Validation of PolyCyano UV: A One-Step Luminescent Cyanoacrylate Fuming Process

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Abstract

PolyCyano UV (Foster + Freeman Ltd) is a new one-step process for developing luminescent fingermarks using cyanoacrylate (CA) fuming without the need for further chemical treatment. Once an exhibit is fumed, it can be imaged under a long-wave UV light source. This method is particularly recommended for substrates that are easily destroyed or degraded during solvent-based staining processes. By avoiding the use of hazardous chemicals and solvents, this method also has significant health and safety advantages.

In this study, conditions including the amount of PolyCyano UV powder, the humidity level of the fuming chamber, and the time and temperature of the fuming process were optimised. A variety of different surfaces were tested and aged fingermark samples were also examined. The PolyCyano UV developed fingermarks were compared to conventional CA-developed fingermarks and subsequently stained with rhodamine 6G. PolyCyano UV was able to develop high quality fingermarks on the surfaces tested, however, when examined under UV light, the luminescence of PolyCyano UV developed fingermarks was found to be weaker than conventional CA-developed fingermarks that were stained with rhodamine 6G. When used in sequence with rhodamine 6G, PolyCyano UV was found to give significantly improved contrast compared to conventional CA-developed fingermarks stained with rhodamine 6G.
Cyanoacrylate Enhancement Techniques

Although cyanoacrylate (CA) fuming is a widely used and reliable fingerprint detection and enhancement technique the developed marks often lack contrast and can be difficult to visualise, particularly on light coloured surfaces. Techniques to increase contrast include optical methods such as episcopic coaxial illumination [1], fingerprint powder and - most commonly - applying a coloured or luminescent stain. The advantage of using a stain is that the dyes will be trapped in the cyanoacrylate polymer, significantly enhancing contrast. Different stains can also be used depending on the surface [2]. Commonly used stains include rhodamine 6G, Ardrox® and basic yellow 40, each with different excitation and emission characteristics. There has been a wide range of studies examining the effectiveness of these dyes as well as proposing alternative methods and dye mixtures [3-5].

Recently, several new products have become commercially available (PolyCyano UV, Lumicyano™, CN-Yellow™) that can develop luminescent fingermarks in a one-stage fuming process, without the need for further chemical enhancement. These techniques have several advantages: the one-step fuming and staining process is more efficient, minimises the use of hazardous chemicals and can be used on surfaces that cannot be treated with a conventional stain solution (e.g., semi-porous surfaces). The concept of a luminescent cyanoacrylate polymer has been investigated since the 1980s; however, there has been limited success. The first reported successful one-step cyanoacrylate fuming process was by Weaver and Clary, who combined methyl cyanoacrylate with dye from the styryl family. This work was published and patented, the resulting product is marketed as CN-Yellow™ [6].

A similar method was proposed by Takatsu, who used p-dimethylaminobenzaldehyde (DMAB) crystals as a vapour staining method of enhancing CA-developed fingermarks. DMAB treated marks exhibited strong luminescence under UV radiation; however, they proposed it as a two-step method [7]. The material safety data sheet (MSDS) for PolyCyano UV confirms that DMAB is used in this product [8]. PolyCyano UV was previously evaluated by Hahn and Ramotowski and developed marks were compared to those treated with different luminescent CA stains. This study found that the PolyCyano UV produced luminescent fingermarks of comparable quality to the stained fingermarks on a range of different surfaces. Similar to conventional CA, the effectiveness of PolyCyano UV was found to be highly dependent on the surface itself [9]. A limitation of the study was that it used a modified fuming cabinet to deliver the PolyCyano UV powder into the glue dish and did not use commercially available equipment.
Aims and Objectives

PolyCyano UV requires validation before it can be accepted into operational forensic laboratories. Since this is a newly developed technique, the performance of PolyCyano UV in a sequence should also be determined as the luminescent properties of PolyCyano UV may interfere with the luminescence of any cyanoacrylate stains subsequently employed. The aim of this study was to determine how effective PolyCyano UV was in developing marks when compared to conventional cyanoacrylate fuming. This was performed by optimising the fuming conditions then comparing the technique to conventional cyanoacrylate (Cyanobloom). Fingermarks developed using both cyanoacrylates were examined under a range of different conditions including white light examination, UV excitation (for PolyCyano UV), post rhodamine staining to determine which technique gave the best enhancement.

Materials and Methods

General Approach

This study was divided into two phases; (1) optimisation of development conditions; and (2) a donor and sequencing study. The first phase aimed to compare different PolyCyano UV development conditions to the reported optimised conditions to determine whether this had an effect on the development quality and fingermark luminescence. Once the conditions were optimised, PolyCyano UV was compared to Cyanobloom (a non-luminescent cyanoacrylate monomer marketed by Foster + Freeman) and stained with different luminescent stains in a sequence. The two CA fuming methods were compared at different stages of the staining sequence based on the quality of fingermark ridge development and contrast between the fingermark and the substrate.

Details about the chemicals and instrumentation used during these experiments can be found in the Appendix.
Phase 1: Optimisation of Development Conditions

Table 1 outlines the manufacturer’s recommended development conditions for PolyCyano UV; for the optimisation study, only the mass, humidity and fuming times were altered. Temperature was not changed as there were only two temperatures available on the MVC 1000/D cabinet (180 °C and 230 °C) and, based on the information provided by Foster + Freeman, 180 °C would not completely vaporise the PolyCyano UV polymer/dye mixture.

The recommended settings were used as a baseline comparison (Table 1) and then each parameter was optimised individually (Table 2). Fresh marks (charged and natural) from a single donor were deposited on glass, aluminium foil, Fanta® soft drink cans and polyethylene bags in duplicate. Luminescence spectroscopy and thermogravimetric analysis were performed on PolyCyano UV powder to determine the most effective visualisation and heating conditions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Recommended Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>230</td>
</tr>
<tr>
<td>Mass of PolyCyano UV (g)</td>
<td>0.6 (for MVC1000/D cabinet)</td>
</tr>
<tr>
<td>Humidity (%)</td>
<td>80</td>
</tr>
<tr>
<td>Fuming Time (minutes)</td>
<td>25</td>
</tr>
<tr>
<td>Visualisation Conditions (nm)</td>
<td>Ex = 365, Em = 415-510</td>
</tr>
</tbody>
</table>

Table 1: Parameters recommended by Foster + Freeman for PolyCyano UV.
Table 2: Parameters used for the optimisation experiments.

<table>
<thead>
<tr>
<th>Mass of PolyCyano UV (g)</th>
<th>Relative Humidity (%)</th>
<th>Fuming Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>70</td>
<td>15</td>
</tr>
<tr>
<td>0.6</td>
<td>75</td>
<td>25</td>
</tr>
<tr>
<td>0.7</td>
<td>80</td>
<td>35</td>
</tr>
</tbody>
</table>

Phase 2: Donor and Sequencing Study

For the sequencing study, four donors (two male and two female) deposited sets of charged and natural three-finger impressions on three surfaces: aluminium, glass and polyethylene bags. Samples were aged from fresh to two months. Each set of three marks was split into two with one half developed with PolyCyano UV and the other half developed with Cyanobloom (Figure 1). After fuming each developed sample was examined under a range of imaging conditions and the results compared according to Figure 2. The rhodamine 6G (R6G) staining solution was prepared according to the methods currently employed by the Australian Federal Police [10].

![Figure 1: Preparation of fingermark samples for the donor and sequencing study.](image)
Comparison Technique

After developing and imaging, the split-sample images were digitally placed side-by-side for comparison. All digital stitching of fingermarks was performed using the GNU Image Manipulation Program (GIMP). No other manipulations were made to the images after stitching. Each three-finger impression was then given a score, using the University of Canberra comparative scale [11] (Table 3). This assessment was based on any differences observed with respect to ridge detail and/or contrast.
Table 3: Comparison scoring system

<table>
<thead>
<tr>
<th>Numerical Value</th>
<th>Qualitative Equivalent</th>
</tr>
</thead>
<tbody>
<tr>
<td>-2</td>
<td>Significant decrease in ridge detail/contrast when compared to Cyanobloom</td>
</tr>
<tr>
<td>-1</td>
<td>Slight decrease in ridge detail/contrast when compared to Cyanobloom</td>
</tr>
<tr>
<td>0</td>
<td>No difference in ridge detail/contrast when compared to Cyanobloom</td>
</tr>
<tr>
<td>1</td>
<td>Slight increase in ridge detail/contrast when compared to Cyanobloom</td>
</tr>
<tr>
<td>2</td>
<td>Significant increase in ridge detail/contrast when compared to Cyanobloom</td>
</tr>
</tbody>
</table>

In an effort to remove the ambiguity of a zero score (where no differences were observed), a supplementary scoring system was implemented. Table 4 outlines the sub-classification of samples that were assigned a zero score.

Table 4: Supplementary scoring system for sample sets that were assigned a zero score.

<table>
<thead>
<tr>
<th>Sub-classification</th>
<th>Qualitative Equivalent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Good Development</td>
<td>Developed fingermarks with clear ridge detail and contrast</td>
</tr>
<tr>
<td>Poor Development</td>
<td>Developed fingermarks but very little ridge detail and/or poor contrast</td>
</tr>
<tr>
<td>No Development</td>
<td>Neither technique produced ridge detail</td>
</tr>
</tbody>
</table>

Results and Discussion

Physical and Chemical Properties

The most noticeable difference between PolyCyano UV and Cyanobloom is that PolyCyano is a solid cyanoacrylate polymer (mixed with a luminescent dye) whereas Cyanobloom is a liquid cyanoacrylate monomer. The thermogravimetric analyse (Figure 3) show that PolyCyano UV must be
heated above 208 °C to be completely depolymerized (liberating CA monomer and the incorporated luminescent dye). The temperature settings on the MVC 1000/D are for 180 °C and 230 °C; therefore, to ensure that adequate CA reagent is generated, the 230 °C setting must be used. This can be explained by the fact that the polymer requires a higher temperature to depolymerise and liberate vaporised monomer, compared to the monomer that has a higher volatility. The luminescence data for pre- and post-fumed PolyCyano UV showed that when excited by UV light the luminescence emission is very strong and broad (Figure 4) with significant emission over the range 380-420 nm (\( \lambda_{\text{max}} = 400 \text{ nm} \)) and less intense emission extending to around 500 nm. This indicates that a range of visualisation conditions can be used if there are interferences from the fingermark substrate. While there is a slight decrease in intensity for the post-fumed samples adequate luminescence emission remains to facilitate the visualisation of developed marks.

![Thermogravimetric analysis of PolyCyano UV.](image)

**Figure 3: Thermogravimetric analysis of PolyCyano UV.**
Mass of PolyCyano UV Optimisation

The amount of PolyCyano UV was determined to be a significant factor impacting on the quality of luminescence in developed fingermarks (Figure 5). The higher mass samples had observable luminescence quenching and over-development, with this effect particularly noticeable on glass. The only surface that produced better fingermark development with 0.7 g of PolyCyano UV was the Fanta® soft drink cans, as the other masses trialled gave reverse development on this substrate. However, this surface is uncommon in casework and, as a result the improvement that 0.7 g provided was not sufficient to warrant it being the optimal mass for the development of all samples. Post fuming, there was also a significant amount of unevaporated residue remaining in the foil dish with this higher starting amount; from a cost point of view such losses need to be minimised. The 0.5 g samples performed the best on the majority of surfaces and, as a result, it was concluded that this was the optimal mass from this study.

Figure 4: Luminescence emission spectra for PolyCyano UV (excitation 365 nm).
Relative Humidity Optimisation

Humidity is an important factor when developing fingermarks by CA fuming: the amount of moisture in the deposit can significantly affect the quality of development [12]. The main issue that arose with this optimisation was ensuring that the cabinet could reach the ideal humidity. It is suggested by Foster + Freeman that a relative humidity (RH) of 90% increases the luminescence of developed marks; however, the fuming cabinet used in this study could not reach over 85% RH. While 75% and 80% RH gave very similar development (Figure 6), some samples developed at 80% RH gave significant over-development (particularly for glass samples). Of the parameters trialled, 75% RH was determined to give the best overall development and was the most practical as the cabinet could reach this humidity without issue.
Figure 6: Representative PolyCyano UV developed natural fingermarks viewed in luminescence mode (365 nm excitation, 400 nm longpass barrier filter) on polyethylene bags: (left) 70% RH, (centre) 75% RH, (right) 80% RH.

Fuming Time Optimisation

Of all the parameters tested, the fuming time played the most significant role in the quality of development (Figure 7). Samples that were fumed for 15 minutes tended to be underdeveloped and exhibited poor luminescence, while 35-minute samples gave good development but exhibited poor luminescence (possibly due to luminescence quenching). A fuming time of 25 minutes was determined to give the best compromise between development and luminescence quality while also allowing for a high throughput of samples in a day, with a total processing time of 45 minutes (including humidification, fuming and purging).
Based on these results, the optimised settings that were used for the donor study are outlined in Table 5. An ageing study was performed to determine the best storage and imaging times for samples. Based on this work, samples should be imaged within 24 hours of development; if samples cannot be analysed within 24 hours, the samples should be stored in the dark to prevent a decrease in luminescence intensity. The decrease in luminescence intensity was very dependent upon the substrate, PolyCyano UV developed fingermarks on glass exhibited the most significant decrease, whereas aluminium and polyethylene bags only a slight decrease was observed.

**Table 5: Optimised parameters for the development of fingermarks using PolyCyano UV.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Recommended Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>230</td>
</tr>
<tr>
<td>Mass of PolyCyano UV (g)</td>
<td>0.5 (for MVC1000/D cabinet)</td>
</tr>
<tr>
<td>Humidity (%)</td>
<td>75</td>
</tr>
<tr>
<td>Fuming Time (minutes)</td>
<td>25</td>
</tr>
</tbody>
</table>
Each sample was examined under white light after development to see how effective each CA fuming process was at developing latent fingermarks. Based on the results shown in Figure 8, there were only minor differences between both CA treatments; there was a slight difference in colour of developed fingermarks as PolyCyano UV developed marks gave pale yellow ridges while Cyanobloom produced white fingermarks. With regards to development, there was no significant donor dependency observed. Male donors tended to give better natural marks than females; however, this was not always the case. There was a degree of degradation with increasing age of the samples (particularly for the two-month samples); however, this trend was not consistent across all donors. With regards to the effectiveness of each cyanoacrylate, PolyCyano UV only outperformed Cyanobloom on glass samples; Cyanobloom developed samples tended to be over-developed (Figure 9), which resulted in a loss of ridge detail. This was observed for older samples with only fresh marks giving better development with Cyanobloom. Fingermarks that were developed on aluminium tended to have very poor contrast due to the colour and reflective nature of the surface. This resulted in a large number (two-thirds of all aluminium samples) of “poor” and “no development” scores for the comparisons that had zero ratings using the University of Canberra comparative scoring system. Polyethylene bags gave good development for most samples, but a noticeable decrease in quality (particularly for the cyanobloom samples) was observed with increasing fingermark age. Based on the white light examination, there was no clear difference between the cyanoacrylates in their ability to develop fingermarks on the surfaces tested. This would be expected as the addition of a luminescent dye such as DMAB is unlikely to alter the mechanics of the development process.
**Figure 8:** Comparison results for all surfaces under white light examination (average McLaren scale values indicated).

**Figure 9:** Representative fingermarks viewed under white light, developed with PolyCyano UV (PC UV) and Cyanobloom (CB) on: (left) aluminium, (centre) glass, (right) polyethylene bags.
Donor and Sequencing Study – UV Examination and Rhodamine Post-Treatment

The main advantage of PolyCyano UV over the traditional cyanoacrylate method is the ability to visualise developed fingermarks in the luminescence mode under UV light without the need for a staining post treatment. However, as the results in Figure 10 indicate, the luminescence of PolyCyano UV developed marks was not as intense as that of rhodamine 6G stained Cyanobloom developed marks. For polyethylene bags there was a significant decrease in quality compared to the white light examination; this is reflected by the increase in negative values across all ages. Similarly for aluminium there was a slight decrease in quality for samples aged up to one week. For both surfaces, the PolyCyano UV developed marks exhibited very low contrast and, when compared to rhodamine 6G, treated marks, there was a significant decrease in quality (Figure 10). Staining samples with rhodamine 6G significantly decreased the number of no development scores for the aluminium samples. This is due to the increase in contrast between the fingermark ridges and the surface when viewing samples in the luminescence mode compared to white light examination. PolyCyano UV developed fingermarks on glass also exhibited a slight decrease in quality when compared to the rhodamine stained marks; however, because there were some samples that had been overdeveloped, this decrease was not as significant. There were also some cases where the luminescence of PolyCyano UV was quenched, possibly due to slight overdevelopment (Figure 11). The only trend that could be ascertained from the age of the samples was an increase in the number of “no development” scores over time. Another potential limitation of the visualisation of PolyCyano UV is that UV excitation of substrates can potentially generate background luminescence. Compared to excitation at longer wavelengths (e.g., when rhodamine 6G is employed) this poses a potential disadvantage of PolyCyano UV. These results indicate that, based on luminescence, PolyCyano UV does not provide any significant advantage over conventional CA fuming with subsequent rhodamine 6G staining for the substrates tested.
Figure 10: Comparison values for all surfaces between PolyCyano UV and Cyanobloom post rhodamine 6G staining (average McLaren scale values indicated).

When PolyCyano UV was used in sequence and developed fingermarks stained with rhodamine 6G, there was a significant improvement in the luminescence of most samples (compared to the unstained UV luminescence). When these marks were compared to Cyanobloom developed and rhodamine 6G stained samples, the PolyCyano UV marks gave better development in the majority of
cases. This can be attributed to two factors: firstly, when examined under white light PolyCyano UV tended to give better development, therefore when these samples were stained with rhodamine 6G it would be expected to outperform Cyanobloom; secondly, the only issue that affected the quality of development when examined under UV light was the weaker luminescence of PolyCyano UV when compared to rhodamine 6G. Therefore, upon staining with rhodamine 6G, the luminescence of PolyCyano UV developed marks would be expected to increase, as was observed. This is illustrated by in the average McLaren values shown in Figure 12. This trend was seen on all surfaces, with aluminium exhibiting the greatest change in scores (35% negative values for UV examination to 4% post staining). A comparison between PolyCyano UV pre and post staining demonstrated the significant increase in quality observed when staining with rhodamine 6G (Figure 12). These results indicate that PolyCyano UV is very effective when used in a sequence; the luminescent dye in the cyanoacrylate polymer does not decrease the luminescence strength of rhodamine 6G (Figure 13). This comparison also had a significantly high amount of zero scores (indicating no significant difference when compared against conventional CA fuming plus staining), which is to be expected as the same enhancement technique was applied to both sides so any variability would be expected to be minimal. However, the main advertised advantage of this technique is that it should develop luminescent marks without the need the further staining. While it was successful to a certain extent, PolyCyano UV was not as effective as conventional CA fuming plus rhodamine 6G staining.

![Figure 12: Comparison results for all surfaces between PolyCyano UV after rhodamine 6G staining and Cyanobloom after rhodamine 6G staining (average McLaren scale values indicated).](image-url)
Discussion Regarding Overall Performance of PolyCyano UV

This study has demonstrated that PolyCyano UV is able to develop fingermarks of a similar quality to conventional CA developed fingermarks. However, the advantage of being able to visualise developed fingermarks in the luminescence mode without the addition of luminescent stains is not as effective as conventional methods. The UV luminescence emission observed in this study for PolyCyano UV developed fingermarks was, in the majority of cases, much weaker than for rhodamine 6G stained fingermarks. While the luminescence can be significantly improved by the addition of rhodamine 6G post treatment, the overall performance of PolyCyano UV was underwhelming. Considering the high cost associated with PolyCyano UV, compared to Cyanobloom or other commercially available cyanoacrylates, it would not be advantageous as a replacement method for routine use. The health and safety issues associated with luminescent stains are minimal when used in a properly equipped forensic laboratory.

Based on this study it was found that, for a MVC 1000D cabinet, 0.5 g was the optimal mass, while Foster + Freeman recommend that 0.5-1.0 g be used per cycle (depending on the number of exhibits and the size of the cabinet). PolyCyano UV costs approximately $150 AUD per 10 g, while Cyanobloom cost $6-7 AUD for a 20 g bottle. For a large volume of samples, it would be a significant
expense to use PolyCyano UV for routine CA fuming. Taking into account the relatively low cost of luminescent dyes and solvents, PolyCyano UV is a costly alternative that is not justified by the results observed on common non-porous substrates. However the use of PolyCyano UV on some semi-porous substrates (not tested in this study), or in situations where conventional staining is problematic, may be justified in some cases. Such a situation would be for CA fuming at the crime scene as PolyCyano UV would remove the need to transport the chemicals required for the application of conventional CA stains such as rhodamine 6G.

Conclusions

PolyCyano UV is marketed as a one-step luminescent cyanoacrylate; this study showed that while UV luminescence could be an advantage, the luminescence was noticeably weaker than conventional CA fumed marks stained with rhodamine 6G. When stained with rhodamine 6G PolyCyano UV developed marks in some cases provided better results than with conventional CA fumed marks stained with rhodamine 6G. This could be due to variability between fuming cycles or slight variations in the amount of cyanoacrylate being vapourised. It is unlikely that PolyCyano UV would replace conventional cyanoacrylate for routine use due to the high cost associated with the product. PolyCyano UV could be used for cases that require DNA examination after fuming (as PolyCyano UV does not potentially damage or decrease DNA recovery like post CA staining can [13]) or in cases where staining may damage or stain the surface itself (e.g., semi-porous surfaces). Using an examination sequence of white light, UV luminescence and luminescence from rhodamine 6G staining allows for imaging of developed fingermarks different regions of the visible spectrum. This could potentially increase the likelihood of recovering exploitable fingermarks.

References


8. Material and safety data sheet PolyCyano UV©. 2011, Foster + Freeman Ltd.


Appendix

Chemicals Used

PolyCyano UV and Cyanobloom were purchased through Foster + Freeman and used as supplied.

Rhodamine 6G dye content 99% [CAS 989-38-8] was obtained from Sigma Aldrich and used as supplied.
Reagent grade isopropanol [CAS 67-63-0] and methyl ethyl ketone [CAS 78-93-3] were obtained through Chem-Supply and used as supplied.

**Instrumentation Used**

A Varian Cary Eclipse luminescence spectrometer was used for measuring the excitation and emission spectra for pre- and post-fumed PolyCyano UV.

A Foster + Freeman MVC1000/D cyanoacrylate fuming cabinet was used to fume all samples throughout the study.

A Foster + Freeman VSC 6000 was used to image all the developed samples.