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Final Summary Overview

for

Combined Temperature and Humidity Control to Tune Latent Fingermark Development by Superglue Fuming

(2015-IJ-CX-K015)

by

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Statement of purpose:

The funding for this project was awarded in January 2016, and 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 these developed fingermarks. These funds primarily support Ms. Leondra Lawson, a graduate student in our group that is working on this project.

This project can be subdivided into three focus areas as defined in the initial proposal, (A) *The Coupling of Temperature and Humidity to Improve the Superglue Fuming of Latent Prints*, (B) *The Importance of Surface Composition on Growth of Polymer during Superglue Fuming of Latent Prints with Controlled Temperature and Humidity*, and (C) *The Importance of Cyanoacrylate Formulation on Optimizing the Fuming of Latent Prints*.

Statement of Hypothesis and Rationale: 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, are completing 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.

Project Design and Methods:

1. The Coupling of Temperature and Humidity to Improve the Superglue Fuming of Latent Prints

We completed a set of experiments to provide insight into the combined impact of humidity and temperature on the molecular level processes that occur during the fuming process, again with the goal of creating a protocol that can be used by forensic scientists to readily improve the efficiency and quality of fumed prints. A well-known effect of temperature in well-controlled anionic polymerizations is that lower temperatures create more beneficial ion-pair initiators. However, the superglue fuming of latent prints is not a well-controlled reaction, and therefore it is not clear whether the increase in polymerization rate at lower temperature is due to increasing initiation by creating more effective ion-pairs or due to minimizing side reactions, or limiting termination. Simultaneously, a lower temperature 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.

Therefore, we examined the effect of temperature for relative humidities that range from ambient to 80% on the amount of poly(ethyl cyanoacrylate) [PECA] (Sirchie OMEGA-PRINT) that grows off of prints deposited on glass microscope slides. The temperature is varied from -10°C to 60 °C as our preliminary experiments show that this is the important parameter range.

This is accomplished by monitoring the fuming of latent prints and the subsequent characterization of the resultant prints and polymer. Characterization techniques that are utilized will include mass analysis, electron microscopy, Fourier Transform Infrared Spectroscopy (FTIR), print quality assessment, and molecular weight analysis of the resultant polymer.

Thus, the results that emanate from this holistic set of experiments offer enhanced insight into the combined role of temperature and humidity on the fuming process and its associated chemical reactions, providing crucial fundamental information that can be utilized by forensic scientists to develop protocols that optimize the fuming process of fresh and aged latent fingermarks.

2. The Importance of Surface Composition on Growth of Polymer during Superglue Fuming of Latent Prints with Controlled Temperature and Humidity

Recent results reported in the literature[1] also indicate that there is a temperature where there is a “greatest visual impact” when fuming latent prints on steel (18 °C), copper (22°C), and glass (8°C), suggesting that the composition of the surface on which the fingermark resides may impact the effect of temperature on the growth of polymer during the superglue fuming of latent prints. It is important to note that these results are consistent with our recent results that have focused on using microscope slides as a model surface, where we determined that the most polymer is formed during the fuming of latent prints on glass at ~10 °C.

As the surface on which a fingermark exists is beyond control at a crime scene, we extend the studies described above to a series of materials beyond glass, with the goal of elucidating the role of the supporting surface in defining the optimal temperature and humidity of the superglue fuming process. With this goal in mind, we planned to examine the combined effect of temperature and humidity on the amount of poly(ethyl cyanoacrylate) (Sirchie OMEGA-PRINT) that grows off of prints deposited on steel, copper, poly(ethylene terephthalate) [Coke bottle], and polyethylene [Ziplock bags]. The materials are chosen as they exhibit a range of thermal conductivities, where the metals have high thermal conductivities and the plastics are thermal insulators. The materials also have varied chemical composition, ranging from inorganic metals to organic plastics. Finally, the materials mimic many common items that may be found at a crime scene including shell casings and weapons (metals), plastic bags containing drugs (polyethylene), and soft drink bottles (poly(ethylene terephthalate (PET)).

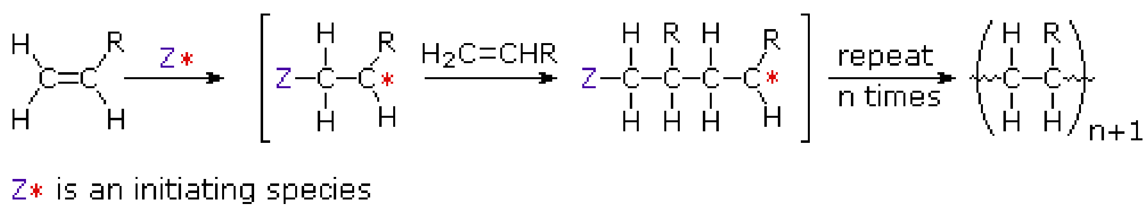
As in the experiments described in Section 1 above, we monitor the fuming of latent prints and subsequently characterize the resultant prints and polymer that are formed via the fuming process under controlled temperature and humidity on each surface. Thus, the results of this set of experiments are designed to document the impact of the supporting surface on the growth of polymer that occurs during development of the latent print, providing insight into the potential inhibiting or catalytic properties of the surface on the polymerization of ethyl cyanoacrylate. This correlation will provide heretofore unavailable information that can be used to rationally optimize the fuming of latent prints in a forensic crime lab by controlling humidity and temperature, two parameters that are readily governable. As noted below, we have made limited progress on this portion of the project with studies that monitor the fuming on PET, PE, and glass.

3. The Importance of Cyanoacrylate Formulation on Optimizing the Fuming of Latent 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 remedy this, several post-deposition treatments have been developed to improve the contrast between the polymer and the substrate. These processes include dusting the fingermark with colored or fluorescent dye powders, or staining with a fluorescent dye solution.[2,3,4] This post-deposition treatment increases the development time, slowing an investigation, and may contain toxic compounds.

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.[5,6] 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. The polymerization of cyanoacrylates occurs by an anionic mechanism, which begins with an anionic Lewis base initiator (Z* in scheme 1 below) attacking a monomer. The negative charge is then transferred to the monomer and subsequently attacks another monomer. This process is propagated until one of two events occurs, either the monomer supply is exhausted or the anion is terminated upon colliding with the terminating agent. These consecutive reactions are shown in Scheme 1.



Scheme 1: Consecutive reactions that occur in an anionic polymerization, initiation, propagation, and termination.

The extreme reactivity of the anionic chain end usually requires the complete absence of terminating agents such as water, oxygen, and especially acids. As trace amounts of impurities are known to inhibit anionic polymerizations, it is important to document the impact of altering the formulation of the cyanoacrylate (i.e. the addition of a fluorescent dye) on the polymerization process in order to develop methods to optimize the fuming process. In particular, we monitor the combined impact of temperature and humidity on the fuming of Lumicyano cyanoacrylate on glass microscope slides, and compare these results to the fuming of Sirchie OMEGA-PRINT on glass microscope slides to document the impact of the

This is realized by following the procedures described above. As described previously, we monitor the fuming of latent prints with Lumicyano and subsequently characterize the resultant prints and polymer with control of temperature and humidity. The conditions of these experiments are carefully controlled to mimic those that were completed in Section 1 above, to allow the direct comparison of the polymerization reactions of Lumicyano to those of OMEGA-PRINT as a function of temperature and humidity. These results therefore clearly reveal the impact of adding a fluorescent dye on the polymerization of a cyanoacrylate during the fuming process. Moreover, the completion of this set of experiments will also provide guidelines for forensic scientists to design different formulations of cyanoacrylates and to optimize the fuming of latent prints with various cyanoacrylates by simultaneously controlling temperature and humidity during fuming.

Findings:

1) *Coupling of Temperature and Humidity to Improve Fuming of Latent Prints*

Based on our findings, ambient relative humidity with surface temperatures near 10 °C provided the optimum quality of visual fingerprints fumed with Sirchie ethyl cyanoacrylate. These results also influence and guide our efforts in regards to investigating optimum parameters for different surfaces and different cyanoacrylate formulations. Our understanding of this results is that the optimum temperature is the result of the balance of competing factors. These factors include the stabilization of propagation centers with lowering temperature, which increases the growth of PECA from the fumed print. This is counterbalanced by a propensity of ambient water vapor to condense onto the print at lower temperatures, where the water acts as terminating and chain transfer agents, slowing the growth of PECA from the fumed print. The optimum balance of these two factors appears to occur at ~ 10 °C.

2) *Importance of Surface Composition on Growth of Polymer during Superglue Fuming of Latent Prints with Controlled Temperature and Humidity*

   Our examination of the impact of surface composition has hit some hurdles, where the accurate monitoring of print growth during fuming on polyethylene surfaces became untenable due to fluctuating mass of the polyethylene itself. Moreover, we found little difference between the PECA formed from prints on glass and polyethylene terephthalate.

3) *Importance of Cyanoacrylate Formulation on Optimizing the Fuming of Latent Prints*

   Overall, LumiCyano proved to be an advantageous alternative to commercial cyanoacrylate when the manufacturer's instructions are followed. For both cyanoacrylate formulations, the larger amount of PECA was formed at surface temperatures near 10 °C. For surface temperatures exceeding 5 °C, PECA grown with Sirchie had molecular weights an order of magnitude lower than those grown with Lumicyano. We believe that this difference is the result of the presence and basic nature of the tetrazine based fluorescent tag in Lumicyano. The tetrazine, therefore, increases the pH of the reaction site, which is known to inhibit termination of the PECA chain growth and increase the amount and molecular weight of PECA formed on the print.

Implications for criminal justice policy and practice in the United States.

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 and humidity 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 and fuming at ambient humidity 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.

Moreover, the insight gained from the understanding of the cyanoacrylate formulation on fuming provides a foundation for further development of additives to cyanoacrylates that provide beneficial properties to the fuming process, where additives that increase the basicity of the cyanoacrylate should be targeted.

Products

Publications:

We do not have any peer reviewed publications submitted yet, but we expect to publish three papers from this research program. At the same time, the results of this research program will serve as the central focus for the Ph.D. Thesis of Ms. Leondra Lawson, which she is expected to defend in 2019.

- *"Enhancing the Cyanoacrylate Fuming Method of Latent Prints by Optimizing Surface Temperature and Humidity*" Leondra S. Lawson-Johnson, Mark Dadmun, *In Preparation*
- *"Importance of Cyanoacrylate Formulation on Optimizing the Fuming of Latent Prints"* Leondra S. Lawson-Johnson, Mark Dadmun, *In Preparation*
- *"Understanding the Chemistry of Superglue Fuming to Improve the Quality of Fumed Latent Prints*", Ph.D. Dissertation, University of Tennessee, Leondra Lawson, *In Preparation*

Presentations:

- "Enhancing the Cyanoacrylate Fuming Method of Latent Prints via Coupling the Effects of Temperature and Humidity" Pittcon Conference and Expo, Orlando, FL, February 26-March 1, 2018 (L. Lawson, Grad. Student, Presenter)"
- "Combined Temperature and Humidity Control to Tune Latent Fingerprint Development by Superglue Fuming" IAI National Conference, Atlanta, GA, August, 2017
- "Enhancing the Cyanoacrylate Fuming Method of Latent Prints via Coupling the Effects of Temperature and Humidity" IAI National Conference, Atlanta, GA, August, 2017 (L. Lawson, Grad. Student, Presenter)
- "Enhancing the Cyanoacrylate Fuming Method of Latent Prints via Coupling the Effects of Temperature and Humidity" Southeast Polymer Forum, Blacksburg, VA, June 2017. (L. Lawson, Grad. Student, Presenter)

- “Applying Polymer Science Principles to Understand the Chemistry of Superglue Fuming” Abertay University, Dundee, Scotland, October 2016”
- “Applying Polymer Science Principles to Improve Materials for Energy Harvesting, Forensic Science, and Advanced Manufacturing” Heroit-Watt University, Edinburgh, Scotland, October 2016”
- “Applying Polymer Science Principles to Understand the Chemistry of Superglue Fuming”, Crime Science Technologies, Paris, France, April 2016”
- “Understanding the Science of Superglue Fuming to Improve the Quality of Developed Latent Prints”, Tennessee Tech University, Cookeville, TN, October, 2015”

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