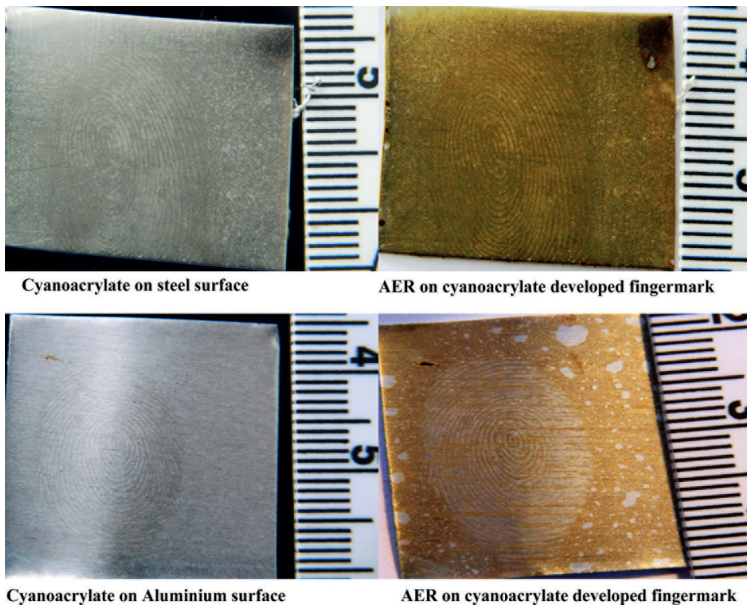


Figure 3: the use of AER in sequence with other techniques

3.6. Lifting of Developed Fingermarks from Dark Colored Surfaces:

The dark colored non-porous round surfaces showed poor contrast of the developed fingermarks. Therefore, developed fingermarks on dark colored glass and plastic surfaces were lifted with the help of transparent adhesive tape to make them useful for further studies (Figure 4).

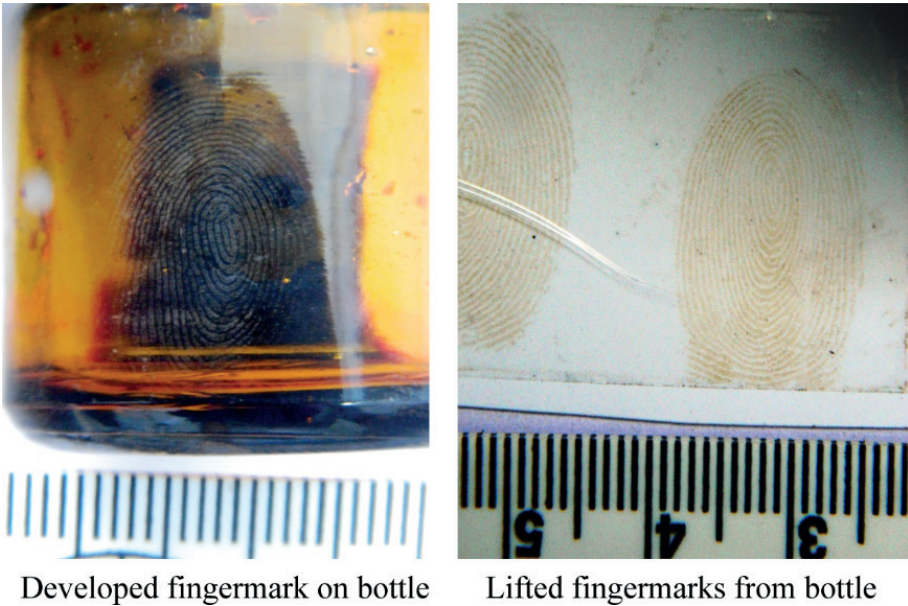


Figure 4: Lifting of developed fingermarks from dark colored surfaces

3.7. Determination of the shelf life of the AER:

The shelf life of the AER has been tested after the storage period of one year in the conical flask with stopper at room temperature under laboratory conditions. After one year the reagent in the flask was visually observed. Few crystals of varying sizes (~ 0.2 cm to 1.5 cm) have been found at the bottom of the flask. The similar type smaller crystals were also formed when few drops of AER were dried (at room temperature) on glass slides. The reagent was then tested for the development of latent fingermarks on stainless steel surface. It has been found that the sensitivity and effectiveness of the AER was not reduced over time which was evident from the developed fingermarks of high quality on different surface. Noteworthy, crystals in the aged reagent has been observed and those could easily be re-dissolved by stirring and by gentle heating of the reagent.

3.8. Matter of Concern:

1. Paper (porous) surfaces showed inconsistent results.
2. AER could damage the coated material surfaces (such as X-ray film, photographic film, poorly coated metal surfaces, paper coated wrappers of candies).

4. Features of AER (Singh,2017):

1. The AER can develop latent fingermarks on non-porous, semi-porous, porous and miscellaneous surfaces as represented in table 4 and figure 5.
2. The AER can develop aged fingermarks (3 months old) on non-porous surfaces.
3. The AER can develop latent fingermarks on (tap/ sewer water, immersed for 1-month period time) wet non-porous surfaces.
4. The AER is stable over passage of time.
5. The AER can be applied in sequence with conventional techniques such as powder, powder suspension and cyanoacrylate fuming.
6. The AER can develop latent fingermark on fired/unfired cartridge cases (brass/nickel).
7. The DNA extraction can be possible from the AER developed fingermarks.
8. The AER is surface independent and develops fingermarks of permanent nature.
9. The AER develops fingermarks of high quality in short time.
10. The AER is safe to handle, economical and easy to prepare.

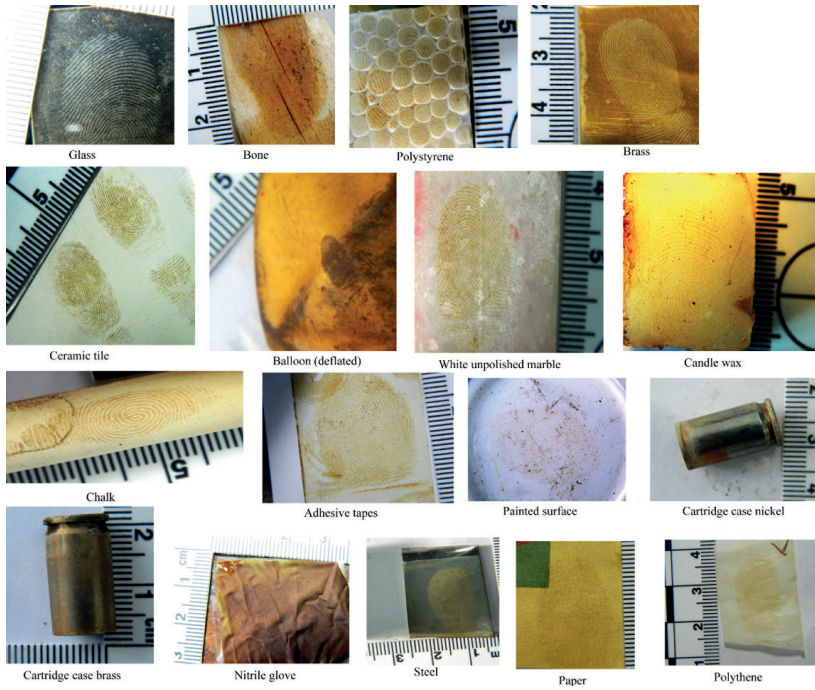


Figure 5: the AER can develop latent fingerprints on non-porous, semi-porous, porous and miscellaneous surfaces

Table 4: The summarized results for fingerprint development on different surfaces by aqueous electrolyte reagent

Surface	Time of Development		Developed fingerprint Grade (SWGFAST grading scheme)
	At room temperature	Between 50° to 55°C	
Steel, Stainless steel	2 minutes	20 seconds	High
Aluminum	3 minutes	30 seconds	High
Copper, Brass	15 minutes	5 minutes	High
Iron	5 minutes	2 minutes	Medium Low
Zinc	5 minutes	2 minutes	High
Nickel	5 minutes	3 minutes	High
Galvanized iron	15 minutes	3 minutes	High
Painted metal	20 minutes	10 minutes	High
Plastics, Balloon	20 minutes	10 minutes	High
Glass	20 minutes	10 minutes	High

Polythene	20 minutes	10 minutes	High
Ceramic tiles (plain and textured)	30 minutes	15 minutes	High
White unpolished marble	20 minutes	10 minutes	High
China bone/porcelain	30 minutes	15 minutes	High
Polished granite	30 minutes	15 minutes	High
Polyvinyl chloride	20 minutes	10 minutes	High
Thermocol/polystyrene	20 minutes	10 minutes	High
Magazine papers	30 seconds	1 dip	High
Polished wood/veneer/sunmica	20 minutes	10 minutes	Medium High
Butter paper	1 minute	1 dip	Low
Thermal papers	15 seconds	1 dip	Low
Papers (A4, notebook and colored papers)	40 seconds	1 dip	Medium Low
Cardboards	20 seconds	1 dip	Low
Nitrile and latex gloves	20 seconds	2 dips	High
Bone	10 seconds	2 dips	Medium Low
Adhesive tapes	15 minutes	9 minutes	High
Candle wax	10 minutes	NR*	High
Chalk	3 minutes	4 dips	High
Crumpled aluminum foil	10 minutes	NR**	High
Cartridge case ¹	15 minutes	5 minutes	Medium Low
Cartridge case ²	5 minutes	3 minutes	Medium Low

(Where, *NR = not recommended because wax may start melting. **NR = not recommended because reagent take time to seep into folds and creases, Cartridge case¹ = brass, fingermark deposited on live cartridge and then case recovered after firing, Cartridge case² = nickel, fingermark deposited on live cartridge and then case recovered after firing)

5. Conclusion:

The technique has shown potential to be used as a universally applicable technique and can assist the fingerprint examiners at the crime scene. The surface independency and permanency of the developed fingerprints were the added advantages of the AER technique.

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