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TR-11-93 "T.E.C. - A New Fluorescent Fingerprint Dye"

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TECHNICAL REPORT

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NOTE: Further information about this report can be obtained by calling the CPRC information number (613) 998-6343

Executive Summary

A patent has been filed through the Canadian Police Research Centre to cover a development made by the Royal Canadian Mounted Police Forensic Identification Support Section. This development allows one to detect cyanoacrylate developed latent fingerprints. D.A. Wilkinson, A.H. Misner and J.E. Watkin collaborated their efforts to develop this TEC dye. The dye is created when three molecules of thenoyltrifluoroacetone bind to one atom of europium in the solution.

The TEC dye is applied to fingerprints after exposure to CA under vacuum. There are two different methods to develop the prints the first is for hard surfaces and skin and the other is for large surface areas, which includes plastic bags.

One of the problems with using cyanoacrylate on its own to develop fingerprints is that it cannot develop weak prints to a stage where they are visible to the naked eye.

Presently permission is given to accredited police agencies only, to make up and use the solutions for their investigative purposes. In the future the material may be supplied commercially as a package.

Résumé

Un brevet a été déposé par l'entremise du Centre canadien de recherches policières en vue de protéger une technique mise au point par la Section de l'assistance à l'identité judiciaire de la Gendarmerie royale du Canada. Cette technique permet de déceler les empreintes digitales latentes révélées avec un cyanoacrylate. D.A. Wilkinson, A.H. Misner et J.E. Watkin ont travaillé de concert pour mettre au point ce colorant TEC qui est obtenu lorsque trois molécules de thénoyltrifluoroacétone se lient à un atome d'europium dans la solution.

Le colorant TEC est appliqué sur les empreintes après exposition au CA dans une enceinte sous vide. Deux méthodes différentes permettent de révéler les empreintes: la première est appliquée dans le cas des surfaces dures et de la peau, tandis que l'autre est utilisée pour les grandes surfaces, dont les sacs en plastique.

Le fait que le cyanoacrylate ne permette pas, à lui seul, de rendre visibles à l'oeil nu les empreintes peu intenses constitue l'un des problèmes liés à son utilisation.

Actuellement, on autorise les services de police accrédités, et eux seuls, à préparer et à utiliser les solutions dans le cadre de leurs enquêtes. Ce matériel pourra, plus tard, être vendu dans le commerce sous forme de trousse.

Thenoyl Europium Chelate: A New Fluorescent Dye with a Narrow Emission Band to Detect Cyanoacrylate Developed Fingerprints on Non-porous Substrates and Cadavers

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Abstract: Reaction of europium chloride with thenoyltrifluoroacetone produces a fluorescent dye that strongly absorbs ultraviolet (UV) light near 350 nm and emits a band only 10 nm wide at 614 nm. Addition of methyl ethyl ketone to an aqueous solution of this dye enables it to penetrate cyanoacrylate (CA) developed latent prints so that a low power, inexpensive UV light source is sufficient to excite brilliant red fluorescence. It can be used to detect CA prints on many surfaces, including cadavers.

Introduction

The polymerization of cyanoacrylate esters, commonly referred to as "super glue fuming" or CA, has become the preferred method of detecting latent prints on non-porous surfaces. The developed latents often can be clearly seen on many surfaces by the use of transmitted or reflected lighting, but the clarity and intensity of the polymerization varies with surface characteristics and development conditions. As a result, the use of a fluorescent stain to increase visible detail has become routine for many examiners [1].

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Most stains bind onto the surface of the CA-developed ridges in such small amounts that a powerful light excitation source is required to produce sufficient fluorescence for the unaided eye to see the print easily. The difference between the wavelengths of light absorbed at peak excitation and the wavelengths of light at peak emission of the fluorescing stain, measured in nanometers, is called the Stokes shift. In practice, the fluorescence from the stained fingerprint is viewed through a filter which blocks the excitation light, but can transmit the dye stain emission. A large Stokes shift, that is, substantial separation between peak absorption and peak emission, allows relative ease in selecting an effective barrier filter to block the excitation light.

Originally the light used for fluorescence excitation was generated by powerful lasers [2], but in recent years several alternate light sources have become commercially available [3,4]. These devices use lamps which produce a broad output across the UV and visible spectrum, and isolate narrow excitation bands, typically 40 nm wide, by filters or gratings. Such alternate high intensity lights can radiate approximately 100 mW/cm^2 of narrow band excitation onto the surface, depending upon distance and wavelength selection. This enables these sources to excite a variety of stains, but only when the filters or gratings effectively prevent the transmission of light in the part of the spectrum where the stain fluorescence occurs. In addition, if the background is fluorescent in the wavelength region of the stain emission, contrast between the stained print and the background can be a problem. This situation sometimes can be improved by changing to a stain with a different wavelength emission, or by varying the excitation or emission filters for other transmission wavelengths.

Almost all fluorescent organic compounds have wide wavelength bands for both excitation and emission, approximately 50 nm at half height. Such broad range absorption and fluorescence limits the filtering approach for increasing contrast. On the other hand, the rare earth element, europium, has a narrow emission band, 10 nm at half height, and this is centered in the red at 614 nm. Unfortunately, the europium ion, Eu^{+++}, absorbs light very poorly. This disadvantage may be overcome by associating the europium ion with a strongly absorbing, organic compound called a ligand. This combination of metal ion and ligand is known as a chelate. The ligand transfers the light energy it absorbs to the europium ion, which then emits light in its characteristic narrow band.

The intent of this paper is to describe such an europium chelate and a method of transferring it from an aqueous solution into a polymerized cyanoacrylate print in sufficient quantity so that a relatively weak UV exciting light, 10 mW/cm^2, provides brilliant fluorescence to the unaided eye.

Principle of Method

Three molecules of thenoyltrifluoroacetone, the ligand, bind to one atom of europium in solution to form a dye, thenoyl europium chelate (TEC). The solution is colorless, but strongly absorbs long wavelength ultraviolet light. The energy absorbed from the UV light is transferred to the europium, which then fluoresces brightly, with narrow band emission, in the red at 614 nm.

Methyl ethyl ketone (MEK), crucial to the successful visualization of cyanoacrylate prints, is incorporated in the dye solution. When an item bearing latent prints coated with cyanoacrylate polymer is immersed into the dye solution, some of the MEK penetrates the polymer although water cannot be absorbed into the CA from the aqueous TEC. The TEC then prefers to dissolve in the pure MEK within the polymer, thus concentrating the TEC by a factor of 100 to 1000. After the item is removed from the solution, the MEK quickly evaporates, leaving the TEC inside the polymer. Any residual TEC deposited on the surrounding surface may be removed by washing with methanol, which dissolves the background TEC but does not remove the dye in the latent print.

Methods and Materials

All chemicals were purchased from Aldrich Chemical Company unless otherwise stated.

A working dye stain is made by mixing two separately prepared solutions. For the first, 1.0 g of thenoyltrifluoroacetone is dissolved in 220 ml of methyl ethyl ketone, and placed in a resealable 2 L container. A second solution is prepared by dissolving 19.0 g of tris (hydroxymethyl) aminomethane in 780 ml of distilled water. The pH of the second solution is adjusted to 8.0 by adding drops of concentrated hydrochloric acid, and then 0.455 g of europium chloride hexahydrate is dissolved in this aqueous tris. The second solution is then poured into the 2L container with the prepared MEK, and the mixture is vigorously shaken. Because the chelate formed is not com-

pletely soluble in the combined liquids, the solution has a faint milky appearance. Sonication in a ultrasonic bath for 5 minutes will increase the uniformity of the solution.

Testing Procedures

Application of the dye and washing of the background was determined to be best accomplished in a darkened room under UV illumination.

For testing purposes, a number of sample exhibits were fumed with CA under vacuum in the CAVAC chamber. Test materials included plastic bags, metal, weapons, and glass. Cadavers were fumed with CA at atmospheric pressure within a plastic tent.

With many smaller items, the TEC solution was poured in a slow running stream from a plastic wash bottle over the areas where polymerized latent prints were anticipated. After the MEK in the stain was allowed to evaporate, the same area was washed with a methanol rinse, consisting of 80% methanol, 15% water, and 5% surfactant, 15-S-7 Tergitol (Union Carbide Corp.).

For larger objects, including plastic bags, a diluted TEC stain was used for practical considerations. The prescribed TEC was diluted by a factor of ten by mixing one part TEC to nine parts of a MEK:water solution prepared in the same ratio, 220 ml MEK to 780 ml distilled water. Exhibits were then immersed in the dilution solution. Test samples were checked for fluorescence at two minute intervals. Once prints were visible, washing was conducted as before. A snug lid was used on the processing container to prevent excessive loss of MEK.

Six separate experiments were conducted on cadavers within 24 hours of death. They had been refrigerated, and then conditioned at room temperature and a low relative humidity (40%) for 4 hours, by which time the skin temperatures were between 13° and 19° C. Sample latent prints from several different donors were deposited on the thigh, knee, shin, ankle, and foot areas from fingers approximating normal conditions, that is, not recently washed nor coated with additional sebum. All were placed using light pressure.

A framework large enough to enclose a cadaver had been constructed of 1/2" copper and polybutylene tubing with tee and elbow

joints, all of which are standard plumbing supplies. A polythene tent was stretched over the framework and sealed at the edges with double sided carpet tape. A Ziploc® bag with the bottom removed was sealed into one edge to produce an airlock entrance to the tent. A small electric hot plate controlled to 200° C was used to volatilize the cyanoacrylate in the tent, and a hygrometer (Cole Palmer) was used to measure the relative humidity.

Each cadaver was placed in the tent along with test prints on aluminum foil. Fuming commenced within 20 minutes of latent print residue deposition, and was continued for 1 hour. The test prints on the foil were visible within 10 minutes, and white friction ridge detail from the sample latents on the skin became discernible usually within 15-20 minutes.

At the end of the 1 hour fuming period, most, but not all, of the sample latents deposited on the skin showed visible white ridge detail under room light. Contrast between the ridges and the background skin was generally poor.

Relative humidity readings within the fuming tent had been noted. In one experiment, the relative humidity rose to 66%, another to 88% and yet another to 98%. This was due to moisture from the cadavers and the effect of heating the CA. Although CA developed visible ridge detail on the skin of each, the best results were obtained at the 66% RH. With higher humidity, the ridge detail lacked continuity. At 98% RH, polymerization began to form on the surrounding skin as well as the latent, making it difficult to observe contrast between the latent and background.

The bodies were examined using only the light from a Spectroline Model B1B-150B UV mercury lamp light source. The dye solution was streamed gently over the skin area where latents had been deposited. The skin area in contact with the dye fluoresced a bright red which resulted in no contrast between the prints and background skin. After approximately 2 minutes to permit evaporation of the MEK, the area was then rinsed with the methanol/water wash solution from a plastic squeeze bottle. Excess background dye was washed off the skin but not from the latents. Several applications of the rinse were necessary, but the final result was good quality, red fluorescent prints. In addition, on several areas of skin where latents had been deposited but

had revealed no visible ridge detail under room light, excellent quality fluorescent prints were exhibited after the dye/rinse procedure.

Photography

Preservation of the fluorescence was performed using Kodak Technical Pan film with a Nikon F3 35mm automatic exposure camera mounted on a tripod. Exposures ranged from 5 to 30 seconds with the Spectronics Model B1B-150B black light mercury lamp used as the light source. The lamp may be hand held or mounted on a tripod approximately 30 cm from the sample surface. If the background surface has low inherent fluorescence, a Schott KV-550 filter is adequate as a barrier filter. For fluorescing backgrounds and for skin, a 620 nm narrow band (10 nm) interference filter (Corion Corp.) produced excellent results.

Health and Safety

Clear polycarbonate safety goggles or face shields provide adequate eye and skin protection from ultraviolet radiation. Lab smocks and rubber or latex gloves must be worn and solutions are to be prepared in a fume hood. Europium trichloride hexahydrate is non-carcinogenic and non-toxic when used as described.

Results

Due to a consistent level of low background fluorescence, the fingerprints visualized on each tested surface displayed good contrast and were easily photographed.

Figure 1 depicts the excitation and emission spectra of TEC, Rhodamine 6G, and the red background of a Coke can. They are not on the same scale of relative sensitivity. TEC has a broad excitation band peaking at 350 nm but retaining 85% of its absorption at 365 nm where the narrow excitation line of the mercury vapor UV lamp occurs. The narrow emission of the europium occurs at 614 nm giving a large Stokes shift of 264 nm. Rhodamine 6G has a Stokes shift of only 36 nm. By use of a narrow band filter it is possible to isolate the emission of the europium and provide contrast even against a broad band red fluorescent background, such as a Coke can.

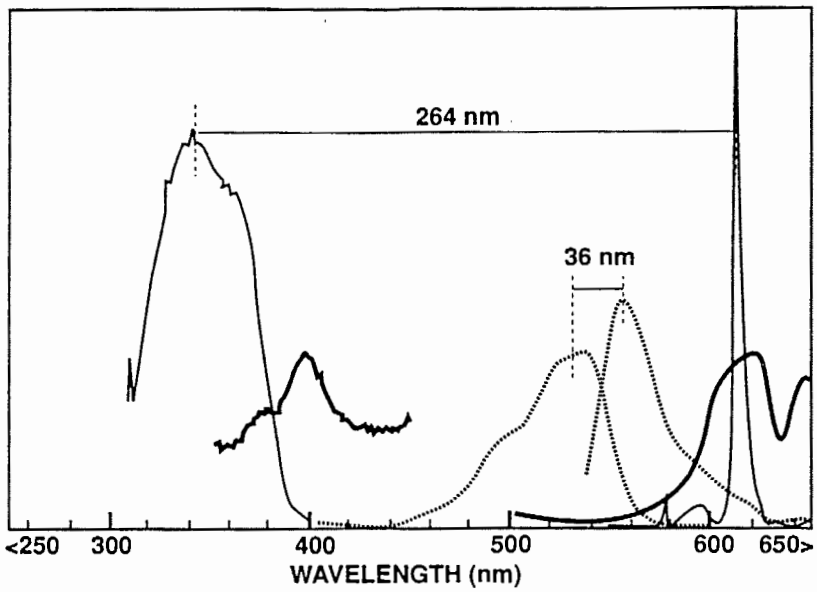

Figure 1

The excitation and emission spectra of TEC (—), Rhodamine 6G (·····), and a Coke can (—)

Figure 2

A cyanoacrylate print developed on a Coke can, dyed by TEC, and photographed through a 620 nm narrow band pass filter

Figure 3

A cyanoacrylate print on a galvanized metal surface dyed by TEC

Figure 4

A cluster of cyanoacrylate prints on skin dyed by TEC

Figure 2 shows a latent CA print developed and photographed using a 620 nm narrow band pass filter on the red colored surface of a Coke can. The Coke can background has a maximum absorption at 400 nm but still retains enough absorption at 365 nm to be excited by the UV lamp (see Figure 1). The color of the broad band red emission of the Coke can looks identical to the eye to that of TEC as they peak at nearly the same wavelength. By use of the 620 nm narrow band pass filter it is possible to block much of the can fluorescence thereby increasing the contrast of the TEC stained print.

Figure 3 shows a TEC dyed CA print on a galvanized metal surface. It is possible to remove all dye from the background by washing so that the irregular reflection pattern of the galvanized surface drops out leaving only the print visible.

Figure 4 shows a cluster of prints deposited on the smooth leg skin of a female cadaver, developed by CA and visualized using TEC.

Figure 5 shows an enlargement of one of these prints. These prints were obtained at a relative humidity of 66% inside the fuming tent and were not visible under room light after fuming.

Discussion

For detecting CA prints developed on smooth surfaces that have little or no background fluorescence, TEC yields fluorescing prints with excellent contrast. Even on red fluorescent backgrounds the narrow emission band allows good contrast.

Most fluorescent stains only adhere to the surface of the cyanoacrylate prints. When prints are washed to reduce the background, some of the surface stain is lost as well. In contrast TEC is absorbed into the bulk of the polymer and washing will now only remove the background dye. The amount of TEC thus locked into the polymer is sufficient so that relatively low intensity UV excitation produces prints easily seen by the eye. For detecting CA prints developed on skin the 620 nm narrow band filter eliminates inherent skin fluorescence.

Control of humidity during fuming is the most important factor in the success of this method on cadavers. High humidity causes condensation to form over the entire skin surface which contributes to CA polymerization on the skin as well as on the print. As a result TEC will

Figure 5

An enlargement of a print from the cluster shown in Figure 4

also penetrate this background polymer, causing background fluorescence which is impossible to remove. Ideally, prior to fuming, cadavers should be at room temperature with the humidity as low as possible.

On cool cadavers, latent print longevity should be similar to that on other surfaces. The work of Delmas [5] supports this. In one case he deposited a print 35 minutes after death, left it for 3 1/2 hours and then successfully developed it with CA and magna powder. This is very encouraging; however, the authors are of the opinion that magna powder lacks sensitivity compared to that of TEC.

There is little hope of ever detecting latent prints on living victims. TEC was added to sebum and this fluorescent "ink" was used to deposit latents on living skin and then observed under UV light. They lost all detail by diffusion within 30 minutes, which is predictable, as latent

print residue will remain essentially liquid at 32° C, the approximate temperature of living skin. When a latent is deposited on a surface at lower temperature, the residue becomes viscous and will persist.

The lifetime of latents deposited on skin near the time of death will be intermediate between these two conditions. The change of the latent from a liquid to a viscous condition and thus the rate of diffusion will depend on the rate of cooling of the body. This will vary a great deal dependent upon existing conditions.

Admittedly these experiments on cadavers do not replicate real life conditions consistent with actual crime victims. It is the opinion of the authors, however, that the results are encouraging and this technique has extensive potential in this regard. Research is continuing and field testing of the technique on actual crime victim cadavers began within Canada during the latter part of 1992.

Conclusion

TEC is a new fluorescent dye stain specifically designed for latent print detection on CA-processed non-porous surfaces and human skin using an inexpensive UV light source. TEC's ideal spectral emission properties, coupled with the ability of MEK to carry the dye inside the CA polymer, make the TEC solution very appealing.

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