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Cultivating Methods to Enhance the Quality of Aged Fingerprints Developed by Cyanoacrylate Fuming.

I. Project Summary:

In many forensic investigations, the recovery and identification of latent fingermarks are vital in recreating a crime scene with the purpose of identifying the individual committing the criminal offense. A standard, cost-effective, and straightforward method for developing these latent prints from a nonporous substrate is the cyanoacrylate fuming method.[i- v] This method involves the exposure of a latent print to the fumes of ethyl cyanoacrylate (ECA), more commonly known as superglue. Unfortunately, the quality of the resultant prints after development is not always ideal. For instance, prints that are exposed to the environment for extended periods of time tend to develop poorly by superglue fuming, presumably due to degradation of the components of a print that inhibits the growth of polymer from the print friction ridges during the fuming process. Moreover, most advances in the application of superglue fuming to develop latent prints, such as increasing the humidity in the fuming chamber, have been discovered empirically. While these empirical improvements aid field agents in the use of superglue fuming to develop fingermarks in the near term, the empirical nature of the progress provides no foundation for further enhancement of the method.

For instance, it has been assumed that the role of the increased humidity in improving print quality is that the water vapor acts as an initiator in the polymerization of the cyanoacrylate during the superglue fuming process. However, our recent results unequivocally demonstrate that water is not the initiator of the cyanoacrylate fumes.[vi,vii] Thus, while this empirical discovery has aided forensic scientists in the near term, it provides no fundamental insight that can be utilized to elaborate new methods to further improve the development of latent prints by ECA fuming. The **only** way that the superglue fuming process for latent print development can be rationally optimized is to cultivate methods to enhance the quality of fingermarks that are developed by superglue fuming by developing a more precise understanding of the molecular level processes that occur during the growth of polymer off of the fingermark ridges during the fuming processes. This information can then be utilized, along with the knowledge of how the chemical structure of a fingermark changes during aging, to provide a valuable suite of fundamental information. This suite of fundamental information can then be utilized by forensic scientists to rationally design and optimize the conditions for the fuming of a latent print to bias the outcome of the fuming process towards a well-developed print, regardless of the condition of the print. It is the goal of this research program to provide this fundamental information.

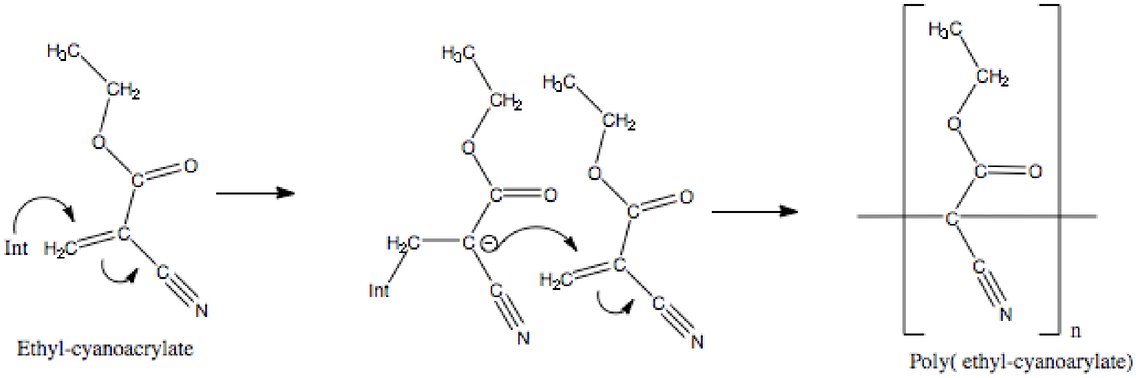
Therefore, the experiments completed in this project investigate the molecular level processes that impact the superglue fuming of a latent print in order to provide fundamental information that can be utilized by forensic scientists to optimize the fuming process. These include experiments to understand the role of water vapor in the chamber on the print development process by fuming, to correlate the changes that occur in a latent print with aging to the processes that occur during the development of aged latent prints, and to understand the role of temperature on the print fuming process.

The results of this research program provide additional insight into the molecular level details of the superglue fuming of fingermarks. It is important to emphasize that these results do not yet provide explicit protocols to improve the quality of latent prints in the field, but offer insight by which to design such protocols. Further research is required to fine-tune and test such protocols. However, it must be underscored that without this foundation, the development of such protocols is empirical and inefficient. Our results provide significant contributions to this foundation.

More precisely, the results indicate that the importance of humidity in the fuming of latent fingermarks comes from its role as a solvation agent for the initiators of the polymerization, creating an accessible solvated ion-pair rather than the less reactive tightly bound ion-pair. It is also found that aging results in UV degradation processes that decrease the pH of the fingermark, inhibiting the polymerization of ECA that is required to effectively fume a latent print. Fingermarks with less exposure to UV radiation will, thus, provide better prints. Finally, the effect of temperature on the quality and amount of polymer formed on a fumed print was studied, showing that lower temperatures provide more polymer and better quality prints. Analysis of the results indicates that lowering the temperature improves the rate of ECA polymerization, and thus appears to be an effective and easily implemented method to improve the efficiency and quality of fumed latent prints.

II. Project Background:

The forensic community has utilized the fuming of cyanoacrylate esters as a method to develop latent fingermarks for over 20 years.[viii,ix] The specific mechanism by which this technique develops the fingermark is that when the fingermark comes in contact with the cyanoacrylate monomer in the vapor, white polymer, poly(ethyl cyanoacrylate) (PECA), grows along the ridges of the print, with virtually no polymer deposited on background areas.[i,iii] The ethyl cyanoacrylate polymerizes on the ridges of the fingermark to form micron size morphologies, such as noodles or blobs. These morphologies provide the optical contrast that is needed to visualize the fingermark. The technique is known to be most effective when the latent print is on a non-porous substrate such as metals or plastics. Additionally, if the substrate on



Scheme 1: Structure and polymerization of ethyl cyanoacrylate to poly(ethyl cyanoacrylate). Int is an initiator

which the print lies is either white or transparent, secondary techniques can be employed to exude contrast.[x]

The structure of ECA and the chemical reaction that results in its polymerization is shown in Scheme 1. Unfortunately, neither the mechanism of polymerization nor the molecular-level reason why polymer grows from the fingermark ridges but not between the ridges is well understood. Nor is it well understood how to optimize this process. Since its inception, there have developed, empirically, many methods by which ECA can be used to develop latent prints. Currently, the method of choice for the fuming of latent prints using ECA involves the rapid heating of the superglue.[i,iii] This produces glue as a vapor, which then reacts with the fingermark residue to grow polymer along the print ridges. Typically prints are completely developed within two minutes.[iii]

Unfortunately, there is very little literature available pertaining to the vapor phase polymerization of cyanoacrylates. Studies observing cyanoacrylate growth from snowflakes, ice droplets, and tobacco smoke utilize the technique but do not investigate the growth process.[xi,xii] Therefore, solution-based chemistry must guide our understanding of the fuming process. The polymerization of ECA in solution has been well documented.[xiii- xix] ECA, in the presence of a Lewis base, is known to polymerize via an anionic mechanism. An anionic polymerization consists of an anionic Lewis base initiator attacking a monomer, where the negative charge is then transferred to the monomer, which subsequently attacks another monomer. This process is propagated to grow the polymer chain until one of two events occurs. In the absence of terminating species, the polymer will continue to propagate until the monomer supply is exhausted. At this time, the anion will remain as what is referred to as a living polymer, which retains the ability to propagate further should additional monomer be introduced to the system. If there is a suitable terminating species present, the anion will be terminated upon colliding with the terminating agent regardless of how far the polymerization progressed. In most cases, successful anionic polymerization requires the careful choice of initiator and the complete absence of terminating agents such as water, oxygen, and especially acids.

There are several other important features of the solution polymerization of ECA that are relevant to the fuming process. Although ECA propagates anionically, the anion is much more stable than other conventional anionic polymers. The polymerization proceeds even in the presence of significant quantities of O_2, CO_2, air, and even H_2O,[iii,xv,xvii,xx] all of which terminate conventional anionic polymerizations.

There have also been recent studies that have sought to create methods to improve the development of latent prints by cyanoacrylate. These include the work of Burns et al[i], who examined the effect of exposing a latent print to basic (ammonia) vapors prior to fuming and correlated this exposure to the extent of polymer deposition during fuming, where Fourier Transform Infrared Spectroscopy (FTIR) was used to quantify the extent of polymer deposition.

Lewis et al[iii] have also examined the development of latent prints by superglue fuming, where their results have shown that the amount of moisture that is present in the print during fuming correlates to the quality of the print, that the cyanoacrylate polymerization is very rapid, and that the concentration of the cyanoacrylate vapors in the enclosure impacts the optimum development time. Finally, it is important to note the work of Mong, Petersen and Clauss[xxi] that also examined the constituents of fingermarks and the changes that occur to the components during aging. This study used chromatographic methods to show that with aging, the components in the fingermark residue, such as squalene, oleic, and palmitoleic acid undergo degradation processes that shorten and oxidize these compounds. This study also found an 85% loss in the fingermarks weight over two weeks, which the researchers attribute to moisture loss. The researchers equate the consolidation of a fingermark upon aging to being analogous to the drying of a varnish from a natural product oil, such as linseed oil, where the oil darkens and thickens to a varnish by oxidation processes upon exposure to air.

Thus, there exists an interesting knowledge base regarding the aging of fingermarks and the cyanoacrylate fuming method to develop latent prints, however there is still lacking a clear understanding of the molecular level interactions of the fingermark with the cyanoacrylate fumes and possible enhancement agents, an understanding that is absolutely required if researchers are to rationally design methods to improve the reliability and utility of the ECA fuming process to develop a broader range of latent prints, including aged prints. For instance, we have developed a method to improve the quality of latent prints by the replenishment of initiators based on our identification of the most effective initiators in the superglue fuming of latent prints.[xxii] We, thus, have completed a set of experiments that will provide additional information, which can then be utilized to optimize, improve, and control the fuming of cyanoacrylates to develop latent prints.

III. Experimental Procedures:

Materials.

The chemicals 11-mercaptoundecanoic acid (MUA) (Aldrich), 11-amino-1-undecanethiol hydrochloride (MUAM) (Dojindo), ethyl cyanoacrylate (Sirchie), sulfuric acid (Fisher), and 30% hydrogen peroxide (Fisher) were used as received. The solvents 200 proof ethanol (Fisher) and toluene (Fisher) were filtered using a 0.45μm PFTE filter prior to use. Nanopure water was obtained using a Milli Pore water treatment apparatus. pH adjustments were performed using perpHect pH buffers 4, 7 and 10 (Fisher). Gold substrates were obtained from Platypus Technologies and consisted of silicon wafers coated in a 5nm titanium adhesion layer and 100nm of gold. Substrates used in QCMB studies were 5Mhz AT-cut quartz crystals with a 1” diameter surface composed of a titanium adhesion layer and coated in gold (Maxtek).

Reproducible Fingermark Deposition

New glass sides were used as the substrate and weighed prior to print deposition. In order to insure the deposition of the most reproducible fingermarks, hands are washed rigorously for 5 minutes, followed by thorough rinsing. While drying for 10 minutes, the hands are kept out of contact with any objects to avoid exposure to any chemical components that are not contained in the natural occurring eccrine sweat prints. Fingermarks are then placed on glass slides and reweighed to obtain the mass of the fingermarks. For consistency, samples that were fumed with ECA within 24 hours of print deposition are referred to as fresh prints while, aged prints are samples that were left under a cover that allowed light and air flow in, yet protected from dust. The aged samples were reweighed after aging for 1, 7, 10, 14, and 30 days. While this research program is not developed as a survey, the fingerprints of 10 graduate students were used throughout this study. Experiments were completed 3-5 times to determine reproducibility and for statistical averaging.

Ethyl Cyanoacrylate Fuming and Temperature Control

Figure 1: Fuming chamber with temperature control

Fuming of ECA (Omega-Print, Sirchie) is completed in an enclosed chamber. The hotplate in the chamber is heated to 150°C, and a temperature bath (Isotemp 3016, Fisher) is set to the appropriate temperature in the range of 20 to 80 °C. The sample is clamped to a heating coil connected to the temperature bath, as shown in Figure 1, and the system is left to equilibrate for at least 10 minutes. In trials of ambient relative humidity (amb. RH), an aluminum weighing pan of ECA is placed on the hotplate directly below the sample (approx. 4” away) once the system has reached equilibrium. The chamber is then closed and the sample is exposed to ECA fumes for 10 minutes.

For trials of high relative humidity (high RH), during equilibration of the system, moisture is introduced through an opening in the lid of the chamber using a standard humidifier (PUM100, Sirchie). The pan of ECA is suspended above the hotplate and the chamber is sealed off to stabilize the moisture. Once the relative humidity reaches ~ 85% for at least 10 minutes, the dish of ECA is lowered onto the hotplate with 4” between the ECA and glass slide and fumed for 10 minutes. For all high RH trials, the RH was kept with within 85-95%. A traceable hygrometer (Control One) is used to record both the temperature and RH of the chamber. After fuming, the sample was reweighed to determine the mass of polymer accumulated on the print during the fuming process.

Self-assembled Monolayer Formation.

Gold substrates were cleaned prior to use with a 3:1 H_2SO_4 :H_2O_2 piranha solution for 1 hour followed by rinsing with nanopure water. The substrates were then immersed in either 10mM solutions of MUA in ethanol or toluene or 1mM ethanolic solutions of MUAM for 24 hours to allow for monolayer formation. After 24 hours the substrates were rinsed in ethanol and nanopure water, dried under a stream of N_2, and stored in an inert atmosphere until needed.

Molecular Weight Determination

Gel Permeation Chromatography (GPC) was used to analyze the molecular weights (number average molecular weight (M_n) and weight average molecular weight (M_w)) of the PECA chains using narrowly disperse poly(styrene) as a calibration standard. To extract the polymer from the fumed print, freshly fumed samples were submerged in 5-10mL of filtered tetrahydrofuran (THF) and sonicated for 20 minutes. Prior to injection this solution was filtered using a 0.45μL filter and concentrated down to less than 1mL. Analyses were performed at room temperature at a flow rate of 1mL/min (THF mobile phase) using a Polymer Labs GPC-20 instrument equipped with two 300mm x 7.5 mm Polymer Labs 5μm Mixed C columns, a 50mm x 7.5mm Polymer labs 5μm guard column and a Knauer K-2301 differential refractometer detector.

Quartz Crystal Microbalance (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 5Mhz 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 fingermark residue and model monolayers.

Mass Balance

To monitor the polymer growth, the mass of the polymer formed on the initiating surface was determined using mass by difference between the fumed and the unfumed surfaces. Mass measurements were performed on a Mettler/Toledo AG245 microbalance with a sensitivity of 0.01mg.

IV. Study Results:

Understanding the Role of Humidity in Superglue Fuming – It is common practice for forensic scientists to fume latent prints that are collected from a crime scene in an environment that is high in humidity, as this has empirically been shown to improve the quality of the final prints. However, it is not known *why* this humid environment provides better quality prints. The improvement has often been attributed to the presence of the water in the atmosphere, which was thought to initiate the polymerization of the cyanoacrylate fumes during the fuming process. However, our recent results unequivocally demonstrate that water is not the initiator of the cyanoacrylate fumes,[6,7] and thus there is a clear need to understand the importance of the presence of the water vapor in the fuming chamber in order to rationally optimize the fuming process.

Pursuant to this, we have completed a set of experiments to provide insight into the role of humidity on the growth of poly(ethyl cyanoacrylate) from fingermarks and functionalized surfaces that serve as models for the reactive groups within a latent print. It is clear that fingermarks are complex systems whose specific composition varies with the ethnicity, habits, and history of the donor, among others. However, in this study, we will exploit the commonality of the components in a latent print to sufficiently simplify the system such that experiments that provide insight into the essential processes that occur during superglue fuming can be completed. To do this, we take into account that our previous results indicate that sodium lactate and amino acids that are present in the latent print are active initiators in the polymerization of the superglue from a latent print.[vii] As such, self-assembled monolayers of carboxylic acid and amines, the two functionalities that can initiate ethyl cyanoacrylate in sodium lactate and amino acids, are prepared in our lab and examined to extract the ability of each functionality individually to initiate the polymerization of ECA as a function of relative humidity. In these studies, quartz crystal microbalance was used to monitor that rate of poly(ethyl cyanoacrylate) growth from latent fingermarks as well as model surfaces that mimic the functionality of latent prints. In each of these systems, the rate of growth of PECA on the latent print, carboxylic acid monolayer or amine monolayer was determined as a function of percent humidity in the atmosphere, which was controlled by a humidifier.

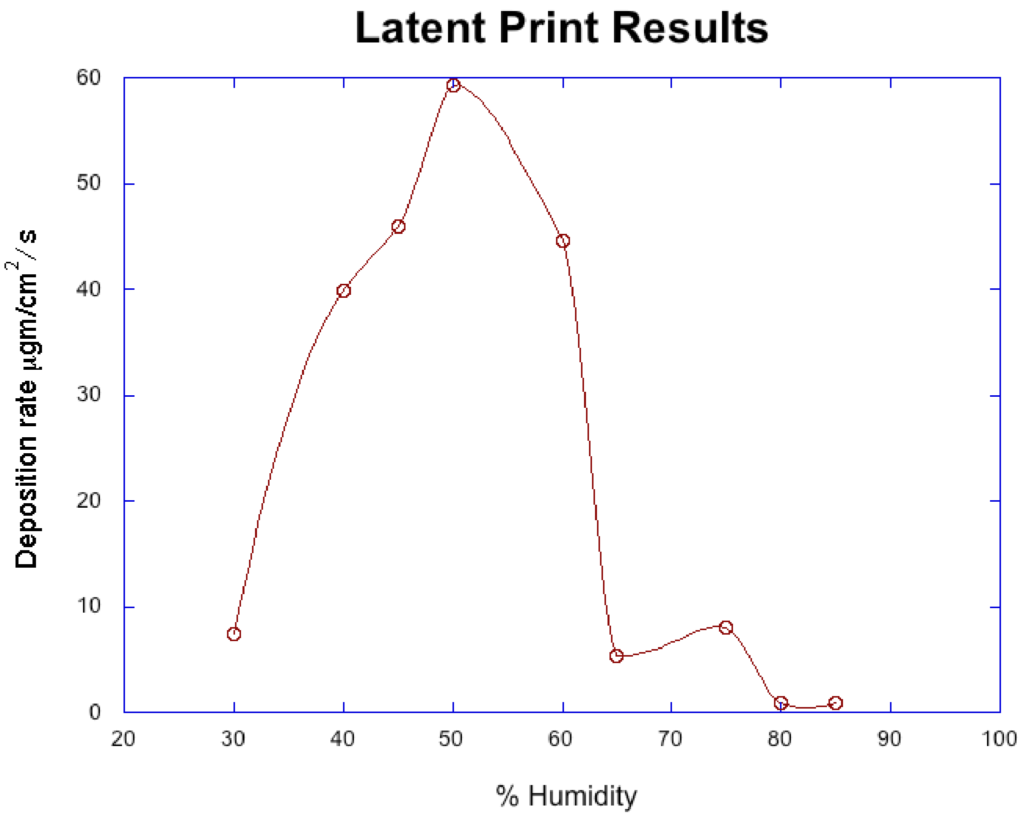


Figure 2 – Change in deposition rate of PECA on latent fingermarks as a function of humidity

The results of this experiment are shown in Figures 2 and 3, which plots the deposition rate of PECA growth as a function of percent humidity for the development of a latent print and of the amine and carboxylic acid monolayers, respectively. These results show that the growth rate reaches a maximum at moderate humidity for the print, while the combined rate of the amine and carboxylic rate in Figure 2 shows similar behavior.

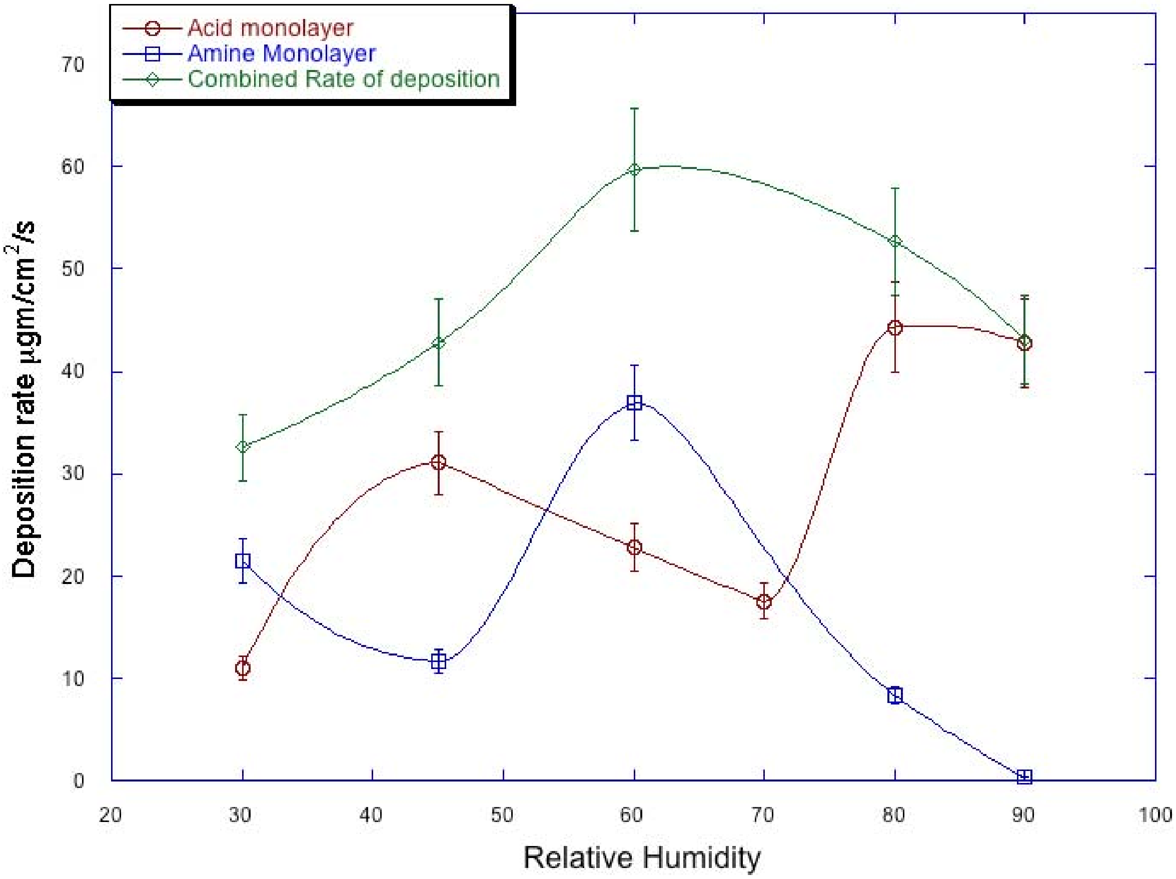
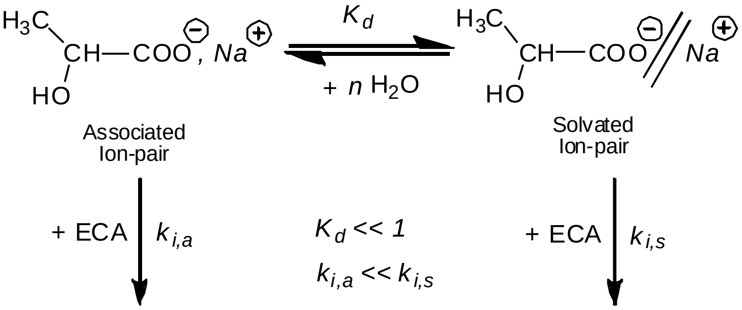


Figure 3 – Change in deposition rate of PECA on carboxylic acid and amine monolayers as a function of humidity

Our interpretation of these results is that the water in the atmosphere is important as it solvates the ion-pair (i.e. sodium-lactate pair) that is responsible for reacting with the ethyl cyanoacrylate monomers to initiate the polymerization, which improves the rate of initiation and propagation in the polymerization of the ECA.

This can be further explained by recalling that the growth of PECA from the latent fingerprint originates from sodium lactate, which acts as the primary anionic initiator for ECA. As the p*K*a value of lactic acid is lower than that of the propagating ECA enolate, a slow or incomplete initiation is expected ($k_i << k_p$). Moisture present in the print keeps the sodium lactate in the form of solvated ion-pairs that are readily able to initiate the ECA. The effect of humidity observed in these experiments can be attributed directly to the behavior of this ion-pair dissociation.[xxiii]



Scheme 2: Initiation of ECA through dissociation of sodium lactate ion pairs from latent fingerprints under fuming condition.

For example, for the sodium lactate system, where the lactate ion is known to be an effective initiator, at low humidity there is very little water present, and most of the sodium lactate is present as a salt, which is a very tightly bound ion-pair. As such, the lactate anion is bound to the sodium and not readily available to grow the polymer chain. Sodium lactate is a weak electrolyte and exists in equilibrium with associated and solvated ion pairs in the presence of moisture (Scheme 2). The rate of initiation of ECA by associated ion pairs of sodium lactate is significantly lower or negligible relative to solvated ion pairs, which have increased inter-ionic distance ($k_{i,a} << k_{i,s}$). Thus the dissociated proportion of sodium lactate determines the number of chains that initiate from the latent prints. Extensive research in the area of ion-pair chemistry of anionic polymerization in polar solvents has indicated that the conversion of such associated (or contact) ion pairs into solvated ion pairs is an exothermic process.[xxiv,xxv] An increase in water vapor allows the ion-pair to solvate, which in turn makes it more accessible to grow polymer chains. The decrease in growth at very high humidity is most likely due to the condensation of water on the surface or the ability of water to terminate the polymerization, both of which slow the polymerization of ECA.

One way to test this interpretation is to *controllably* alter the strength of the ion pair in an anionic polymerization of ECA and monitor the change in the polymerization rate and molecular weight as a function of the strength of the ion pair binding. Because the anion is "chaperoned" by its cation, the reactivity of the ion pair is reflected in the reactivity of the anion.[xxvi] Theoretically the distance between the ion pair, or how loosely the two ions are bound together, increases through solvation of the counter ion with increased humidity, which can account for improved initiation by the anion and propagation of the monomer. It is also known that larger counter ions are more loosely bound[xxvii] therefore creating a mechanism to tune the strength of the ion pair and test whether the state of the ion pair in the initiator and at the end of the growing polymer chain is the dominant factor that controls the polymerization with humidity. Therefore, monitoring the PECA that is grown from a group of initiators where the strength of ion pair bonding is systematically decreased by increasing the size of the counter-ion will test our interpretation of the role of humidity in the fuming process.

Therefore, we have superglue-fumed droplets of aqueous solutions (4.9 mol%) of sodium lactate, potassium lactate, and tetrabutyl ammonium lactate to quantify the impact of the availability of the ion pair to reaction during the polymerization process. Figure 4 and Table 1

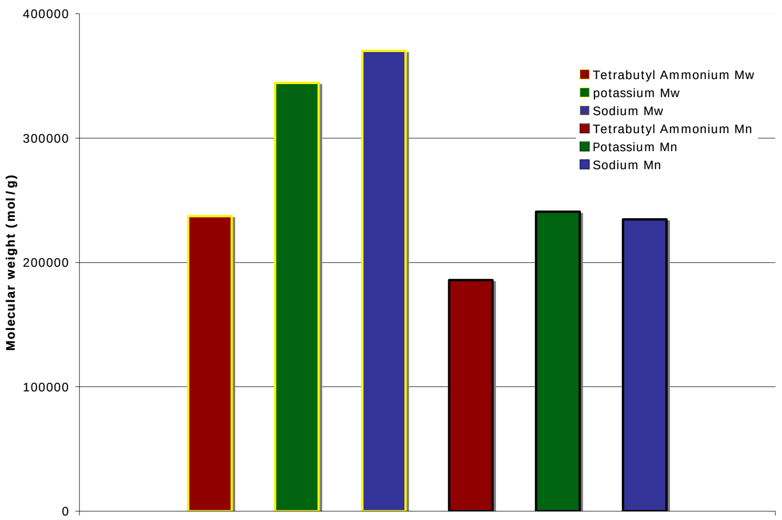


Figure 4 – Molecular weight results for 4.9% lactate solutions exposed to fuming ECA for 10 minutes under ambient conditions.

show these results, which documents the molecular weight as determined by size exclusion chromatography and mass of the resultant polymer from the fuming of each initiator solution for 10 minutes at ambient humidity (~ 40%). These results are quite interesting, in that the larger, more loosely bound ion pairs give lower molecular weights and more polymer. The more loosely bound ion pairs will initiate and propagate more quickly than the more tightly bound ion-pairs. More initiation means more chains, and if all else is equal (amount of monomer to react with, propagation rate, etc…) will result in more, shorter chains, i.e. a lower molecular weight. Thus, these results indicate that the ion pair availability dominates the initiation and polymer chain growth, where the increased initiation and propagation results in the production of more polymer.

Table 1

Initiator	Mass of PECA formed (mg)
Sodium Lactate	1.75
Potassium Lactate	2.36
Tetra butyl ammonium Lactate	3.09

Thus, these results indicate that improved accessibility of the anion to grow a polymer chain during ECA fuming dominates and promotes polymer growth. This result supports our interpretation that the role of the humidity on the growth of polymer during the superglue fuming of fingermarks is dominated by its role of solvating the ion-pair that acts as initiator, improving its accessibility. This change in structure increases the growth of poly(ethyl cyanoacrylate) from latent prints during superglue fuming, which in turn improves the quality of the developed fingermark.

Understanding the Aging Process of Latent Prints and its Impact on Superglue Fuming

It is well known that the visual quality of a fumed fingermark that has aged in the environment is much poorer than that of a fumed fresh print. It appears that the polymerization of the ECA fumes does not readily initiate from the older print due to changes in the print structure during aging. A significant amount of information is known about the constituents of latent prints[xxviii,xxix] and the chemical changes that occur in fingermarks as they are aged in the environment.[xxi] As was mentioned in the background, there is evidence[xxi] that the larger organic compounds that exist in a fresh fingermark undergo oxidation upon aging in the atmosphere by which these compounds degrade and the chemical composition of the prints is altered. This oxidation is also accompanied with substantial weight loss in the first two weeks of aging, attributed to moisture loss.

However, given that water is not the initiator for the polymerization that occurs during fuming,[6,7] the poor print development and polymer deposition that occurs upon fuming an aged print is not merely due to the "drying out" of the print, but must correlate to specific changes in the chemical structure of the print that occur during aging. Recent results indicate that the lactate ion is an important initiator in the fuming of latent prints and readily degrades to the pyruvate ion, as depicted in Figure 5. As can be seen in this figure, pyruvic acid also contains a carboxylate functionality, and thus it is not clear whether this

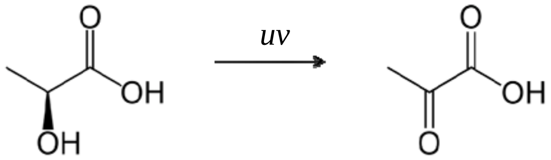


Figure 5 – Degradation of lactic acid to pyruvic acid

compound will also initiate the polymerization of ECA during superglue fuming. If it will, then this degradation process is not critical to the loss of quality of aged prints. It is worth noting that pyruvic acid is a stronger acid than lactic acid, and thus has a lower pK_a value than lactic acid (2.49 vs. 4.756). This means that a solution of unbuffered pyruvic acid has a lower pH than a unbuffered lactic acid solution.

To test the ability of pyruvic acid to initiate the polymerization of poly(ethyl cyanoacrylate), we dotted aqueous solutions of sodium lactate or pyruvic acid onto silicon wafers, with concentration equivalent to the total ion concentration that would be expected in eccrine sweat. These wafers were then fumed with ethyl cyanoacrylate at 150 °C at 40% RH,

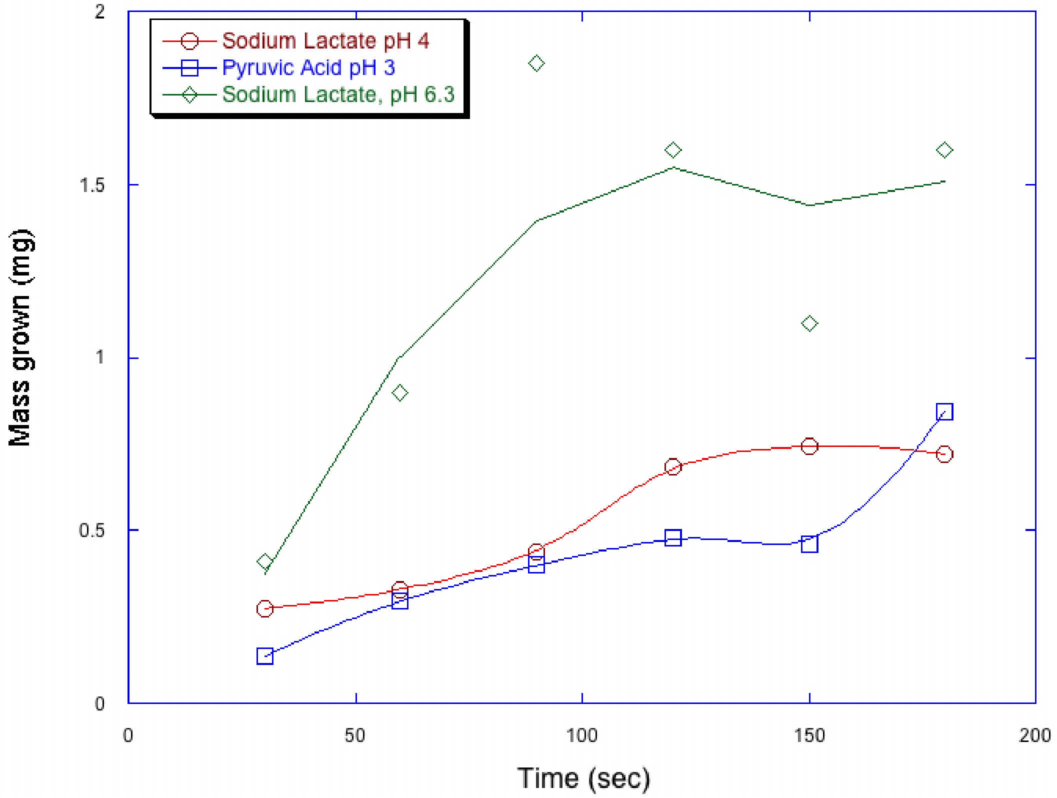


Figure 6 – Growth of PECA by fuming droplets of sodium lactate and pyruvic acid

varying the pH and fuming time. In these experiments the amount of polymer formed is monitored, which is shown in Figure 6. These results show that the pyruvic acid can polymerize ECA at a pH of 3, which is the resultant pH of the solution due to the strength of the acid. However the amount of polymer grown is less than that of the sodium lactate solution at its natural pH (~6.3). When the pH of the sodium lactate is brought down by introduction of a buffer to that of the pyruvic acid solution, its ability to initiate the polymerization of ECA approaches that of pyruvic acid.

Therefore, these results indicate that the degradation of sodium lactate to pyruvic acid during aging does deteriorate the ability of the components of the latent print to polymerize ECA and develop the print. However, this is primarily due to the fact that the pyruvic acid lowers the pH of the print, increasing the amount of H^+ ions that are present and available to terminate the growing polymerization reaction.

This is interesting for the forensic scientist from two perspectives. First, limiting the degradation by exposure to UV radiation becomes one method to limit the decrease in print quality. Obviously this is not possible for all samples, as the history of the print is not controlled, however, when it is in the forensic scientists hands, protocols should be developed that limit *further* UV degradation. Second, increasing the pH of aged prints should improve print quality, where this has been shown to be a factor in our work to investigate the enhancement of aged prints by replenishment of initiators.[xxii] Further optimization of the pH control may provide additional improvement in the quality of aged print, and the utility of pH control in improving the quality of aged prints should be more carefully studied in the future.

Improving the Quality of Aged Latent Prints – Temperature

Recent discussion with forensic scientists have brought to our attention the fact that the quality of latent prints that are developed by superglue fuming are improved at lower temperature. More precisely, it appears that the growth of the PECA polymer chain from the print occurs much more rapidly at lower temperatures.

In order to more fully understand the fundamental reasons for, and to potentially exploit this phenomenon to improve the quality of prints developed by forensic scientists, the mass accumulated on reproducibly deposited fingermarks and the molecular weight characteristics of the resultant polymers have been determined and analyzed to provide insight into the fundamental driving force of this behavior.

The results of this experiment are shown in Figures 7 and 8, which clearly indicate that the mass of polymer that is grown from a print dramatically increases as the temperature decreases. Moreover, and somewhat surprisingly, the molecular weight of the polymer does **not** increase significantly with a decrease in temperature. This combination of trends (increase

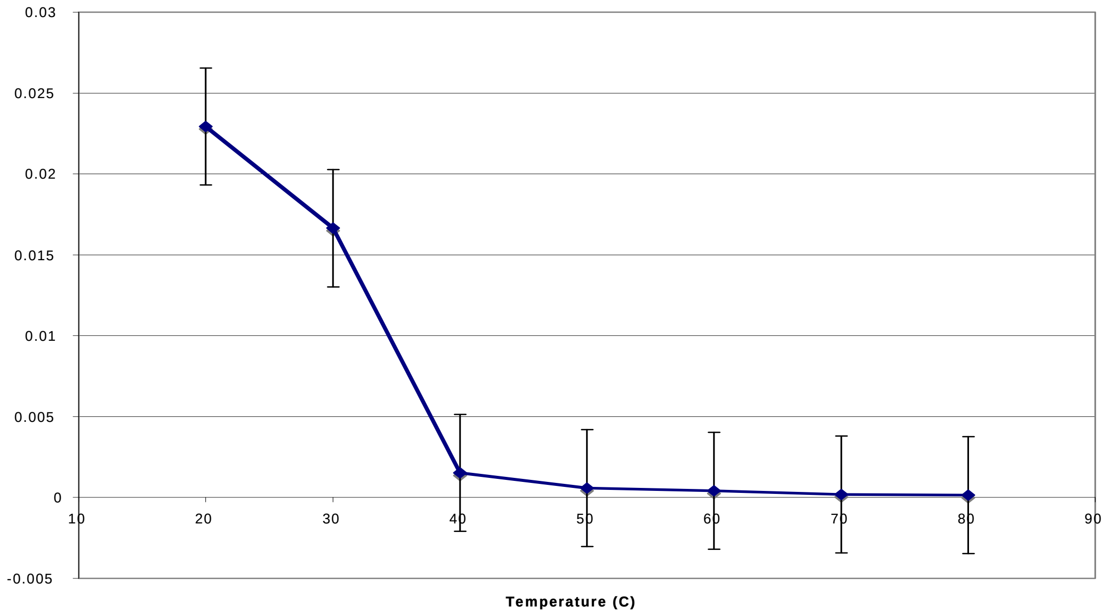


Figure 7– Mass of ethyl cyanoacrylate that polymerizes from latent prints as a function of temperature.

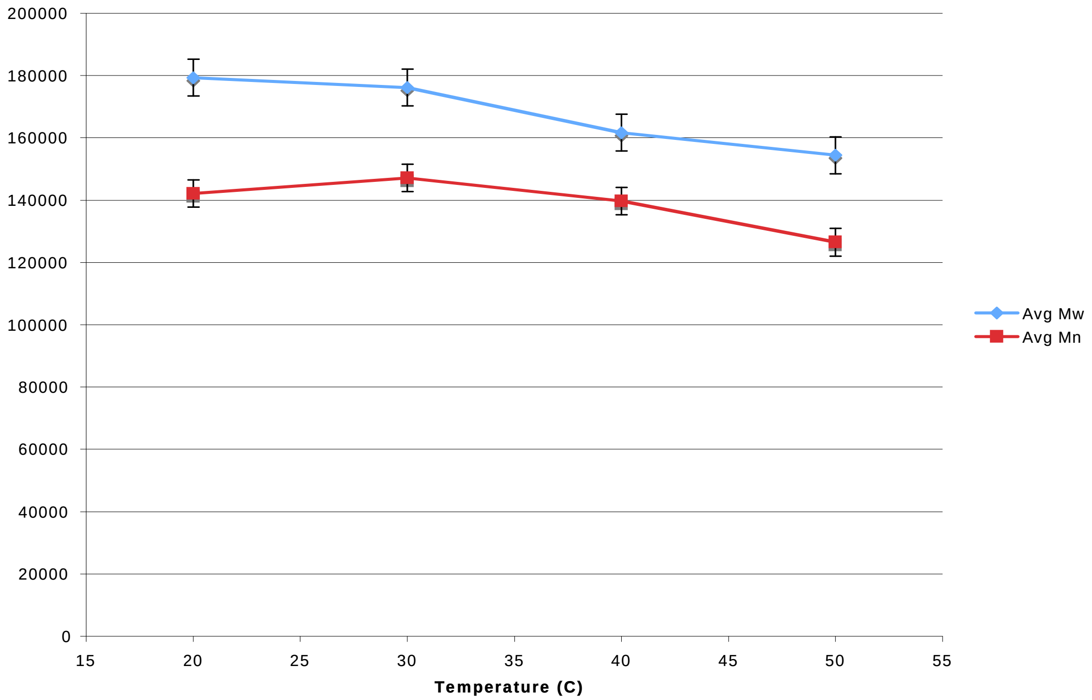


Figure 8 – Molecular weight of ethyl cyanoacrylate that polymerizes from latent prints as a function of temperature.

polymerization rate, but little or no change in molecular weight) can only be realized if the change in temperature results in an increase in the rate of initiation and propagation. This implies that lowering the temperature improves the ability of the present initiators to initiate the polymer growth, and thus lowering the temperature should improve the quality of aged prints.

It is well known that lowering the reaction temperature of a solution anionic polymerization increases the availability of the ion pair that resides at the end of the growing polymer chains, increasing the rate of initiation and polymerization and this may explain the observed increase in amount of polymer formed with decreasing temperature in the fuming of latent prints. In fact the ion-pair results discussed in Figure 4 provide insight into this phenomena, where the larger ion pair creates smaller chains, and thus indicating that an increase in initiation dominates the behavior of the system at low temperature.

This is particularly important in developing methods to improve the quality of aged prints that are developed by superglue fuming. It is abundantly clear that aging decreases the number of active initiators present, and in order to improve the quality of the print, the initiators that are present must be more efficient or additional initiators must be added. Our results on the effect of temperature on the growth of PECA from superglue fumed prints strongly suggests that lowering the temperature will make the initiators that are present in the fingermark more efficient in growing polymer chains, and therefore this is an extremely promising and easy method to improve the quality of aged latent prints. Further study is underway to precisely define and optimize the protocol for such an enhancement procedure.

V. Synopsis:

We have completed a set of experiments to provide a fundamental understanding of the molecular level interactions of the fingermark with the cyanoacrylate fumes and possible enhancement processes so that researchers can rationally design methods to improve the reliability and utility of the ECA fuming process to develop a broader range of latent prints, including aged prints. In these studies, we have identified the role of humidity in the development of latent prints as a solvation agent of the anion-cation pair that resides at the end of a growing polymer chain. In the absence of water, this pair is tightly bound and cannot initiate or polymerize the ECA monomer. As the humidity increases, the water solvates the ion pair, making it accessible to the ECA monomer and allowing its polymerization. In a similar manner we have shown that lowering the temperature of the fuming process increases the rate of polymerization and quality of the print due to a similar mechanism, lowering the temperature loosens the ion pair, which in turn increases the rate of polymer growth. We are extremely interested in completing further research to utilize temperature control as a method to improve the quality of aged latent prints developed by superglue fuming. Finally, our results show that one important mechanism in the degradation of latent prints upon aging is the degradation of the lactate ion to pyruvate ion, where this degradation results in a lowering of the pH of the sample, which in turn provides more terminating agents (H^+ ions) for the polymerization process.

VI. Application to The Practitioner

As stated in the title of this project, a primary goal of this research project is to cultivate methods to improve the quality of latent prints developed by superglue fuming. In this project the 'cultivation' has been to provide fundamental insight into the molecular level processes that occur during the superglue fuming of fingermarks, so that protocols can be *rationally* developed to improve their quality. Each set of results presented here provides important and previously unavailable information that can be used to develop, test, and promote such protocols.

For instance, our understanding of the role of water vapor/humidity in the development of latent prints by superglue fuming indicates that for any print, aged or new, the solvation by water of the ion that initiates the polymerization process is critical to the formation of PECA. In aged prints, it is known that water is readily lost with aging. Moreover, previous work has shown that merely rehydrating aged prints is not sufficient to improve their quality when developed by fuming; One way to reconcile these two facts is to consider that the aged prints are not readily re-hydrated. Additional protocols to improve the uptake of water by aged prints, such as super saturation or increased temperature or pressure, become interesting methods to improve the quality of aged prints. These methods are under investigation in our labs to more fully relate our current results to developing protocols to improve the quality of aged prints developed by superglue fuming.

Similarly, Our results that describe the chemical changes that occur in a print by UV degradation and its impact on the superglue fuming process provide guidelines for forensic scientists to minimize these changes and potentially optimize fuming procedures to favorably bias the quality of the developed print. While the history and environmental exposure of a fingermark is not controllable, the results presented here do accentuate the importance of minimizing UV exposure once the fingermark is in the forensic scientists control. Protocols for storage and transportation should be developed that minimize UV exposure. Additionally, our results expose the importance of the pH of the latent print on its ability to effectively initiate and polymerize the ECA fumes. Degradation lowers the pH of the fingerprint, which in turn increases the termination of growing PECA chains.[vii] Control of the aged fingerprint pH becomes another method for a forensic scientist to improve the growth of PECA from the print ridge, a process that is necessary to improve the quality of the latent print developed by superglue fuming. To exploit this information, the ability of increased pH combined with novel rehydration methods to improve the quality of aged prints is currently under investigation in our lab.

Finally, our results show that decreasing the temperature of the latent print increases the rate of the development and improves the print quality. Moreover, the understanding of the molecular level processes that are responsible for this behavior indicates that the decrease in temperature *improves* the effectiveness of the present initiators. This in turn implies that decreasing the temperature is a simple and effective method to improve the quality of aged prints developed by superglue fuming. Preliminary results in our lab verify this conclusion, and a more thorough protocol that uses temperature control to improve the quality of aged prints developed by superglue fuming is underway in our lab.

It is important to emphasize that the descriptions above and rational design of promising and potential methods to improve the quality of latent prints developed by superglue fuming are only possible because of the foundation of fundamental understanding that have been cultivated in this research program. We have concentrated on developing the fundamental information necessary to logically develop protocols that can be used by forensic scientists, and emphasize the success in building this foundation as a result of this research program. This was the original goal of this research program, to cultivate the understanding in order to rationally design methods to improve the quality of latent prints developed by superglue fuming, and the results presented in this report emphasize the success of this research program.

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