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An alternative carrier solvent for fingermark enhancement reagents

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Highlights

- Solstice® PF is a viable carrier solvent alternative to HFE7100.
- Solstice® PF is non-ozone depleting with a lower GWP, surface tension and cost.
- Number of fingermarks detected by HFE7100 and Solstice® PF formulations was comparable
- 1,2-indanedione developed 1.2 times as many fingermarks as DFO in a pseudo-operational trial.

Abstract

Solstice® Performance Fluid (PF), trans-1-chloro-3,3,3-trifluoropropene, is presented as an alternative to HFE7100, methoxy-nonafluorobutane, as a carrier solvent in a number of chemical formulations used for the visualisation of latent fingermarks. The supply of HFE7100 may be at risk due to a recent European Union regulation to control global warming. Laboratory trials using split depletions and a pseudo-operational trial of 1000 porous samples have shown that Solstice® PF is a viable alternative to HFE7100 for the chemical formulations of ninhydrin and 1,2-indanedione. Other preliminary trials have also indicated that Solstice® PF can be used as a carrier solvent for the zinc toning of marks found using ninhydrin as well as the α-naphtholflavone fixative solution for iodine developed marks. Results from the pseudo-operational trial demonstrate that the number of marks detected by ninhydrin and 1,2-indanedione formulations for each carrier solvent is comparable. When compared to HFE7100, advantages of Solstice® PF include a very low global warming potential and atmospheric lifetime in addition to a higher wetting index and lower costs. This study also provides a validation study that supports the potential replacement of DFO with 1,2-indanedione.

Keywords
ninhydrin; DFO; 1,2-indanedione; HFE7100; Solstice® PF; fingermark; pseudo-operational trial

Introduction

Due to the global warming effect contributed by fluorinated greenhouse gases, the European Parliament is considering a ban on some of the hydrofluorinated solvents listed in Annex II of Regulation (EU) No 517/2014 of 16 April 2014 [1]. Fluorinated gases listed in Annex I of the regulation will see a reduction year on year until 2030 whereas those listed in Annex II are currently only subject to reporting quantities placed on the market to the EU commission. Therefore, an alternative and effective replacement for HFE as the carrier solvent in a number of chemical formulations used in latent fingermark development needs to be investigated due to the potential withdrawal, partial or otherwise, of HFE products.

The reaction of ninhydrin with amino acids and proteins to produce a purple colouration (Ruhemann's complex) has been known for over 100 years. The carrier solvent for amino acid reagent formulations has changed many times since the first reported use of ninhydrin as a fingerprint reagent in 1954. Such changes were applied to improve the safety of the reagent (e.g. non-flammable ninhydrin), the performance of the reagent (addition of acetic acid to ninhydrin formulation) and environmental regulations (replacement of CFC-113). Oden and van Hofsten [2] reported one of the first instances of ninhydrin (acetone-based) for the detection of latent fingermarks on paper. Other studies have investigated the use of petroleum ether, 1,1,2-trifluorotrichloroethane (CFC-113) and heptane as carrier solvents for the ninhydrin reaction [3–5]. The UK Home Office Centre for Applied Science and Technology (CAST) does not recommend the use of petroleum ether or heptane due to its flammability. In the UK, CFC-113 was the main solvent carrier from 1974 up to the late 1990s until it was banned under the Montreal Protocols of 1987. CAST embarked on a research project to find an alternative for CFC-113 formulations that was non-flammable, non-toxic, volatile and relatively non-polar to minimise the diffusion of ink [6,7]. Ideally, the alternative solvent should also provide equivalent, or superior, performance in the detection of

latent fingermarks on porous surfaces. An early study identified Genesolv 2000 as a possible replacement for both ninhydrin and DFO; however, the solvent resulted in ink removal or diffusion [8]. CAST identified hydrochlorofluorocarbons (HCFC), hydrofluorocarbons (HFC) and hydrofluoroethers (HFE) as potential replacements to CFC-113. It may be assumed that the efficiency of the reagent is largely unaffected by the choice of carrier solvent; however, trials by CAST have indicated otherwise. Ninhydrin formulations based on two solvents, 2,3-dihydrodecafluoropentane (HFC-4310mee) and 1-methoxynonafluorobutane (HFE7100) outperformed CFC-113 formulations based on laboratory trials which were also confirmed by pseudo-operational trials [7,9]. Similar results were reported by Petruncio [10] whereby HFC-4310mee and HFE7100 provided an increased detection rate and reduced ink diffusion in a comparative study including petroleum ether. Around 2009 [11], in an effort to reduce costs to police forces, CAST investigated an alternative solvent for ninhydrin formulations, Asahiklin AE-3000. Initial price estimates were quoted as 30% cheaper than HFE7100; however, further estimates from the supplier indicated that there will be little, if any, cost saving. A pseudo-operational comparative trial between ninhydrin formulations of HFE7100 and AE-3000 indicated that there was no statistical difference between the effectiveness of these two ninhydrin formulations [11,12]. Research has also investigated analogues of ninhydrin to improve the detection of fingermarks by means of better contrast or fluorescence [13–17]. These have largely been replaced by the use of DFO and 1,2-indanedione (1,2-IND) which can be prepared using HFE solvents [18–20].
The UK Home Office Fingermark Visualisation Manual (FVM) classifies ninhydrin and DFO as 'category A' processes which are defined as "*processes extensively evaluated by the Home Office and considered suitably effective. Standard processes for routine operational use. They must be used in preference to other category processes where possible*" [21]. 1,2-IND is currently classified as a category B process that is generally less effective but has not been fully evaluated by the Home Office CAST. Nonetheless, in recent newsletter updates, CAST have indicated that 1,2-IND may replace DFO and provided an updated 1,2-IND formulation that supersedes the FVM formulation [22,23].

This study presents a comparative pseudo-operational trial to assess the possible replacement of HFE7100 as the carrier solvent in the ninhydrin and 1,2-IND formulations. The possible replacement solvent is Solstice® Performance Fluid (Solstice® PF), trans-1-chloro-3,3,3-trifluoropropene, manufactured by Honeywell Research Chemicals. At the same time, this trial also provides a validation study for the potential replacement of DFO with 1,2-IND.

Methodology

The methodology used in this study is based on recommendations for fingermark research from CAST [24] and the International Fingerprint Research Group [25].

Laboratory trials

Split depletion trials using 5 donors (4 female and 1 male) were tested on white paper. Donors were asked not to wash their hands for at least half an hour prior to deposition. Each donor made a total of 4 depletion series', each containing 8 marks in the depletion. Each series of depletion was divided into half and enhanced with the appropriate enhancement technique. The following comparisons were carried out: ninhydrin-HFE7100 and ninhydrin-Solstice® PF; 1,2-IND-HFE7100 and 1,2-IND-Solstice® PF; DFO-HFE and 1,2-IND-HFE7100 as well as DFO-HFE and 1,2-IND-Solstice® PF. Results were evaluated by putting the split series' back to the original position and grading the developed fingermarks as recommended by CAST [24]. The use of Solstice® PF was also assessed and compared to HFE7100 in the formulations of zinc toning as well as iodine fixing.

Pseudo-operational trials

The extensive pseudo-operational trial was carried out on a variety of porous surfaces (paper, magazines, junk mail, newspaper and envelopes). The substrates were obtained from family, friends, colleagues and recycling bins. A maximum of 10 items was taken from each person. 1000 samples were included in this study and grouped as 250 papers, 250 envelopes, 250 junk mail/magazines and 250 newspaper pages. In the case of newspapers and magazines, the first and last page were included as well as another random two pages in between. The items were treated in 10 batches of 100 samples (25 of each substrate). Each item was split into five equal sections and labelled A (ninhydrin-HFE7100), B (ninhydrin-Solstice® PF), C (DFO-HFE7100/71DE), D (1,2-IND-HFE7100) and E (1,2-IND-Solstice® PF) [figure 1]. Sequential treatment with ninhydrin was carried out on processes C-E. The item labeling and treatment was rotated for each sample to eliminate any bias, so, for example, for item no. 2 the order was B, C, D, E and A. Any marks developed with continuous ridge detail and an area greater than 64 mm^2 were included in the count for the number of latent marks detected.

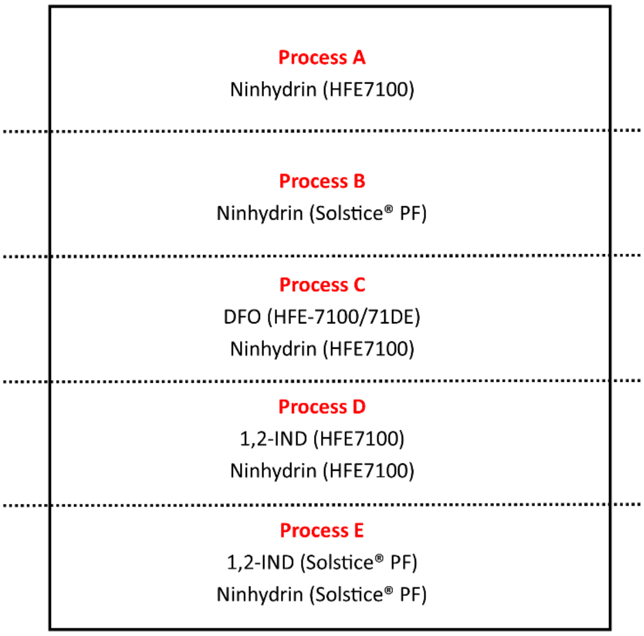


Figure 1 - Scheme of sample division for a substrate in the study.

Formulations

The effectiveness of the Solstice® PF solvent used for both ninhydrin and 1,2-IND processes was compared to the standard HFE7100 solvent. The DFO process was included in the study as a validation study for the possible replacement with 1,2-IND. The formulations for processes A, C and D were prepared according to CAST [21,23]. For the Solstice® PF processes (B and E), the same formulations as recommended by CAST were used by directly replacing the HFE7100 with Solstice® PF. To minimize evaporation, shallow troughs with a curved, corrugated bottom surface were used for passing through the items [21].

Ninhydrin

A concentrated solution of ninhydrin was prepared by dissolving ninhydrin (25 g, Sigma Aldrich) in ethanol (225 mL, Fisher), glacial acetic acid (25 mL, Fisher) and ethyl acetate (10 mL, Fisher). A working solution was then prepared by measuring 52 mL of the ninhydrin concentrated solution together with HFE7100 (1 L, 3M Novec) or Solstice® PF (1 L, Honeywell). The articles under examination were drawn through the working solution in the trough and the excess liquid allowed to drain back before drying completely in a fume hood. The articles were then placed in a humidity oven (Gallenkamp FDC018) at 80 °C and 65% humidity for 4 minutes. Observations of developed marks were checked immediately and over the next 10 days.

DFO

A DFO working solution was prepared by dissolving DFO (0.25 g, Sirchie) in methanol (30 mL, Fisher) and glacial acetic acid (20 mL, Fisher) followed by the addition of HFE71DE (275 mL, 3M Novec) and HFE7100 (725 mL, 3M Novec). The articles under examination were drawn through the working solution in the trough and the excess liquid allowed to drain back before drying completely in a fume hood. The articles were then placed in a dry oven (Hereaus) at 100 °C for 20 minutes. Fluorescence examination was carried out with a Quaser 2000 equipped with a green excitation source (band-pass filter 473-548 nm at 1% cut-on and cut-off points) and viewed with a long-pass 549 nm filter (1% cut-on point).

1,2-Indanedione

A working solution of 1,2-IND was prepared by dissolving 1,2-indanedione (0.25 g, BVDA) in ethyl acetate (45 mL Fisher), methanol (45 mL Fisher), glacial acetic acid (10 mL, Fisher) and zinc chloride stock solution (1 mL) followed by the addition of HFE7100 (1 L, 3M Novec) or Solstice® PF (1 L, Honeywell). The chemicals were added in the order described as the solution may become unstable or go cloudy. The zinc chloride stock solution was prepared by dissolving zinc chloride (0.1 g, Sigma) in ethyl acetate (4 mL, Fisher) and acetic acid (1 mL, Fisher). The articles under examination were drawn through the working solution in the trough and the excess liquid allowed to drain back before drying completely in a fume hood. The articles were then placed in a dry oven (Hereaus) at 100 °C for 10 minutes. Fluorescence examination was carried out with a Quaser 2000 equipped with a blue/green excitation source (band-pass filter 468-526 nm at 1% cut-on and cut-off points) and viewed with a long-pass 529 nm filter (1% cut-on point).

Ninhydrin Enhancement - zinc toning

A working solution for zinc toning was prepared by dissolving zinc chloride (1.2 g, Acros) in ethanol (10 mL, Fisher), 2-propanol (2 mL, Fisher) and acetic acid (2 mL, Fisher) followed by the addition of HFE7100 (40 mL, 3M Novec) or Solstice® PF (40 mL, Honeywell). The solution was then applied through an Ecospray® fine mist sprayer (nozzle diameter: 0.70 mm, flow rate: 0.45 mL/s) at a distance of approximately 15–20 cm. After drying, the articles were then placed in a humidity oven (Gallenkamp FDC018) at 80 °C and 65% humidity for 4 minutes. Fluorescence examination was carried out with a Quaser 2000 equipped with a blue/green excitation source (band-pass filter 468-526 nm at 1% cut-on and cut-off points) and viewed with a long-pass 529 nm filter (1% cut-on point).

Iodine

Iodine crystals were heated gently to about 50 ^{0}C in a cabinet loaded with the articles under examination. To prevent fading, developed marks were treated with a fixing solution. An iodine fixing solution was prepared by dissolving α-naphthoflavone (0.1 g, Acros) in acetic acid (5 mL, Fisher) followed by the addition of HFE7100 (30 mL, 3M Novec) or Solstice® PF (30 mL, Honeywell). The fixing solution was then applied through an Ecospray® fine mist sprayer (nozzle diameter: 0.70 mm, flow rate: 0.45 mL/s) at a distance of approximately 15–20 cm.

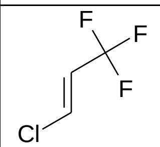
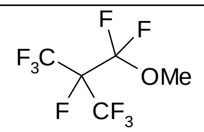
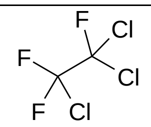
Results and Discussion

Solvent Properties

A suitable alternative solvent to HFE7100 should ideally be non-flammable, non-toxic, volatile, environmentally friendly and relatively non-polar to minimise the diffusion of ink. Solstice® PF, manufactured by Honeywell, fulfills these criteria and when compared to HFE7100 has a lower toxicity and surface tension as well as a higher wetting index. The high wetting index indicates that the solvent can be absorbed easier by the substrate to reach amino acids ingrained in the pores of the porous substrate. Although a fluorinated solvent itself, Solstice® PF has a very low global warming potential (GWP) rate of 1 and atmospheric lifetime of 26 days compared to a GWP of 320 and an atmospheric lifetime of 4.1 years for HFE7100. GWP is defined as the “climatic warming potential of a greenhouse gas relative to that of CO_2 calculated in terms of the 100-year warming potential of one kilogram of a greenhouse gas relative to one kilogram of CO_2 [1]. Table 1 summarises the solvent properties of Solstice® PF, HFE7100 and CFC-113. Solstice® PF has a boiling point of 19°C but a high enthalpy of vaporisation which limits the evaporation of the solvent. According to UN regulations (UN3163), that classifies it as non-flammable liquefied gas, the solvent is shipped in pressure-rated cylinders. It also prevents loss of product by evaporation during transportation and storage. In addition to the environmental friendly attributes when compared to HFE7100, Solstice® PF has a lower cost of about a third on a single unit which increases to about a half cost-saving on bulk orders.

Figure 2 – Solstice® PF 6kg container.

Table 1 – Physical Properties of three different carrier solvents.

	Honeywell Solstice® PF Performance Fluid	3M Novec HFE7100	CFC-113
Chemical name	Trans-1-chloro-3,3,3-trifluoropropene 1233zd	Methoxy-nonafluorobutane	1,1,2-trichloro-1,2,2-trifluoroethane
Chemical family	Hydrochlorofluoro-olefin (HCFO)	Hydrofluoroether (HFE)	Chlorofluorocarbon (CFC)
Chemical formula	CF_3-CH=CClH	$C_4F_9OCH_3$	Cl_2FC-$CClF_2$
Chemical structure			
Molecular weight	130	250	187
Appearance	Colourless	Colourless	Colourless
Boiling Point (°C)	19	61	48
Latent heat of vaporisation at bp (kJ/kg)	194	112	146
Freezing point (°C)	-107	-135	-35
Vapour pressure at 25°C (kPa)	126	28	44
Liquid density at 25°C (g/mL)	1.26	1.52	1.56
Surface tension at 25°C (mN/m)	12.7	13.6	17.3
Viscosity at 25°C (mPa.s)	0.45	0.61	0.68
Wetting index: 1000 x density/(surface tension x viscosity)	220	183	133
Solubility of water in solvent at 25°C (ppmv)	460	95	110
Solubility of solvent in water (ppmv)	1900	12	170
Flash point (°C)	None	None	None
Flammability range in air	None	None	None
Atmospheric lifetime	26 days	4.1 years	85 years
Occupational exposure limit (ppm)	800	750	1000
Global warming potential [1]	1	320	6000
Ozone depletion potential [2]	0.00	0.00	0.80
Cost (£)/L (inclusive of VAT) [3] **(minimum order)**	64.66 (6kg drum equates to 4.76L which costs £307.80) Delivery charge £36	90.93 (5.4kg drum equates to 3.55L which costs £322.80) Free Delivery	N/A

Cost (£)/L (inclusive of VAT) [3] **(bulk order)**	43.87 4 x 6kg drums equate to 19.05L which costs £835.20 Delivery charge £36	85.33 15kg drum equates to 9.87L which costs £842.24 Free Delivery	N/A

[1] GWP–100 year Integration Time Horizon (ITH) [2] CFC-11 = 1.0 [3] Prices as given by Samuel Banner Chemicals and Severn Biotech for Solstice® PF and HFE7100 respectively (September 2017).

Laboratory Trials
Split depletion series were done to compare the effectiveness of HFE7100 and Solstice® PF as the amino acid reagent carriers. Each half of the depletion series was treated with a different processing technique and then recombined. For both ninhydrin-HFE7100 and ninhydrin-Solstice® PF treatment only the first few depletions (up to the fourth) were observed (Figure 3). The fingermarks were weakly visible but no obvious difference was seen between HFE7100 and Solstice® PF ninhydrin formulations. There was no significant quality differences between the split depletion series halves of fingermarks recovered with DFO and 1,2-IND-HFE (figure 4b) and 1,2-IND in both solvents (figure 4c). A slightly difference in fluorescence intensity was observed from the camera response but not visually.

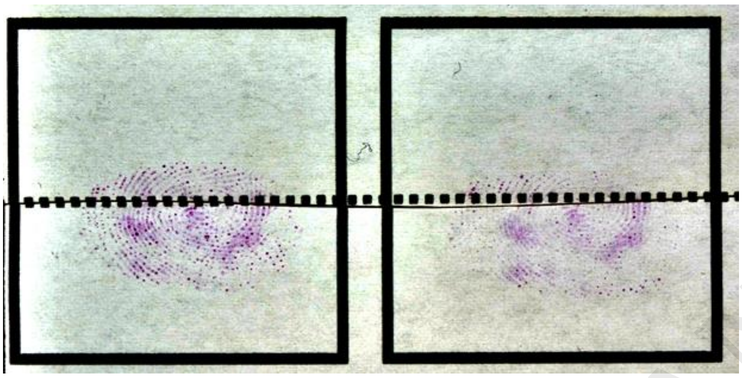
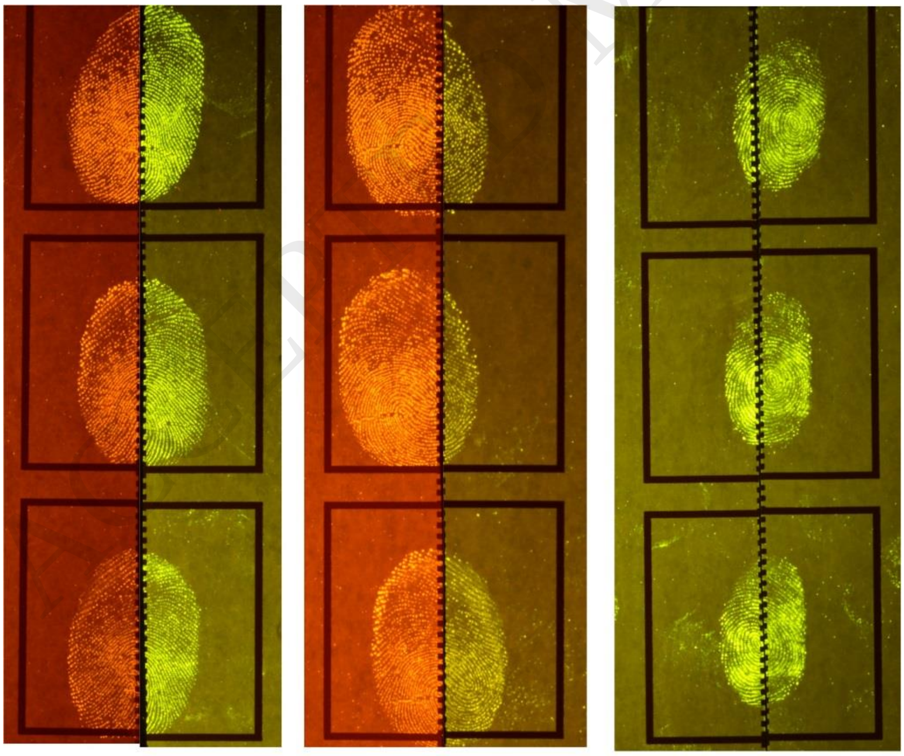


Figure 3 – Depletion series on paper: ninhydrin-HFE7100 (lower half), ninhydrin-Solstice® PF (upper half).



(a) (b) (c)

Figure 4 Depletion series on paper by different donors: (a) DFO (left) and 1,2-IND-HFE (right); (b) DFO (left) and 1,2-IND-Solstice® PF (right); (c) 1,2-IND-HFE (left), 1,2-IND-Solstice® PF (right).

Pseudo-operational trial

A pseudo-operational trial was then set-up following the successful results with split depletions under laboratory conditions. A pseudo-operational trial can be used to "establish whether the results obtained in laboratory trials are replicated on articles/surfaces typical of those that may be submitted to a fingerprint laboratory, or to distinguish between closely equivalent formulations that cannot be separated in laboratory trials" [24]. The number of fingermarks detected for each process is presented in tables 2 and 3. Figures 5 and 6 are the graph representatives of table 2. The results obtained show that both ninhydrin and 1,2-IND are comparable for the two carrier solvents tested, HFE7100 and Solstice® PF. There are slightly more fingermarks developed with ninhydrin-HFE7100 (3.6% more) than with ninhydrin-Solstice® PF, whereas 1,2-IND-Solstice® PF appeared to develop the highest number of fingermarks which is 1.0% higher than with 1,2-IND-HFE7100 (3.8% higher for the Solstice® PF formulation when taking into account ninhydrin sequencing). Figure 7 represents the cumulative increase of fingermarks detected by batches of 100 samples. Figures 8-10 show several examples of enhanced latent marks with the different processes employed in this study.

Before ninhydrin sequencing

There is little difference in the number of fingermarks detected when comparing the two carrier solvents for ninhydrin and 1,2-IND for each substrate. 1,2-IND-HFE7100 detected considerably higher amount of fingermarks on envelopes whereas the opposite was true for newspapers and 1,2-IND-Solstice® PF. A further observation is that ninhydrin-Solstice® PF developed more latent fingermarks on grey papers (44% more) as well as brown and grey envelopes (61% more). A second examination of ninhydrin developed marks after 10 days indicated an increase of approximately 11% in fingermark recovery. A higher number of additional marks using the ninhydrin-Solstice® PF process was found on paper (8%) and newspaper (21%), whereas while using the ninhydrin-HFE7100 formulation the quantity of new marks reached 7% and 15% respectively. An equivalent number of new marks on magazines/leaflets (11%) was observed whereas an increase of 11% was detected with envelopes treated with the ninhydrin-HFE7100 formulation and 8% for the ninhydrin-Solstice® PF formulation. DFO (HFE formulation) was included in this study as a validation study for its possible replacement with 1,2-IND [23]. The results show that the total number of fingermarks developed with the DFO formulation is 20% lower in comparison to 1,2-IND-HFE7100 and 21% lower than 1,2-IND-Solstice® PF formulation. The HFE7100 and Solstice® PF formulations for 1,2-IND developed 1.2 times as many marks as DFO. In contrast, a recent CAST study [23] on 432 porous items (paper and cardboard) reported that 1,2-IND-HFE7100 (same formulation as this study) developed 1.6 times as many marks as DFO.

After ninhydrin sequencing

The DFO-ninhydrin sequence produced an increase of 27% new marks and 60% of DFO recovered marks were also visualised with ninhydrin treatment. Ninhydrin sequencing of 1,2-IND enhanced fingermarks yielded an increase of 20% and 23% for the HFE7100 and Solstice® PF formulations respectively. Furthermore, 63% of previously recovered 1,2-IND-HFE7100 marks and 66% of 1,2-IND-Solstice® PF marks were also visualised with ninhydrin treatment. DFO-ninhydrin sequencing was particularly effective on newspaper (61% new marks) whereas 1,2-IND-ninhydrin sequencing was effective for magazines (72% and 61% new marks for HFE and Solstice® PF respectively).

Zinc Toning

A zinc toning solution was prepared using both HFE7100 and Solstice® PF. Successful enhancement was achieved for both formulations on split depletions as well as on marks recovered during the pseudo-operational trial (figure 11).

Table 2 - Total number of fingermarks detected for each process and substrate (including sequencing).

Surface	A	B	C	C (DFO/NIN)	C (NIN New)	D	D (IND/NIN)	D (NIN New)	E	E (IND/NIN)	E (NIN New)
envelopes	65	60	115	71	37	134	80	32	101	73	20
papers	318	311	503	300	114	594	386	94	587	387	124
magazines	45	37	47	29	14	39	24	28	51	41	31
newspapers	65	68	33	21	20	72	37	15	108	56	24
TOTAL	**493**	**476**	**698**	**421**	**185**	**839**	**527**	**169**	**847**	**557**	**199**

Table 3 - Cumulative number of fingermarks detected for each process and substrate.

	envelopes					paper					magazines					newspaper				
Batch	**A**	**B**	**C**	**D**	**E**	**A**	**B**	**C**	**D**	**E**	**A**	**B**	**C**	**D**	**E**	**A**	**B**	**C**	**D**	**E**
1	16	12	34	58	40	49	39	65	80	51	0	0	1	0	1	8	6	1	4	7
2	30	25	71	86	57	79	71	135	163	119	3	2	1	9	16	14	10	7	14	14
3	36	29	89	100	62	96	93	193	242	199	11	5	2	21	24	15	10	9	14	18
4	37	34	96	111	72	116	108	221	297	277	15	6	9	25	33	16	13	16	23	31
5	43	43	115	125	84	135	127	265	355	348	34	26	36	51	71	31	33	36	44	70
6	45	46	118	131	88	160	148	337	434	418	41	28	43	57	77	33	33	36	46	71
7	46	47	131	136	98	187	185	417	502	507	44	36	53	57	78	40	42	39	56	95
8	48	49	144	152	107	243	236	500	588	608	45	37	58	57	78	43	44	42	66	109
9	52	54	145	156	109	262	255	551	637	659	45	37	61	64	80	54	58	44	74	121
10	65	60	152	166	121	318	311	617	688	711	45	37	61	67	82	65	68	53	87	132

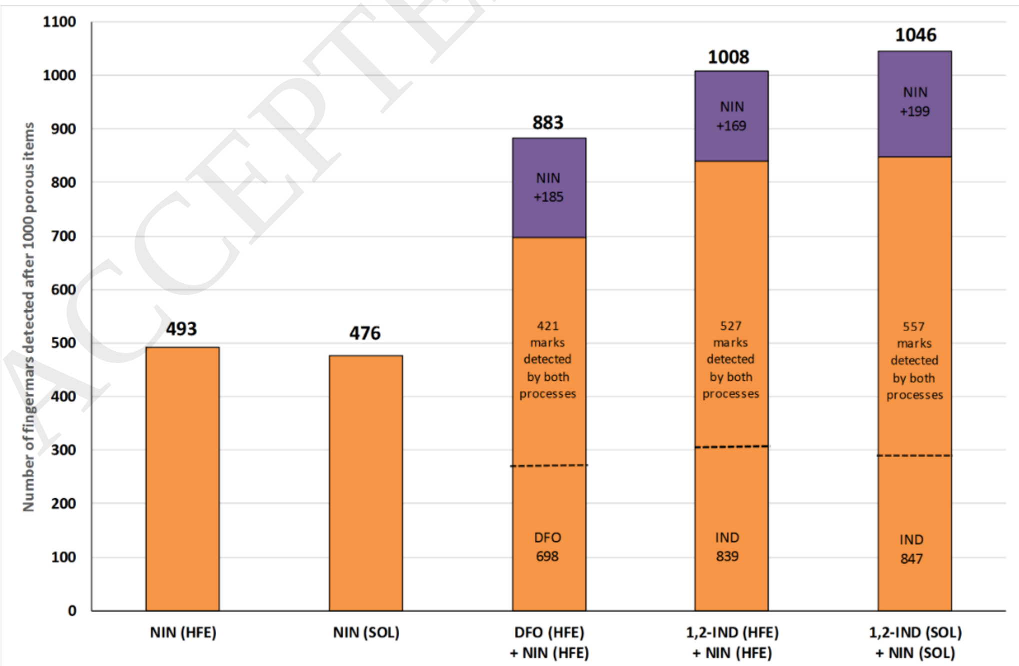


Figure 5 - Number of detected fingermarks for each process on all substrates.

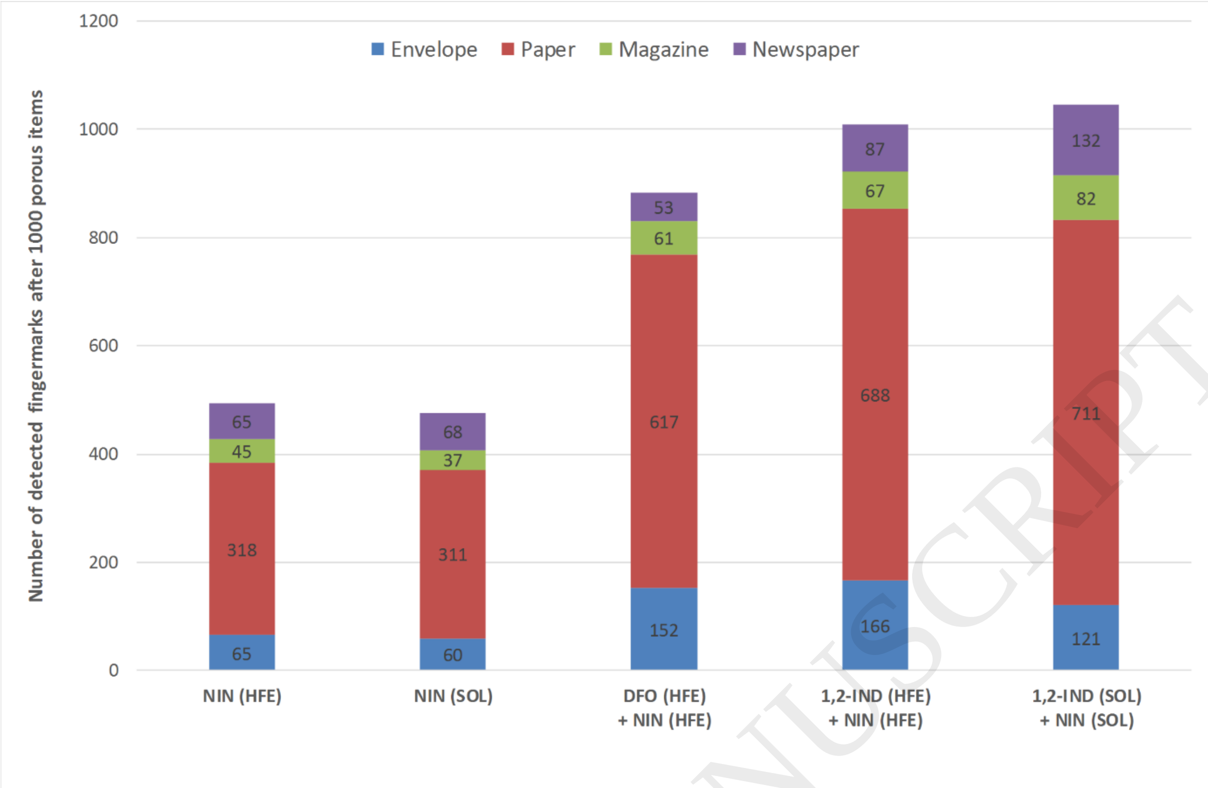


Figure 6 - Number of detected fingermarks for each process and substrate.

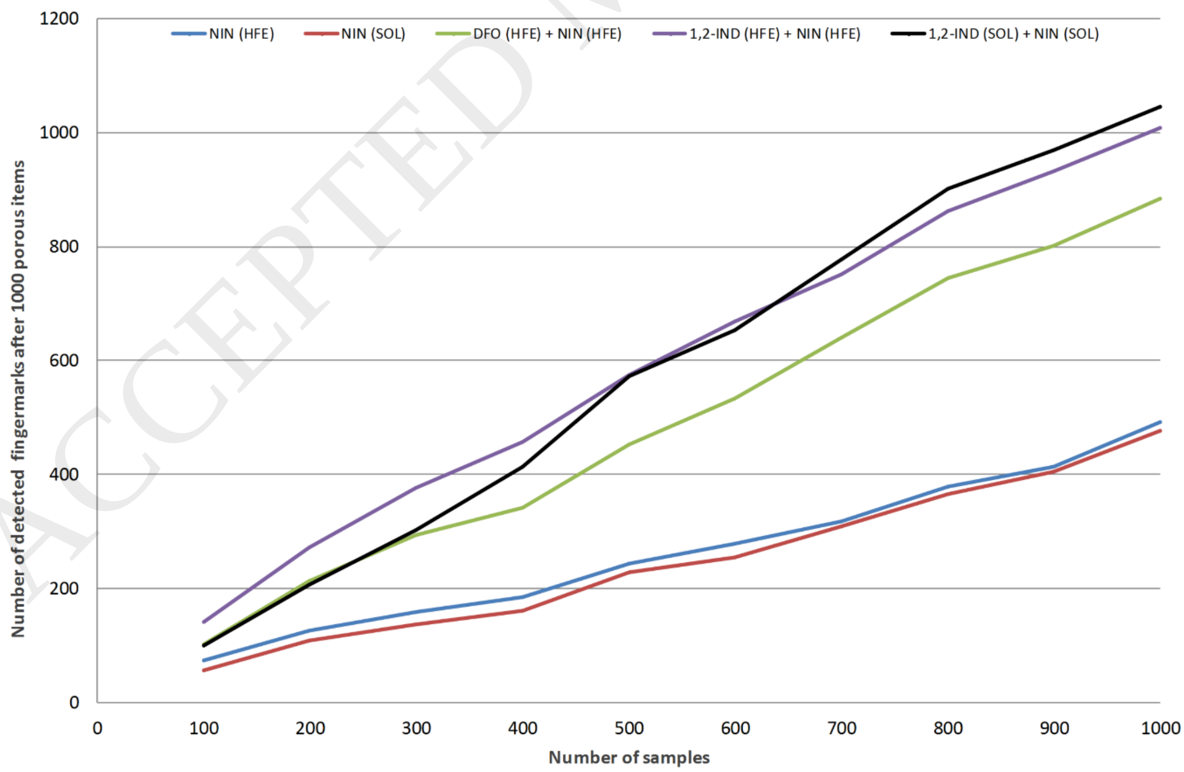


Figure 7 – Cumulative number of fingermarks detected on all substrates for each process.

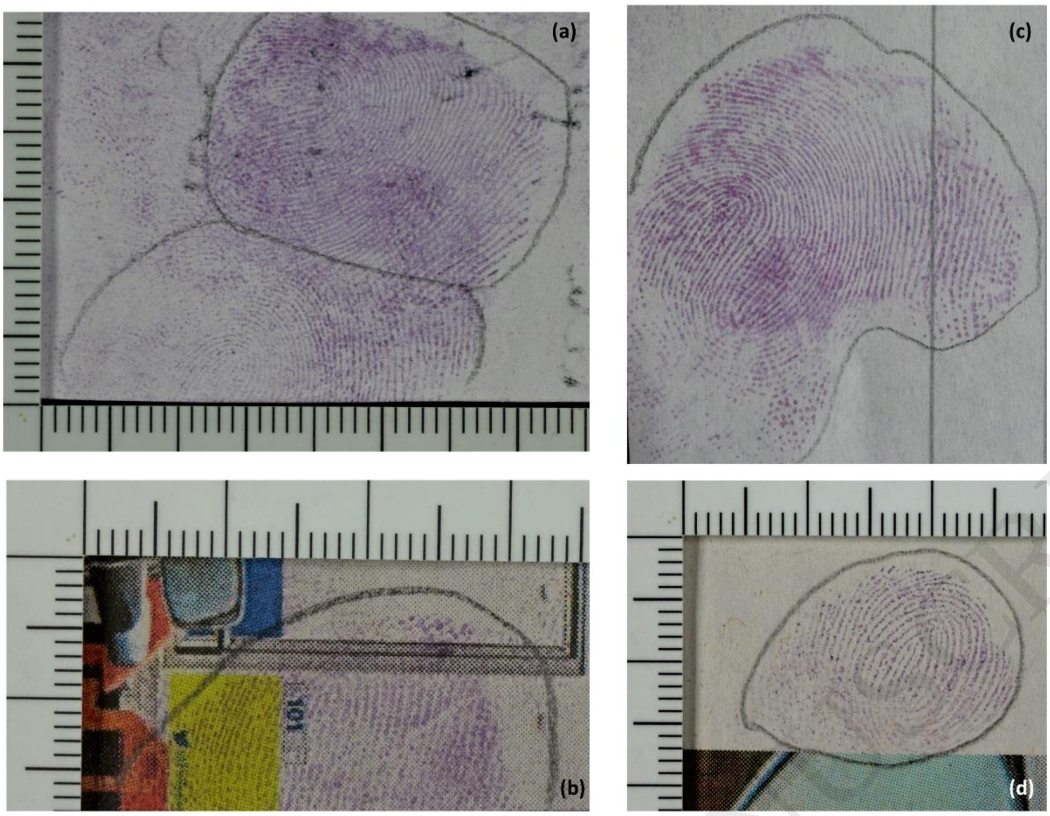


Figure 8 – Latent fingermarks enhanced with ninhydrin-HFE7100 (a,b) and ninhydrin-Solstice® PF (c,d) on paper (a,c) and on newspaper (b,d).

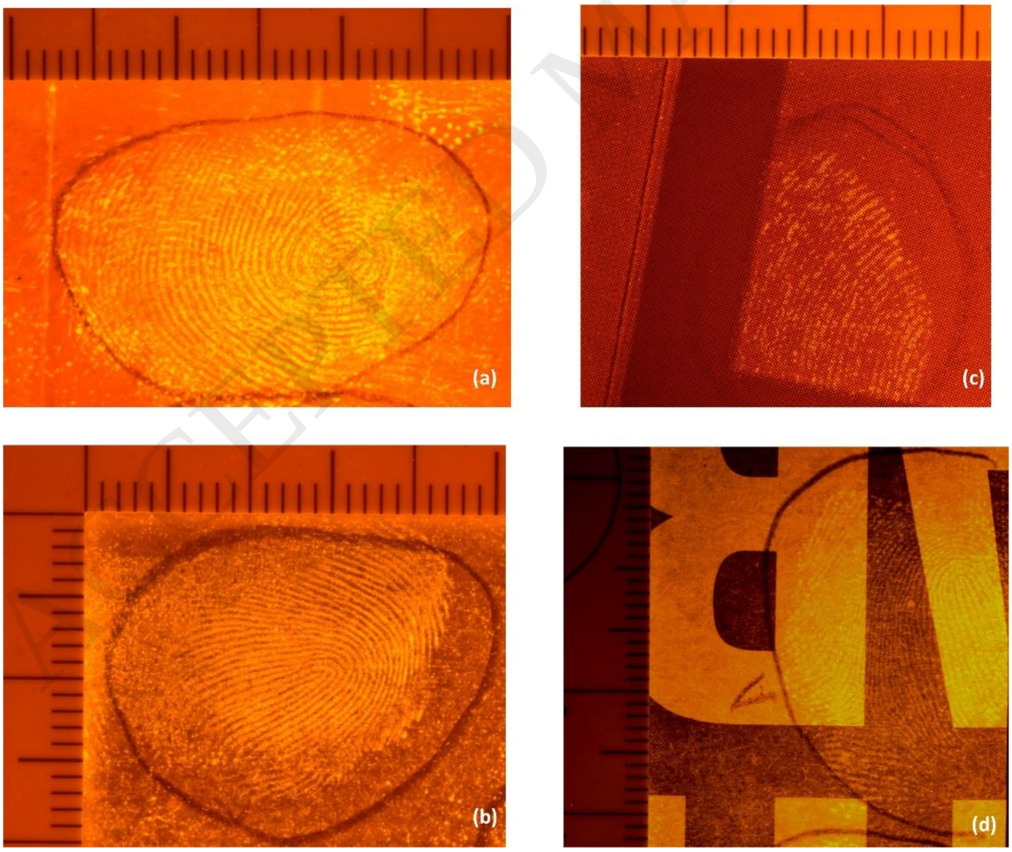


Figure 9 – Latent fingermarks enhanced with DFO on various substrates: envelope (a); paper (b); magazine (c) and newspaper (d).

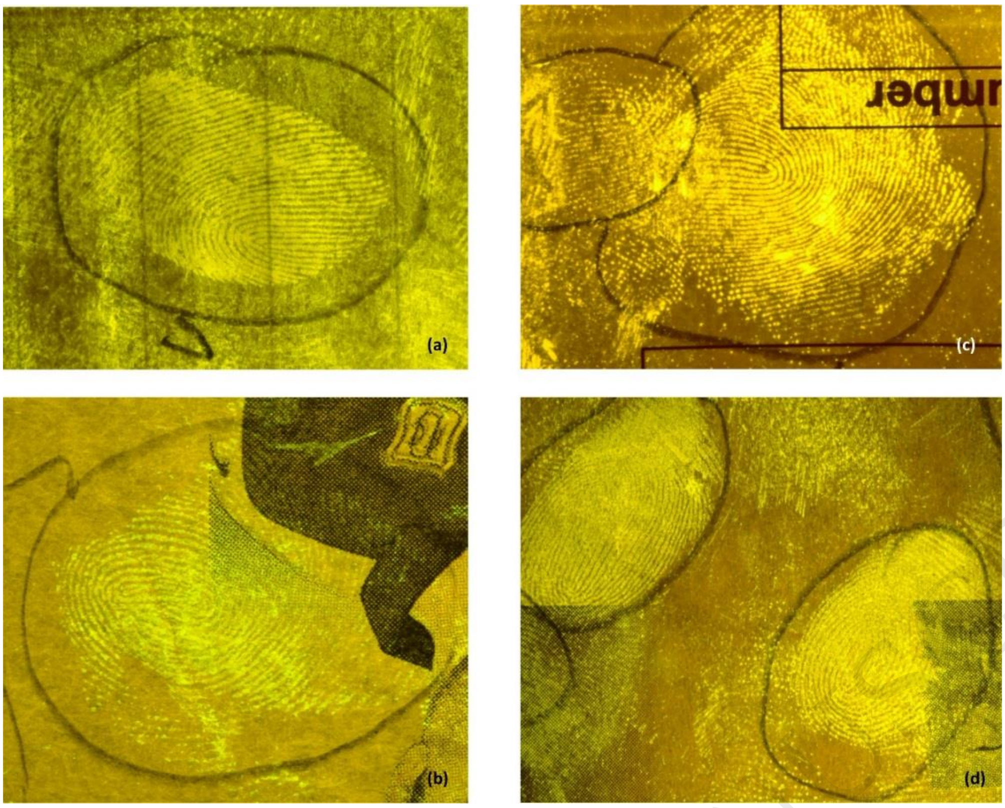


Figure 10 – Latent fingermarks enhanced with 1,2-IND-HFE7100 (a,b) and 1,2-IND-Solstice® PF (c,d) on paper (a,c) and on newspaper (b,d).

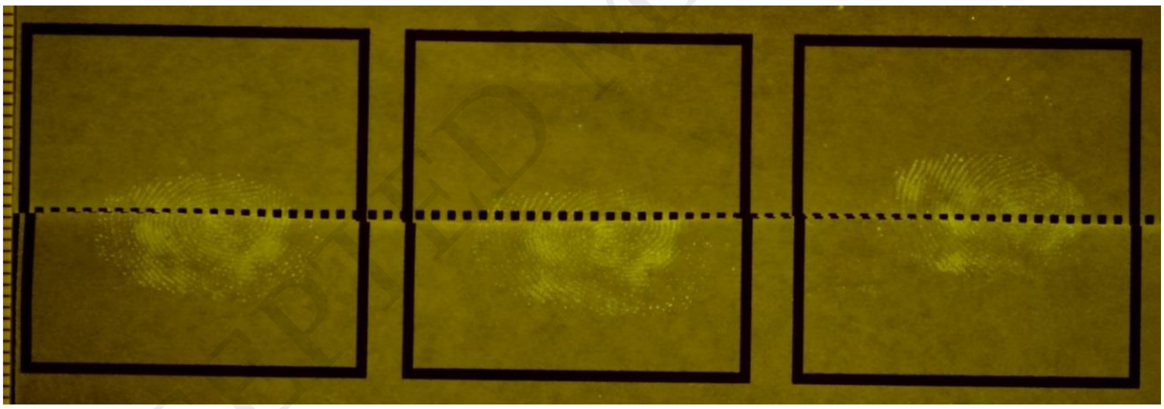


Figure 11 – Depletion series on paper: ninhydrin-HFE7100-Zinc toning (lower half), ninhydrin-Solstice® PF-zinc toning (upper half).

Solvent Usage

500 mL solutions were prepared for all formulations just prior to use for every two batches (200 samples). During the pseudo-operational study, the age of the solution varied from one to fourteen days; however, ageing consistency across each batch of 100 samples was maintained. Solutions were stored in a refrigerator at 4°C with parafilm on the bottle caps and were allowed to reach room temperature prior to use. Preliminary trials showed that the Solstice® PF working solutions for ninhydrin and 1,2-IND were still effective after 6 months. All solutions showed good stability and no precipitation or phase separation was observed. The total amount of solvent used during the pseudo-

operational trial of 1000 samples is given in table 4. For the ninhydrin and 1,2-IND formulations, an average of about 20% more solvent was required for Solstice® PF as compared to HFE7100 which may be explained by the lower boiling point of Solstice® PF. There appears to be no correlation between the quantity of solvent used for sample processing and weather conditions like temperature or humidity. The temperature and humidity in the laboratory were not controlled; however, external temperatures and relative humidity ranged from 11-19^{O}C and 35-95% respectively during the trial. There were slight differences in solvent usage between each batch which may be due to varying sample size, sample wetness or porosity. The ninhydrin-HFE7100 solution became cloudy after processing approximately 25 samples. This may occur due to sample contaminants or ninhydrin precipitation caused by solvent evaporation. For the 1,2-IND-HFE7100 formulation no cloudy solution was noticed; however, the solution became slightly milky when the solvent was left to evaporate completely. DFO-HFE solution remained clear during the processing of samples. When the solution was left to evaporate, yellow oily droplets appeared on the surface. These droplets are formed due to water from the samples which is immiscible with the HFE solvent. For the ninhydrin and 1,2-IND Solstice® PF formulations there was no issues with cloudy solutions, oily droplets, phase separation or reagent precipitation. Two magazine samples were observed to release some dye during treatment with 1,2-IND-Solstice® PF.

Due to the low boiling point of Solstice® PF, shallow troughs with a curved, corrugated bottom surface should be used to minimise evaporation. This is also advised for solutions prepared with HFE-7100 [21]. To further minimise evaporation, solutions prepared with Solstice® PF could be prepared just prior to use, otherwise appropriately sealed bottles should be used to store solution in a refrigerator. The fact that Solstice® PF is shipped in pressure-rated cylinders prevents loss of product by evaporation during transportation and storage.

Table 4 - Solvent usage for the pseudo-operational trial.

Process	**A Ninhydrin (HFE-7100)**	**B Ninhydrin (Solstice® PF)**	**C DFO (HFE/7100/71DE)**	**D 1,2-IND (HFE-7100)**	**E 1,2-IND (Solstice® PF)**
Solvent usage /mL	2150	2500	2100	1945	2480

Ink Diffusion

The common ink constituents are a mixture of dyes, resins and carrier components such as glycol-based solvents or water. Exposure to polar solvents of these constituents may cause the ink to run and diffuse [26]. An assessment of the diffusion properties for the Solstice® PF and HFE formulations was carried out. A random selection of 14 different ink types and colours was prepared on A4 white paper and treated with the different formulations. For 1,2-IND, two writing implements, Staedtler (black ink felt-tip pen) and Apex (blue ball-point pen), showed minimal ink running when treated with Solstice® PF but not with HFE when observed under white light; however, under fluorescence examination, ink diffusion was observed for both carrier solvents (figure 12). No ink diffusion was observed when Solstice® PF was used on its own suggesting that the polar components (e.g. methanol, acetic acid), although in small quantities, in the 1,2-indanedione formulation also play a role in the minimal ink diffusion observed. Ink diffusion was also monitored during the pseudo-operational trial. Figure 13 shows a split paper sample with no ink diffusion observed, the lower half treated with ninhydrin-HFE7100 formulation and the upper half treated with the ninhydrin-Solstice® PF formulation. The results indicated that neither HFE nor Solstice® PF caused diffusion of handwritten or printed inks. From the 1000 samples in the pseudo operational trial, two samples showed slight ink diffusion.

Iodine fixing solution

An iodine fixing solution was prepared in both carrier solvents to assess their suitability to fix iodine treated marks on paper. Both solvents performed as expected where the fixative solution of α-naphthoflavone provided a blue colour enhancement to provide further contrast. Figure 14 shows an example of a split handprint where one side was only fumed with iodine (right) and the other side was fumed with iodine followed by fixing with a α-naphthoflavone solution prepared with Solstice® PF (left).

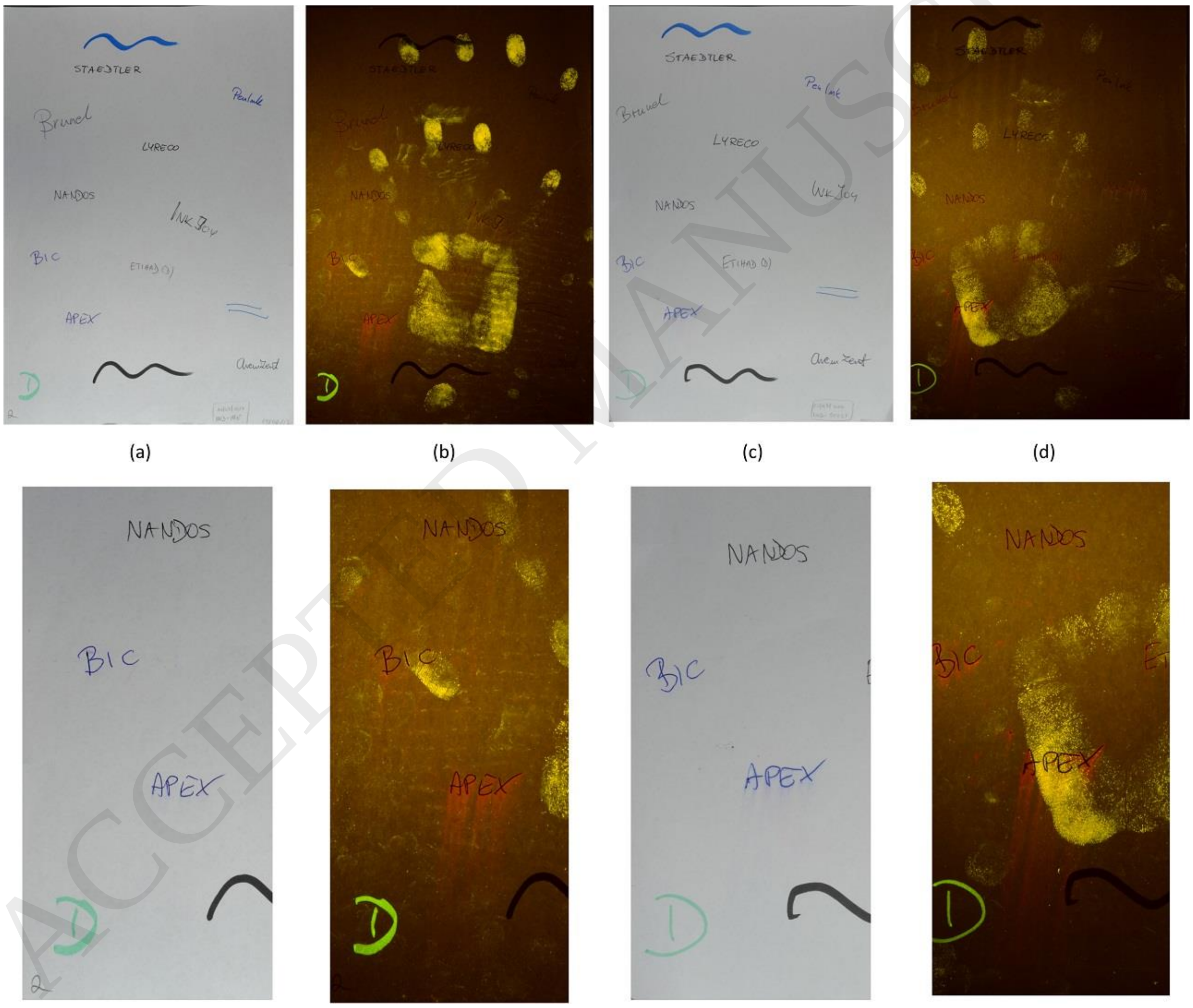


Figure 12 – A4 white paper with various inks as viewed under white light and fluorescence (blue-green light and 529 nm orange filter) after treatment with 1,2-IND: HFE7100 (a,b) and Solstice® PF (c,d).

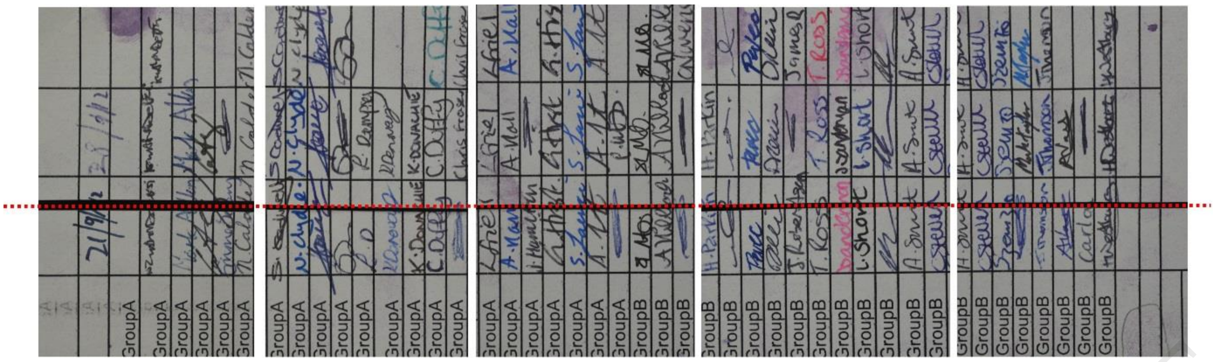


Figure 13 – Split paper sample from the pseudo-operational trial treated with ninhydrin: HFE formulation (bottom) and Solstice® PF formulation (top).

Figure 14 – A split handprint treated with iodine fuming with no fixing (right) and fixing with α-naphthoflavone- Solstice® PF (left).

Conculsions

As the EU is considering a ban on some of the hydrofluorinated solvents, including HFE7100, research into alternative solvents used in fingermark enhancement techniques is required. This study assessed Solstice® PF as a possible replacement to HFE7100 for the preparation of various chemical formulations used in the development of latent fingermarks. A pseudo-operational trial of 1000 porous samples showed that the number of marks detected by ninhydrin and 1,2-IND formulations for both carrier solvents is comparable. Both solvents are fluorinated and non-ozone depleting; however, Solstice® PF has a much lower GWP and atmospheric lifetime as well as a higher wetting index (lower surface tension). Furthermore, Solstice® PF can have a cost saving of about 50% at current prices although an average of 20% more solvent was used during the pseudo-operational trial of 1000 samples. Ink diffusion for both solvents was comparable with minimal ink running. Although it is recognised that further research is required, this study shows that Solstice® PF is a viable substitute to HFE7100 as a carrier solvent in a number of chemical formulations used in the visualization of latent fingermarks.

The increased detection rate and the reduction of heating time (10 vs 20 minutes) of 1,2-IND when compared to DFO provides support for the potential replacement of DFO with 1,2-IND as a category A process.

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