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Developing Methods to Improve the Quality and Efficiency of Latent Fingermark Development by Superglue Fuming

ABSTRACT:

The completed research program was designed to provide fundamental information that can be used to improve the superglue fuming method of developing latent fingermarks, by optimizing the acquisition of developed latent fingermarks and enhancing the quality of aged fingermarks. This has been realized by, first, using our expertise in polymer chemistry to explain the role of temperature on the superglue fuming of aged fingermarks and developing protocols to implement temperature control in a forensic laboratory. Our results show that fuming at lower temperatures improves the rate of polymerization that occurs during superglue fuming and thus, provides an easy and cost-effective method to improve the quality of aged prints developed by superglue fuming. More precisely the results of this project indicate that the optimum temperature of fuming is between 10 and 15 °C. Furthermore, any protocols that are devised to control the temperature of fuming must take into account the presence of the warm superglue fumes. The decrease in temperature also appears to improve the quality of aged latent prints.

Previous results also suggest that rehydration of an aged fingermark is critical to its successful development by superglue fuming, and thus we have investigated aggressive rehydration methods of aged latent fingermarks as a method to improve the quality of aged prints. Unfortunately, simply rehydrating fresh or aged prints by exposure to room temperature or boiling water vapor is not a sufficient method for improving print quality. In fact, exposure to boiling water vapor harms prints, presumably by removing initiators by dissolving them into the steam and releasing them from the print before fuming. Finally, we have completed Fourier Transform Infrared spectroscopy (FT-IR) experiments to monitor the molecular level changes during the polymerization of ethyl cyanoacrylate and the hardening process that occurs after polymerization, to provide guidelines that can be used to improve the turn-around time of obtaining a print that can be recorded and compared to a database. Thus, we have completed a series of experiments that provide fundamental information that forensic scientists in the field can use to create protocols to improve the effectiveness and optimize the process of the superglue fuming method to develop, visualize and analyze latent fingermarks.

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Executive Summary:

The cyanoacrylate fuming method (CFM) is a highly effective and well-accepted method for developing latent fingermarks on non-porous substrates. Interactions between the fingerprint residue and the cyanoacrylate vapor cause rapid polymerization resulting in a white polymer coating that enables print visualization. In this process, ECA is fumed onto a non-porous surface containing fingerprints, which forms a white polymer, poly(ethyl cyanoacrylate) (PECA), only on the print ridges, which in turn provides the optical contrast that enables the visualization of a print. ECA not only develops the print, but also fixes and improves visibility of other biological samples, such as saliva, that can be used to identify a criminal without inhibiting the collection and investigative use of DNA information. The chemistry of this process is that there exist chemicals in the latent print that serve as the initiators for the polymerization of ethyl cyanoacrylate to form poly(ethyl cyanoacrylate), which can be easily detected by the human eye. This process is possible because cyanoacrylates are extremely reactive due to their polarized carbon-carbon double bond, which includes two electron-withdrawing groups. The polymerization of highly reactive ECA can be initiated even with a small amount of weak bases and anions.

Though a useful technique, the superglue fuming process requires a waiting period to harden and does not always provide a quality fingermark, particularly if it has been exposed to the environment for extended periods of time. Unfortunately, our current understanding of the molecular level processes that occur during superglue fuming is inadequate to provide guidelines

that can be used to remedy these shortcomings. Thus, in order to develop methods to improve the efficiency and optimize the superglue fuming process, a more careful understanding of the molecular level processes that occur during fingermark fuming and subsequent hardening is needed. For that reason, we have completed a series of experiments that provide insight into the chemical reactions that occur during the superglue fuming and hardening process to provide fundamental information that can be utilized by forensic scientists to rationally optimize the superglue fuming process. We have focused on expanding on our previous results to more completely understand the ability of temperature control and hydration of prints to improve the quality of latent fingermarks. We have also examined the changes that occur to a latent fingermark during the hardening process, with the goal of developing a protocol that will optimize the turn-around time of obtaining a print that can be recorded and compared to a database.

The proposed experiments were designed to provide *crucial fundamental information* that will define and describe the chemical and physical processes that occur during the superglue fuming of latent fingermarks. This in turn will provide a scientific foundation for the validity of the ability of superglue fuming to accurately and truthfully develop the structure of latent fingermarks, providing scientific validation of its ability to faithfully preserve and present the latent fingermark as it was left at the scene.

The expertise in our laboratory is polymer science and chemistry. Thus, we view the development of the fingermark during superglue fuming as the polymerization of the cyanoacrylate monomers from the fingermark surface during the fuming process. This polymerization process creates structures that are visible to the eye, which creates the contrast that is needed to visualize the print. The polymerization proceeds by the initiation and chain growth of the cyanoacrylate monomer by chemical components that exist in the latent fingermark deposit. *The quality of the developed print is intimately linked to the ability of the chemicals that exist in the fingermark to successfully polymerize the cyanoacrylate monomer, grow structures off the print ridge, and develop the optical contrast needed to view the print.*

Our previous work in this area provides an interesting foundation and fascinating potential avenues to develop methods to improve the quality of developed fingermarks. 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 exposing aged prints to room temperature water vapor 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, are therefore examined as methods to improve the quality of aged prints.

Even more exciting is our recent results that begin to explain the role of temperature in the development of latent fingermarks by superglue fuming. These results show that the polymerization of the polymer from the print occurs much more rapidly at lower temperatures. In order to more fully understand the fundamental reasons for, and 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. This suggests that lowering the temperature *improves the ability of the present initiators* to initiate the polymer growth.

This is particularly important in relation to 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. We have therefore completed further research to utilize temperature control as a method to improve the quality of fresh and aged latent prints developed by superglue fuming.

Findings and Conclusions

The Effect of Temperature on the Superglue Fuming of Latent Prints:

Using Temperature to Improve the Quality of Aged Latent Prints

Our initial experiments in this area were completed to document the impact of lowering the temperature of the superglue fuming process on the growth of poly(ethyl cyanoacrylate) from aged latent prints. These results show that lowering the temperature does improve the polymerization of ECA when applied to aged prints as it does to fresh prints. Notably the molecular weight of the grown polymer approaches that which is found in un-aged fumed prints, indicating that the change in initiation and chain growth with temperature is similar for aged and un-aged print and is not affected by degradation or loss of mass of a print during aging. These results therefore suggest that lowering the temperature may improve the quality of the aged print.

Determination of the Optimum Temperature for Superglue Fuming

Our previous results demonstrate that lowering the temperature of the latent print from 50 to 20 °C dramatically improves the amount of poly(ethyl cyanoacrylate) (PECA) formed on the print during fuming, as well as increases print quality. The current research program focused on optimizing the temperature for fuming to easily characterize the latent fingerprints. These results show that the optimum temperature of the item that is being fumed for fresh latent prints is 8-10 °C. These results are the focus of a manuscript that is in preparation to disseminate this information to Forensic scientists, so that they may take advantage of this information in their fieldwork.

Developing methods to control print temperature during superglue fuming in a forensic laboratory

The results above clearly demonstrates that the optimum temperature of fuming is ~ 10 °C, which is ~50 °F. These results were expanded to evaluate the quality of fumed latent prints on duct tape, plastic "Ziploc" bags, and soda bottles that were cooled in a refrigerator or freezer, as this cooling protocol is more readily applied in a forensic lab. *The goal of these studies is therefore to develop a protocol that may readily be used in Forensic laboratories that will improve the quality of latent prints by cost-effectively lowering the temperature of the fumed prints*.

Therefore, the effect of placing the sample with the deposited fingerprint in a refrigerator or freezer prior to fuming the print on PECA formation is examined. In particular, the ability of the sample to retain the colder temperature long enough to effect its PECA formation during fuming is assessed. In this experiment, each sample was placed in a refrigerator or freezer for 2 days; then removed from the colder environment and brought to the fuming station. Prior to fuming, the temperature of the sample was continuously monitored using an infrared thermometer. In both cases, the plastic substrates return to room temperature within two minutes. Thus, it is clear that the use of a standard refrigerator or freezer is not sufficient to keep the sample at ~ 10 °C during fuming to take advantage of temperature effects of the polymerization of ethyl cyanoacrylate that occurs during the fuming process.

The temperature of the three samples was also monitored during fuming of the print surfaces that are placed on a temperature controlled block at 2 °C, 10 °C, 20 °C, and at room temperature. The fuming process brings hot ECA fumes to the print surface, which increases the temperature of the print during fuming. These results indicate that optimum temperature of fuming is between 10 and 15 °C when taking into account the warming of the sample that occurs due to the presence of the warm superglue fumes. Moreover, any protocols that are devised to control the temperature of the fuming process must take into account the presence of the warm superglue fumes.

Role of Hydration on the Superglue Fuming of Aged Latent Fingermarks:

The goal of this portion of the research program is to investigate methods to aggressively expose aged fingermarks to water with the goal of improving the *selective* polymerization of ethyl cyanoacrylate from aged prints, consequently improving the quality of the superglue fuming process of aged prints. To realize this goal, we exposed aged prints to water vapor by suspending them above room temperature water vapor or positioning them over a beaker of boiling water.

A quartz crystal microbalance monitors the change in mass of new and aged prints during their exposure to boiling or room temperature water vapor to document their ability to take-up water. Somewhat surprising is the fact that the slope of the mass vs. time line for the print suspended above boiling water is *negative*. This indicates that the mass of the print is decreasing with exposure to boiling water vapor, i.e. that the boiling water vapor washes away the print. Clearly, the exposure of the latent print to boiling water primarily results in loss of print material, a process that is detrimental to the development of the print by superglue fuming. Also, somewhat surprisingly, the exposure of the print to the vapor of room temperature water modestly increases the mass of the print.

The completed experiments therefore demonstrate that exposure of prints to plain water has very little, if any, effect on the PECA formation during the fuming of fresh or aged latent fingerprints. Exposure to boiling water, however, decreases the amount of PECA grown off of the fresh or aged print; this is attributed to the removal of initiators from the print during exposure, hindering PECA formation and therefore decreasing the quality of prints. Therefore, although eccrine sweat is a water based mixture, these results are consistent with the conclusion that components of the prints other than water initiate polymer growth from superglue fuming, not the water itself. Furthermore, simply rehydrating fresh or aged print by exposure to room temperature or boiling water is not a sufficient method for improving print quality. Boiling water harms prints, presumably by removing initiators by dissolving them into the steam and releasing them from the print before fuming.

Optimizing the Turn-around Time of the Superglue Fuming Method

The focus of this portion of the project centered on understanding and improving the requirement that fumed prints often necessitate 12-24 hours to 'harden' to ensure that the print will not smudge during further analysis. Multiple members of our research team have spent significant time attempting to determine under what circumstances superglue fumed latent prints will smear, and when they won't. For instance, our group has attempted to identify a set of reproducible conditions that result in fumed latent prints that have a tendency to smear. A variety of factors have been examined in this endeavor, concentrating on the print donors gender and the surface on which the print is deposited. Unfortunately, these investigations have not yielded a reproducible condition where the fumed print smears.

With no clear conditions that can be used to reproducibly examine fumed prints that smear, we completed experiments to provide a more careful understanding of the molecular level processes that occur during fingerprint fuming and subsequent "hardening". We have completed Fourier Transform Infrared spectroscopy (FT-IR) experiments to monitor these molecular level changes during the polymerization of ethyl cyanoacrylate and the hardening process that occurs after polymerization.

The results show that there exist differences in the structure of the PECA that is formed by curing and that which is formed on a fumed print, differences that must be understood. These differences could be due to the presence of water in the cured sample that is not as prevalent in the fumed sample due to the increased temperature of fuming. The fumed print grows from surface bound initiators, which may result in a different reaction than occurs in the atmospheric curing of the monomer. The current FTIR data is being further analyzed to address these continuing uncertainties.

IMPLICATIONS OF POLICY AND PRACTICE: The results of this research program which are most promising to impact policy and practice are the results that provide additional insight into the impact of temperature on the fuming of latent prints. This research program clearly indicates that lowering the temperature of the object on which a fingerprint resides to ~8-10 °C will increase the amount of PECA that is formed during fuming, which in turn improves the quality of the developed print. This has clear implications to the practicing forensic scientists, in that fuming chambers with temperature control should be developed.

The results also indicate that the quality of fumed *aged* latent prints can also be improved by lowering the temperature. Our interpretation of this phenomenon is that the lower temperature improves the efficiency of utilizing the remaining initiators that exist in the print after aging. This provides another parameter to control in lab that can offer an improvement of print quality of aged latent prints.

The results that investigated the hardening of the print appear to indicate that there are very few conditions (surfaces, print composition, etc.) that exist for print fuming that result in a latent print that smears. Our interpretation of this result is that the formation of a fumed print that smears is due to specific local environment conditions. This implies that the observation of a print that smears shortly after fuming is indicative of an alteration in the fuming chamber environment, which should be investigated. A reproducible chamber environment should provide the practicing forensic scientist with a fumed print that is robust after a few minutes.

I. Introduction:

Statement of the Problem: In many forensic investigations, the recovery and identification of latent fingermarks are vital in recreating a crime scene. A standard, cost-effective, and straightforward method for developing these latent marks from a nonporous substrate is the cyanoacrylate fuming method.[1-6] This method involves the exposure of a latent mark to the fumes of ethyl cyanoacrylate (ECA), more commonly known as superglue. The most effective procedure for fuming latent marks using ECA involves the rapid heating of the superglue,[1,3] which causes the heated glue to turn into a white vapor. This vapor then reacts with the fingermark residue it contacts and begins growing polymer along the mark ridges. The result is a fixed and durable, visible coating of the fingermark friction ridges.[5] Throughout this report, the term fingermark will primarily be used, but due to long-term habits, the term 'print' will occasionally be used, and should be viewed as equivalent to the term 'fingermark'.

Though a useful technique, the superglue fuming process requires a waiting period to harden and does not always provide a quality fingermark, particularly if the latent fingermark has been exposed to the environment for an extended period of time prior to development. Unfortunately, our current understanding of the molecular level processes that occur during superglue fuming is inadequate to provide guidelines that can be used to remedy these shortcomings. In fact, methods to enhance the development of prints by fuming, such as increased humidity or addition of ammonia to the fuming chamber,[1] have been empirical in nature due to this lack of understanding of the fundamental chemical processes that occur during the fuming process. Thus, in order to develop methods to improve the efficiency and optimize the superglue fuming process, a more careful understanding of the molecular level processes that occur during fingermark fuming and subsequent hardening is needed. For that reason, we have completed a series of experiments that provide insight into the chemical reactions that occur during the superglue fuming and hardening process to provide fundamental information that can be utilized by forensic scientists to optimize the superglue fuming process and improve the quality of aged prints.

We have focused on expanding on our previous results to more completely understand the ability of temperature control and hydration of prints to improve the quality of latent fingermarks. We have also examined the changes that occur to a latent fingermark during the hardening process, with the goal of developing a protocol that will optimize the turn-around time of obtaining a print that can be recorded and compared to a database.

The proposed experiments are designed to provide *crucial fundamental information* that will define and describe the chemical and physical processes that occur during the superglue fuming of latent fingermarks. This in turn will provide a scientific foundation for the validity of the ability of superglue fuming to accurately and truthfully develop the structure of latent fingermarks, providing scientific validation of its ability to faithfully preserve and present the latent fingermark as it was left at the scene.

Literature Citations and Review: Initially, developing a latent fingermark by ECA fuming included the placement of the print in an enclosed tank with a dish of cyanoacrylate (superglue) at ambient temperature and pressure for extended periods of time.[7,8] This process was slow and usually resulted in significant background of polymer. Further research demonstrated that heating the cyanoacrylate or fuming in the presence of a base[9] (sodium hydroxide) speeds up the process and results in better quality prints.

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 grows along the ridges of the print, with virtually no polymer deposited on background areas.[1,3] The ethyl cyanoacrylate polymerizes on the ridges of the fingermark to form micron size morphologies, such as noodles or blobs, as shown in Figure 1. 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 which the print lies is either white or transparent, secondary techniques can be employed to exude contrast.[10]

In addition to the quality of the obtained print, the cyanoacrylate fuming method also reveals traces of blood and sweat that are exposed to the vapor.[2] The cyanoacrylate will coat the droplets much the same way ECA is used to coat ice crystals.[11,12] More important than the ability to reveal these traces of blood and sweat is the non-destructive nature of the ECA fuming method. A study using a variety of forensic PCR kits found that presence of the ECA did not prevent successful DNA testing of the blood or sweat.[2]

Unfortunately, it is not well understood what are the most important controlling parameters of a successful polymerization of ECA during the fuming process. Nor is it well understood how to optimize this process. For instance, the noodle morphology provides a much better visual print than the blob morphology, yet the reason for the appearance of the two morphologies is still unclear.

It is assumed that some component of the fingermark that resides on the ridge of the fingermark serves as an initiator to the polymerization of the ECA to form a polymeric layer only in those spots that contain the initiator. Eccrine sweat, which makes up the fingermark residue, has numerous components, many of which may initiate the polymerization of cyanoacrylates, including amino acids, water, and sodium lactate. Thus, in order to rationally optimize the development of fingermarks in a broad range of conditions by ECA fuming, it is necessary to determine the controlling molecular actors in this process. Motivated by this need, our research efforts, which were funded by NIJ (2006-DN-BX-K031), have clearly identified the carboxylate groups of the amino acids and sodium lactate in eccrine sweat as the primary initiator of ECA during the fuming process.[6] These results, in turn, provided a foundation to develop methods to reinvigorate the ability of aged prints to grow polymer during the superglue fuming process by replenishing the initiators available, improving the quality of the developed fingermarks.[30]

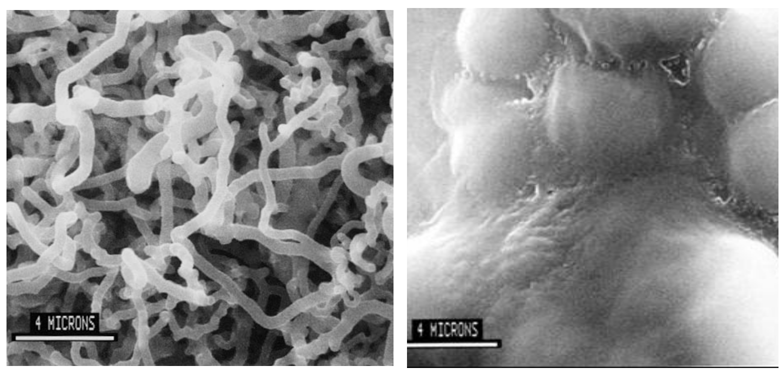

Figure 1 - (left) Cyanoacrylate polymer formed on the ridge of an eccrine sweat latent fingermark. (right) Cyanoacrylate polymer formed on the ridge of an oily, sebaceous latent fingermark.

This work built off of earlier efforts to better understand the print development process, where researchers examined the chemical composition of fingermarks.[13] In this work, the common adult fingermark was found to contain predominately eccrine sweat.[3,13,14] Eccrine sweat is secreted from the palms of the hands, soles of the feet as well as all other non-hairy surfaces.[3,14] Although the exact composition of an individuals' eccrine sweat will vary with lifestyle and diet,[14] the general chemical make-up of eccrine sweat is presented in Table 1. These purely eccrine prints can however, become contaminated when the hands come into contact with other regions of the body.[14] The hairy surfaces of the body have sebaceous glands buried deep within the hair follicles. These sebaceous glands secrete sebum, an oily mixture composed of fatty acids, triglycerides, and other components.[3,14] Fortunately, sebum contamination was found to contribute less than 5% by weight to the total composition of a latent print and thus eccrine sweat remains the primary source for initiators of the ECA upon fuming. Lewis et al found that the presence of sebum contamination did influence the aging of a fingermark, but its presence was not required for print development.[3] Inspection of Table 1 indicates that the primary components of eccrine sweat are NaCl, lactate, and various amino acids.

Table 1: *Composition of Eccrine Prints*

Components of Eccrine Sweat	**Abundance (wt%)**
NaCl	43.83%
Lactic Acid	29.22%
Urea	11.69%
Amino Acids	7.79%
Others	4.97%
NaH_2PO_4	1.75%
Glucose	0.44%
K_2PO_4	0.31%

Unfortunately, the vapor phase polymerization of cyanoacrylates is not studied extensively outside the forensic field, as such studies could provide additional insight. Studies observing cyanoacrylate growth from snowflakes, ice droplets, and tobacco smoke utilize the technique but do not investigate the growth process.[11,12] Foley et al. reported the use of superglue fuming to form neat poly(ethyl cyanoacrylate) (PECA) nanofibers from distributed surface-bound initiators at relatively high humidity and room temperature.[15] The same group[16] also examined the impact of initiator and counter-ion on the resultant morphology of PECA formed from superglue fuming, observing nanofiber and film morphologies. In this study, they varied the anion, while keeping the counter-ion (sodium) constant. They invoke the Hard Soft Acid Base (HSAB) theory[17] developed by Pearson to explain the different morphologies obtained via ECA polymerization. Their rational is that the electron withdrawing effects of the cyano and carbonyl groups on the monomer renders it a positive hard acid. The nucleophilic attack of that β-carbon in the initiation step is successful when accomplished by a species of the same hard nature. Their results showed that the increased hard quality of an anion yielded more polymer coverage, which suggests higher initiation rates. So, as the hardness of the anion increased, they obtained a film morphology which was the result of more and easier initiation, while and anion with softer character gave nanofibers or no polymer at all, the result of very little or slow initiation. They conclude that the formation of the polymer and its structure is dependent on the anion involved; however, further experiments are needed to clarify whether it is the anion or the structure of the ion pair as a whole that controls the polymer growth.

Additionally, solution-based chemistry can guide our understanding of the fuming process. The polymerization of ECA in solution has been well documented.[18-24] 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 process is unaffected by significant quantities of O_2, CO_2, air, and even H_2O,[3,20,22,25] all of which terminate conventional anionic polymerizations.

The polymerization of cyanoacrylates has also been studied for their use in other applications including adhesives, nanomaterials,[26] and the production of sub micron resists. In one study, the examination of the vapor phase deposition of cyanoacrylate polymers was achieved by polymerizing off of a silicon surface that had been exposed to an amine vapor in a closed chamber.[27] In this study, the researchers were able to create micron-size, well defined, smooth, and homogeneous layers of cyanoacrylate that could then be etched to form resist structures that could be used by the semi-conductor industry.

There have also been studies that have sought to create methods to improve the development of latent prints by cyanoacrylate fuming and other methods. These include the work of Burns et al[1], 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. Importantly, this quantification of the amount of polymer deposited during the fuming as determined by FTIR correlates very well to the observed visual quality of the prints as determined by four fingermark experts. This result indicates that FTIR can be used as a method to quantify the success of the development of a print by the fuming process, and that the exposure of a latent print to a base prior to fuming appears to improve the quality of the developed print.

Lewis et al[3] 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[28] 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.

Our recent research in the growth of poly(ethyl cyanoacrylate) from latent prints, which was funded by NIJ (2006-DN-BX-K031), has also provided important insight into the molecular level processes that occur during superglue fuming of latent prints. These results show that the presence of water is needed in the superglue fuming process, not as an initiator, but to solvate the carboxylate salt that is the initiator to create an ion pair, which readily initiates the polymerization of ethyl cyanoacrylate. We have also provided insight into the impact of the aging process on the growth of polymer during fuming. These results identify two environmental factors, exposure to UV and air currents, when coupled with a loss of water from the print residue, that results in a loss of the initiator that is needed to grow the polymer from the print and results in a decrease in the ability of the print to polymerize ethyl cyanoacrylate.[29] This data was then utilized to develop a methodology by which the ability of aged latent fingermarks to polymerize ECA is recovered. In this protocol initiator was reintroduced to the system by the exposure of the aged print to the vapor of acetic acid or ammonia. These two small molecule enhancement agents improve the growth of the polymer from the print ridges by over an order of magnitude, while retaining the integrity of the print structure.[30] Comparison between the two enhancement agents provides insight into the mechanism by which this enhancement occurs.

Even more exciting is our recent results that begin to explain the role of temperature in the development of latent fingermarks by superglue fuming. Our results show that the polymerization of the ECA monomer from the print occurs much more rapidly at lower temperatures.[31]

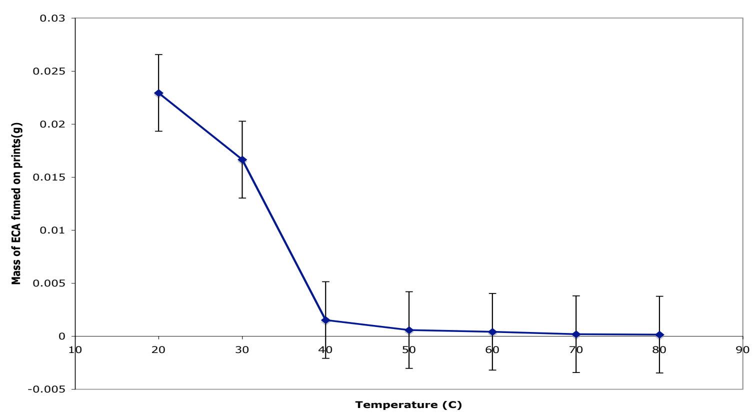

Figure 2– Mass of ethyl cyanoacrylate that polymerizes from latent prints as a function of temperature.

The results of this experiment are shown in Figure 2, which clearly indicate that the amount of polymer that is grown from a print dramatically increases as the temperature decreases. In these studies, it is shown that the amount of PECA formed during the polymerization of ECA from a latent fingerprint increases with decreasing temperature, while the polymer molecular weight varies little. This is interpreted to be the result of the opening of the ion pair that initiates the polymer chain growth and resides on the end of the growing polymer chain with decreasing temperature. Comparison of temperature effects and counter-ion studies show that in both cases loosening the ion pair results in the formation of more polymer with similar molecular weight, verifying this interpretation.[31] In the current project, we have completed further research to utilize this temperature control as a method to improve the quality of latent prints developed by superglue fuming.

Statement of Hypothesis and Rationale: 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, 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. We, thus, have completed a set of experiments that provide this information, which can then be utilized by the practicing forensic investigator to optimize, improve, and control the fuming of cyanoacrylates to develop latent prints.

II. <u>Methods</u>:

Materials.

The chemicals 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). 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

For clean fingermarks, new glass sides were used as the substrate and weighed prior to print deposition. In order to ensure 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 eccrine secretions. Fingermarks were 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. 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. For oily prints, the same procedure is completed, except that the fingertip was rubbed across the forehead and nose prior to deposition.

Ethyl Cyanoacrylate Fuming and Temperature Control

Fuming of ECA (Omega-Print, Sirchie) was completed in an enclosed chamber. The hotplate in the chamber was heated to 150°C, and a temperature bath (Isotemp 3016, Fisher) was set to the appropriate temperature in the range of 20 to 80 °C. The sample was clamped to a heating coil connected to the temperature bath, as shown in Figure 3, and the system was left to equilibrate for at least 10 minutes. In trials of ambient relative humidity (amb. RH), an aluminum weighing pan of ECA was placed on the hotplate directly below the sample (approx. 4” away) once the system has reached equilibrium. The chamber was then closed and the sample is exposed to ECA fumes for 10 minutes.

Figure 3: Fuming chamber with temperature control

For trials of high relative humidity (high RH), during equilibration of the system, moisture was introduced through an opening in the lid of the chamber using a standard humidifier (PUM100, Sirchie). The pan of ECA was suspended above the hotplate and the chamber was sealed off to stabilize the moisture. Once the relative humidity reaches ~ 85% for at least 10 minutes, the dish of ECA was 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 within 85-95%. A traceable hygrometer (Control One) was 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.

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.

III. Study Results:

The Effect of Temperature on the Superglue Fuming of Latent Prints:

Using Temperature to Improve the Quality of Aged Latent Prints

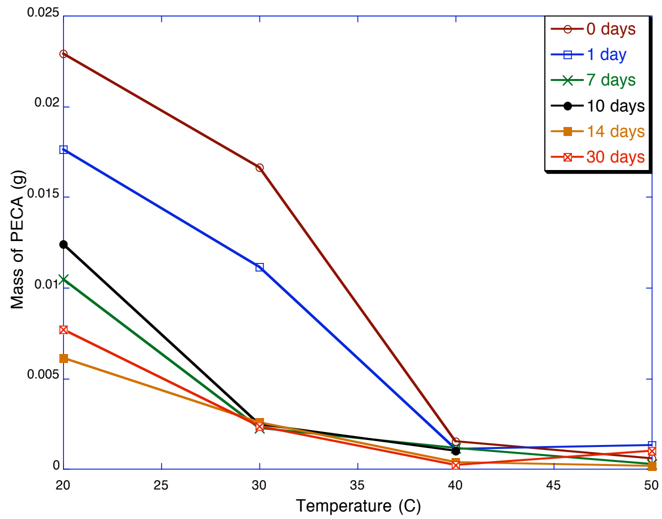

Figure 4: Mass of PECA accumulated on fingerprints and surroundings as a function of temperature of substrate/prints fumed at 85-95%RH.

Our initial experiments in this area were completed to document the impact of lowering the temperature of the item that is exposed to fumes during the superglue fuming process on the growth of poly(ethyl cyanoacrylate) from aged latent prints. Our previous results (Fig. 2) show that lowering this temperature can improve the ability of initiators that are present in a fingermark to grow polymer chains. With this in mind, we completed a set of experiments to quantify the effect of temperature on the amount and molecular weight of polymer that is formed from aged latent prints that are developed by superglue fuming. In these experiments, fingerprints were laid on clean glass slides and placed under a cover so that they were exposed to light and air while limiting dust exposure. The samples were allowed to age for 1, 7, 10, 14, and 30 days, and subsequently re-weighed to determine the mass loss due to aging. These prints were then fumed with ethyl cyanoacrylate (ECA) for 10 minutes at both high and ambient humidity. Regardless of changes that occur in the print during the aging process, poly(ethyl cyanoacrylate) *is* formed from the print during superglue fuming, indicating that there remain *some* initiators present in the aged print.

The mass and molecular weight of polymer formed by superglue fuming these aged prints at various temperatures are illustrated in Figures 4-5, respectively, as a function of aging time and temperature. These results follow the trends of the temperature dependence of fresh prints that are fumed with ECA; lowering the temperature of an aged print during superglue fuming creates more polymer on the print, but the molecular weight of that resultant polymer does not change significantly with temperature. Thus, these preliminary results show that, generally, lowering the temperature of the latent print provides a method to improve the effectiveness of growing PECA from the print.

Thus, the trend of decreasing the temperature and improving the polymerization also applies to aged prints as it does to fresh prints; the rate of polymerization increases and the degree of polymerization stays static, as the temperature of the substrate is lowered.[32] Notably the molecular weight of the grown polymer approaches that which is found in un-aged fumed prints, indicating that the initiation and chain growth is similar at all temperatures and is not affected by degradation or loss of mass of a print. These results therefore suggest that lowering the temperature may improve the quality of the aged print.

Determination of the Optimum Temperature for Superglue Fuming

Our previous results demonstrate that lowering the temperature of the latent print from 50 to 20 °C dramatically improves the amount of poly(ethyl cyanoacrylate) (PECA) formed on the print during fuming (Fig. 2), as well as an increase in print quality. The current research program focused on optimizing the temperature for fuming to easily characterize the latent fingerprints. Thus our research in this program has focused on measuring the fuming of latent prints at temperatures below 20 °C. These results are shown in Figure 6, which more precisely shows that the optimum fuming temperature for fresh latent prints is 8-10 °C. These results are the focus of a manuscript that is in preparation to disseminate this information to Forensic scientists, so that they may take advantage of this information in their fieldwork.

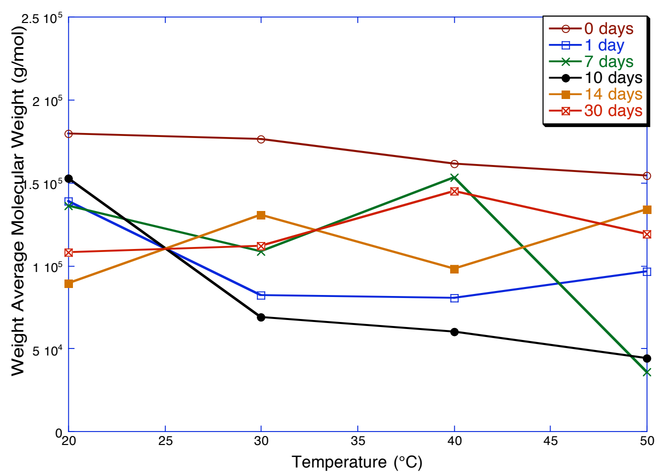

Figure 5: Average molecular weight of PECA chains as a function of temperature of the fingerprints being fumed at high (85-95%) relative humidity

This is an interesting result in that it can be explained as a competition of the temperature dependence of two competing molecular level processes. The growth of the poly(ethyl cyanoacrylate) (PECA) polymer chain is an anionic polymerization, which means that the growing chain end consists of a negatively charged chain end and a positively charged counter-ion. Growth of the polymer chain occurs by the insertion of a monomer between the chain end and counter-ion (step 1) followed by the reaction of the monomer with the chain end (step 2). The rate of the monomer insertion (step 1) *increases* with decreasing temperature as the counter-ion is more loosely bound at lower temperatures. Conversely, the rate of the reaction of the monomer with the chain end *decreases* with decreasing temperature. Thus, the rate of PECA polymer chain growth at temperatures above ~10 °C is dominated by the rate of step 1, while the PECA polymer chain growth at temperatures below ~10 °C are controlled by the slower rate of step 2.

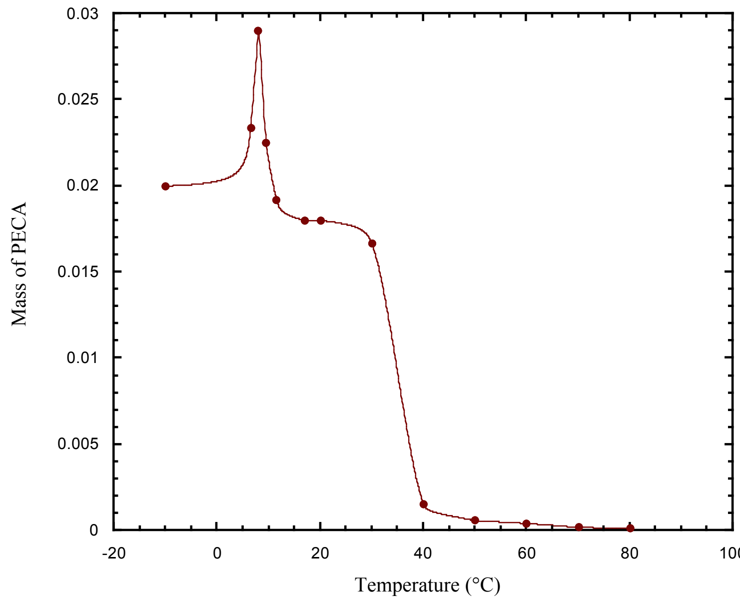

Figure 6: Effect of temperature on the amount of PECA grown from fresh latent prints.

Developing methods to control print temperature during superglue fuming in a forensic laboratory

The results above clearly demonstrates that the optimum temperature of fuming is ~ 10 °C, which is ~50 °F. Prof. Dadmun discussed these results with ATF Specialist Andrew McIntyre when he visited him in October 2012. It was agreed that it would be interesting to expand these results to evaluate the quality of fumed latent prints that were cooled in a refrigerator or freezer, as this cooling protocol is more readily applied in a forensic lab. It was also agreed that investigating if fumed prints on everyday objects such as duct tape, plastic "Ziploc" bags, and soda bottles are also improved by cooling. *The goal of these studies is therefore to develop a protocol that may readily be used in Forensic laboratories that will* *improve the quality of latent prints by cost-effectively lowering the temperature of the fumed prints*.

As shown in Figure 6 above, our previous work has clearly demonstrated that the amount of PECA that grows off of a latent print after superglue fuming is optimized at ~10 °C. This observation leads to the search for a cost-efficient and convenient method to bring latent prints to ~ 10 °C. Pursuant to this goal, the effect of placing the sample with the deposited fingerprint in a refrigerator or freezer prior to fuming the print on PECA formation is examined. In particular, the ability of the sample to retain the colder temperature long enough to effect its PECA formation during fuming is assessed. The impact of the precise surface on which the print is deposited on the fuming is also examined, where surfaces that are studied include duct tape, Ziploc bags (polyethylene), and coke bottle fragments (polyethylene terephthalate).

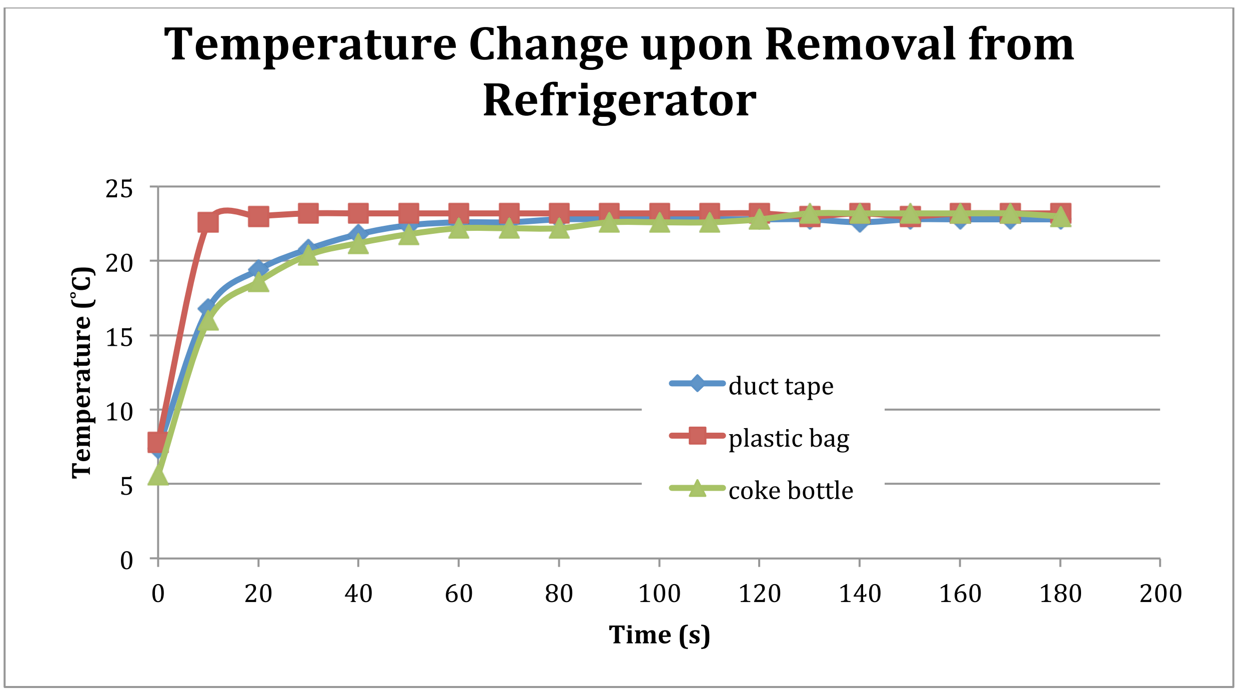

Figure 7: Time evolution of the temperature of duct tape, a polyethylene bag, and a poly(ethylene terephthalate) bottle after removal from a refrigerator at 5°C.

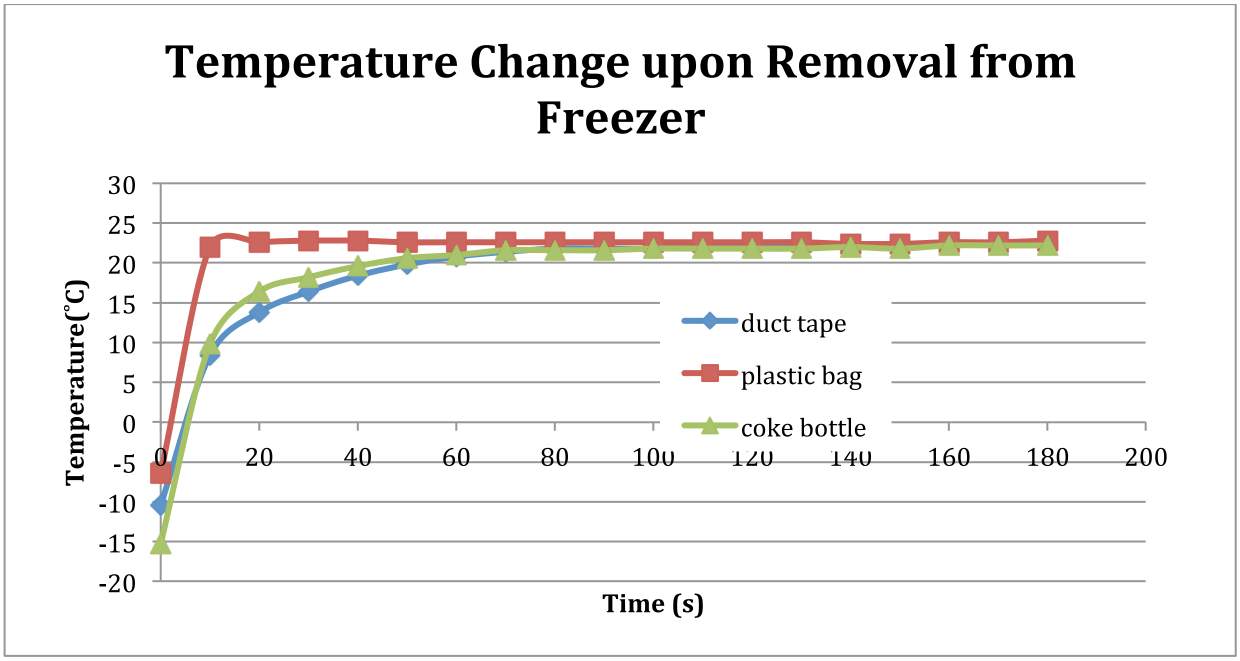

Figure 8: Time evolution of the temperature of duct tape, a polyethylene bag, and a poly(ethylene terephthalate) bottle after removal from a Freezer at -20°C.

Each sample was placed in a refrigerator or freezer for 2 days; then removed from the colder environment and brought to the fuming station. Prior to fuming, the temperature of the sample was continuously monitored using an infrared thermometer. The Figure 7 and 8 below show the change in temperature of the duct tape, plastic bag and coke bottle upon removal from the refrigerator and freezer, respectively. In both cases, the plastic substrates return to room temperature within two minutes. Thus, it is clear that the use of a standard refrigerator or freezer is not sufficient to keep the sample at ~ 10 °C during fuming to take advantage of temperature effects of the polymerization of ethyl cyanoacrylate that occurs during the fuming process.

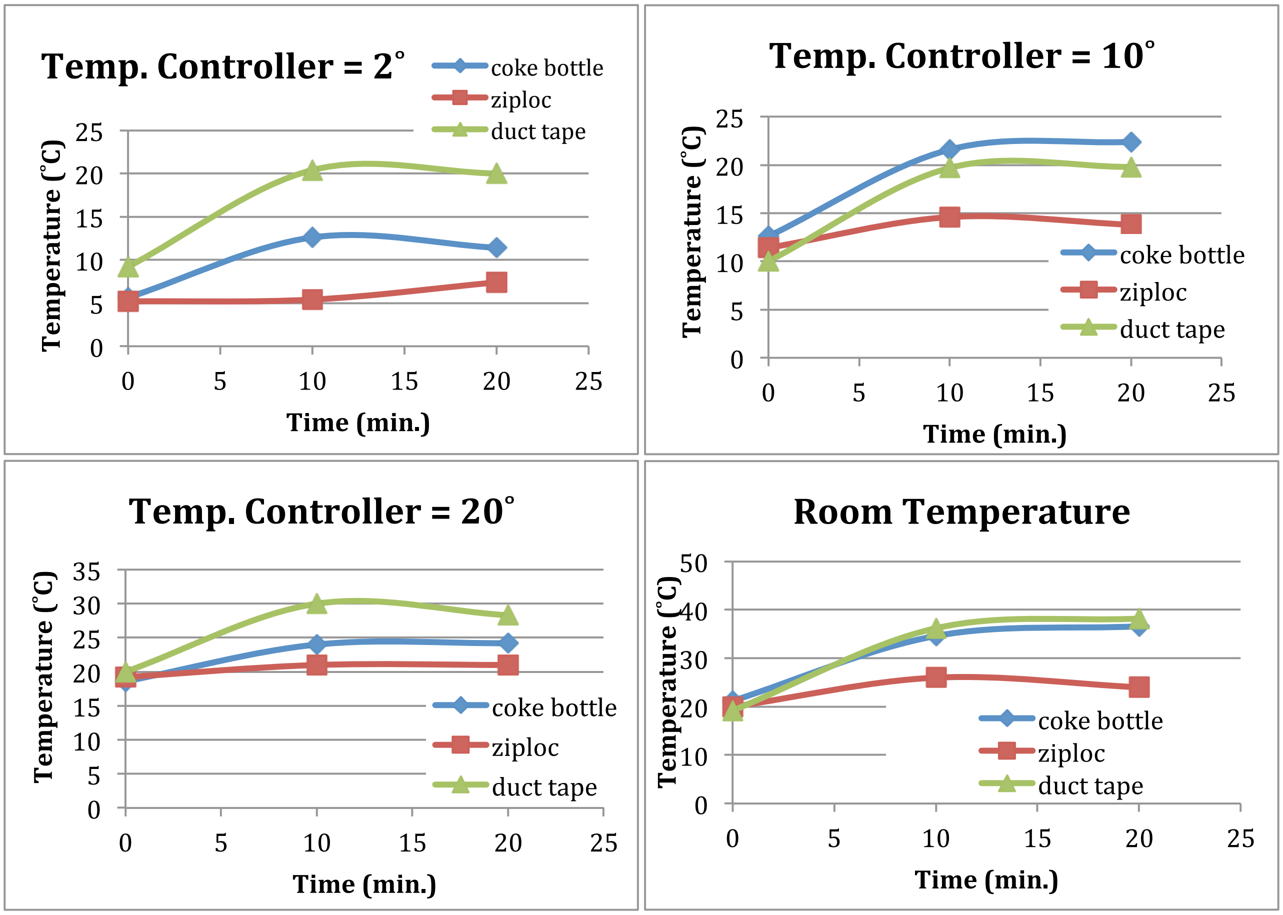

Figure 9: Time evolution of the temperature of duct tape, a polyethylene bag, and a poly(ethylene terephthalate) bottle during fuming.

The temperature of the three samples was also monitored during fuming of the print surfaces that are placed on a temperature controlled block at 2 °C, 10 °C, 20 °C, and at room temperature. The fuming process brings hot ECA fumes to the print surface, which increases the temperature of the print during fuming. Figure 9 shows the time evolution of the increase of the print surface temperature during fuming. These result show that the fuming process increases the temperature of the print by 2-20 °C, depending on the surface and the initial temperature. Further inspection shows that the Ziploc bags exhibit the smallest increase in temperature upon exposure to the hot superglue fumes, which is probably because the Ziploc bag is sufficiently flexible to remain in close contact with the temperature controlled block throughout the fuming process. The Coke bottle did not conformally coat the temperature-controlled block, and this results in a warming of the surface when exposed to the hot superglue fumes.

These results therefore indicate that optimum temperature of the samples during fuming is between 10 and 15 °C when taking into account the warming of the sample that occurs due to the presence of the warm superglue fumes. Moreover, any protocols that are devised to control the temperature of the fuming process must take into account the presence of the warm superglue fumes.

Role of Hydration on the Superglue Fuming of Aged Latent Fingermarks:

The goal of this portion of the research program is to investigate methods to aggressively expose aged fingermarks to water with the goal of improving the *selective* polymerization of ethyl cyanoacrylate from aged prints, consequently improving the quality of the superglue fuming process of aged prints. To realize this goal, we expose aged prints to water vapor by suspending them above room temperature water vapor or positioning them over a beaker of boiling water. The procedure and results of experiments to determine the impact of these hydrating procedures on the ability of new and aged latent prints to grow poly(ethyl cyanoacrylate) is described below.

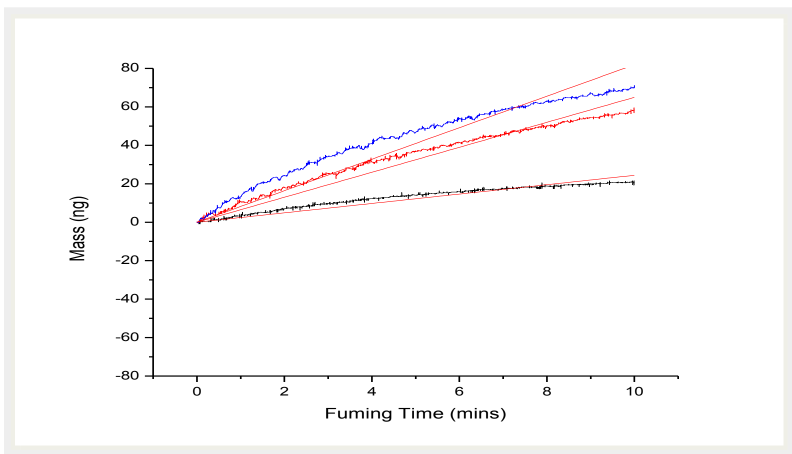

Figure 10: Change in mass of an aged clean latent print with exposure to the vapor of room temperature water, plotted as a function of exposure time.

Fingerprints were laid on a glass slide and the slides were weighed in order to determine the weight of the print. The samples were then covered to protect the prints from collecting dust. After 30 days, the samples were reweighed to determine the weight of the aged print. The slides with fingerprints were then placed about 4 inches above a 250 ml beaker of boiling water, so that it was far enough that the water would not splash on the slide but that the vapor would reach the slide. A set of slides was exposed to the boiling water vapor for 5 minutes and another set for 10 minutes. Another set of slides were placed about 4 inches above a beaker of room temperature water for 5 minutes and another set for 10 minutes.

The fingerprints were fumed on the slides that were exposed to boiling water vapor, the set of slides that were exposed to room temperature water vapor, the set of slides that were not exposed to water, and a set of clean slides with no prints. The slides were then removed and reweighed to determine the mass of the polymer that formed on the print after fuming.

A quartz crystal microbalance monitors the change in mass of new and aged prints during their exposure to boiling or room temperature water vapor to document their ability to take-up water. The results, shown in Figures 10 and 11, are very interesting in that they show that exposure to boiling water vapor washes away part of the print and thus this exposure is detrimental to the print integrity.

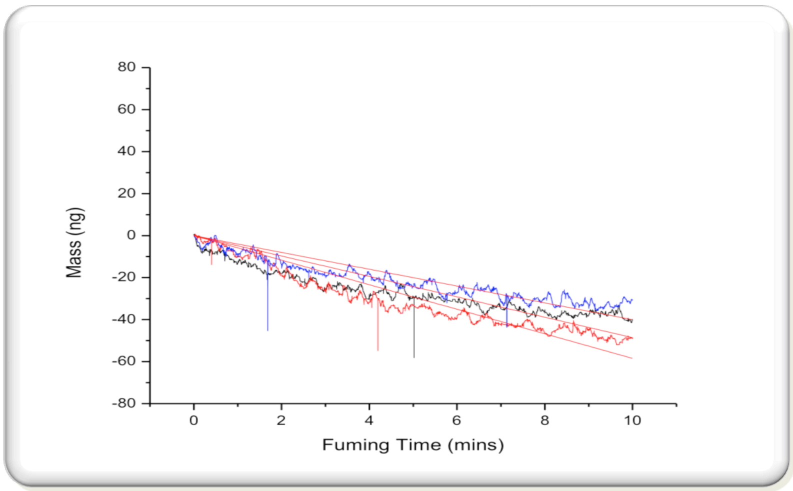

Figure 11: Change in mass of an aged oily latent print with exposure to the vapor of boiling water, plotted as a function of exposure time.

Somewhat surprising is the fact that the slope of the line for the print suspended above boiling water is *negative*. This indicates that the mass of the print is decreasing with exposure to boiling water vapor, i.e. that the boiling water vapor washes away the print. Clearly, the exposure of the latent print to boiling water primarily results in loss of print material, a process that is detrimental to the development of the print by superglue fuming. Also, somewhat surprisingly, the exposure of the print to the vapor of room temperature water modestly increases the mass of the print.

Further experiments were completed to verify that the exposure of aged latent prints to room temperature water vapor hydrates the aged prints; and more accurately determine the impact of this hydration procedure on the quality of fumed aged latent prints. Both clean and oily latent prints were deposited, then exposed to room temperature water vapor or boiling water vapor. These prints were then fumed with ECA for ten minutes, and the amount of poly(ethyl cyanoacrylate) that is grown on each print was determined by the careful determination of the mass of the fumed print. Figures 12 and 13 show the result of these experiments, which plot the fractional increase in mass of each print after fuming, where Figure 12 shows the results for the fresh print, while Figure 13 shows the results for aged prints.

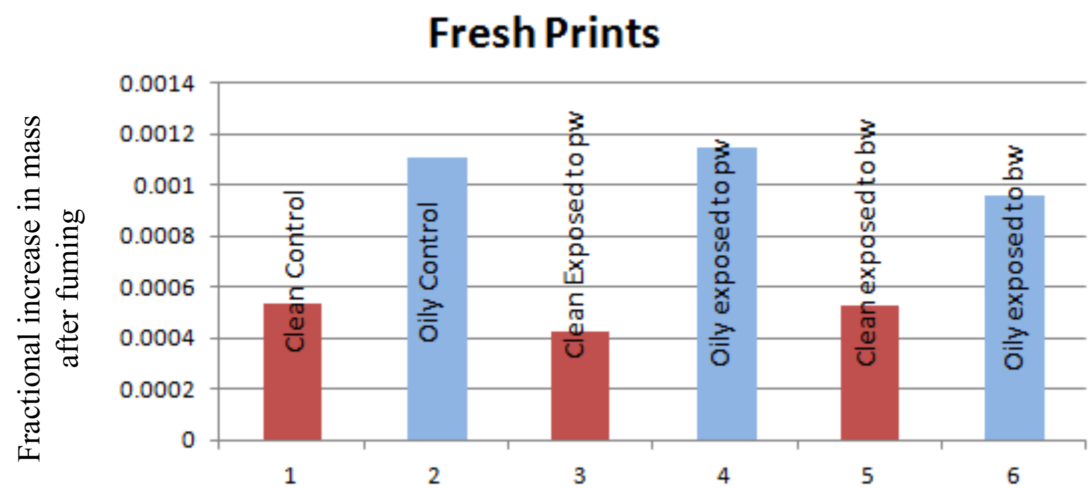

Figure 12 The fractional increase in mass of the fumed print after water exposure for fresh prints.

Unfortunately, the results are not promising. The fresh clean prints that are exposed to plain water (pw) do not show an increase in the amount of PECA grown off of the print compared to the clean print that is not exposed to water. The exposure of the print to boiling water (bw) shows no significant improvement for the clean prints and a slight decrease in PECA growth for the oily prints. Figure 13 shows similar results for the latent prints that have been aged for 14 days. For these prints, the plain water shows a modest increase in PECA growth for the clean prints, though within error. The oily prints exhibit a decrease in PECA growth. Exposure to boiling water, however, shows a strong decrease in PECA formation for both oily and clean prints

The completed experiments therefore demonstrate that exposure of prints to plain water has very little, if any, effect on the PECA formation during the fuming of fresh or aged latent fingerprints. Exposure to boiling water, however, decreases the amount of PECA grown off of the fresh or aged print; this is attributed to the removal of initiators from the print during exposure, hindering PECA formation and therefore decreasing the quality of prints. Therefore, although eccrine sweat is a water based mixture, these results are consistent with the conclusion that components of the prints other than water initiate polymer growth from super glue fuming, not the water itself. Furthermore, simply rehydrating fresh or aged print by exposure to room temperature or boiling water is not a sufficient method for improving print quality. Boiling water harms prints, presumably by removing initiators by dissolving them into the steam and releasing them from the print before fuming.

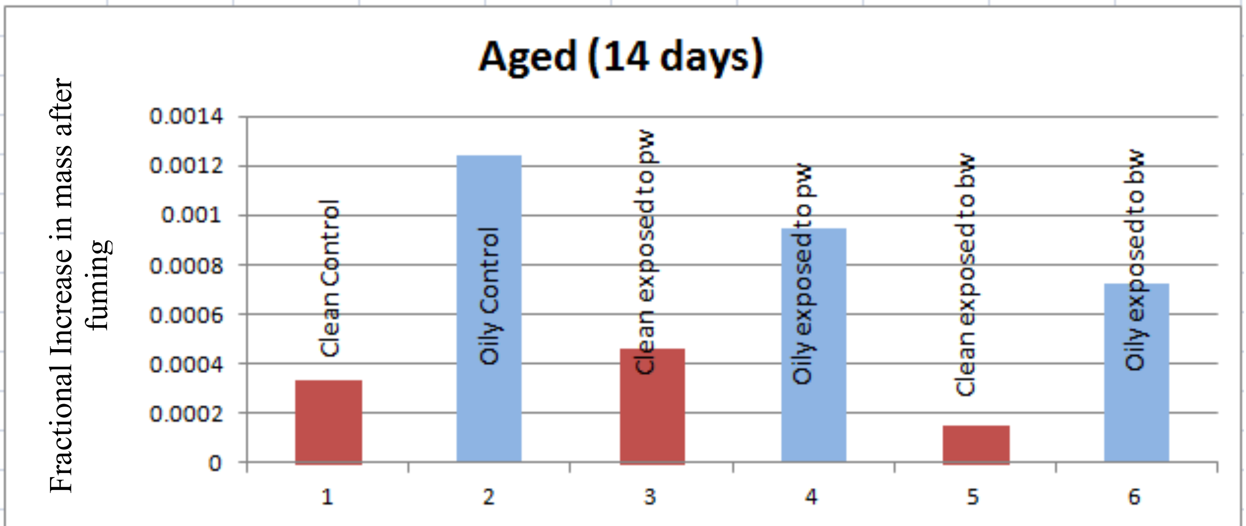

Figure 13 The fractional increase in mass of the fumed print after water exposure for prints that have been aged for 14 days. Note the relative decrease in mass due to aging as well as similar trends to the behavior of fresh prints.

Optimizing the Turn-around Time of the Superglue Fuming Method

The focus of this portion of the project centered on understanding and improving the requirement that fumed prints often necessitate 12-24 hours to 'harden' to ensure that the print will not smudge during further analysis. Multiple members of our research team have spent significant time attempting to determine under what circumstances superglue fumed latent prints will smear, and when they won't. Discussions with ATF Specialist Andrew McIntyre have clarified that not all fumed fingerprints smear. For instance, our group has attempted to identify a set of reproducible conditions that result in fumed latent prints that have a tendency to smear. A variety of factors have been examined in this endeavor, concentrating on the print donor's gender and the surface on which the print is deposited. Table 2 below shows the conditions and results of the recent tests.

As can be seen in Table 2, the investigations have not yielded a reproducible condition where the fumed print smears.

Table 2

Substrate	Subject Gender	Results and Notes
Glass Slide	Female #1	No Smear
Dr. Pepper Aluminum Can	Female #1	No Smear
Aluminum Foil	Female #1	No Visible Smear however Polymer easily scratched off substrate
9mm Bullet	Female #1	No Smear
Samsung Cell Phone	Female #2	No Smear
Razor	Female #1	No Smear
Toothbrush	Female #1	No Smear
Plastic Cup	Female #3	No Smear
Pencil	Female #4	No Smear
Spoon	Female #5 (Pregnant)	No Visible Smear however Polymer easily scratched off substrate
Spoon	Male #1	No Visible Smear however Polymer easily scratched off substrate
Cardboard	Female #1	Print did not show
Textbook	Female #1	No Smear
Medication Bottle	Male #2	No Smear
Metal Knife	Female #1	No Smear
Lid of Medication Bottle	Female #4	No Smear
Metal Slide	Female #5 (Pregnant)	No Smear
Rubber Eraser	Female #5 (Pregnant)	Did Not Show
409 Cleaner Bottle	Female #1	No Smear
Balloon	Female #1	No Smear
Plastic Book Cover	Female #1	No Smear
Computer Mouse	Female #1	No Smear
Computer Cable	Female #1	No Smear
Mechanical Pencil	Female #1	No Smear
Mechanical Pencil	Male #1	No Smear

With no clear conditions that can be used to reproducibly examine fumed prints that smear, we completed experiments to provide a more careful understanding of the molecular level processes that occur during fingerprint fuming and subsequent "hardening". We have completed

Fourier Transform Infrared spectroscopy (FT-IR) experiments to monitor these molecular level changes during the polymerization of ethyl cyanoacrylate and the hardening process that occurs after polymerization.

Initially, the FT-IR spectrum of ethyl cyanoacrylate (ECA) was monitored as it polymerizes. In these experiments, a small amount of ECA was applied to a glass slide and the IR spectrum was collected every two hours over a twenty-four hour time period. These results are shown in Figures 14 and 15 that demonstrate the change in the peaks at 3130 cm^{-1} and 2240 cm^{-1}, respectively. The 3130 cm^{-1} corresponds to the stretching vibration of the –CH=CH– double bond that reacts during the polymerization, while the 2240 cm^{-1} peak corresponds to the vinyl –CN group.

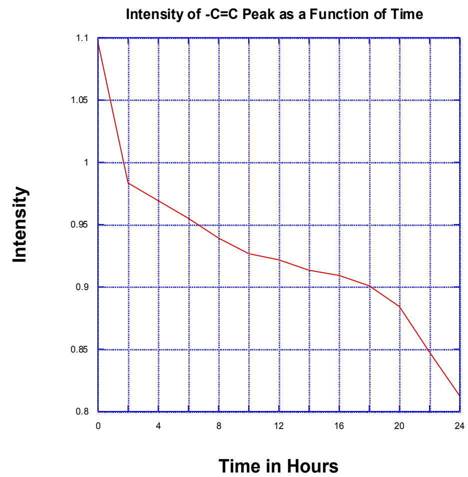

Figure 14: Decrease in intensity of the 3130 cm^{-1} peak with curing, which corresponds to the –CH=CH– double bond

The results show that both peaks decrease during polymerization. While the decrease in the –C=C– stretching is expected due to the reaction of this double bond during polymerization, the loss of the –CN group was not similarly expected. These results can be interpreted to indicate that the polymer chains are crosslinking during the polymerization.

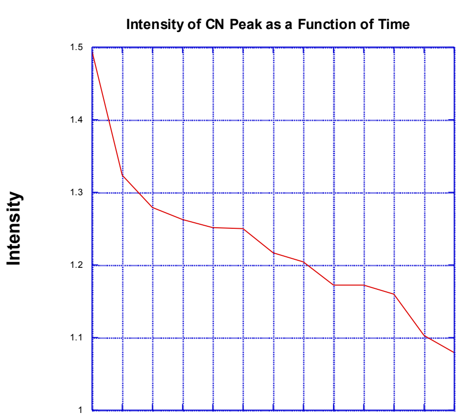

Figure 15: Decrease in intensity of the 2240 cm^{-1} peak with curing, which corresponds to the –CN bond

We therefore conducted additional experiments to further understand the chemistry of the hardening of the poly(ethyl cyanoacrylate) that is formed during the fuming of latent prints. In these experiments, the FTIR spectra of the fresh monomer, of the polymer formed on fumed prints, and of the "cured" monomer after 5 hours of reaction were obtained. The "cured" sample is formed by placing ethyl cyanoacrylate onto a glass slide and allowing it polymerize. The fumed print was obtained by fuming a latent print that was applied to a gold-coated slide for 10 minutes.

The variation in the three spectra is shown in Figures 16, where the difference in the two spectra is found in the analysis of numerous peaks. The peak at 810 cm^{-1} decreases when the monomer reacts as a result of print fuming or when it is cured. Similarly, the 990 cm^{-1} and 1021 cm^{-1} peaks merge to form one peak at 1015 cm^{-1} in both PECA formation reactions, but result in differing final spectra. The peak at 1207 cm^{-1} disappears with polymerization that occurs during fuming or curing of the superglue. The peaks at 1319 cm^{-1} and 1288 cm^{-1} are both due to the C-O stretching vibration, and these peaks shift to 1223 cm^{-1} for the cured sample. This can be attributed to an alteration of the local chemical environment associated with the loss of the adjacent C=C bond. The peak around 1732 cm^{-1} exhibits different behavior for the fumed and cured PECA. This peak is associated with the –C=O group. Interestingly, the PECA formed by fuming and the PECA formed by curing exhibit different C=O peaks, implying that the interaction of the carbonyl groups with its environment differs based on the polymerization process. These results are currently being more thoroughly analyzed and interpreted to understand the polymerization process and products.

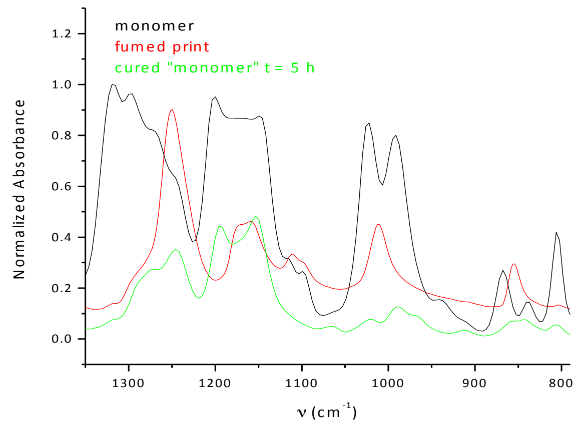

Figure 16: FTIR spectra of ethyl cyanoacrylate monomer, fumed poly(ethyl cyanoacrylate) and cured poly(ethyl cyanoacrylate).

Lastly, the change in the chemical structure of the poly(ethyl cyanoacrylate) during the fuming of a latent print was monitored *in-situ* with FTIR. These *In*-situ IR spectra provide time-resolved information of the chemical reactions that are occurring during the fuming process. To realize these experiments, a latent print was applied to the tip of the In-situ IR diamond tipped probe and exposed to monomer vapors as in the standard fuming process.

The results show that there exist differences in the structure of the PECA that is formed by curing and that which is formed on a fumed print, differences that must be understood. These differences could be due to the presence of water in the cured sample that is not as prevalent in the fumed sample due to the increased temperature of fuming. The fumed print grows from surface bound initiators, which may result in a different reaction than occurs in the atmospheric curing of the monomer. The current FTIR data is being further analyzed to address these continuing uncertainties.

IV. Conclusions:

DISCUSSION OF FINDINGS: This project seeks to provide fundamental information that will enable the straightforward improvement of the superglue fuming method of developing latent fingermarks, by optimizing the acquisition of developed latent fingermarks and enhancing the quality of aged fingermarks. The project has been subdivided into three focus areas as defined in the initial proposal, (A) The Effect of Temperature on the Superglue Fuming of Aged Latent Prints, (B) Role of Hydration on the Superglue Fuming of Aged Latent Fingermarks, and (C) Optimizing the Turn-around Time of the Superglue Fuming Method, where we have made significant progress in all three areas.

The Effect of Temperature on the Superglue Fuming of Latent Prints:

Using Temperature to Improve the Quality of Aged Latent Prints

The results that document the impact of lowering the temperature of the superglue fuming process on the growth of poly(ethyl cyanoacrylate) from aged latent prints show that lowering the temperature improves the ECA polymerization when applied to aged prints, as it does to fresh prints.[32] Notably the molecular weight of the grown polymer approaches that which is found in un-aged fumed prints, indicating that the initiation and chain growth is similar at all temperatures and is not effected by degradation or loss of mass of a print. These results therefore suggest that lowering the temperature may improve the quality of the aged print.

Determination of the Optimum Temperature for Superglue Fuming

Our previous results demonstrate that lowering the temperature of the latent print from 50 to 20 °C dramatically improves the amount of poly(ethyl cyanoacrylate) (PECA) formed on the print during fuming (Fig. 2), as well as an increase in print quality. Further experiments completed in this research program focused on optimizing the substrate temperature for fuming. These results indicate that the optimum fuming temperature for fresh latent prints is 8-10 °C. These results are the focus of a manuscript that is in preparation to disseminate this information to forensic scientists, so that they may take advantage of this information in their fieldwork.

Developing methods to control print temperature during superglue fuming in a forensic laboratory

The research program then focused on developing an experimental procedure that can be more readily applied in a forensic lab than adhering the sample to a temperature controlled block, as was utilized in these laboratory scale experiments. Thus, the quality of fumed latent prints that were cooled in a refrigerator or freezer prior to fuming was evaluated for duct tape, plastic "Ziploc" bags, and soda bottles. The first experiment was to verify the ability of the sample to retain the colder temperature long enough to effect its PECA formation during fuming.

These results show that the samples return to room temperature within two minutes upon removal from the refrigerator or freezer. Thus, it is clear that the use of a standard refrigerator or freezer is not sufficient to keep the sample at ~ 10 °C during fuming to take advantage of temperature effects of the polymerization of ethyl cyanoacrylate that occurs during the fuming process.

The temperature of the three samples was also monitored during fuming of the print surfaces that are placed on a temperature controlled block at 2 °C, 10 °C, 20 °C, and at room temperature to document the impact of the hot ECA fumes on the print temperature. These results indicate that optimum substrate temperature of fuming is between 10 and 15 °C when taking into account the warming of the sample that occurs due to the presence of the warm superglue fumes. Thus, any protocols that are devised to control the temperature of the fuming process must take into account the presence of the warm superglue fumes.

Role of Hydration on the Superglue Fuming of Aged Latent Fingermarks:

The goal of this portion of the research program is to investigate methods to aggressively expose aged fingermarks to water with the goal of improving the *selective* polymerization of ethyl cyanoacrylate from aged prints, consequently improving the quality of the superglue fuming process of aged prints. To realize this goal, we expose aged prints to water vapor by suspending them above room temperature water vapor or positioning them over a beaker of boiling water.

These completed experiments demonstrate that exposure of prints to plain water has very little, if any, effect on the PECA formation during the fuming of fresh or aged latent fingerprints, though the print does appear to take up some of the water. Exposure to boiling water, however, decreases the amount of PECA grown off of the fresh or aged print, where this is attributed to the removal of initiators from the print during exposure. Therefore, although eccrine sweat is a water based mixture, these results are consistent with the conclusion that components of the prints other than water initiate polymer growth from super glue fuming, not the water itself. Furthermore, simply rehydrating fresh or aged print by exposure to room temperature or boiling water is not a sufficient method for improving print quality. In fact, boiling water harms prints, presumably by removing initiators by dissolving them into the steam and releasing them from the print before fuming.

Optimizing the Turn-around Time of the Superglue Fuming Method

The focus of this portion of the project centered on understanding and improving the requirement that fumed prints often necessitate 12-24 hours to 'harden' to ensure that the print will not smudge during further analysis. Multiple members of our research team have spent significant time attempting to determine under what circumstances superglue fumed latent prints will smear, and when they won't. For instance, our group has attempted to identify a set of reproducible conditions that result in fumed latent prints that have a tendency to smear. A variety of factors have been examined in this endeavor, concentrating on the print donors gender and the surface on which the print is deposited. Unfortunately, these investigations have not yielded a reproducible condition where the fumed print smears.

With no clear conditions that can be used to reproducibly examine fumed prints that smear, we completed Fourier Transform Infrared spectroscopy (FT-IR) experiments to provide a more careful understanding of the molecular level processes that occur during fingerprint fuming and subsequent "hardening. The results show that there exist differences in the structure of the PECA that is formed by curing and that which is formed on a fumed print, differences that must be understood. These differences appear to be due to the presence of water in the cured sample that is not as prevalent in the fumed sample due to the increased temperature of fuming. The fumed print grows from surface bound initiators, which may result in a different reaction than occurs in the atmospheric curing of the monomer. The current FTIR data is being further analyzed to address these continuing uncertainties.

IMPLICATIONS OF POLICY AND PRACTICE:

The results of this research program which are most promising to impact policy and practice are the results that provide additional insight into the impact of temperature on the fuming of latent prints. This research program clearly indicates that lowering the temperature of the object on which a fingerprint resides to ~8-10 °C will increase the amount of PECA that is formed during fuming, which in turn improves the quality of the developed print. This has clear implications to the practicing forensic scientists, in that fuming chambers with temperature control should be developed.

The results also indicate that the quality of fumed *aged* latent prints can be improved by lowering the temperature. Our interpretation of this phenomenon is that the lower temperature improves the efficiency of utilizing the remaining initiators that exist in the after aging. This provides another parameter to control in lab that can offer an improvement of print quality.

The results that have investigated the hardening of the print appear to indicate that there are very few conditions (surfaces, print composition, etc.) that exist for print fuming that result in a latent print that smears. Our interpretation of this result is that the formation of a fumed print that smears is due to specific local environment conditions. This implies that the observation of a print that smears shortly after fuming is indicative of an alteration in the fuming chamber environment, which should be investigated. A reproducible chamber environment should provide the practicing forensic scientist with a fumed print that is robust after a few minutes.

IMPLICATIONS FOR FURTHER RESEARCH:

The results of this project do offer potential pathways for further research. These include:

- There remains a need to understand the combined impact of humidity and temperature on the molecular level processes that occur during the fuming process. Lowering the temperature of the fuming reaction may also cause condensation of water vapor from the air onto the surface, which will likely decrease print quality by either inhibiting polymer growth (water can be a terminating agent in the polymerization) or allowing polymer growth outside the print ridge (water may also be an initiator for chain growth). It therefore becomes extremely important to simultaneously control the temperature and humidity of the fuming process in order to truly optimize the growth of the polymer during fuming and bias the development process towards better quality prints.

- While the fuming of latent fingermarks is a simple and effective method to develop the fingermark, a main limitation of this technique is the white color of the polymer that is formed, which often exhibits insufficient contrast with light colored or transparent surfaces. To improve this process, the development of a fuming process that includes a fluorescent dye with the cyanoacrylate during fuming has been a topic of significant recent interest.[33,34] Commercially available products that enable the superglue fuming of a print in the presence of a fluorescent dye include CN-Yellow from Arrowhead Forensics, Lumicyano, and PolyCyano UV. However, in each of these products, the presence of the colorant/fluorescent dye may alter the polymerization of the cyanoacrylate during the fuming process. It is therefore important to document the impact of altering the formulation of the cyanoacrylate (i.e. the addition of a fluorescent dye) on the polymerization process and optimum temperature of the fuming process.
- Similarly, the chemical composition of aged latent prints is known to differ from that of fresh prints, and therefore, the optimum temperature of fuming aged latent prints should also be studied.
- The development of a chamber with control of both temperature and humidity for the fuming process that can be adapted in a Forensic Laboratory should be examined. While the result of this research program are completed in a fuming chamber with temperature and humidity control, the use of a small refrigerator that is adapted to allow for humidity control should be examined as a novel chamber to control temperature and humidity in a forensic laboratory.

V. References:

All references are listed at the end of the report.

VI. Dissemination of Research Findings

Publications:

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Presentations:

"Understanding the Science of Superglue Fuming to Improve the Quality of Developed Latent Prints" University of North Carolina Pembroke, Pembroke, NC, April, 2014

"Developing Methods to Improve Superglue Fuming of Latent Fingerprints" International Association for Identification, Providence, RI, Aug 2013

"Understanding the Science of Superglue Fuming to Improve the Quality of Developed Latent Prints" Eastern Kentucky University, Richmond, KY, Nov, 2012

"Understanding the Science of Superglue Fuming to Improve the Quality of Developed Latent Prints" East Tennessee Section of the American Chemical Society Meeting, Morristown, TN, Sept, 2012

"Understanding the Science of Superglue Fuming to Improve the Quality of Developed Latent Prints" Knox County Forensic Science/CSI program, Karns, TN, Nov, 2011

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