

RECENT ADVANCES IN LATENT PRINT VISUALIZATION RESEARCH

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The U.S. Secret Service has been actively involved in investigating new methods for the visualization of latent prints. Summarized below are several of our most recent projects, which were presented at the Chesapeake Bay Division IAI meeting in Richmond, VA, on April 4, 1998.

Gentian Violet

Gentian violet (GV), a triphenylmethine dye, has been used for many years as a biological stain. GV has also been used for a number of years by the law enforcement community as a processing technique for the visualization of latent prints on sticky surfaces (e.g., adhesive tapes, and in some cases, plastics, and cans). The dye stain attaches itself to dead skin cells (squamae) deposited on contact with surfaces as well as some sebaceous-type material [1]. The first alleged use of gentian violet on evidence was in Italy and England during the late 1960s [2]. One of the first published accounts of the use of gentian violet was by Takashi Arima, a Medical-legal Examiner, Scientific Investigation Research Section, Fukushimaken Police Headquarters, Japan, during the early 1980s [3]. One problem that was soon encountered using gentian violet was that it was not particularly useful on dark tapes. An article by Wilson and McCloud offered a potential solution [4]. This technique involved sandwiching the GV-treated item between two pieces of welled photographic paper (emulsion side). The technique was somewhat cumbersome and resulted in prints that were in "reverse position" on the photographic paper.

Another study examined the use of commercial fabric dyes and biological stains [5]. This indicated that gentian violet exhibited a weak fluorescence when excited with long-wave ultraviolet radiation. On black electrical tape, another study recommended the use of basic fuchsin (rosaniline chloride) instead of gentian violet because of the formers ability to fluoresce [1]. In an effort to develop prints on the adhesive side of black or dark colored tapes, one study advocated the use of a fluorescent gentian violet solution [6]. The reagent contained a small quantity of rhodamine 6G and was applied by dipping or bashing. It was noted that excessive amounts of rhodamine 6G added to the reagent left a prominent dark red residue on the evidence. Fluorescence examinations were conducted using a 5 watt Spectra-Physics Model 164-09 argon ion laser. Work done during the mid 1980s at the London Metropolitan Police Serious Crimes Unit laboratory presented the first indications of the deep red to near-infrared (NR) fluorescence of gentian violet-treated items [7]. The authors reported a weak fluorescence in the region of 730-750 nm using the 514.5 run line of an argon ion laser.

An effort to explore gentian violet fluorescence was conducted by Galvin Long, University of Hull, under the supervision of Dr. Simon Bramble, of the Home Office Forensic

Science Service, Metropolitan Laboratory [8]. The spectrum obtained showed that gentian violet had strong fluorescence with a maximum excitation peak at 530 nm and a maximum emission peak at 720 nm. They also studied the effects of concentration on this fluorescence intensity. The U.S. Secret Service was also interested in experimenting with this gentian violet fluorescence. An inexpensive system for viewing this fluorescence was constructed. The excitation source was a slide projector (with an IR absorbing filter). The excitation filter was a Coming blue-green filter no. 4-96 (spectral output is between 375-600 nm). The emission filter was a Kodak Wratten filter no. 92 (approximate cut-on at 625 nm). A Sony Hyper HAD 0.1 Lux 1/3" CCD camera with a Computar 16 mm f/1.4 lens was used for viewing the samples. This approximate configuration produced very good results on the sticky side of black electrical and cloth-like tapes. Further experiments showed that viewing the fluorescence of gentian violet-treated items in the deep red to NIR resulted in significantly better detection limits than viewing the visible stain with white light.

Gun Blueing

The practice of "blueing" or "browning" iron and steel parts of objects probably dates back to the early days of metalworking. Skilled craftsmen would use these solutions to impart dark blue or brown color to their work- The first known instances of blueing gun metal date back to the early 17th century. The primary reasons for blueing gun metal, aside from improving the weapon's overall appearance, included removing reflections from polished surfaces and preventing rust. One firearms blueing and browning text from the mid-1930s provides a warning with regard to touching the metal surfaces prior to blueing them. The author stated, "...from this moment onwards [after cleaning] the degreased parts must not be touched with the naked hand, as the skin is always slightly fatty..." [9]. In other words, the presence of fingerprint residues on the metal surface prevents the deposition of the blue/black color. This is the underlying principle that is exploited during the gun blueing process.

Although many gun blueing formulations exist today, they essentially all work in a similar fashion. In short, blueing involves inducing an artificial rusting process using a specially prepared oxidizing solution containing primarily selenous acid and copper sulfate. These two compounds are responsible for the blue/black color. While the metal is in contact with the solution, copper and selenium are removed from the solution and deposited together on the surface of the metal, possibly as the alloy copper selenide (CuSe) [10]. The presence of any fingerprint residues, oils, etc. on the metal surface inhibits the deposition of the dark colored alloy. The resulting print detail appears light against a dark colored metallic background. The process was first introduced to the U. S. Secret Service in early 1995 by Mr. Edward R. German, from the U. S. Army Crime Laboratory in Ft. Gillem Georgia, and Mr. Donald Coffey, from the U. S. Army Crime Laboratory in Fr, Germany. Mr. Coffey had learned of

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the process from a chemist and gun owner who worked for the Bundeskriminalamt in Wiesbaden, Germany. Independent evaluations of the process were conducted by the U. S. Secret Service and the results recently published in the Chesapeake Bay Division Examiner [11]. The time required for development was dependent upon the gun blue concentration. Experiments showed that diluting the gun blue solution by a factor of forty to eighty times (i.e., one part gun blue to forty to eighty parts distilled water) provided the best results. At these dilutions, development would occur in a controlled fashion over the course of a few minutes. The process could be sped up or slowed down by increasing or decreasing the gun blue concentration, respectively.

Dr. George Saunders, under contract with the Secret Service, found that gentle Cyanoacrylate ester (CAE) fuming prior to the gun blueing process often produced superior results to just gun blueing alone [12]. It was emphasized that over-fuming with CAE (which would impart a uniform coat of polymer over the metal surface) would destroy any possibility of subsequent development with gun blue. A method has also been proposed for the removal of gun blueing solution deposits (in cases where over development has occurred). In some instances, tool-mark identifications can be complicated by over development with gun blue solutions. A mixture of 14.1 ml of household vinegar (5% acetic acid) and 20 ml of 3% hydrogen peroxide has been found to remove excess buildup of gun blue on cartridge cases [13]. *This solution has also been found to visualize latent prints on cases by itself.* Gentle stirring of the solution is recommended while the cases are immersed.

1,2-Indanediones

Although ninhydrin was first synthesized by Ruhemann in 1910, little work had been done to try and improve or enhance its latent print development abilities until the early 1980s. After the discovery by Dalrymple, et al., that lasers could promote fluorescence of untreated latent prints [14], the focus shifted to finding reagents that would produce strongly fluorescent reaction products with latent prints. During the early 1980s, a research initiative was launched by Dr. Joseph Almog, Israel National Police, to produce compounds that were structurally similar to ninhydrin, but differed by the presence of fluorescence enhancing substituents. The requirements for the ideal compound were: good initial color, superior fluorescence of the reaction product with latent prints (preferably without cooling to liquid nitrogen temperatures or secondary zinc chloride treatment), low cost, ability to dissolve in an array of different solvents (preferably non-polar), and low toxicity. While no compound was subsequently found to meet all of these criteria, several synthesized compounds were promising.

The current standard for fingerprint fluorescence intensity was established in 1989 when the non-ninhydrin reagent, 1,8-diazafluoren-9-one (DFO) was introduced [15]. This compound, although producing weak initial color development, produced an intensely fluorescent reaction product with latent print residue.

In September of 1995, chemists at the University of Pennsylvania Department of Chemistry synthesized a new type of latent print visualizing compound. The compound, 6-methylthio-1,2-indanedione, was similar to the triketo ninhydrin analog 6-methylthioninhydrin except that the new compound lacked a carbonyl group in the 3-position. This seemingly minor modification may have significantly altered the reaction mechanism and the reaction product. This development encouraged the syntheses of other substituted 1,2-indanediones as well as the unsubstituted 1,2-indanedione parent compound. Several of these compounds were evaluated (including the 6-methylthio, 5-chloro, 6-bromo, 6-nitro, 5-methoxy, 5,6-dimethoxy 6-fluoro, and unsubstituted 1,2-indanedione) [16]. Results indicated that the 5-methoxy and 5,6-dimethoxy analogs produced the best results. Although visible color development was negligible (when reacted with glycine), significant fluorescence was observed even without secondary zinc chloride treatment. Efforts are now underway to begin commercializing some of these compounds to make them available for evidence processing.

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