An Evaluation of a Novel One-step Fluorescent Superglue Process

INTERNATIONAL ASSOCIATION FOR IDENTIFICATION
Phoenix, AZ
July 26, 2012

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Background

Background

- Dr. Harry Coover was the first to work with cyanoacrylate monomers in 1942 while searching for the best material for making clear gun sights – he rejected the material initially because it was too sticky
- Cyanoacrylates also synthesized by Ardis in 1949
- First discovery of the strong adhesive properties was in 1951
- Joyner and Shearer (working for Coover at Eastman) accidently bonded the glass prisms of a refractometer together
- This material (ethyl cyanoacrylate) was subsequently marketed as Eastman 910 and ultimately as Superglue® in 1958

Background*

- Cyanoacrylate fuming for developing latent prints was discovered independently by three separate groups around the same time period
- In May 1977, Fuseo Matsumura (trace evidence examiner) at the Saga Prefectural Crime Laboratory (National Police Agency of Japan) observed his fingerprint ridges developed on glass slides
- Latent print examiner Masato Soba performed some preliminary research and found that cyanoacrylates had the potential to develop latent prints on many different surfaces (including adhesive tape)
- In 1979, the technique was demonstrated to examiners from the U.S. Army Crime Laboratory, who ultimately transferred the technology back to the United States

*Source: http://onin.com/

Background*

- In May 1979, L.W. Wood, from Police Headquarters in Northampton, UK, noticed his prints developing on a film tank that had been repaired with cyanoacrylate glue
- In 1980, scientists with the Home Office Central Research Establishment found it to be a promising technique
- In mid-1980, Louis Bourdon (Ontario, Canada) applied for patents in both Canada and the United States for using cyanoacrylates for developing latent prints
- U.S. Patent 4,297,383 was issued on October 27, 1981
- Patent claim successfully challenged by U.S. Army JAG

*Source: http://onin.com/

Background – Acceleration Methods

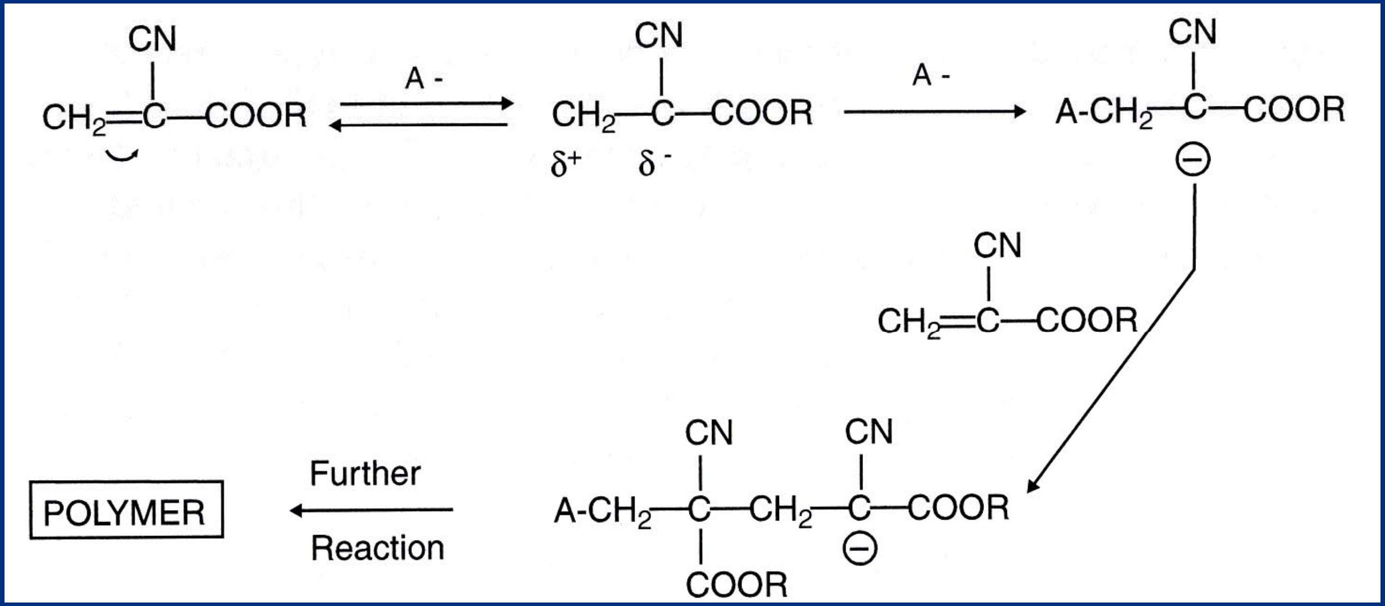
- Chemical methods for accelerating the CA fuming process were suggested by Kendall and Rehn in 1982, including amines, esters, and ethers
- Sodium hydroxide/cotton recommended in 1982 by Kendall and Rehn
- Olenik suggested using heat in 1983
- Sodium carbonate was recommended by Martingale in 1983
- Sampson recommended sawdust in 1984
- Cyanoacrylate "gel" (Hard Evidence™) reported in 1984

Cyanoacrylate Fuming Mechanism

Mechanism

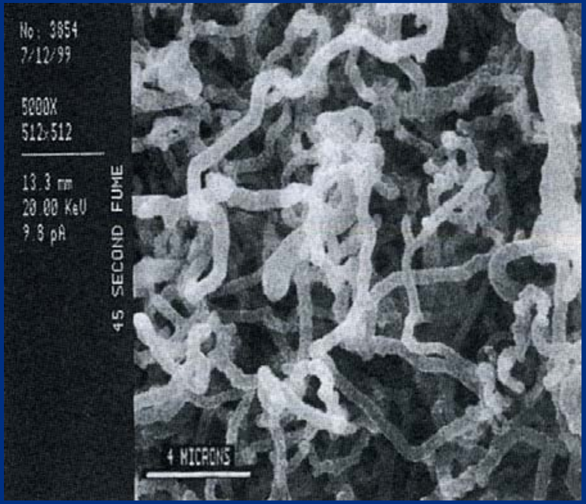
- Cyanoacrylate polymerization has been studied extensively
- It is known that basic compounds can act as initiators
- The reaction mechanism with LP residue is less well understood
- Proposed initiators:
  - Water/basic compounds (Lee/Gaensslen, 1984)
  - Non-polar hydrocarbons (Czekanski et al., 2006)
- Use of pretreatments to enhance CA fuming proposed:
  - Ammonia (Burns et al., 1998)
  - Acetic acid (Lewis et al., 2001)
  - Methylamine (McLaren et al., 2010)

Mechanism



- Reaction is less effective in acidic environments; hydrogen ions act as polymerization chain termination agents

Mechanism



Source: Lewis LA, Smithwick RW, Devault GL, Bolinger B, Lewis SA. (2001) Processes involved in the development of latent fingerprints using the cyanoacrylate fuming method. J Forensic Sci 46(2):241-246.

- Eccrine-rich LP residue produces a “noodle”-like structure (l)
- Sebaceous-rich LP residue produces a “nodular”-like structure (r)

Previous One Step Colored or Fluorescent Cyanoacrylate Fuming Methods

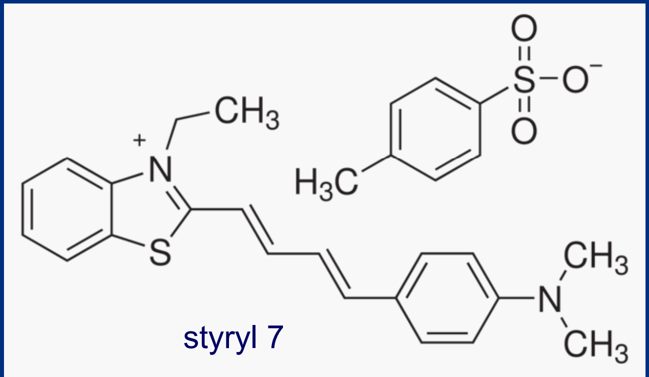
Early Efforts

- Grimm MR, Taylor RA. (1984) Superglue sticks it to the bad guys! Ident News 34(3):11
- Reported the use of iodine in the form of Iodettes™
- Material from the Iodette™ ampoule is spread over a piece of cotton soaked with sodium hydroxide and then the cyanoacrylate was added
- Good results on waxy surface and white lined paper

Source: http://store.sirchie.com/IODETTE-Ampoules-6-ea-P401.aspx

Early Efforts – Alaska/3M

- Weaver, Clary, and Rao report on the use of a proprietary 3M magenta colored dye from the styryl family to “co-fume” with CA
- The magenta dye was used by 3M for thermal dye diffusion printing
- The dye sublimed very well at low temperatures when mixed with methyl cyanoacrylate
- A portable heat wand was developed in conjunction with 3M



styryl 7

A ONE STEP FLUORESCENT CYANOACRYLATE
FINGERPRINT DEVELOPMENT TECHNOLOGY

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5500 E. Tudor Road
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and

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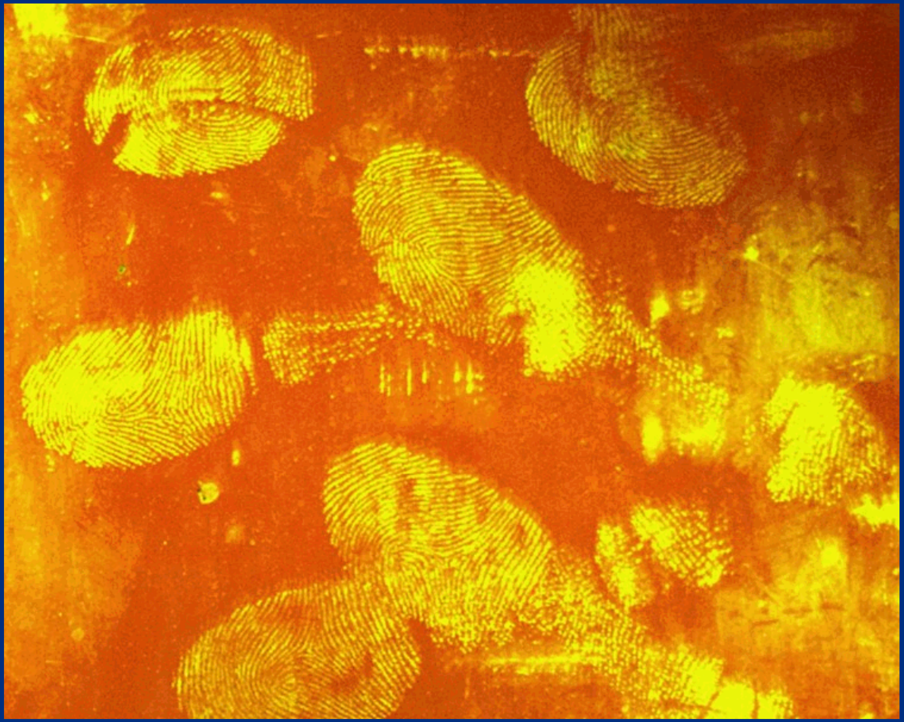
St. Paul, Minnesota 55043

Early Efforts – Alaska/3M

- Arrowhead Forensics now markets a product called CN-Yellow™
- CN-Yellow™ is cured into a steel wool cartridge
- Fumes are generated by heating the CN-Yellow™ cartridge with a butane torch
- Optimal excitation is 450 nm



Source: http://www.crime-scene.com/store/A-CNYP-1.shtml

Early Efforts – BKA

- Gros, Spring, and Deinet report in 1995 on the unsuccessful effort to chemically modify the cyanoacrylate monomer to make it fluorescent/colored
- Attempts to reproduce work of SJ Yong from the Australian National University in 1966
- Reaction of anthracene with the ethyl cyanoacrylate monomer to produce an ethyl ester adduct
- The adduct typically decomposed rather than produce a fluorescent CA reagent

Visualisation of Latent Fingerprints with Cyanoacrylates

Summary of research projects of the private Fresenius Technical College/University in Idstein commissioned by the Bundeskriminalamt Wiesbaden

Project Head
Prof. Dr. Leo Gros

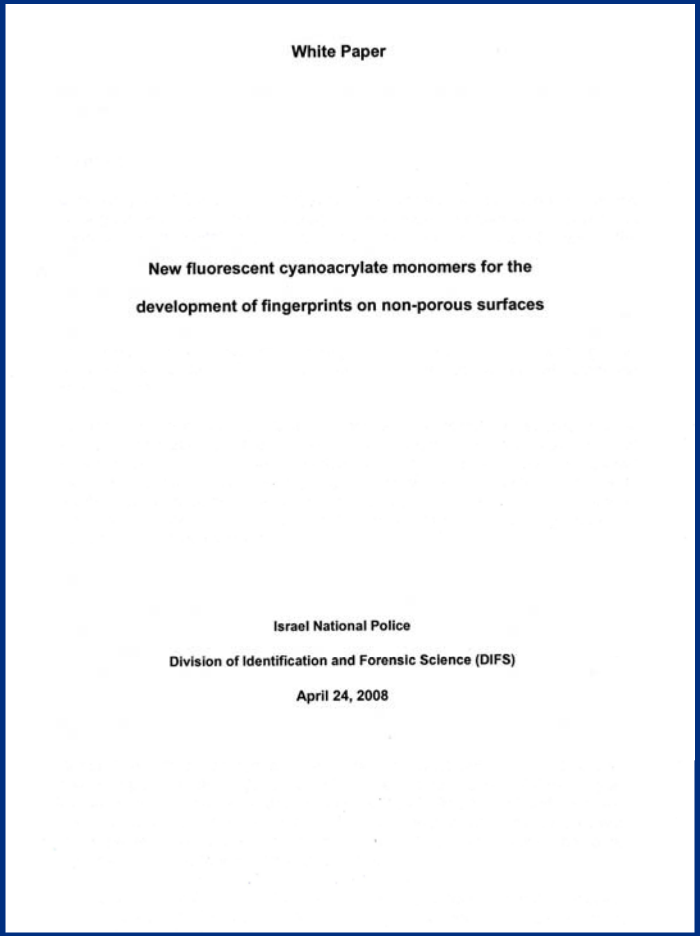
Autor
Dipl.-Ing. (FH) Matthias Spring

Project Assistance by the BKA
Dr. Werner Deinet

December 1995

Recent Efforts – Israel National Police

- Attempts were made to chemically modify the CA monomer
- Similar to BKA effort - they synthesized Diels-Alder adducts of anthracene and ethyl cyanoacrylate
- Anthracene-cyanoacrylic acid is then formed and then subjected to a retro-Diels-Alder reaction to liberate a fluorescent CA monomer
- The anthracene sublimed too fast and ended up coating the entire exhibit without developing latent prints



White Paper

New fluorescent cyanoacrylate monomers for the development of fingerprints on non-porous surfaces

Israel National Police

Division of Identification and Forensic Science (DIFS)

April 24, 2008

Evaluation of the Poly Cyano UV One-Step Fluorescent Cyanoacrylate Fuming Method

Poly Cyano UV

- Foster & Freeman introduced a new product called Poly Cyano UV, which produces fluorescent cyanoacrylate development in one step
- Does not require solvents, which could harm the substrate and possibly the developed CA polymer
- A luminescent powder is mixed with the cyanoacrylate monomer and heated at 230°C for the normal duration of the MVC 1000 auto-cycle sequence

Materials and Methods

Materials – Sample Substrates

- Fold top sandwich bag
- Freezer bag
- Evidence bag
- Black trash bag
- Sheet protector
- Acetate
- Bubble wrap
- Birthday bag
- Multi-colored, glossy surface
- Rough plastic surface

Materials – Dye Stain Formulations

Ardrox working solution

2 mL	Ardrox
10 mL	acetone
25 mL	methanol
10 mL	2-propanol
8 mL	acetonitrile
945 mL	petroleum ether

MBD stock solution

100 mg	MBD
100 mL	acetone

MBD working solution

10 mL	MBD stock solution
30 mL	methanol
10 mL	2-propanol
950 mL	petroleum ether

Materials – Dye Stain Formulations

R6G stock solution

100 mg	rhodamine 6G
100 mL	methanol

R6G working solution

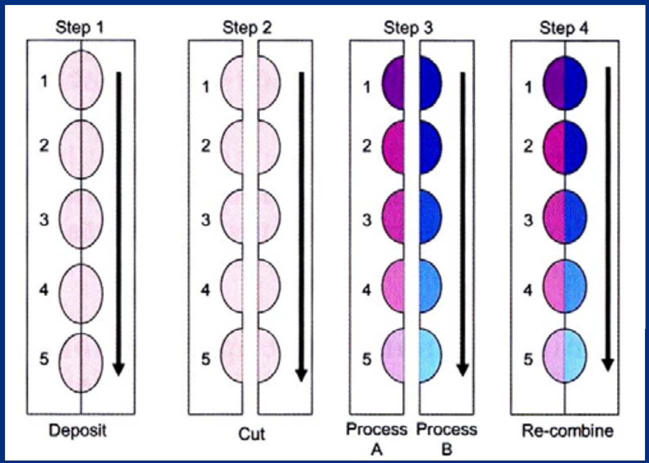
3 mL	R6G stock solution
15 mL	acetone
10 mL	acetonitrile
15 mL	methanol
32 mL	2-propanol
925 mL	petroleum ether

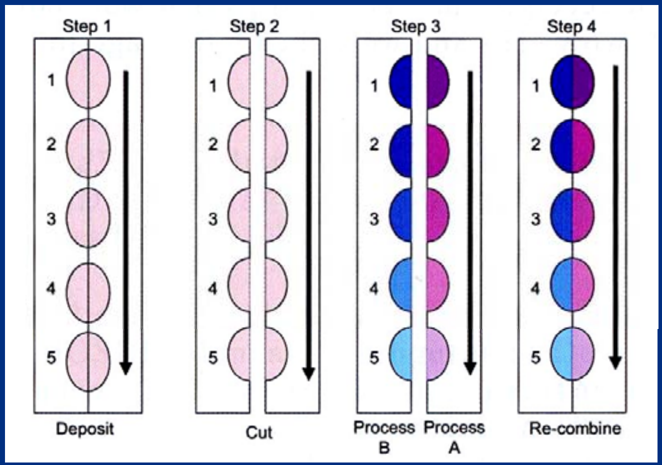
RAM (R6G/Ardrox/MBD)

3 mL	R6G stock solution
2 mL	Ardrox
7 mL	MBD stock solution
20 mL	methanol
10 mL	2-propanol
8 mL	acetonitrile
950 mL	petroleum ether

Method – MVC 1000

- Eccrine- & sebaceous-rich depletion series from 8 donors (3M/5F)
- 8 prints per depletion series; all samples aged 2-3 weeks
- Split each series; each ½-sample processed two different ways
- All optical evaluations performed using Lumatec® Superlite 400





Source: UK Home Office Centre for Applied Science & Technology, St. Albans, HERTS, UK

Method – Processing Samples

- The total number of prints evaluated for each process (these numbers represent split or half prints):

Ardrox	108
RAM	96
R6G	72
MBD	120

- This represents a total of 396 “half” prints. The other remaining 396 “half” prints were processed with the one-step method.

Method – MVC 1000

- Modified MVC 1000 fuming cabinet
- Temperature set for 230°C (80% RH)
- 0.5 g of Cyano UV powder was placed on the modified shelf unit (released into the CA after the heating plate temperature reached 230°C)
- 3 minute purge; 40 minute fuming cycle; 10 minute purge

Method – MVC 1000 Modifications

Method – MVC 3000

- Standard MVC 3000 unit used for two step process
- Temperature set for 120°C (80% RH)
- 5 minute purge; 30 minute fuming cycle; 20 minute purge
- Dye stains applied subsequently using a wash bottle or pipette
- Dye stains used: Adrox P133D, MBD, rhodamine 6G, RAM

Results

Results – Ardrox

- Three week old eccrine-rich print on trash bag – depletion #6
- Left side dyed with Ardrox and right side was developed with Cyano UV
- Ardrox was best on the black plastic trash bag (2), glossy bag (2), and evidence bag (3) material

Results – Ardrox

2 week old	ARDROX	ONE-STEP FLUOR SG
Sandwich Bag	0	0
Freezer Bag	–	+
Evidence Bag	–	+
Black Trash Bag	+	–
ULINE Bubble Wrap	0	0
Glossy Bag	+	–
Textured plastic substrate	±	±
Acetate Sheet	–	+
Sheet Protector	–	+

KEY: +: results were better –: results were worse ±: results inconclusive 0: no results

3-week old	ARDROX	ONE-STEP FLUOR SG
Sandwich Bag	±	±
Freezer Bag	–	+
Evidence Bag	+	–
Black Trash Bag	–	+
ULINE Bubble Wrap	0	0
Glossy Bag	0	0
Textured plastic substrate	–	+
Acetate Sheet	–	+
Sheet Protector	0	0

KEY: +: results were better –: results were worse ±: results inconclusive 0: no results

Results – MBD

- Two week old sebaceous-rich print on black trash bag material – depletion #3
- Left side dyed with MBD and right side was developed with Cyano UV
- MBD was best on the textured plastic surface (2) and the acetate sheet (2) material

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Results – MBD

2 week old	MBD	ONE-STEP FLUOR SG
Sandwich Bag	0	0
Freezer Bag	–	+
Evidence Bag	±	±
Black Trash Bag	±	±
ULINE Bubble Wrap	±	±
Glossy Bag	±	±
Textured plastic substrate	+	–
Acetate Sheet	+	–
Sheet Protector	±	±

KEY: +: results were better —: results were worse ±: results inconclusive 0: no results

3-week old	MBD	ONE-STEP FLUOR SG
Sandwich Bag	0	0
Freezer Bag	0	0
Evidence Bag	±	±
Black Trash Bag	0	0
ULINE Bubble Wrap	0	0
Glossy Bag	0	0
Textured plastic substrate	±	±
Acetate Sheet	–	+
Sheet Protector	±	±

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Results – Rhodamine 6G

- Three week old eccrine-rich print on sandwich bag material – depletion #1
- Left side developed with Cyano UV and the right side is rhodamine 6G
- R6G was best on the acetate sheet (2), the evidence bag (3), and glossy bag (3) material

Results – Rhodamine 6G

2 week old	R6G	ONE-STEP FLUOR SG
Sandwich Bag	0	0
Freezer Bag	0	0
Evidence Bag	±	±
Black Trash Bag	0	0
ULINE Bubble Wrap	0	0
Glossy Bag	0	0
Textured plastic substrate	0	0
Acetate Sheet	+	–
Sheet Protector	±	±

KEY: +: results were better –: results were worse ±: results inconclusive 0: no results

3-week old	R6G	ONE-STEP FLUOR SG
Sandwich Bag	±	±
Freezer Bag	±	±
Evidence Bag	+	–
Black Trash Bag	0	0
ULINE Bubble Wrap	0	0
Glossy Bag	+	–
Textured plastic substrate	0	0
Acetate Sheet	0	0
Sheet Protector	0	0

KEY: +: results were better –: results were worse ±: results inconclusive 0: no results

Results – RAM

- Two week old sebaceous-rich print on evidence bag material – depletion #1
- Right side developed with Cyano UV and the left side is RAM
- RAM was best on the textured plastic substrate (2) and the sheet protector (2) material

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Results – RAM

2 week old	RAM	ONE-STEP FLUOR SG
Sandwich Bag	±	±
Freezer Bag	±	±
Evidence Bag	±	±
Black Trash Bag	±	±
ULINE Bubble Wrap	0	0
Glossy Bag	0	0
Textured plastic substrate	+	–
Acetate Sheet	–	+
Sheet Protector	+	–

KEY: +: results were better –: results were worse ±: results inconclusive 0: no results

3-week old	RAM	ONE-STEP FLUOR SG
Sandwich Bag	±	±
Freezer Bag	±	±
Evidence Bag	0	+
Black Trash Bag	0	0
ULINE Bubble Wrap	0	0
Glossy Bag	±	±
Textured plastic substrate	0	0
Acetate Sheet	0	0
Sheet Protector	0	0

KEY: +: results were better –: results were worse ±: results inconclusive 0: no results

Discussion

Discussion – Health & Safety

- 180ºC - No CA monomers or polymers generated detectable levels of HCN when heated for 30 minutes
- 200ºC - Low levels detected for most samples.
- 260ºC - A significant increase in HCN levels was observed at temperatures above
- Results are in good agreement with those reported by Mock (1985)

Forensic Science International 212 (2011) 143–149

Contents lists available at ScienceDirect

Forensic Science International

journal homepage: www.elsevier.com/locate/forsciint

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Investigation of hydrogen cyanide generation from the cyanoacrylate fuming process used for latent fingermark detection

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ARTICLE INFO

Article history:
Received 20 April 2011
Received in revised form 30 May 2011
Accepted 2 June 2011
Available online 6 July 2011

Keywords:
Cyanoacrylate fuming
Hydrogen cyanide (HCN)
Cyanide quantitation
Picrate–resorcinol
Fingermark detection
Occupational health and safety

ABSTRACT

Cyanoacrylate fuming is one of the most common techniques employed for the detection of latent fingermarks on non-porous surfaces such as plastic and glass. The technique is generally applied by exposing items of interest to the vapours generated by heating a suitable quantity of commercial cyanoacrylate adhesive. In this study, the potential for highly toxic hydrogen cyanide (HCN) to be generated from the overheating of cyanoacrylate was investigated. Two commercial cyanoacrylate adhesives and two quantitative methods for the determination of HCN were employed: (i) the sodium picrate method; and (ii) the picrate–resorcinol method. ^{13}C nuclear magnetic resonance (NMR) analysis was used to confirm the presence of cyanide. In addition, the thermal decomposition of cyanoacrylate was studied using simultaneous thermogravimetric and differential thermal analysis (TGA–DTA). It was determined that detectable and quantifiable amounts of HCN were generated from the thermal decomposition of cyanoacrylate monomer and polymer at temperatures as low as 200 °C. Using an optimised picrate–resorcinol method, it was shown that around 10 μg of HCN could be generated from the heating of 1 g of cyanoacrylate monomer at 200 °C. For one of the adhesives tested, this increased to above 100 μg of HCN when 1 g of cyanoacrylate monomer was heated at 280 °C. Recommendations are provided that, if followed, should ensure that the cyanoacrylate fuming process can be safely applied with minimal risk to the operator.

1. Introduction

Cyanoacrylate (CA) fuming is a well-established method for the detection of latent fingermarks on a wide range of non-porous substrates, including plastic, glass, and metallic surfaces. This is generally achieved by exposing evidential items to the fumes generated by heating a small quantity of commercial cyanoacrylate adhesive in an enclosed chamber. The fuming chamber may be a home-made, improvised system (e.g., a plastic tent or a modified glass fish tank), or a commercial unit. The cyanoacrylate vapour selectively polymerises on latent fingermark ridges to form a hard, white polymer known as polycyanoacrylate, with the reaction believed to be initiated by certain eccrine and sebaceous components in the latent deposit [1]. The temperature used to vapourise the cyanoacrylate can vary significantly, with some commercial units heating the adhesive to around 180–190 °C [2]. With certain uncontrolled heating systems, such as those based on the use of a hot plate or butane torch, temperatures well above 200 °C may be encountered.

While cyanoacrylate monomer (i.e., liquid cyanoacrylate adhesive) is generally used to produce the vapour necessary for fingermark development, solid cyanoacrylate polymer – polycyanoacrylate – may also be employed [3]. However, in this case, higher temperatures are required for depolymerisation to occur, which results in the release of cyanoacrylate vapour.

Cyanoacrylate vapour is classified as an eye and respiratory tract irritant; therefore, it is generally recommended that exposure to the vapour is minimised [4]. Several reports have suggested that the thermal decomposition of cyanoacrylate may generate irritating organic vapours, such as oxides of carbon and nitrogen [5,6]. In 1985, Mock indicated that heating cyanoacrylates to temperatures above 400 °F (approximately 204 °C) generated highly toxic hydrogen cyanide (HCN) gas [7]. He based this on results from a study conducted by the Loctite Corporation in February 1983 (Dobiecki, J.W.; "Quantitation of Hydrogen Cyanide Generated from Thermal Decomposition of Cyanoacrylate in a Closed System"). In this study, researchers placed 1 mL of cyanoacrylate adhesive in an enclosed chamber that was heated at the desired temperature for 30 min. The chamber was then

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0379-0738/$ – see front matter © 2011 Elsevier Ireland Ltd. All rights reserved.
doi:10.1016/j.forsciint.2011.06.004

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Discussion – Health & Safety

- HCN is considered lethal at concentrations from 100 mg/m^3
- Even in the worst case scenario (~200 µg/m^3) the value is well below the lethal threshold – but caution is advised for less controlled field applications (rooms, tents, etc.)

Approximate temperature (°C)	Loctite® 406		Loctite® Hard Evidence		Mock [7]
	Monomer	Polymer	Monomer	Polymer	
180	0	0	0	0	–
200	0	9.2	10.7	12.9	0
220	3.9	17.0	17.5	26.6	5.6
240	4.7	23.9	22.0	32.9	–
260	6.7	48.8	27.2	122.0	–
270	–	–	–	–	98.2
280	76.1	53.8	100.8	>166	–

"–", not tested.

Sources: Mock JP. (1985) Fingerprint Whorld 11(41):16-17
Fung TC et al. (2011) Forensic Sci Int 212:143-149.

Conclusions

- The one-step fluorescent CA fuming method appeared to produce comparable development to the two-step method (involving dye stains)
- Some variation occurred depending on the substrate
- Sebaceous-rich prints developed better than eccrine-rich ones for both techniques
- The one-step process does not involve the use of harsh solvents that could potentially damage the substrate and/or the cyanoacrylate polymer.

Acknowledgements

- William Hahn, Student Intern, West Virginia University (fluorescent CA work)
- John Morgan, CLPE, Lead Fingerprint Specialist, U.S. Secret Service (print evaluation)
- Anthony Clay, CLPE, Lead Fingerprint Specialist, U.S. Secret Service (print evaluation)

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