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## Enhancing the Quality of Aged Latent Fingerprints Developed by Superglue Fuming: Loss and Replenishment of Initiator

**ABSTRACT:** The recovery and identification of latent fingerprints from a crime scene are crucial to many investigations. The cyanoacrylate (superglue) fuming method (CFM), which develops fingerprints by growing a polymer coating over the print residue, is a powerful method but encounters severe limitations when prints are aged or exposed to harsh environmental conditions. We examine the aging process and how the changes that occur to a fingerprint residue over time influence the growth of polymer during development. We identify loss of initiator by erosion and degradation that, when coupled with a loss of water from the print residue, result in a decreased ability to polymerize ethylcyanoacrylate. Then, we present a methodology by which the ability of aged latent fingerprints to polymerize ethylcyanoacrylate is recovered. Two print enhancement agents, acetic acid and ammonia, are demonstrated to improve the growth of polymer from the print ridges by over an order of magnitude, while retaining the integrity of the print structure. Comparison between the two enhancement agents indicate that the enhancement occurs due to ridge coating by the ammonia or acetic acid and pH control of the latent print.

**KEYWORDS:** forensic science, fingerprints, aging, recovery, cyanoacrylate, enhancement, polymerization, quartz crystal microbalance

The cyanoacrylate (superglue) fuming method (CFM) is a highly effective and well-accepted method for developing latent fingerprints on nonporous substrates (1–4). Interactions between the fingerprint residue and the cyanoacrylate vapor cause rapid polymerization resulting in a white polymer coating that enables print visualization. As a latent fingerprint ages, however, changes to the print residue results in a decrease in the quality of the impression obtained using the CFM (1,5). The nature of this change in the fingerprint residue and how it affects the polymerization of ethylcyanoacrylate (ECA) is not well understood.

The residue that is deposited by an individual leaving a fingerprint is comprised primarily of eccrine sweat, which is secreted through pores in the hand (1,6,7). The water-based mixture contains a variety of salts but consists predominantly of NaCl, sodium lactate, urea, and amino acids. Many fingerprints also become contaminated with sebum, an oily mixture secreted from hair follicles. The contribution of sebum to the fingerprint residue is nominally 5% by weight (varies based upon personal habits), but adds a mixture of glycerides and fatty acids to the residue (1). Unlike sebaceous prints, eccrine prints do not contain hygroscopic materials such as di- and monoacyl glycerols and glycerol. As a result, clean prints are not able to maintain a hydrated print composition.

The volatile components of the fingerprint residue, primarily water, are known to evaporate out of the fingerprint residue during the aging process (8). It is unclear, however, exactly how the loss of water from the print residue affects its ability to polymerize ECA vapor. Simple re-hydration of aged, eccrine prints with

water vapor has been unsuccessful in regenerating prints (9). We have previously reported that the eccrine-based salts based in the print are primarily responsible for the initiation of the polymerization of the ECA vapor during the CFM. Moreover, these components are nonvolatile and should remain during the aging process (10). This raises several questions such as why does aging reduce the effectiveness of the CFM, if nonvolatile components of the residue are responsible for cyanoacrylate initiation? Additionally, might there be a method to regenerate the ability of an aged fingerprint to initiate the growth of cyanoacrylate during fuming?

The initial part of this paper will present results of an investigation that has examined how aging of latent prints impacts the growth of poly(ethyl cyanoacrylate) from the print during fuming. To this end, fingerprints consisting solely of eccrine sweat were deposited onto a highly sensitive mass balance known as a quartz crystal microbalance (QCMB). The latent prints in this study were aged in environmental conditions where the temperature varied from 23°C to 25°C and humidity ranged from 50% to 80%. The aging prints were also exposed to indirect light, and small amounts of air flow through a small gap in the casing. To account for this, a control set of fingerprints was also aged in containers that prevented exposure to light and airflow. From the results of this experiment, the primary contributing factors that lead to the ineffectiveness of the CFM to develop aged latent fingerprints are presented.

Additionally, a method was established by which the latent fingerprints that have deteriorated by aging can recover the ability to initiate and polymerize the cyanoacrylate vapor along the fingerprint ridges. This was accomplished by exposing the latent fingerprint to vapors of either ammonia or acetic acid prior to development by the CFM.

Ammonia was chosen as a potential enhancement agent for several reasons. Firstly, the enhancement agent needed to have a

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vapor pressure such that simple evaporation allows the agent to readily interact with the fingerprint without damaging the structural integrity of the fingerprint ridges. Secondly, previous research suggests that a more basic pH environment results in improved polymer growth during the CFM (9,10). Furthermore, work reported by Burns et al. documented the effectiveness of ammonia on increasing polymer deposition and print quality when used as an intermediary agent between an initial and secondary period of cyanoacrylate fuming (4). The work presented here seeks to understand the role of the vapor and how it interacts with the print residue to allow for additional polymer growth during the CFM.

The second enhancement agent explored in this investigation, glacial acetic acid, was chosen for similar reasons. Again, the enhancement agent needed to have a sufficient vapor pressure that would allow the vapor to interact with the print without damaging the structural integrity of the fingerprint ridges. Acetic acid also contains carboxylic acid groups which were identified as the primary initiating species of ECA polymerization present in latent fingerprint residue from previous studies. Thus, if this enhancement agent coats the fingerprint ridges and improves the supply of initiators on the print ridge for the polymerization that occurs during the CFM, then the enhancement agents will be effective. Additionally, recent research results indicate that acids such as acetic and propionic are capable of regenerating clean prints under humid conditions. Acetic acid has been used to regenerate an 8-month-old clean print deposited by a prepubescent child to yield a cyanoacrylate-developed print equal in quality to that of a freshly deposited print (9). During this preliminary effort, Lewis et al. optimized a method of regenerating clean prints using a hot (65°C) fine-vapor mist of 75% acetic acid. This method consistently regenerated adult-ecrine and children prints that have aged up to 8 months prior to fuming. The quality of these regenerated and developed ecrine prints was found to be equivalent to fresh-fumed clean prints.

Previous studies of the kinetics of ECA polymerization during cyanoacrylate fuming from monolayer surfaces revealed that the carboxylic acid functionality, present in acetic acid, initiates and polymerizes the cyanoacrylate vapor at a deposition rate that is an order of magnitude higher than the deposition rates observed from surfaces containing the amine functionality, found in the ammonia vapor (11). Therefore, a direct comparison of the influences of the two enhancement agents will provide insight into the mechanism by which the enhancement agents alter the development of latent fingerprints by the CFM.

## Method

### *Fingerprint Deposition*

Reproducible deposition of latent fingerprints is a necessary condition for any quantitative fingerprint study. Therefore, all foreseeable measures were taken to ensure that the latent prints used in this study are as consistent and reproducible as possible. For all fingerprints used in this study, the researcher's right hand was washed thoroughly using nonfragrant hand soap and dried using a lint free cloth (Betawipe). The researcher's hand was then kept out of contact with all surfaces (even itself) for a period of 5 min. This provides a standard amount of time during which ecrine sweat is accumulating at the fingertip. The fingertip is then depressed onto the chosen substrate for 5 sec. After this, the fingertip is removed and the substrate containing the latent print is ready for either development or aging.

### *Substrate Preparation*

Substrates used in this investigation are designed for use with the QCMB. For these samples, the substrate is a 5 Mhz gold-coated QCMB crystal (Maxtek, Cypress, CA). These substrates were used as received.

### *The CFM*

Fingerprint development by the CFM was achieved by transferring approximately 2 g of ECA (Sirchie, Youngsville, NC) to an aluminum-weighing dish (VWR), which is heated by a hot plate to a temperature of 150°C. Once white fumes began evolving from the dish, the system was enclosed in a chamber of volume 2500 cm<sup>3</sup> with the surface to be developed suspended 5 cm above the vapor source for 10 min. While the length of cyanoacrylate fuming is longer than fingerprint developers will often expose a latent print, this extended fuming time was designed so that the entire kinetics of the polymerization that occurs during development could be captured.

### *Latent Fingerprint Enhancement*

Two enhancement agents, ammonia (Fisher Scientific, Suwanee, GA) and glacial acetic acid (Fisher Scientific), were investigated for their ability to enhance the amount of polymer growth onto a finger print surface. Print deposition onto the QCMB sensors was achieved by using the method described above using a partial right index finger. The finger was depressed such that only the piezoelectrically active area of the sensor received print residue. The restriction of the size of the print to the piezoelectrically active area of the crystal necessitated the use of a partial print rather than an entire normal print. To establish a reference from which any enhancement could be gauged, the fuming of unaltered, aged prints was also examined. This provides information about the deposition rate of poly(ethyl cyanoacrylate) (PECA) onto an aged print that can be used as a baseline to determine the influence of the enhancement agents on the CFM efficiency.

To observe the effect of the exposure of the print to small molecule gases on the print development process, the aged prints were exposed to vapors of ammonia or glacial acetic acid. The exposure was carried out by mounting the aged print 3 inches above a 100-mL beaker containing 25 mL of the desired liquid for a period of 5 or 10 min. This allows sufficient time for the vapor of the liquids to interact with the print residue. After the exposure period, the sensors were immediately moved to the fuming chamber where they were developed under standard fuming conditions. After monitoring the deposition onto the print surface, the print was photographed using a Nikon 5.0 Mpixel digital camera for visual comparison of the developed prints.

### *QCMB*

The QCMB is a highly sensitive acoustic wave sensor, where the inverse piezoelectric effect allows an applied current to generate a transverse acoustic wave throughout the quartz sensor. The addition of material onto the sensor surface is detected through shifts in the frequency of the oscillating crystal as the acoustic wave expands to include the material. In this investigation, a Maxtek QCMB equipped with a 5 Mhz gold-coated quartz sensor is utilized to monitor the growth of the PECA on the QCMB crystal that is formed as the cyanoacrylate vapor polymerizes from the fingerprint residue.

## Results and Discussion

### *Effects of Aging on Latent Fingerprints and How It Influences the CFM*

This study seeks to address the influence of fingerprint aging on the growth rate of polymer formed during cyanoacrylate fuming. It is well known that the quality of a latent fingerprint that is developed by the CFM decreases as a function of aging (1,5). However, the primary components of the print residue that are responsible for the initiation of the cyanoacrylate polymerization are not volatile and should therefore remain anchored to the substrate during the aging process. This suggests that other environmental factors must be impacting the ability of the CFM to develop the print. To examine this phenomenon, additional aspects of the aging process are considered. These variables include the exposure of the print to air currents and light. Control prints were also aged in containers that shielded the prints from both light and air flow. To examine the influence of these variables on the aging process, QCMB is used to monitor the deposition of ECA onto the fingerprint ridges during the CFM. The developed prints were subsequently photographed using a Nikon 5MP digital camera to allow for qualitative judgment of print quality.

During the fuming process, the mass of the PECA that grows off the print was monitored as a function of fuming time by QCMB to produce a graph of mass on the print as a function of time, seen in Fig. 1. The mass is found to consistently increase throughout the duration of the fuming period. The slope of the line is then extracted to quantify the rate of polymer growth from the print during fuming, known as the average deposition rate (adr). The adr is extracted from the development of prints that are aged up to 7 days and is plotted as a function of aging time in Fig. 2. Here, the deposition rate of PECA onto the fingerprint ridges decreases dramatically as a function of aging for prints that are exposed to light and air currents. The prints that were not exposed to light and air flow during the week of aging retained the same rate of deposition as the freshly deposited fingerprints. Clearly, the exposure of the print to light and airflow during aging cause a reduction in the deposition rate during cyanoacrylate fuming.

One explanation for the observed decrease in deposition rate when the print ages is that the print loses water and becomes brittle. The brittle print is then susceptible to erosion from air currents

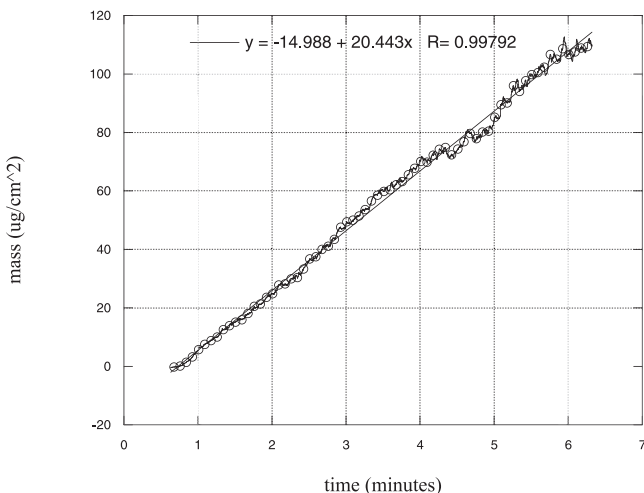


FIG. 1—The growth of ECA onto a freshly deposited latent print on a QCMB crystal as a function of time exposed to the monomer vapor.

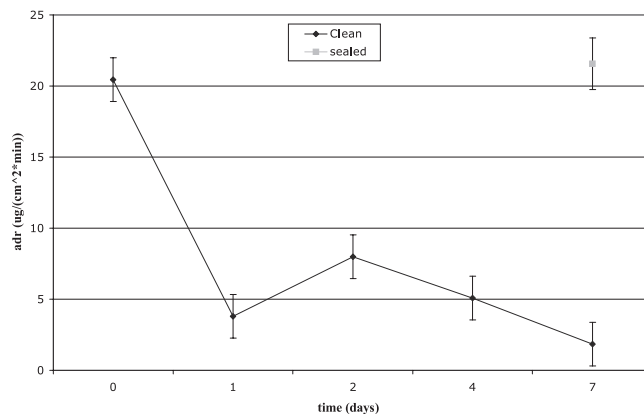


FIG. 2—A comparison of the average deposition rates of PECA from latent prints that are allowed to age in the presence of light and air flow to that of week-old prints that were aged in containers that prevented exposure to air flow.

that cross the print surface. This process can be thought of much like the weathering of a hillside. Therefore, the initiators that remain on the print surface retain the ability to polymerize the ECA vapor; however, there are fewer of them. Fewer available initiating sites on a fingerprint residue results in a decrease in the deposition rate of polymer onto that surface, as is consistent with the results of this experiment.

A second possible reason is that the primary initiator of the fingerprint residue, the lactate ion, degrades due to the exposure to ultraviolet light. This degradation also destroys potential initiating sites and results in a decrease in the rate and amount of polymer grown from the fingerprint surface.

Photographs of the aged prints that were developed by ECA fuming were taken with a digital camera. Figure 3 shows the images of the developed fingerprints for various stages of aging with exposure to light and air current as well as the image of a week-old print that was sealed from light and air flow during aging. The fresh print (aged 0 days) has good ridge definition and contrast with the substrate. After just 1 day of aging, however, periodic breaks in the ridgelines become evident. After an entire week of aging in the presence of light and airflow, the ridge definition is very poor with the points of development becoming increasingly sporadic. The contrast between the polymer and the substrate is still good; however, there exist fewer areas where polymer grows. In contrast, the print that was aged in the absence of light and airflow retains most of the ridge definition.

These results conclusively show that the exposure of the print to air current and light during that aging period plays a significant role in the loss of print quality associated with older prints when developed by cyanoacrylate fuming. Dehydration during aging, by itself, does not alter the ability of the fingerprint residue to initiate and polymerize the ECA vapor during development with the CFM.

Additionally, closer inspection of the developed prints provides some insight into the relative importance of the exposure to light and airflow on the degradation process. If the exposure to air flow is considered, the erosion of the brittle salt from the surface should leave periodic gaps in fingerprint ridges. However, the degradation of the polymerization initiators due to exposure to light would be expected to provide a more uniform loss of initiator across the print. Inspection of Fig. 3 shows that the initiator is lost in a periodic fashion, suggesting that the exposure to airflow is an important process by which latent prints degrade, presumably simultaneous to UV degradation due to exposure to light.

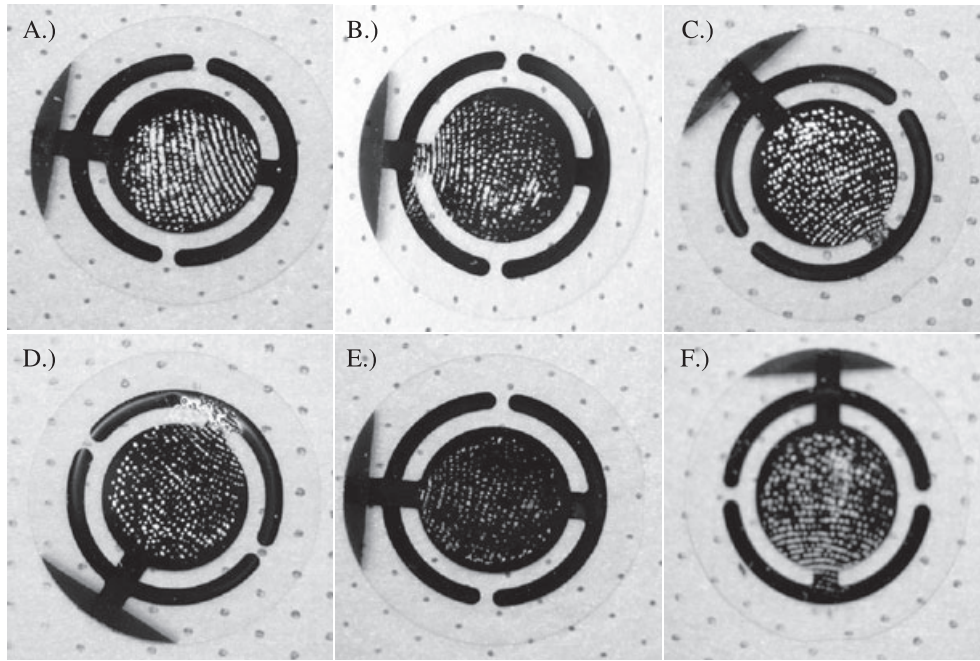


FIG. 3—Eccrine-based latent fingerprints developed, on QCM crystals, by the CFM that have been aged for (A) 0 days, (B) 1 day, (C) 2 days, (D) 4 days, (E) 7 days, and (F) 7 days sealed from air current during aging.

Regardless, these results indicate that the aging of latent prints can be mitigated, and the subsequent decrease in print quality that can be attained by developing using cyanoacrylate fuming, by sealing the print such that exposure to air currents and light can be eliminated. Moreover, the results also indicate that the loss of the initiator in the print is the fundamental process that is responsible for the common observation that latent fingerprints that are aged in the environment do not develop well by cyanoacrylate fuming, and provides critical fundamental information that can be utilized to develop methods to enhance the quality of aged prints that are developed by superglue fuming, as will be described in the next section.

#### *The Enhancement of Aged Latent Fingerprints to Polymerize ECA Vapor During the CFM*

In the previous section, the results suggest that the decrease in the quality of aged latent fingerprints that were developed using the CFM is due to the loss of initiator. However, other techniques are able to develop aged fingerprints, thus print residue must remain on the surface. That remaining residue is, however, no longer capable of initiating polymerization to produce a visible impression of the fingerprint ridges with cyanoacrylate fumes. Thus, developing a methodology through which the ability of a degraded latent fingerprint to polymerize the ECA vapor is recovered would be very beneficial. This is attempted by reintroducing initiator to the print by exposing them to small molecule vapors.

The first enhancement agent studied was gaseous ammonia. Previous studies have suggested that the creation of a more basic environment enhances an initiator's ability to polymerize ECA vapor. To explore this potential, latent prints that had been degraded for 1 week in the presence of light and airflow were exposed to the vapor above conc. ammonia for either 5 or 10 min immediately prior to development with the CFM. The influence of the exposure to ammonia is shown in Fig. 4A where the growth of PECA onto the fingerprint surface is plotted as a function of

fuming time for both the enhanced prints as well as prints that received no enhancement. Exposing the prints to the ammonia vapor prior to development with the CFM does, in fact, lead to an increase in the amount of observed polymer growth. A quantitative measure of this observed enhancement can be obtained from the average deposition rate extracted from each curve, as seen in Fig. 4B. The 10-min exposed prints show clear enhancement leading to a deposition rate that is an order of magnitude higher than that of the unaltered aged print. Additionally, if the images of the developed prints are examined (Fig. 5), it becomes clear that the additional growth occurs along the fingerprint ridges. Although it is difficult to determine print quality from this photograph, the enhanced prints do appear to have better ridge definition than the unaltered print.

Thus, exposing a degraded latent print to ammonia vapor increases polymer growth and improves ridge definition. However, so as to understand how this process occurs, an additional enhancement agent must be examined. Here, acetic acid is chosen to provide carboxylate groups, which have been shown to be effective initiators for cyanoacrylate fumes.

The enhancement of degraded latent fingerprints with glacial acetic acid occurred using the same conditions as with ammonia. The development process was again monitored using the QCM and the growth of polymer from the acetic acid-enhanced prints can be seen in Fig. 6A. In the case of acetic acid, both the 5- and 10-min exposed prints show large increases in rate of polymer growth. Quantification of the deposition rates of PECA onto the acetic acid enhanced prints (Fig. 6B) shows that even the prints that were exposed to acetic acid for 5 min produced deposition rates that were an order of magnitude greater than the unaltered prints. Also, similar to the ammonia-enhanced prints, images of the developed fingerprints (Fig. 7) show significantly more ridge definition than the aged, unaltered fingerprint.

Thus, these data show that both ammonia and acetic acid vapor effectively recover the ability of a degraded latent fingerprint to polymerize ECA vapor. Moreover, if the enhancement produced by

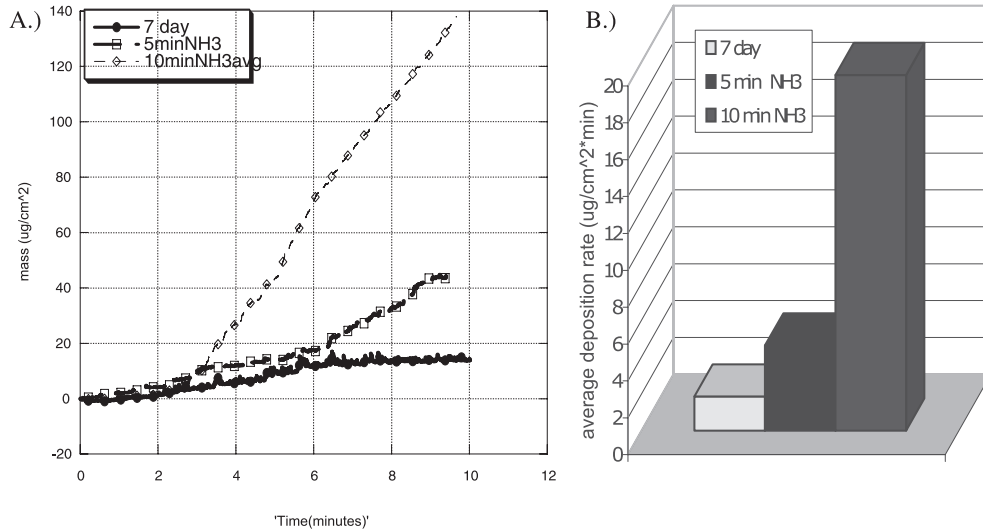


FIG. 4—(A) A comparison of the mass of ECA accumulating on the QCM crystal containing week-old latent prints that either received no enhancement (filled circle), enhancement from 5-min exposure to ammonia vapor (open square), or enhancement by 10-min exposure to ammonia vapor (open diamond) prior to development with the CFM. (B) A direct comparison of the effect of exposure to ammonia vapor on the average deposition rate of ECA onto week-old latent prints.

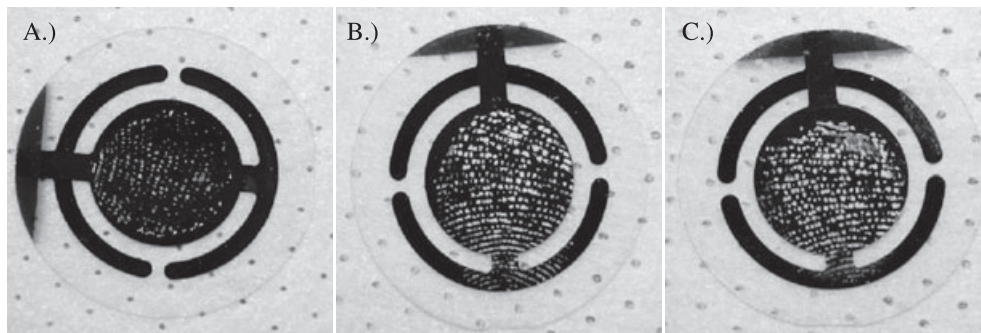


FIG. 5—Photographic images of latent prints aged for 1 week, then receiving (A) no enhancement, (B) 5-min enhancement with ammonia, and (C) 10-min enhancement with ammonia prior to development with the CFM.

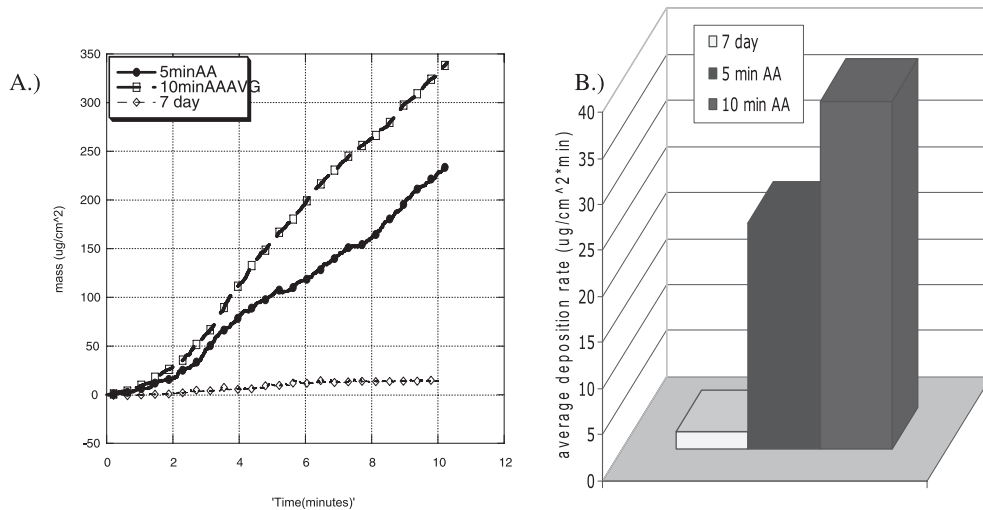


FIG. 6—(A) A comparison of the mass of ECA accumulating on the QCM crystal containing week-old latent prints that either received no enhancement (open diamond), enhancement from 5-min exposure to acetic acid vapor (closed circle), or enhancement by 10-min exposure to acetic acid vapor (open square) prior to development with the CFM. (B) A direct comparison of the effect of exposure to acetic acid vapor on the average deposition rate of ECA onto week-old latent prints.

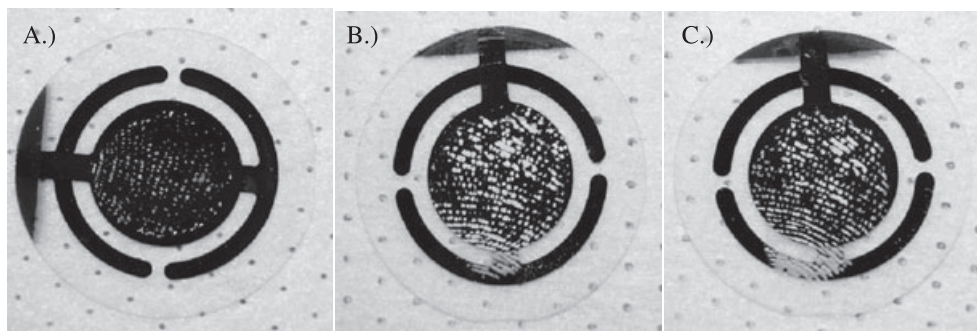


FIG. 7—Photographic images of latent prints aged for 1 week, then receiving (A) no enhancement, (B) 5-min enhancement with acetic acid, and (C) 10-min enhancement with acetic acid prior to development with the CFM.

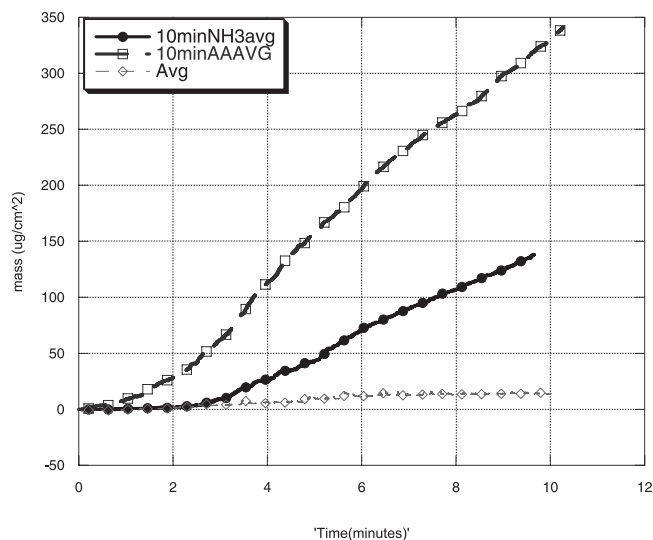


FIG. 8—A comparison of the mass of ECA accumulating on the QCM crystal containing week-old latent prints that either received no enhancement (open diamonds), enhancement from 10-min exposure to ammonia vapor (closed circles), or enhancement by 10-min exposure to acetic acid vapor (open squares) prior to development with the CFM.

the ammonia is compared to that produced by the acetic acid, insight into the nature of the enhancement can be attained. Figure 8 shows a direct comparison of the observed enhancement of the two enhancement agents after exposure for 10 min. Clearly, the acetic acid is significantly more effective at increasing the amount of polymer growth. In a previous investigation into model fingerprint surfaces, the carboxylic acid functionality was found to polymerize ECA vapor with a deposition rate that is an order of magnitude greater than that of a primary amine. The ability of acetic acid to enhance print quality suggests that the enhancement agent is coating the fingerprint ridges and providing a new source of initiators. This implies that a significant portion of the polymerization is occurring from the amine or carboxylate groups that are deposited from the ammonia or acetic acid vapors, respectively. In this case, the carboxylic acid would be more effective at polymerizing the ECA vapor than the amine, which is consistent with these reported data. If the nature of the enhancement were a result of altering surface composition by exposure to the enhancement agents, then it would be expected that the ammonia would provide greater enhancement, due to its basic pH.

TABLE 1—A comparison of the effectiveness of the two enhancement agents studied (acetic acid and ammonia) to increase the average deposition rate of ECA onto the print surface during development with the CFM.

Type of Enhancement	Average Deposition Rate ( $\mu\text{g}/\text{cm}^2/\text{min}$ )	% Increase
None	1.85	—
5 min $\text{NH}_3$	$4.62 \pm 1.15$	250
10 min $\text{NH}_3$	$19.28 \pm 4.82$	1042
5 min AA	$24.58 \pm 6.14$	1329
10 min AA	$37.88 \pm 9.46$	2048

However, a comparison of the magnitude of the enhancement of the deposition rate, as seen in Table 1, suggests that the enhancement process is more complicated than merely fingerprint ridge coating. The 10-min exposure to ammonia produced an increase in the deposition rate of just over an order of magnitude over that of the unaltered aged print, while the 10-min exposure to acetic acid produced an increase in the deposition rate that is double that of ammonia. However, model studies indicate that the carboxylate is an order of magnitude more effective as an initiator than the primary amine (11). This discrepancy may be explained by the fact that each agent alters the pH of the residue as well as coating it. The acid, thus, lowers the pH of the print, while the basic ammonia raises it. This pH effect will slightly reduce the deposition rate of the acetic acid-enhanced prints, while increasing the deposition rate of the basic ammonia-enhanced prints. Therefore, rather than an order of magnitude difference between the efficacy of the two enhancement agents, the mediated difference of a factor of two is observed.

It should be noted that this enhancement process has been found to be effective on aged fingerprints that reside on surfaces other than gold, including glass slides and silicon wafers, and thus we expect that this enhancement process will be useful to forensic agents on a wide range of latent prints obtained in the field. Additionally, it is curious that the enhancement occurs only on the print ridge, when one might naively assume that the exposure of the print to the vapors would result in the deposition of the enhancement agent across the whole surface, including between the ridges of the print and on the surface surrounding the print. Our results show that this does not occur, presumably because the organic nature of the print residue attracts the acetic acid and ammonia vapor more than the inorganic surrounding surface, and thus there exists more enhancement agent on the ridge than the surrounding surface.

## Conclusions

In this paper, the decrease in print quality of aged latent prints that are developed by superglue fuming is examined. It was found that the dehydration of the fingerprint residue is not the reason for the decrease in the rate of polymer growth during fingerprint development of aged prints. However, when the dehydration of a latent print is coupled with exposure to light and air currents, significant decreases in the amount of polymerization, as well as the apparent print quality, was observed. It appears that the erosion of the dried print by airflow and UV degradation of the initiators present in the print results in a loss of the initiators on the print surface as the print ages, and this translates into a decrease in the amount of cyanoacrylate that polymerizes off of the aged print and a concurrent decrease in developed print quality.

Additionally, a methodology was established by which an aged latent fingerprint can recover its ability to initiate and polymerize ECA by exposure to select vapors. Two enhancement agents, ammonia and acetic acid, were tested for their ability to enhance degraded latent fingerprints. Exposure of the aged prints to both enhancement agents showed increases in the amount of polymerization that occurred during fuming, as well as increases in apparent print quality. The nature of the enhancement appears to be primarily that of a ridge coating process; however, additional studies are needed to verify this. Regardless of the mechanism of enhancement, the feasibility of enhancing aged latent fingerprints is demonstrated and shows great promise as a tool for forensic scientists to recover aged latent fingerprints using cyanoacrylate fuming. Due to the greater observed enhancement, as well as the toxic nature of ammonia, which may interfere with DNA testing, acetic acid holds the greatest promise as an enhancement agent.

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