Document Title:	**Co-Polymerization of Sublimation Dyes and Expanding the Micro-Crystalline Vapors of Cyanoacrylate in Fingerprint Development**
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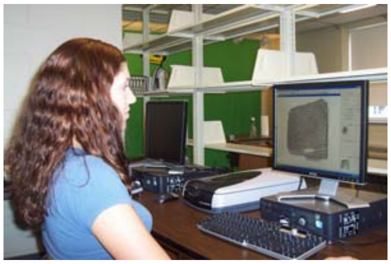
Document No.:	**227937**
Date Received:	**August 2009**
Award Number:	**2006-DN-BX-K037**

Co-Polymerization of Sublimation Dyes and Expanding the Micro-Crystalline Vapors of Cyanoacrylate in Fingerprint Development

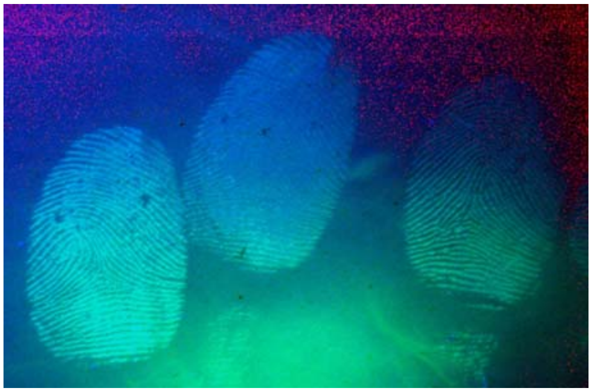
In October of 2006, the National Institute of Justice (NIJ) awarded Mountain State University's Forensics Division of Justice Studies with funding to conduct research to enhance latent print visualization by combining co-polymerize sublimation dyes with the cyanoacrylate deposition process.

Mountain State University, founded in 1933, is a not-for-profit, independent institution in Beckley, West Virginia, serving more than 6,500 students a year from all 50 states and a host of other countries. In addition to its main campus in Beckley, MSU has four branch campuses: MSU Martinsburg, serving the eastern panhandle of West Virginia and the quad-state area near Washington, D.C.; MSU Center Township, serving greater Pittsburgh; and MSU Orlando, serving central Florida. Its newest location is at the Hickory Metro Higher Education Center in Hickory, N.C.



The forensic investigation curriculum at MSU is as diverse as the backgrounds of its full and part-time professors. The team operates under the direction of Dr. Michael Kane, with faculty and staff bringing a real-world experience from across the nation. Instructors have firsthand knowledge and hands-on skill from such backgrounds as the military, state and local police and fire departments, crime labs, and even the FBI. MSU's forensic and criminal justice instructors provide students with a proficient understanding of the crime scene investigation processes. Students at Mountain State University can earn an Associate of Science in Fire Science and/or a Bachelor of Science in Forensic Investigation. Both degrees offer hands-on learning experiences in all of the forensic-related classes. Outside of the traditional classroom, MSU provides forensic students with a two-story (plus basement) crime scene house where practical events are conducted with realistic, simulated crime scene investigation.

. This research focused on co-polymerization simultaneously with cyanoacrylate and dye materials. The photo on right depicts our first success.



MSU/NIJ research began in January of 2007, with numerous MSU students participating in the processes. Two individual branches make up the research project:

1. Attempting to co-polymerize sublimation dyes with cyanoacrylate for latent fingerprint development that is visible with Ultra Violet (UV), Alternate Light Source (ALS) and room light color. Numerous families of sublimation dyes have been tested with varying thermal parameters along with multiple concentrations of differing solvents, thermal range modifiers and two types of cyanoacrylate.

2. Expanding the micro-crystalline vaporization of liquid cyanoacrylate and sodium hydroxide cellulose pads. In this branch of research numerous chemistries have been tested. We have increased the micro crystalline blume from two minutes to four and eight minutes, however the thermal parameters were not expanded sufficiently to accomplish the heat required to sublimate the thermal dyes.

New Patents/Research Tools: Fuma-Dome and Press and Fume

This research project has been working towards a one-step co-polymerization of several families of sublimation or airborne dyes with cyanoacrylate as a fingerprint development methodology. The research was devised around two new patented devices by Certified Latent Fingerprint Examiner, David E. Weaver. These devices are the Fuma-Dome and the Press and Fume, recently launched by Tri-Tech Inc. of Southport, North Carolina. The Fuma-Dome provides for a sublimation heat device as well as an enclosed chamber to concentrate the cyanoacrylate and sublimation dyes for rapid fingerprint development on any non-porous surface. The Press and Fume device is a low-cost, low-tech paper-thin glass ampoule system that when crushed creates instant fingerprint development on nonporous surfaces within a 3-cubic foot container.

The Fuma-Dome is a new and revolutionary system for developing latent prints by means of cyanoacrylate (Superglue) fumes. Unlike other fuming guns, the Fuma-Dome combines a fuming gun and fuming chamber into one system specifically designed for use at a crime scene; however, it can also be used in the crime laboratory. This innovative design also incorporates a rechargeable cyanoacrylate cartridge.

At pennies per charge, the Fuma-Dome is extremely cost effective. Developing latent prints with Fuma-Dome is simple, straightforward, and happens very rapidly. Often within 30-seconds fingerprints are visible on nonporous surfaces. After the cyanoacrylate is depleted, recharging is quick and easy. The operator can import liquid cyanoacrylate into the copper rechargeable sublimation device. A recharged cartridge will provide you with approximately five to ten minutes of fuming. The clear, 11" diameter plastic dome allows monitoring of the prints as they develop. The Fuma-Dome can be used for developing prints on larger surfaces such as glass windows, doors, tabletops, or even vehicles, as shown below.

Background

The use of airborne colorants for co-polymerization with cyanoacrylate presents two basic challenges. The colorant must have preferential affinity for cyanoacrylate. The colorant must also have a similar thermal parameter to the cyanoacrylate. Colorants may be defined as either pigments or dyes with many sub-classes. Pigments are microscopic colored particles that are insoluble in the substrate that they are coloring. Pigments tend not to migrate out of the substrates they are imbedded in. By contrast, dyes can be more prone to migration into and out of substrates than pigments as they are soluble colorants. They tend to be transparent colorants, but their molecule by molecule dispersion imparts more color on a mass to mass ratio than do pigments. This is because all of the dye mass contributes to color whereas only the pigment mass at the surface contributes to coloration.

Colorants may become airborne following a variety of mechanisms. Pigments or dyes can be dispersed in an air, dust, liquid or plasma stream. Dyes can be sublimed or vaporized. Cyanoacrylate may be colored with dyes or pigments. Pigments need to be added to the uncured resin before cured. Dyes can be added before the resin cures or applied after curing and allowed to migrate into the resin to provide color. In the context of fingerprint development, transparent colors are preferred so that the detail of the fingerprint is not obscured, also due to the molecular weight of these transparent dyes they are more likely to migrate in the vaporization process at similar thermal or vapor pressure parameters and co-polymerize with cyanoacrylate. In addition, because of the mechanism used, the resin impacting the fingerprint may cure either before or concurrent with the dye application, therefore, migratory colorants are preferred. Because the intent of this research was on color transfer through sublimation, and because the purpose was to resolve the detail of the print, we focused on dyes rather than pigments.

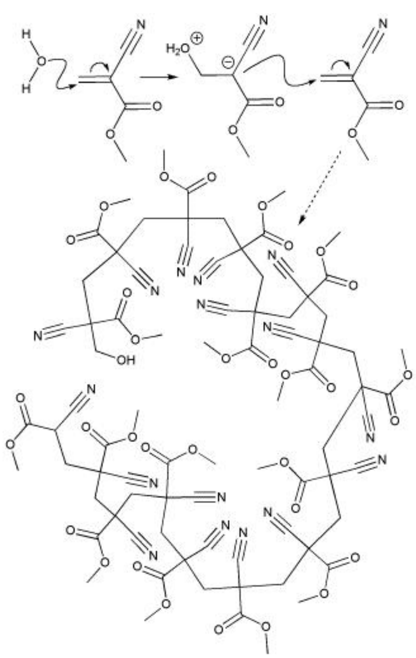
In its simplest form, cyanoacrylate was vaporized and allowed to cure to a fingerprint. Under various conditions dyes were vaporized or sublimed and the dye cloud was allowed to contact the polymerized fingerprint, this yielded less specificity to the latent fingerprint and most dyes used as a secondary application yielded strong background coloration sometimes obscuring the fingerprint entirely. It is the focus of this research to simultaneously introduce the sublimation dye and cyanoacrylate in the vapor wand format, and we proceeded with a protocol; which focused on the co-polymerization process with simultaneous volatilization of Cyanoacrylate and sublimation dyes

The first dyes selected were a sub set of disperse dyes called sublimation dyes. Disperse dyes are a special class of solvent soluble colorants that are typically mixed with dispersing aids to make water based dispersions for textile dyeing. In textile applications, the dye is introduced in a water bath at an elevated temperature. Because the dye has a greater affinity for the textile than it does for the water, the warm dye particle impacts the surface of the textile it dissolves into the fabric. Because it is not water soluble, it will not migrate back out the dye bath.

These dyes are soluble in many polymer systems including cyanoacrylate. In polymer applications no dispersing aid is needed. They are co-mixed directly with the resin and dissolved into the resin as a manufactured part is produced. Whether a particular colorant is classified as a solvent dye or a disperse dye depends on the application and on whether a dispersing aid is added to the chromaphore. There are many dyes, where the core chromaphore is sold as a solvent dye under one name and mixed with a dispersing aid and then sold as a disperse dye under a different name.

As the name implies the sub class of sublimation dyes, sublime rather than melt when their phase transition temperature is met. These dyes are used in a variety of applications ranging from smoke bombs to printing on textiles. In textile printing, the dyes are printed onto transfer paper. The paper is then applied to textiles (c.f., polyester) and heat is applied driving the dye into a gas state. The gas invades the textile where, as in the dye bath, it dissolves into the fabric allowing very detailed patterns. In smoke bombs the dye is heated or burned and becomes colored smoke until the gas cools back to room temperature. The colored smoke is a dye vapor. It can and will color compatible substrates it impacts.

Cyanoacrylate:



In its cured state Cyanoacrylate has many polar sights available for electronic affinity with solvent soluble dyes.
Many traditional plastics colorants, such as solvent red 1, solvent blue 36 solvent yellow 43 will all color this resin. Previous applications have used solvent blue 36 and solvent yellow 43 to bath dye already cured prints. In these applications, the dye migrates out of alcohol solutions into the resin. As with the water dispersions, the dye has more affinity for the resin than the alcohol bath. The mechanism of migration is important to the overall project. Dyes are

more susceptible to migration than pigments because of the relative mass. When thinking in molecular terms, a pigment is a huge, massive particle. As such is not greatly affected by the random movement caused by thermodynamic vibration.

Dyes on the other hand are discrete molecular sized particles. Unless they are bound to a substrate they will move around freely compelled by random thermodynamic energy. This is why dyes are able to leave dye baths and migrate into another object. In the case of coloring materials like resins, the dye is unbound in the dye bath and can move freely into the resin. If the dye has affinity for the dye bath it can just as easily move back out. In the case of disperse dyes in water, once the dye is in the resin it looses the dispersing aid and has no affinity for the water so it will not migrate back into the batch. The dye can however move freely on the resin and if the resin contacts something that the dye also has affinity for it can migrate, or bleed, into the new object.

Therefore when coloring something through a bath or any migratory process, it is important to find a dye that will migrate in and get stuck. For cyanoacrylate, dyes which will, by nature of their polarity bond to the available electrons in the oxygen groups will move into the resin and stay there.   For this application sublimation dyes that would have affinity for the resin in their solvent dye state were selected. It was not critical that the dyes would not be able to bleed out.

A variety of dyes were tested including the full commercial range of sublimation and smoke dyes. Other classes of dyes tested included: solvent, acid, basic, polymeric and some specialty colorants included keyplasts and petroleum dyes were also tested. Each dye tested has a different phase transition temperature and some do not sublime. For this research, lower transition temperature parameters were a secondary goal as the equipment that would be utilized in the field is somewhat limited to moderate heat output. Unfortunately most dyes that sublimed at a sufficiently low temperature did not have preferential affinity for the fingerprint. Preferential affinity for the print simply means that the dye would color the print and not the background and can be done in a variety of ways. First is that the dye will adhere to or solubalize in the cyanoacrylate and not the background. Second would be for the dye to have a color effect in or on the cyanoacrylate that is easily distinguishable from the effect in the rest of the background.

Research protocols

1. All dyes are first tested alone in the sublimation device at a full range of temperatures, low, (275-300 degrees F) medium, (400-525 degrees F), and high, (625-750 degrees F). This test is performed by exposing the generated vapor onto white ceramic tile with known exemplars of the investigator’s finger impressions placed on them. The tiles are held approximately eight to twelve inches away from the exhaust of the butane torch. Results are monitored and documented. Several times we have developed specificity of the sublimation dye to the fingerprint.

Room light, visible red and blue materials as well as a very strong and consistent UV/ALS co-polymerization have occurred, up to the date of this writing. Specifically, Yellow 43 sublimation dye shows consistent fingerprint development and moderate to great sensitivity under UV and ALS.

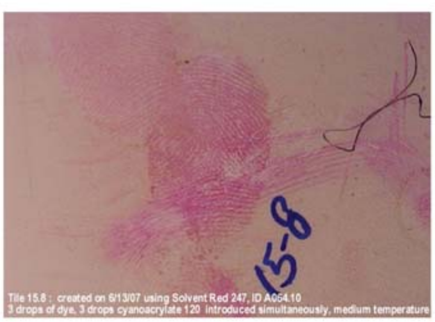
2. All dyes are tested in a combined format with the cyanoacrylate (CN) impregnated into the sublimation device, as well as the dye materials. This branch of the research is giving us optimum results, as the developing fingerprints are stabilized by the CN polymer.

Because of the tincitorial strength of dyes, colored residue left on surfaces after the fuming process can often be noticeable as an invasive color. However, many dyes produce different colors in their crystalline state than they do in their solubalized state. One of the best performing dyes was solvent yellow 43. As mentioned above, solvent yellow 43 will migrate into cured cyanoacrylate in a bath dyeing application. Solvent yellow 43 is also smoke dye and will sublime when heated to its phase transition temperature. This dye gave the best results in the vapor wand, co-polymerization branch of our research, with dye impregnated tightly into the polymerized cyanoacrylate developed print. This dye has also shown discrete co-polymerization, specific to the fingerprint in the breakable cartridge format that uses Sodium Hydroxide for the exothermic event. Research continues as the photo-luminescent yield is low.

The testing of sublimation dyes in the new Fuma-Dome system has produced interesting results, also we have achieved injection of the CN vapor and Yellow 43 into standard fingerprint development chambers with extreme success. Subsequently, three U.S. Patents have been filed (PATENT PENDING) for the various configurations of dye blends and we are continuing to refine the product CN-Yellow (tm).

We are finding a great variance in the families of the other dye materials with sometimes very specific polymerization at the fingerprint ridge site but nothing as specific and robust as the Yellow 43.

Solvent Red 247



Right; Co-polymerization of Red 247.

Left; Close up image of latent print developed with cyanoacrylate and Red 247.

Thus far we have three families of dyes that are co-polymerizing with variable specificity. We have also had an event which has opened a very direct route of investigation: One particular dye, a red subliming dye called 247 gave instant and prolific results and co-polymerization with the cyanoacrylate. Unfortunately, we only received approximately 1 gram of this dye. We ordered more of the material and when we received the second batch it did not work. Variables in dye batch manufacturing and de-dusting oils may be the reason for the variability. The original dye was sent to a premier microscopy resource laboratory, McCrone Associates, Inc. of Westmont, IL, for further analysis. Their analysis identified as the only difference in the two batches of solvent red 247 is the quantity of twitchell de-dusting oil present. It would appear that the twitchell is acting as a vapor carrier and migratory agent that when present in the proper ratio enables the 247 dye to preferentially adhere to the latent print. Currently our chemist, Charles Steele, is developing line blends with varying ratios of Red 247 and the twitchell de-dusting oil in hopes of duplicating and improving on the initial success.

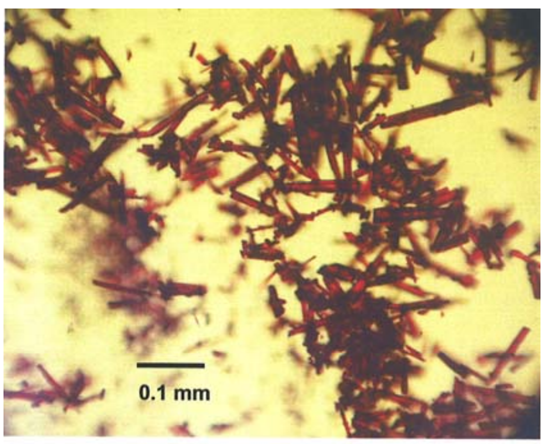


Figure 1. Solvent Red 247, Original sample (transmitted light, in air)

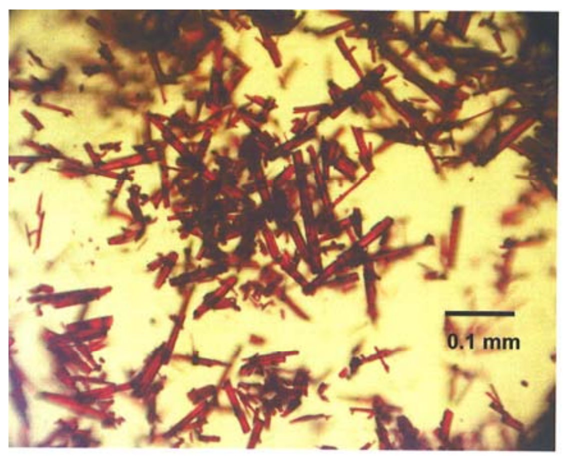
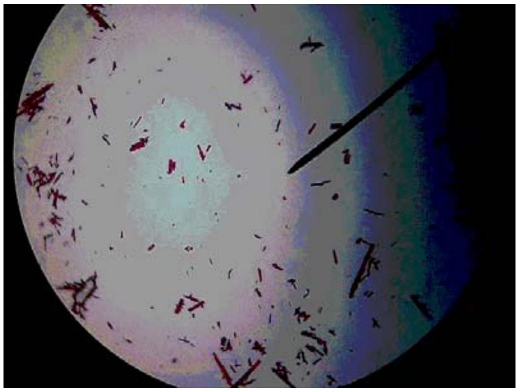
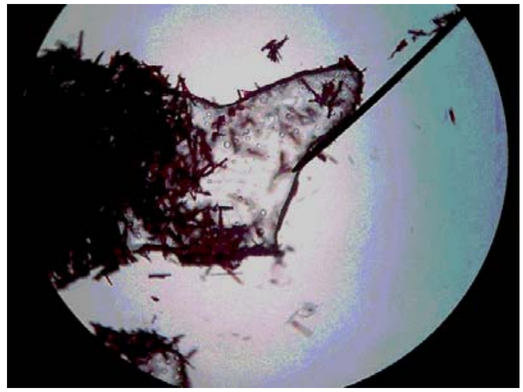


Figure 2. Solvent Red 247, Second sample (transmitted light, in air)

The original 247 dye batch preferentially adhered to the fingerprint ridge site as opposed to most other red dyes tested, which avoided the fingerprint entirely and provided a reverse development of the fingerprints by completely coloring the background of the non-porous test tile. Fingerprints developed with 247 here in the laboratory are a strong red color and have remained light fast for a 6-month period. The de-dusting oils are commonly used to “wet” dyes to keep the dust from getting all over when barrels are open. And the oils used are not evenly mixed through the batches which are supported by the findings in the McCrone analysis.

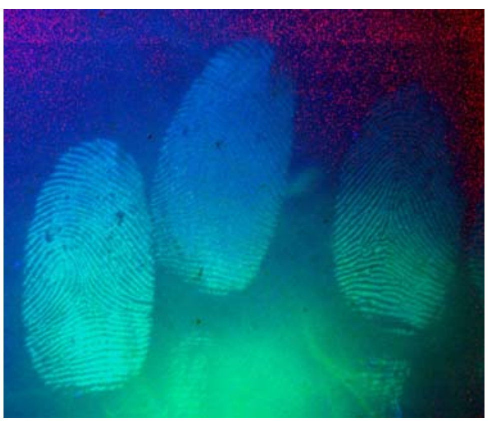


Solvent Red 247 without Twitchel Oil



Solvent Red 247 with Twitchel Oil

Like other dyes in this study, solvent yellow 43 will dissolve into the cyanoacrylate when the dye vapor impacts the cured resin. And like other dyes in this study, the dye vapor will also solidify when it comes into contact with surfaces that absorb its heat. In the case of many colorants this causes a nonspecific coloration where the fingerprint and the background are equally colored. But with the solvent yellow 43 the dye has a fluorescent functionality that is only present in its solubalized state. Crystallized dye around the cyanoacrylate will not fluoresce whereas the dye that has solubalized into the resin will produce photo-luminescence.

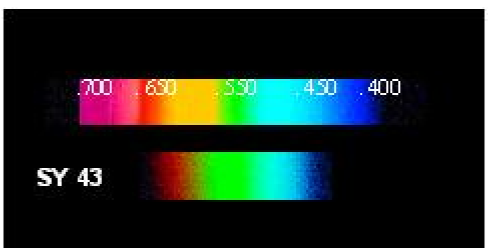


Early success with Yellow 43 and ethanol.

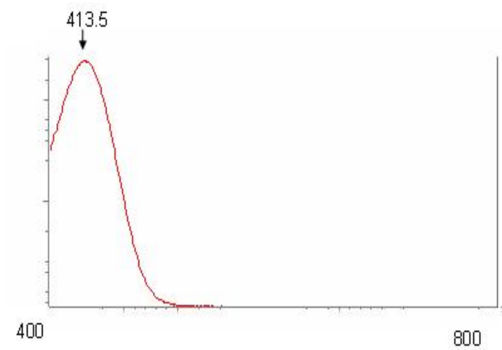
The phenomenon of quenching.

In one form of the Yellow 43 dye, Peg 50 Tallow Amide was used as vapor carrier. Peg 50 Tallow Amide is an easily vaporized semi-solid wax. When heated it become a heavy lighter than air vapor. Several solvent/ disperse dyes will dissolve in this wax. A preparation of solvent yellow 43 and Peg 50 Tallow Amide was used in a variety of combinations. When heated the vapor is dense enough to act as a carrier solvent for the dye.

In addition to acting as a carrier, the Peg 50 Tallow amide vapor leaves an amorphous wax coating on the surfaces it condenses on. This coating also has some solvent value. Just like coloring prints in a dye bath, dye dissolved into the Peg 50 residue have a better chance to migrate into the resin because the dyes are already in a molecular state and therefore susceptible to random thermal motion. Combinations of peg 50 tallow amide and subliming dyes that had solubility in the peg 50 tallow amide were also tried. The best of these was smoke blue 180 which could be dissolved into the tallow but produced only weak color on the print, and these latent prints were transient, fading within three days.



Shown above is the fluorescent emission spectrum of Solvent Yellow 43. Note that although the dye has a primary emission in the yellow/green wavelengths, the dye gives off a broad spectrum of visible light ranging from red to blue when exposed to UV energy. This allows for easy visualization against many backgrounds.

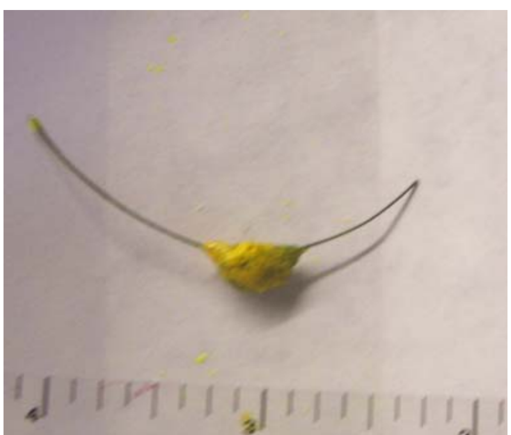


Show above is a typical visible absorption spectrum for Solvent Yellow 43. The spectrum was collected in acetone and shows a primary absorption peak at 413.5 nm.

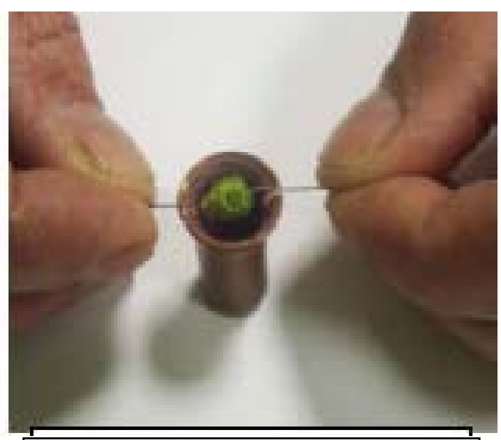
Optimized Yellow 43 Dye with Cyanoacrylate Fuming Using a Butane Torch

Although the yellow 43 dye is specific to the fingerprints and visible under UV in most tests when using different liquid agents such as ethanol, acetone, or a water/sodium silicate solution, there have been recurring problems with development. Some applications, especially when using the dye in a tallow blend, lead to over-saturation or quenching of the fingerprint and reduced or no polymerization. Blending the dye in either powder or tallow form with ethanol produces the required polymerization but with unacceptably high levels of background illumination. The ratio of dye to cyanoacrylate also affected the degree and timing of the print polymerization. The formula that initially produced the best results and maintaining stability with the longest possible shelf life was to immediately saturate steel wool with the solution. The solution is not stable in the liquid form which limited the ability to scale up the fuming event for larger areas but is ideal for use with a butane torch in small to mid-sized chambers and in the Fuma-Dome device. We have since resolved the shelf life and scalability issues by developing a new product which will soon be released under our third patent.

Ten grams of the cyanoacrylate/Yellow-43 based blend (PATENT PENDING) is a sufficient for approximately 20-25 charges. The steel wool will accept four to six drops of the solution and polymerization is rapid. The steel wool ball with polymerized glue-dye blend is easy to store and will provide two or three fuming events per charge, depending on the size of the fuming chamber.



Steel wool impregnated with CN and Yellow 43 powder



Steel wool inserted into self-manufactured copper sublimation adapter.

The steel wool ball is inserted into a ¾ inch copper tube that has been flared and slots cut into one end to attach the wire. This tube is placed on the adapter of a hand-held butane torch burning at a medium temperature setting (440 degrees F or above) then inserted into a fuming chamber. Smoke fumes from the cyanoacrylate and dye begin immediately and are allowed to fill the chamber. Depending on the size of the chamber this could be from 30 seconds to 1 minute. When the chamber is full of fuming material the torch is turned off and removed and the chamber sealed. The material in the chamber needs to set in the fumes for at least 5 minutes but not more than 10 and then removed. Polymerized prints will be developed and exhibit exceptional luminescence with either short or long wave UV, or under an alternate light source such as blue-green laser. The CN-Yellow product peak absorption and emission occurs at 450 nm. in the cyanoacrylate polymer matrix in our opinion.

Breakable Cartridge

In the second branch of the research we are testing various chemistries to advance and optimize the microcrystalline vapor of the Press and Fume device generation. Currently the mechanism utilizes the traditional reaction of sodium hydroxide and cellulose with 10cc of liquid cyanoacrylate. This exothermic event allows for evidence processing that fits within a 3-cubic foot chamber. One research goal is to expand the cubic foot exposure of the cyanoacrylate vapor to allow the development of fingerprint evidence in larger chambers or entire interiors of a vehicle and expand this technology to entire rooms in crime scenes. Another goal in which we have obtained moderate success was to introduce sublimation dyes into this exothermic process. A Yellow 43 blend of the dye powder, peg 50 tallow, and acetone, has produced high quality but inconsistent photo-luminescence print development.

Press-n-Fume Device (above), Print Developed with Press and Fume (below).

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Dye Chemist: Charles Steele
Current Research Assistants: Mason Hines, Alissa Doss, Andrea Shockey, Sara Farmer
Grants Financial Assistance: Sheryl Logan
Dept. of Justice Studies Administrative Secretary: Bobbi Brown

This Project was supported by Award No. 2006-DN-BX-K037, awarded by the National Institute of Justice, Office of Justice Programs, US Department of Justice. The opinions, findings, and conclusions or recommendations expressed in this publication/program/exhibition are those of the authors and do not necessarily reflect the views of the Department of Justice.