TECHNICAL NOTE: EVALUATION OF ONE-STEP LUMINESCENT CYANOACRYLATE FUMING

Alicia Khuu[a]*, Scott Chadwick[a], Xanthe Spindler[a], Rolanda Lam[a], Sébastien Moret[a], Claude Roux[a]

[a]Centre for Forensic Science, University of Technology Sydney (UTS), Sydney NSW, Australia
*Corresponding author

Contact details:
Alicia Khuu
Centre for Forensic Science, Faculty of Science
City Campus, Broadway, Bldg 7
PO Box 123 Broadway NSW 2007 Australia
alicia.khuu@uts.edu.au

Highlights

- Conventional cyanoacrylate typically gave better development on fresher fingermarks
- Rhodamine 6G gave superior luminescence compared to that of one-step treatments
- Fingermarks on polystyrene surfaces are better visualised with a one-step treatment

Abstract

One-step luminescent cyanoacrylates have recently been introduced as an alternative to the conventional cyanoacrylate fuming methods. These new techniques do not require the application of a luminescent post-treatment in order to enhance cyanoacrylate developed fingermarks. In this study, three one-step polymer cyanoacrylates: CN Yellow Crystals (Aneval Inc), PolyCyano UV (Foster + Freeman Ltd) and PECA Multiband (BVDA), and one monomer cyanoacrylate: Lumikit™ (Crime Scene Technology), were evaluated against a conventional two-step cyanoacrylate fuming method (Cyanobloom (Foster + Freeman Ltd) with rhodamine 6G stain). The manufacturers' recommended conditions or conditions compatible with the MVC™ 1000/D (Foster + Freeman Ltd) were assessed with fingermarks aged for up to 8 weeks on non-porous and semi-porous substrates. Under white light, Cyanobloom generally gave better development than the one-step treatments across the substrates. Similarly when viewed under the respective luminescent conditions, Cyanobloom with rhodamine 6G stain resulted in improved contrast against the one-step treatments except on polystyrene, where PolyCyano UV and PECA Multiband gave better visualisation. Rhodamine 6G post-treatment of one-step samples did not significantly enhance the contrast of any of the one-step treatments against Cyanobloom/rhodamine 6G-treated samples.

Keywords: latent fingermarks; Cyanobloom UV; Lumikit™; CN Yellow Crystals; PolyCyano UV; PECA Multiband

Introduction

Cyanoacrylate (CA) fuming is the preferred laboratory technique for the detection of fingermarks deposited on non-porous substrates. In this technique, CA is vaporised and the fumes react with components from fingermark secretions forming a hard white polymer extending along the ridges of the fingermark [1]. Limitations arise with CA development due to the lack of contrast that occurs on light-coloured substrates, where white fingermarks can be difficult to visualise, and with the development of aged fingermarks, where transparency of the CA ridges is increased [1]. The contrast of developed fingermarks can be improved through post-treatment with luminescent stains which penetrate the CA development and become trapped within the polymer [2, 3]. While contrast on non-porous substrates is generally improved, the use of post-stains is associated with a number of limitations: increased handling times [2]; absorption of stains into semi-porous substrates [4]; health and safety concerns associated with the use of hazardous chemicals during staining [5]; and the potential loss of integrity of the developed fingermark as well as the exhibit.

One-step luminescent CA fuming products incorporating a luminescent dye with CA have been researched since the early 1980s. However, it is only recently that a number of commercial products have become available including: CN Yellow Crystals (Aneval Inc), PolyCyano UV (Foster + Freeman Ltd), PECA Fluor Extra, PECA Multiband (BVDA), and Lumikit™ (Global Forensics Ltd).

The initial report of a one-step luminescent CA was in 1993, when Weaver and Clary successfully produced luminescent fingermarks following co-sublimation of a styryl dye with CA monomer [6]. Weaver subsequently conducted work on the optimisation of CN Yellow, the first commercially available one-step luminescent CA. This product incorporates CA in a solid polymer form with yellow 43, a dye which was reported to show selectivity for CA-polymerised fingermark ridges [7]. Groeneveld et al. found that while CN-Yellow produced visible CA-developed fingermarks, luminescent contrast was poor [8]. A review of the technical notes indicates that a slow heating of the product may degrade the luminescent component of CN Yellow Crystals [9].

More recently, PolyCyano UV and the PECA products have been developed and commercialised. Like CN-Yellow, these products are also in a solid polymer form and require a temperature of 230°C to vaporise. The luminescent compound of PolyCyano UV and PECA formulations is dimethylamino benzaldehyde (DMAB), which differs in concentrations from 5 % in PolyCyano UV and up to 15 % in PECA Fluor Extra and PECA Multiband [10-12]. In a study conducted by Takatsu et al., DMAB was reported to selectively bind to the CA polymer following a two-step enhancement process and could offer sufficient contrast on exhibits which were sensitive to solvents [13]. Previous studies conducted with PolyCyano UV on a number of non-porous surfaces have determined that its ability to develop fingermarks is similar to that of conventional CA [8, 14, 15]. However, in most cases, the luminescence of PolyCyano UV lacked intensity when compared to post-stains used following the fuming with Cyanobloom [14, 15]. At the time of writing, no published research was available on either of the PECA products.

Lumicyano™ was formerly available as a prepared solution of luminescent dye incorporated with CA. This has since been superseded by Lumikit™ which requires the combination of Lumicyano Powder™ dye ($C_4H_5ClN_4O$) and Lumicyano Solution™ in a two-step preparation process. Following preparation, Lumikit™ is fumed under the same conditions as that of conventional CA [16-18]. The manufacturers recommend a concentration of equal to or less than 5 % w/w (powder to solution) prior to fuming [16]. Studies on both Lumicyano™ [4, 19] and a 4 % preparation of Lumikit™ [20] showed that the CA development under white light was comparable to that of conventional CA

when the technique was applied to non-porous substrates. Farrugia et al. [19] found a similar rate of detection under luminescent lighting conditions, while it was also found that Lumicyano™ gave inferior luminescence to CA-developed fingermarks stained with basic yellow 40 (BY40) [4, 20]. Further, semi-porous substrates treated with 4 % Lumicyano™ resulted in inferior CA-development compared to that of the conventional method [20]. However, post-treatment of 4 % Lumicyano™ samples with BY40 revealed a further 30 % of previously undetected fingermarks [20].

While one-step luminescent CAs offer the convenience of reduced handling and processing times, and show good potential for use on semi-porous substrates, they are associated with significantly greater costs than conventional CA fuming and staining reagents. The aims of this study were to evaluate the quality and performance of commercially available one-step luminescent CA fuming techniques (CN Yellow Crystals, PolyCyano UV, PECA Multiband and Lumikit™) in comparison to conventional CA fuming with a post-treatment of rhodamine 6G (R6G) and to evaluate the one-step luminescent techniques against each other. The manufacturers' recommended fuming conditions were firstly assessed to determine their compatibility with a commercial fuming cabinet. Comparisons of the different treatments on non-porous and semi-porous substrates were then performed. This study was conducted in accordance with the International Fingerprint Research Group guidelines [21].

Materials and Methods

Materials and Equipment

The control treatment consisted of fuming with the monomer CA: Cyanobloom (Foster + Freeman Ltd), followed by staining with R6G working solution (R6G (Sigma Aldrich); methyl ethyl ketone (Chem-Supply); isopropanol (VWR); deionised water) [22]. The one-step luminescent CAs evaluated in this study were polymer CAs: PolyCyano UV (Foster + Freeman Ltd), CN Yellow Crystals (Aneval Inc) and PECA Multiband (BVDA); and a monomer CA: Lumikit™ (Global Forensics Ltd). The relative performances of these techniques were investigated on polyethylene bags (Woolworths Select Resealable Sandwich Bags), polystyrene cups (Woolworths Essentials Foam Cups) and glossy cardboard (Kleenex Facial Tissue box) surfaces (method described below).

A MVC™1000/D (Foster + Freeman Ltd) fuming cabinet was used for all treatments in this study. Samples were imaged with a Nikon AF Micro Nikkor 60 mm lens and QImaging Peltier Cooling CCD Camera. Ultraviolet (UV) excitation and luminescent examination were performed using the Poliview IV (Rofin) with V++ Precision Digital Imaging System version 4.0 and Polilight PL500 forensic light source. A VSC6000 (Foster + Freeman Ltd) was also used to image CA development on glossy cardboard and polystyrene for episcopic coaxial illumination.

Procedure

Fingermark Collection and Ageing

Three donors (one male, two females) were used in this study. Based on previous research, these donors were identified as either a weak, average or strong donor. Each donor provided three sets of natural, single fingermark depositions over three depletions on each of the test surfaces. Fingers were allowed to naturally recharge prior to the depositions onto each surface. For the comparison study, each set of the collected fingermarks were stored in the dark, under ambient laboratory conditions (21°C/50 % relative humidity (RH)) for either one, four or eight weeks. Following ageing, fingermarks were halved, with each half depletion series exposed to a different treatment. A total of 810 fingermarks were collected for the comparison study.

Fuming Conditions

Samples were then exposed to the respective CA treatment for a maximum of 60 minutes, until sufficient development was observed or until it was deemed that no development or further enhancement could be achieved. Within three hours after sufficient fuming, Cyanobloom-treated samples were imaged under white light only, while other samples were imaged under the respective recommended luminescent conditions (**Table 1**) followed by white light. All samples were then left to cure for at least 18 hours before being stained with a R6G solution (**Table 2)** and again imaged within three hours of staining at the recommended visualisation conditions for R6G [22]. Corresponding fingermark halves were digitally stitched using GNU Image Manipulation Program (GIMP). No further digital enhancements were performed on any of the imaged fingermarks. The CA treatment for each fingermark half was then directly compared to the treatment on the corresponding half and scored using the comparative scale shown in **Table 3** [14, 23].

Table 1: Fuming conditions for each treatment used in the MVC™1000/D CA fuming cabinet and visualisation conditions using the Poliview

Conditions	Cyanobloom/ R6G	PolyCyano UV	PECA Multiband	CN Yellow Crystals	Lumikit™
Temperature (°C)	120	230	230	230*	120
Mass (g)	0.5	0.6	0.2	0.6*	0.4* (5 % w/w)
Humidity (%)	80	80	80	80	80
Visualisation (nm)	Ex = 490; Em = 555	Ex = 350; Em = 450	Ex = 440; Em = 505	Ex = 450; Em = 555	Ex = 350; Em = 555

*Values adjusted for use in this study.

Table 2: Preparation of rhodamine 6G staining solutions for non-porous and semi-porous substrates

Component	Rhodamine 6G Stock Solution (SS) (500 mL)	Working Solutions	
		Non-Porous Substrates [22]	Semi-Porous Substrates
Rhodamine 6G	0.2 g	1:3 SS:H_2O	1:15 SS:H_2O
Isopropanol	200 mL		
Methyl ethyl ketone	300 mL		

Table 3: Comparison scoring system [14, 23]

Score	Definition	
-2	Significant decrease in enhancement when compared to alternative treatment	
-1	Slight decrease in enhancement when compared to alternative treatment	
0	No enhancement when compared to alternative treatment	
	Sub-Classification for Zero Scores	
	Good Development	*Fingermarks give clear ridge detail and contrast*
	Poor Development	*Fingermarks have very little ridge detail and poor contrast*
	No Development	*No evidence of fingermarks from either technique*

1	Slight increase in enhancement when compared to alternative treatment
2	Significant increase in enhancement when compared to alternative treatment

Results and Discussion

Preliminary Tests

From preliminary tests of all CA products in this study, fuming for over 60 minutes resulted in no further discernible enhancement or development. Rather, extended fuming caused CA to develop on the background of the substrate in some instances. For the polymer treatments, yellow powder also deposited on the substrate resulting in spotty background luminescence. As such, fingermarks were fumed for no more than 60 minutes in the comparison study.

The equivalent manufacturers' recommended conditions for each of the CAs were used for a MVC1000^{TM}/D in this study except for with Lumikit^{TM} and CN-Yellow Crystals. A 5 % w/w mixture of Lumikit^{TM} was found to give good development and luminescence in preliminary tests; however, the 0.8 g quantity suggested was excessive and did not completely vaporise when cycles of less than 20 minutes were used. A 0.4 g preparation of a 5 % w/w mixture was found to completely vaporise with no noticeable effect on the quality of the developed fingermark and was subsequently used in the comparison study.

As the suggested fuming temperature and quantity of CN Yellow Crystals [9] were incompatible with the fuming chamber used in this study, changes to these conditions were made in order for adequate CA development to be achieved. As a consequence, it was found that the luminescent component of the formulation did not specifically adhere to the CA development. Under luminescent examination, samples fumed with CN Yellow Crystals generally exhibited very poor contrast between the fingermark and the background, hence was found to be inferior to other treatments, similar to preliminary findings by Groeneveld et al. [8]. Comparisons to CN Yellow Crystals, although performed, are therefore not shown in subsequent graphs.

Comparison Study

The relative performance of each technique can only be assessed where visible fingermark development has occurred on at least one side of the reconstructed fingermark following exposure to the respective techniques. Therefore, fingermarks which gave comparison scores of 0 which resulted from *No Development* (**Table 3**) were not included in subsequent graphs. These accounted for 36 % of the total number of fingermarks in this study; the majority of these were found to correspond to fingermarks deposited by the weak donor.

Cyanoacrylate Development

Cyanobloom-treated fingermark halves were compared to fingermark halves treated with PolyCyano UV, PECA Multiband and Lumikit^{TM} on the three substrates under white light. **Figure 1** shows the CA development of respective one-step luminescent treatments in comparison to that of Cyanobloom on glossy cardboard; polystyrene; and polyethylene. A negative score indicates a decrease in enhancement when fingermarks were treated with the respective one-step luminescent CA compared to Cyanobloom.

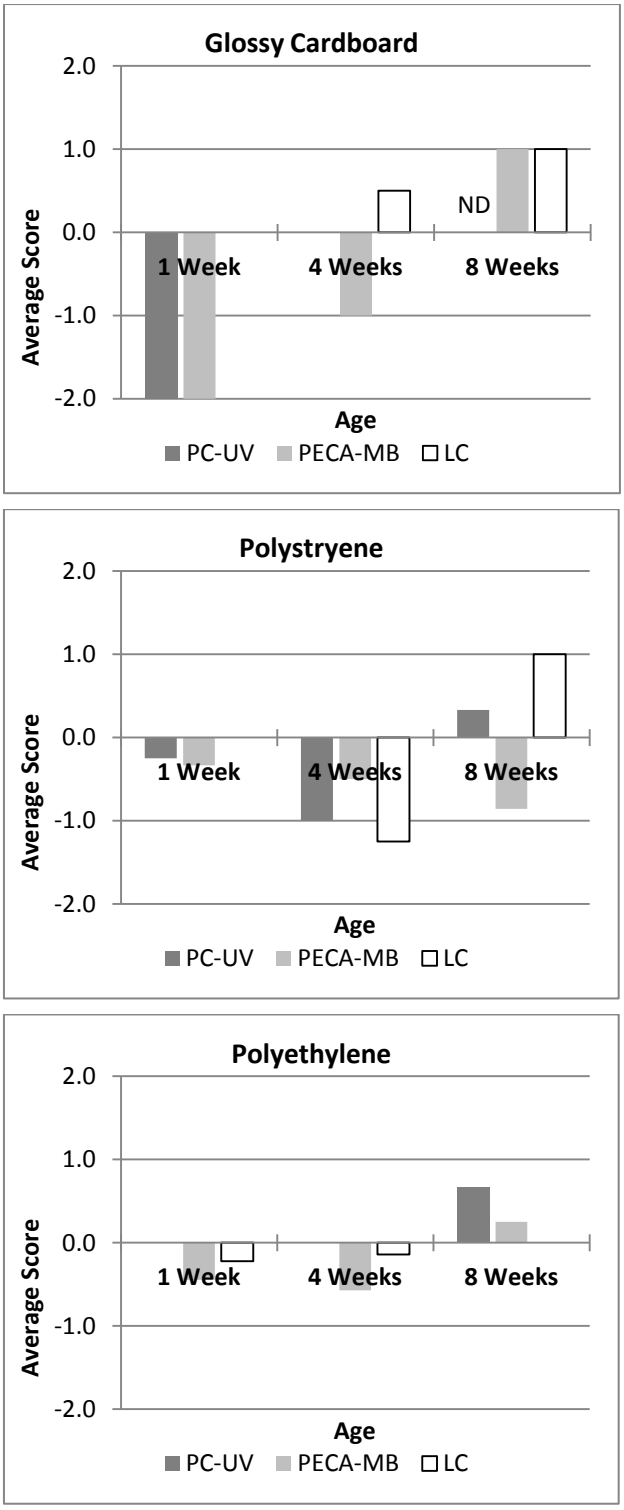

Figure 1: Average comparison scores for PolyCyano UV (PC-UV), PECA Multiband (PECA-MB) and Lumikit™ (LC) against Cyanobloom on: glossy cardboard; polystyrene; and polyethylene with fingermarks aged for 1, 4 and 8 weeks under white light examination. ND indicates instances where all fingermarks in a corresponding set achieved a zero score due to *No Development* (see Table 3).

The most notable differences in CA development were observed on the semi-porous substrates. While the liquid monomer treatments (Cyanobloom and Lumikit™) tended to act similarly on samples aged for 1 week on all substrates, Lumikit™ offered improved CA development on both of the semi-porous substrates as the samples aged (**Figure 1**).

On polystyrene, one-step treatments gave comparable enhancement to that of Cyanobloom on samples up to 4 weeks old, where Cyanobloom showed slightly inferior development to Lumikit™ for 8 week old samples, as indicated by the positive value (**Figure 1**). However, the CA-developed fingermarks from Cyanobloom and one-step luminescent CAs on polyethylene were found to be comparable for samples aged for up to 8 weeks (**Figure 1**). A consistent emerging trend across the substrates was that the quality of Cyanobloom development decreased as the age of the fingermark increased. This would account for the more comparable results in older fingermarks between Cyanobloom and the one-step treatments (**Figure 1**). A similar trend was also seen in a previous study on polyethylene samples treated with PolyCyano UV [14]. The results from the white light observation suggest that both the substrate and age of the fingermark impact the quality of the CA development.

One-Step Luminescent CAs Compared to Cyanobloom/R6G

Figure 2 shows the comparison of the one-step luminescent CAs to Cyanobloom/R6G under luminescent conditions on glossy cardboard, polystyrene and polyethylene. PolyCyano UV gave significantly inferior enhancement when compared to Cyanobloom/R6G on glossy cardboard for samples aged up to 8 weeks (**Figure 2**). PECA Multiband gave slightly inferior enhancement to that of Cyanobloom/R6G on glossy cardboard with fresher samples. This was seen to decrease with the age of the sample, which can be contributed to the decrease in the quality of the Cyanobloom development (**Figure 1**).

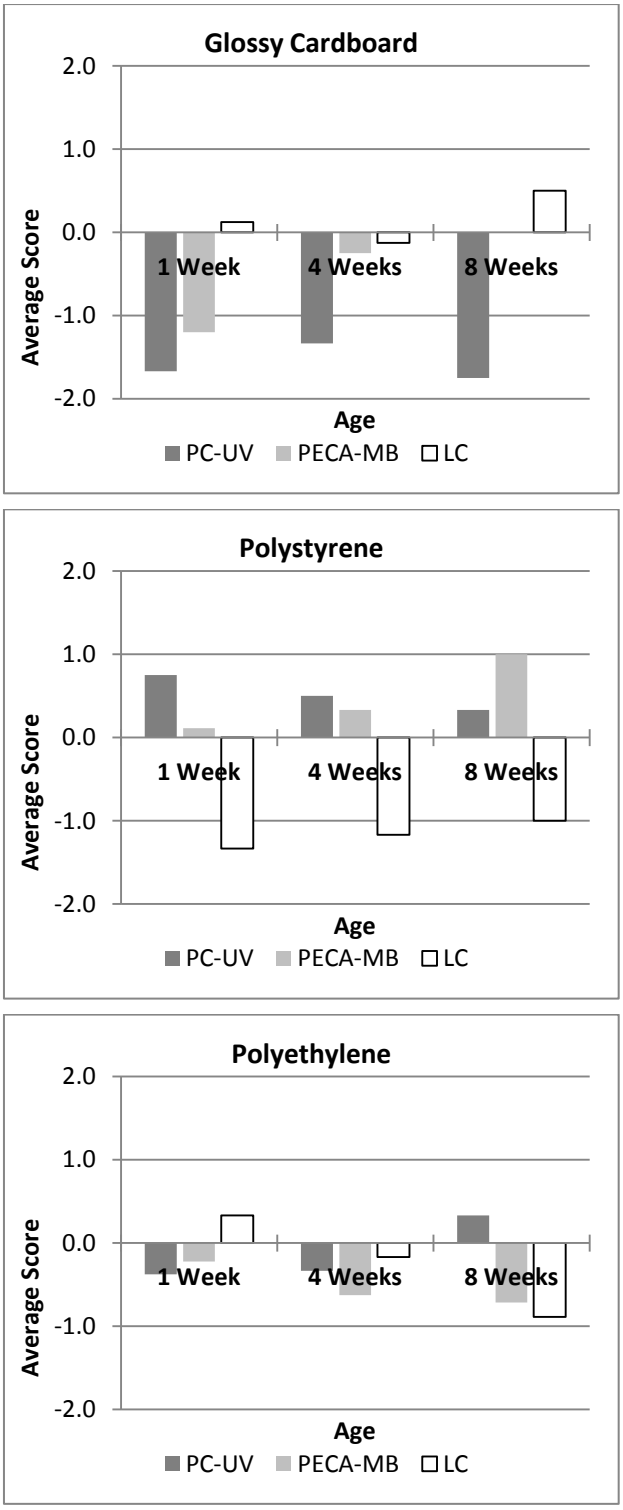

Figure 2: Average comparison scores for PolyCyano UV (PC-UV), PECA Multiband (PECA-MB) and Lumikit™ (LC) against Cyanobloom/R6G on: glossy cardboard; polystyrene; and polyethylene with fingermarks aged for 1, 4 and 8 weeks viewed under their respective luminescent conditions.

A weaker R6G working solution than that currently recommended by the National Centre for Forensic Studies [22] was used to stain samples on the semi-porous substrates (**Table 2**), as preliminary results showed strong staining and background luminescence when the standard formulation was used. Slight discolouration of glossy cardboard was observed, however, this rarely affected the visualisation of the fingermarks during luminescent examination unless the substrate was previously flexed or had suffered surface damage in the region of the fingermark. In these cases, the stain bled into the substrate and emitted strong localised luminescence.

On polystyrene, two emerging trends were seen with PolyCyano UV and PECA Multiband with respect to Cyanobloom/R6G: PolyCyano UV appeared to give greater contrast when used on fresher samples; while PECA Multiband showed superior contrast on older samples (**Figure 2**). Similar to glossy cardboard, slight discolouration was observed in control samples stained with the weaker R6G working solution. However, in this instance, poorer visualisation of the control samples tended to result as R6G did not appear to fully penetrate the ridges hence interrupted ridge detail was observed (**Figure 3**; **Polystyrene**). Fingermarks developed with the one-step treatments (except CN Yellow Crystals) generally had complete luminescent ridges.

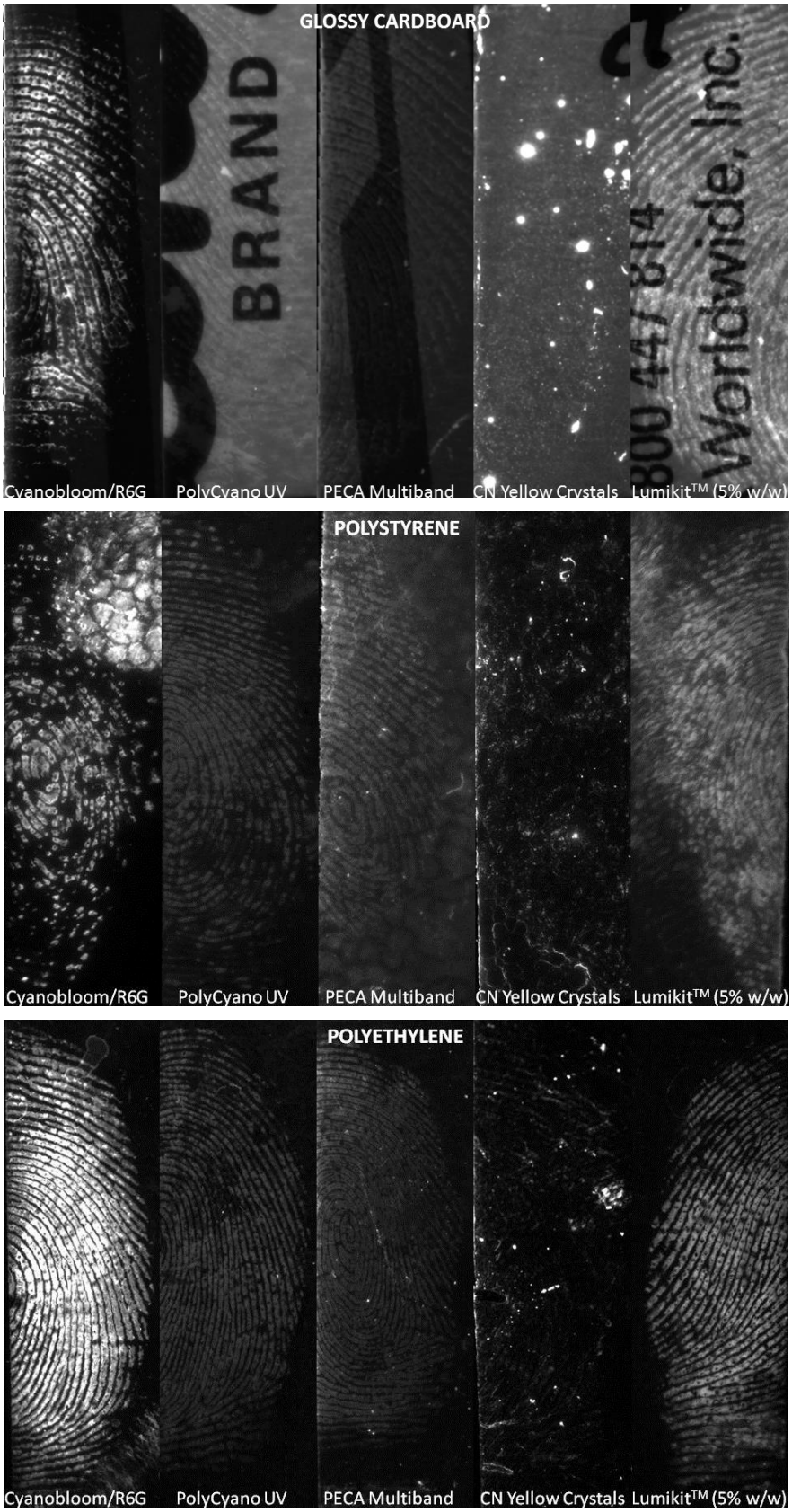

Figure 3: Representative 1 week-aged fingermark halves on glossy cardboard, polystyrene and polyethylene developed with Cyanobloom/R6G, PolyCyano UV, PECA Multiband, CN Yellow Crystals and Lumikit™ and viewed under their respective luminescent conditions.

Similar to under white light examination (**Figure 1**), no significant differences in enhancement were observed on polyethylene with Cyanobloom/R6G under luminescence (**Figure 2**). Generally, the increased enhancement of Cyanobloom/R6G over the one-step treatments can be attributed to the intensity of R6G, as the CA development of the treatments all tended to be similar (**Figure 1**).

Typically R6G gave more intense luminescence across the range of surfaces than the one-step treatments. A previous study also reported stronger luminescence from fingermarks developed with Cyanobloom/R6G when compared to that of PolyCyano UV on a range of non-porous substrates [14]. Another study found the intensity of luminescence from fingermarks developed with Cyanobloom/BY40 was much stronger and more persistent than that from Lumicyano™ on various compositions of plastic bags [4]. In a pilot formulation of CN-Yellow, Weaver found that while solvent yellow 43 could be vaporised at the appropriate temperature and showed specificity for CA development, the luminescence exhibited was low [7]. Hence, there may be a trade-off between these three properties of dye compounds used in one-step luminescent CAs. However, in conventional CA fuming a luminescent post-treatment is selected in order to minimise background interference.

Comparison of One-Step Luminescent CAs

Representative images of fingermark halves fumed with the respective CAs are shown in **Figure 3.** Overall, no significant enhancement was observed from any one-step luminescent CA compared to another under luminescent conditions except in comparison to CN Yellow Crystals, where luminescent fingermarks were lacking. It is possible that the slow heating conditions of CN Yellow Crystals caused the loss of specificity of the luminescent component for CA-developed ridges.

Between the two polymer treatments, PolyCyano UV was consistently inferior to PECA Multiband on glossy cardboard (**Figure 3**). On polystyrene, Polycyano UV samples gave poorer contrast to that of PECA Multiband samples (**Figure 3**). This could be attributed to the lesser amount of DMAB in the PolyCyano UV formulation (5 %) [10] compared to the PECA Multiband formulation (10-15 %) [12]. Although the CA development was slightly better than that of the polymer CAs, Lumikit™ gave inferior luminescence on older samples.

On polyethylene, Polycyano UV consistently outperformed PECA Multiband. Contrast tended to be lacking in PECA Multiband-treated samples as the luminescent component appeared to lose its specificity for the fingermark ridges on this substrate. This again could be contributed to the higher concentration of DMAB in PECA Multiband where the excess had an affinity for the substrate, whereas with PolyCyano UV no background luminescence was observed on polyethylene. Lumikit™ showed no consistently notable differences in enhancement from the polymer treatments on polyethylene. Representative images of each of the CAs used in this study are shown in **Figure 3** under their respective luminescent conditions.

Rhodamine 6G Post-Stain

Following post-staining of samples, the one-step treatments typically did not show an increase in enhancement against Cyanobloom/R6G-treated samples (**Figure 4**). While no direct comparison of unstained and post-stained one-step treatments was conducted in this study, it appears that post-staining further enhances the visualisation of fingermarks treated with one-step luminescent CAs. It was noted that there was less difference in the level of enhancement between post-stained one-step lumincescent CAs and Cyanobloom/R6G-treated samples shown in **Figure 4** than compared to the same sample set in **Figure 2**, where the one-step luminescent CA-treated samples were compared to Cyanobloom/R6G-treated samples. Another study reported an increase in

enhancement against Cyanobloom/R6G samples when PolyCyano UV-treated fingermarks were post-stained with R6G, compared to when PolyCyano UV samples were unstained [14]. Similarly, Farrugia et al. reported a significant increase in the proportion of detected fingermarks when 4 % Lumicyano™-treated fingermarks were post-stained with BY40 [20].

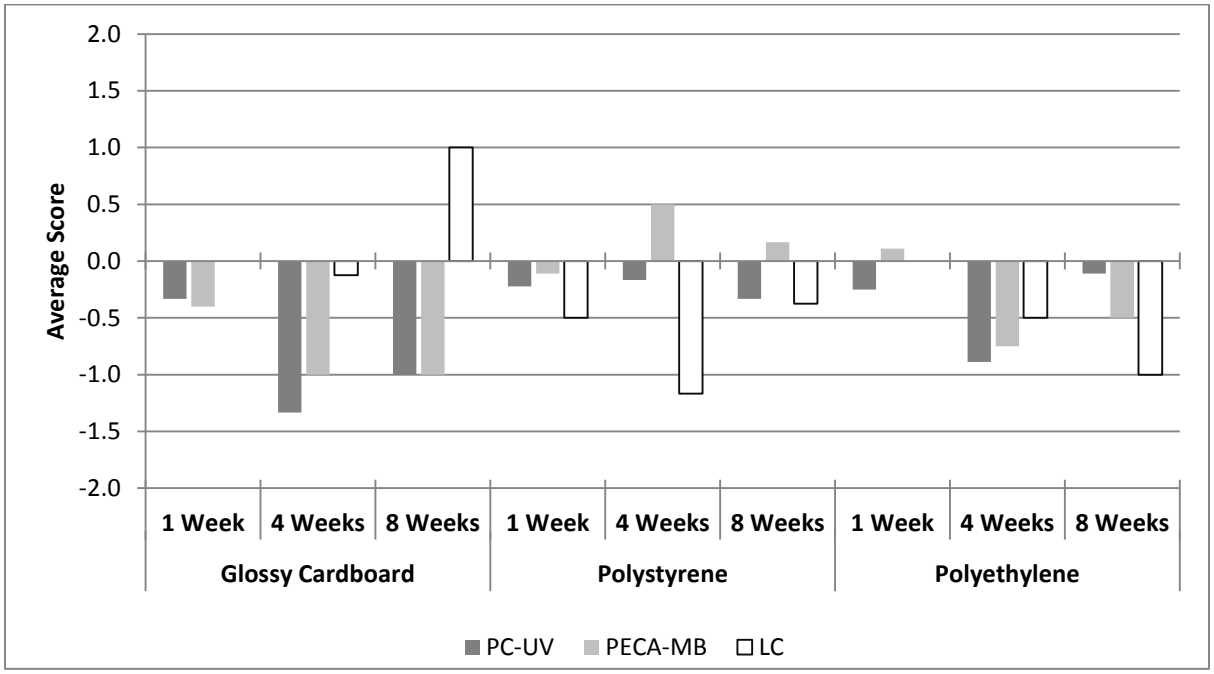

Figure 4: Average comparison scores for PolyCyano UV (PC-UV), PECA Multiband (PECA-MB) and Lumikit™ (LC) against Cyanobloom/R6G after post-treatment with R6G on: glossy cardboard; polystyrene; and polyethylene with fingermarks aged for 1, 4 and 8 weeks viewed under R6G conditions listed in Table 1.

For fingermarks developed with Lumikit™ on glossy cardboard, post-staining with R6G did offer increased enhancement when compared to the polymer treatments; whereas on polystyrene, post-treated Lumikit™ samples exhibited a decrease in enhancement when compared to Cyanobloom/R6G and other post-treated polymer samples. On this substrate, it was noted that Lumikit™ did not readily uptake the R6G stain into the CA development. While Farrugia et al. [20] detected 30 % more fingermarks following BY40 post-staining of Lumicyano™ samples on various plastic bags, that was not observed on the polyethylene bags used in this study. This could be attributed to different plastic substrates, difference in stain formulations and the vastly different sample sizes.

Conclusions

In this study, one-step luminescent CA fuming techniques: CN Yellow Crystals, PolyCyano UV, PECA Multiband and Lumikit™, were each directly compared to conventional CA fuming (Cyanobloom) with R6G stain and to each other, with the development quality and luminescence of the techniques assessed. While this study was limited by a small sample size and substrate range, notable trends were observed. With the exception of CN Yellow Crystals, the one-step luminescent CAs evaluated in this study produced luminescent fingermarks. While the luminescence of these techniques was weaker than that of Cyanobloom/R6G-enhanced fingermarks, PolyCyano UV and PECA Multiband gave slightly superior luminescent ridge detail than the conventional method. Based on the results of this study, these one-step techniques show potential to better visualise

ridge detail on polystyrene. One-step luminescent CAs may also give better enhancement on older fingermarks where development by Cyanobloom appears to decline with age of the fingermark. Future research could be conducted to investigate this emergent trend.

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