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Replacing Synperonic® N in the Physical Developer fingermark visualisation process: Reformulation[☆]

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A B S T R A C T

The Physical Developer solution currently recommended for use in the United Kingdom for fingermark visualisation uses two surfactants: n-dodecylamine acetate (nDDAA) and Synperonic® N. Synperonic® N is covered by the EU directive 82/242/EEC, which sought to phase out chemicals with degradation products more harmful than their precursor. This study explores the replacement of Synperonic® N with alternative detergents and examines their ability to produce clear, stable solutions that are effective at developing fingermarks. The critical properties of the detergents were investigated, such as the critical micelle concentration and the hydrophilic-lipophilic balance, and planted mark comparisons were performed on promising formulations. Tween® 20 was deemed unsuitable due to the production of cloudy solutions and the requirement to age the formulation to improve effectiveness. Brij® C10 produced clear formulations; however, these were too stable causing unacceptably long exhibit processing times, and an additional preparation stage was necessary. Brij® L23, Brij® S10, Igepal® CO-630, Polyoxyethylene (10) tridecyl ether and Tergitol™ 15-S-9 also proved to be unsuccessful alternatives. Decaethylene glycol monododecyl ether (DGME) was found to be a suitable alternative to Synperonic® N and depletion series experiments suggested that a range of DGME and nDDAA detergent quantities were effective at developing marks. The processing time using DGME was similar to Synperonic® N and the most favourable ratio of reagents is proposed in this paper as a reformulated Physical Developer solution.

1. Introduction

Physical Developer (PD) is a process principally used for the development of fingermarks on porous surfaces. The process originates from the wet photographic industry and it was first proposed by Jonker et al. in the late 1960s to use these stabilised PD solutions as a means of depositing metal on printed circuit boards [1,2]. It was adapted as a fingermark development process by researchers at the Atomic Weapons Research Establishment, Aldermaston during the 1970s and found to be effective both for sequential use after ninhydrin [3] and as a process for visualising fingermarks on surfaces that had been wetted [3–7]. It has subsequently been found to be capable of developing fingermarks on surfaces exposed to elevated temperatures [8,9] and where fingermarks are decades old [10]. As such, PD is an essential process for the recovery of fingermarks from porous surfaces exposed to adverse conditions, and can also develop an appreciable proportion of marks not detected by the amino acid reagents [11].

The performance of PD is critically dependent on the surfactants included in its formulation. The surfactants are responsible for the stabilisation of silver nanoparticles in the working solution and it is

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postulated they do this by the formation of micelles as shown in Fig. 1. It is the destabilisation of these micelles by the fingermark constituents that causes the silver particles to first deposit and then grow, enabling the ridge detail to be seen [12].

The PD solution currently recommended for use in the United Kingdom uses two surfactants: n-dodecylamine acetate (nDDAA) and Synperonic® N [2]. The nDDAA acts as a cationic surfactant, forming micelles around any silver nuclei forming in the PD working solution. Synperonic® N (isononylphenol, ethoxylated) is a non-ionic surfactant added to prevent precipitation of the nDDAA from solution. There are issues of availability for both these surfactants. nDDAA is commercially available but is not a standard product and is therefore made to order, making it relatively expensive and available from a restricted number of suppliers. Synperonic® N was one of the class of chemicals covered by EU directive 82/242/EEC [14], which sought to phase out chemicals with degradation products more harmful than their precursor. It was subsequently banned from industrial use and marketing (EU directive 2003/53/EC [15]) and, although the quantities used in PD are well below these limits, Synperonic® N is not commercially viable to manufacture and hence it is no longer available. Remaining supplies of Synperonic® N that have been retained to make the stock detergent are depleting and potentially degrading in quality, and therefore PD formulations based on alternative surfactants are required.

Finding a replacement for Synperonic® N has been explored previously by groups of researchers [16–18]. In earlier work by this research group, Wright [16] investigated a range of formulations where Synperonic® N was replaced with Tween® 20, Tween® 80, Synperonic® 91/5, Synperonic® 91/6, Synperonic® 13/6.5 and Caflon®-N. Of these formulations, only the Tween® 20-based formulation gave comparable performance to Synperonic® N, and, although it even appeared superior on freshly deposited marks, its performance relative to Synperonic® N appeared to decrease as the age of the deposited mark increased. It was noted during this work that the silver in the working solutions would precipitate during processing if the temperature was below 17 °C. Other formulations that replace Synperonic® N with Tween® 20 have subsequently been proposed and are in operational use in some countries. However, there is little agreement on the amount of Tween® 20 to use in the stock detergent solution, with 1.5 mL/L used in Australia, 2.8 g/L used by Swedish researchers, 3 mL/L used in Switzerland and the United States of America and 4 g/L used in Germany (all with an equal volume or weight of nDDAA) [17,19–22]. The United Kingdom (UK) has not yet migrated from the Synperonic® N formulation but is now in a position where an alternative formulation has become essential to retain the capability to develop fingermarks on wetted porous exhibits.

The work described here involved two stages:

1. To explore the potential to implement a formulation based on Tween® 20 in the UK.
2. If Tween® 20 formulations were not considered viable alternatives, identify another formulation based on an alternative surfactant and characterise its performance.

Before any formulation can be implemented on operational casework, it is necessary to conduct a comparison of the new formulation with the existing Synperonic® N formulation to establish the potential impact on casework (positive or negative). This aspect of the work will be reported in a subsequent publication [23].

In parts of this paper, reference is made to several terms relating to surfactants and these are described here to aid the reader.

The critical micelle concentration (CMC) is defined as the concentration of surfactant needed for micelles to form. If the CMC is reached or exceeded, micelles form spontaneously and the majority of the surfactant is present in the micelles; if the concentration is below the CMC then no micelle formation occurs [24].

The hydrophilic-lipophilic balance (HLB) of a surfactant is an empirical value based on the chemical structure of the surfactant. It is determined by calculating the relationship between the different

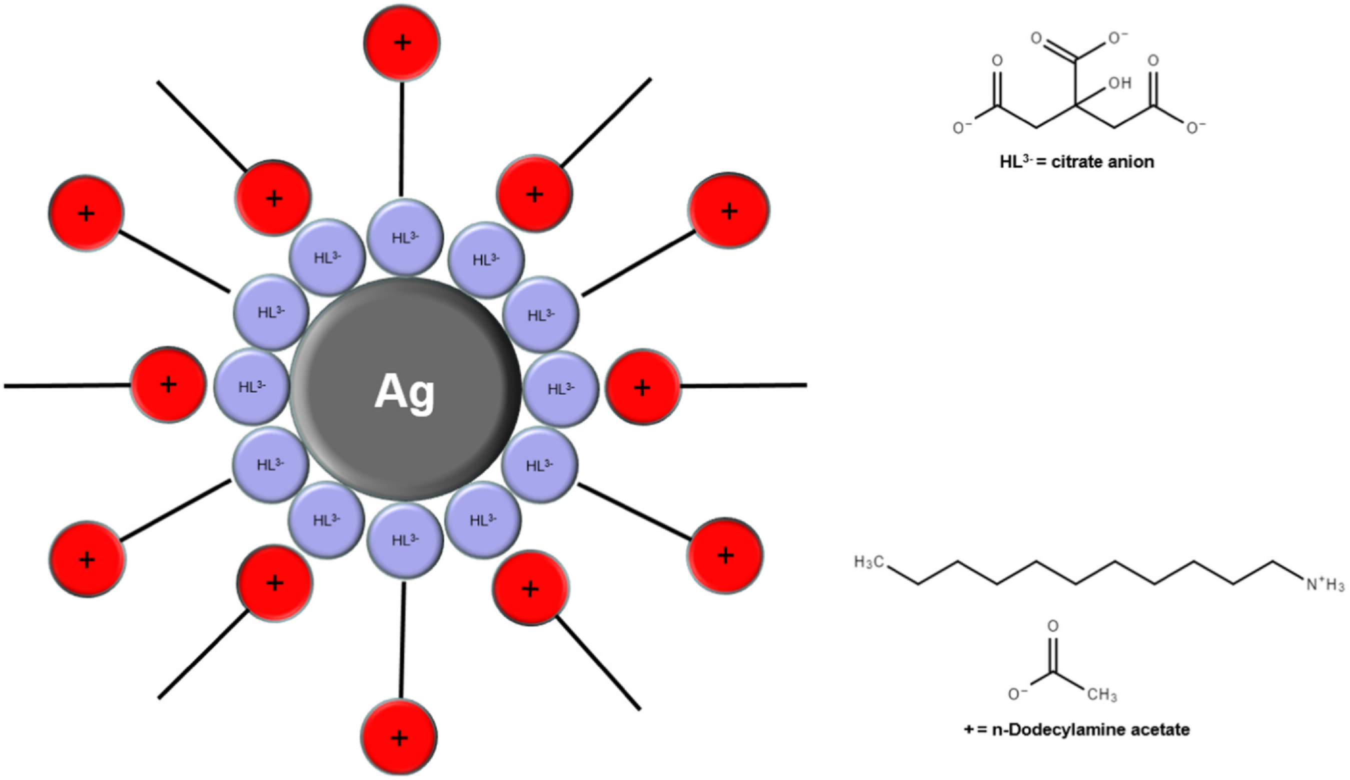


Fig. 1. Schematic diagram showing the formation of micelles around a silver particle by the n-dodecylamine acetate surfactant used in the PD working solution [1,13].

Table 1
Chemicals used in the PD formulations used in this study.

Chemical	CAS No.	Grade (s)	Supplier (s)
Maleic acid	100–16–7	ReagentPlus®, ≥99% (HPLC)	Sigma Aldrich[a] (Gillingham, UK)
Ammonium iron (II) sulphate hexahydrate	7783–85–9	ACS reagent 99% BioXtra ≥98% BioUltra ≥99.0%	Sigma Aldrich[a] (Gillingham, UK)Honeywell Fluka (Bucharest, Romania)
Citric acid anhydrous	77–92–9	Redi-Dri™, ACS reagent, ≥99.5%	Sigma Aldrich[a] (Gillingham, UK)
Iron (III) nitrate nonahydrate	7782–61–8	ACS reagent, ≥98% BioReagent EMSURE® ACS Reagent pHEur	Sigma Aldrich[a] (Gillingham, UK)Honeywell Fluka (Bucharest, Romania)
Silver nitrate	7761–88–8	ACS reagent, ≥99.0% Tested according to pHEur 99.9999% trace metals basis EMSURE® ACS, ISO, Reagent pHEur	Sigma Aldrich[a] (Gillingham, UK)
Surfactants			
Brij® C10	9004–95–9	As supplied average M_n~683	Sigma Aldrich[a] (Gillingham, UK)
Brij® L23	9002–92–0	30% (w/v) in H2O	Sigma Aldrich[a] (Gillingham, UK)
Brij® S10	9005–00–9	As supplied average M_n~711	Sigma Aldrich[a] (Gillingham, UK)
Decaethylene glycol monododecyl ether (DGME)	9002–92–0	As supplied	Sigma Aldrich[a] (Gillingham, UK)
Igepal® CO-360	68,412–54–4	As supplied average M_n ~617	Sigma Aldrich[a] (Gillingham, UK)
n-Dodecylamine acetate (nDDAA)	2016–56–0	As supplied	ICN Pharmaceuticals (Plainview, NY, USA) Pfaltz & Bauer (Waterbury, CT, USA) City Chemicals (West Haven, CT, USA)
Polyoxyethylene (10) tridecyl ether	78,330–21–9	As supplied mixture of C_{11} to C_{14} iso-alkyl ethers with C_{13} iso-alkyl predominating	Sigma Aldrich[a] (Gillingham, UK)
Synperonic® N	9016–45–9	As supplied	BDH Chemicals (Now Merck[a])
Tergitol™ 15-S-9	84,133–50–6	As supplied	Sigma Aldrich[a] (Gillingham, UK)
Tween® 20	9005–64–5	As supplied	VWR (Lutterworth, UK) Sigma Aldrich[a] (Gillingham, UK)

[a] Sigma Aldrich and Merck Chemicals were consolidated into Merck Life Science UK Ltd in July 2020.

regions of the molecule based on their solubility in water or lipids [25].

The cloud point is the temperature above which an aqueous solution of a water-soluble surfactant becomes turbid and separates into a surfactant-rich phase and an aqueous phase. Cloud points only apply to non-ionic surfactants. The cloud point is useful when determining storage stability as separation is likely to occur with surfactants kept at temperatures significantly higher than the cloud point phase. Generally, non-ionic surfactants show optimal effectiveness when used near or below their cloud point [26].

2. Materials and methods

2.1. Chemicals

Throughout the course of the project, the potential variabilities between chemicals of different purities and from different suppliers were explored. None of these variations were found to have a significant impact on the effectiveness of the resultant working solutions [27]. However, obtaining a quality source of nDDAA reagent in order to replace the stock piled supply from ICN Pharmaceuticals proved challenging. The analysis of one supplier's product revealed the absence of nDDAA entirely so this was not used in the study. The City Chemicals product did not fully dissolve so its use was halted after Experiment 1 and the Pfaltz & Bauer (P&B) product was used in preference.

A summary of the chemicals used is provided in Table 1.

The dynamic light scattering study in Experiment 3 used deionised water. The water used throughout the rest of the experiments was reverse osmosis, deionised, grade 2 (as defined in BS EN ISO 3696:1995) produced from a Sartorius water purification system. It is known that some impurities found in water will cause the silver to precipitate prematurely from the solution so a higher quality of water was utilised to avoid these issues.

2.2. Substrates

A range of different paper types representative of those encountered in casework were utilised, and these are summarised in Table 2.

Not all of the substrates were used throughout; the number and type of those selected being determined according to the design of the individual experiment.

Table 2
Overview of the substrates used in this study.

Manufacturer	Paper type	Details
3M	Yellow Post-it® note	Super sticky big notes yellow Post-it® note pad
Banner	Plain white paper	100% recycled A4 copier paper, 80 gsm
Blake	Plain brown envelope	Recycled business envelopes, 120 gsm
NCR	Thermal paper	Thermal POS Printer Rolls
Owl Brand	Plain brown envelope	A4 manilla envelope, 115 gsm
Pukka Pad	Lined white paper	Jotta writing paper, 80 gsm
Purely Everyday	Plain white envelope	A4 seal-self envelope, 90 gsm
Ryman	Lined yellow paper	Superior conference pad, 80 gsm
Wilkinson	Plain white paper	A4 paper, 80 gsm
Xerox	Plain white paper	A4 performer copier paper, 80 gsm

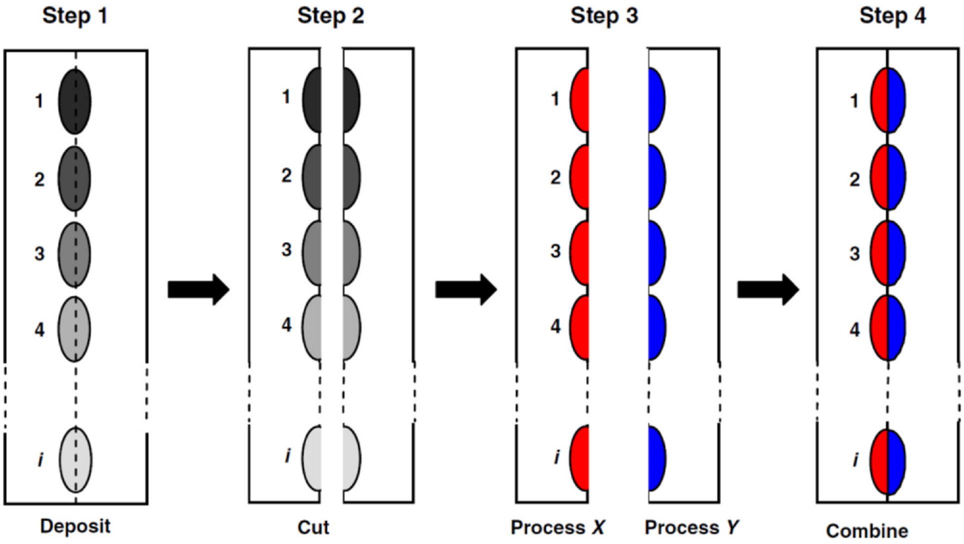


Fig. 2. Schematic diagram showing the concept of a split depletion series [30].

Table 3
Grading scheme used for assessment of developed marks.

Grade	Description of level of detail present
0	No evidence of fingermark
1	Evidence of contact but no ridge detail observed
2	Less than ⅓ clear ridge detail present across original contact area
3	⅓ to ⅔ clear ridge detail present across original contact area
4	Over ⅔ clear ridge detail present across original contact area

2.3. Fingermark deposition and grading

For all of the experiments 'natural' fingermarks were deposited. The residue left when depositing a natural mark is not controlled or groomed; it is therefore considered to be a good representation of marks found on evidence at a crime scene. Donors were asked not to wash their hands or apply hand lotion for at least 30 min before depositing marks. Fingermarks were obtained from a range of donors to provide a varied representation of gender and age, all of whom had read and signed a consent form, in accordance with the Centre for Applied Science and Technology (CAST) ethics methodology [28].

The split depletion method [29,30] was used throughout the experiments, see Fig. 2. Use of a split depletion series allows each half of the fingermark to be processed under different conditions e.g. using different solutions, so that the relative effectiveness can be directly compared on the same fingermark.

The PD process was carried out as per the Home Office 2014 Fingermark Visualisation Manual [31], which involves a maleic acid wash, followed by treatment with the PD working solution and then rinsing with water baths. Scratch-free, glass processing trays were used to minimise premature silver precipitation and white paper sheeting was placed underneath the trays to enable greater visibility of the solution. Each substrate was monitored in the working solution until a sufficient contrast between the mark and background was achieved, or, if no marks were observed, until the background became sufficiently darkened. The time in the working solution was not fixed and depended on the substrate, marks and test solution in use. After completing fingermark processing and recombination of the strips, the half marks were graded and compared against each other. Each mark was given a value of zero to four depending on the area of useful ridge detail available [29,30]. The grading scheme used is shown in Table 3. Marks given a score of three or four would be considered to be potentially identifiable if encountered in an operational scenario. One evaluator was used to grade all of the marks in each experiment.

2.4. Experiment 1 Stability Assessment of a Tween 20-based PD Formulation

The initial phase of the work was based on the theory that it would be possible to implement the Tween® 20-based formulations previously researched by this group [16] in place of the current Synperonic® N formulation.

International groups that have implemented PD formulations incorporating Tween® 20 in the stock detergent suggest that some of these formulations are less effective at developing fingermarks when used shortly after preparation [32]. Researchers have also found that PD solutions containing Tween® 20 can remain effective after several months [33]. However, at the time the work was carried out, the change in effectiveness over time had not been determined, nor had a 'cut-off' date after which the solution should be discarded. A study has since been published exploring the longevity of Tween® 20-based PD, which noted the solution failed to remain stable and that the effectiveness varied with age, with a fresher solution generally yielding stronger background development [34]. Stock detergent refrigeration is recommended by de la Hunty [32] but there is no research into the stability of Tween® 20-based PD working solutions at low temperatures. Establishing the formulation stability relative to the effectiveness was the aim of Experiment 1.

Preliminary work for this study indicated that a PD working solution based on Tween® 20 that had been aged for seven days was more effective than a two day old solution [27], and that a two week old solution gave better results than a one week old solution [35]. The processing time of the items in the working solution typically ranged between 35 and 45 min, which was approximately double the time of the current formulation (~20 min).

For this experiment, seven PD working solutions were produced using Tween® 20-based stock detergent, see Table 4. These solutions were stored for various lengths of time and at different temperatures before visual assessment in order to see the effect on stability. A duplicate of solution 1 was made using an alternative supplier of nDDAA (solution 2) and an alternative batch of Tween® 20 was used for solution 5 in order to exclude reagent quality issues.

Table 4
Solutions prepared in Experiment 1.

Solution reference	Age of solution	Storage conditions	Comments
1	2 days	Refrigerated at ~4 °C	City Chemical nDDAA
2	2 days	Refrigerated at ~4 °C	Pfaltz & Bauer nDDAA
3	1 week	Incubated at ~30 °C	Pfaltz & Bauer nDDAA
4	2 weeks	Room temperature at ~21 °C	City Chemical nDDAA
5	2 weeks	Room temperature at ~21 °C	City Chemical nDDAA and alternative batch of Tween® 20
6	1 month	Room temperature at ~21 °C	City Chemical nDDAA
7	2 months	Room temperature at ~21 °C	City Chemical nDDAA

The solutions were prepared as follows:

Maleic acid solution

1. In a beaker, add 25 g of maleic acid.
2. Add 1 L of Grade 2 RO water and stir until fully dissolved.

Stock detergent

1. In a beaker, add 2.8 g non-ionic surfactant (Tween® 20).
2. Add 2.8 g cationic surfactant (n-dodecylamine acetate).
3. Add 1 L of Grade 2 Sartorius RO water.
4. Cover and leave to stir for a minimum of four hours at room temperature.

Redox solution

1. In a beaker, add 900 mL Grade 2 RO deionised water.
2. Add 30 g of iron (III) nitrate nonahydrate and stir until fully dissolved.
3. Add 80 g of ammonium iron (II) sulphate and stir until fully dissolved.
4. Add 20 g of anhydrous citric acid and stir until fully dissolved.

Silver nitrate solution

1. In a beaker, add 10 g of silver nitrate.
2. Add 50 mL Grade 2 RO water and stir until fully dissolved.

PD working solution

1. Slowly pour 40 mL of the pre-made stock detergent solution into the 900 mL redox solution and stir for at least ten minutes.
2. Add the silver nitrate solution and stir for a further ten minutes.
3. Bottle, label and store the working solution in the dark until required.

During preparation, the solution temperature was maintained at 20 °C or above before being placed into storage at the specified temperature as detailed in Table 4. The ‘minimum’ preparation temperature of 20 °C was used in order to avoid the formation of cloudy or precipitated solutions as seen previously at 17 °C and this temperature was maintained throughout processing [16].

Planted mark studies were conducted using solutions aged for two weeks and one month. The two week old solution was chosen as the starting point because preliminary tests had indicated that this performed better than a one week old solution. This experiment would indicate whether performance continued to improve or started to degrade again.

For this experiment three porous substrates were used:

- Banner plain white paper.
- Xerox plain white paper.
- Owl Brand plain brown envelope.

Twelve donors deposited a split depletion series consisting of six natural marks on each paper type and marks were aged for two weeks before being processed.

2.5. Experiment 2 Identification of Alternative Surfactants

The possibility of using an alternative surfactant to Synperonic® N in the stock detergent solution was explored because of the stability issues with the Tween® 20 formulation encountered in Experiment 1. Based on a knowledge of the performance of the PD working solutions, and the properties of the different surfactants used to date, the following theories were formulated to inform the selection of alternative surfactants [36]:

- The non-ionic surfactant (e.g. Synperonic® N or Tween® 20) is responsible for the emulsion of the cationic surfactant (n-dodecylamine acetate).
- The non-ionic surfactant should have a similar HLB value to its cationic counterpart. As Synperonic® N creates a clear and effective stock detergent when combined with nDDAA, it is thought that nDDAA has an HLB value similar to Synperonic® N (≈12).
- Similar HLB values reflect similar micelle structure and hydrophobicity.
- If the HLB of the non-ionic detergent is too high then the micelle system will be less stable and will collapse over time.
- Tween® 20 has a higher HLB value that Synperonic® N, making it more hydrophilic and less likely to adsorb to fatty fingerprint residue.

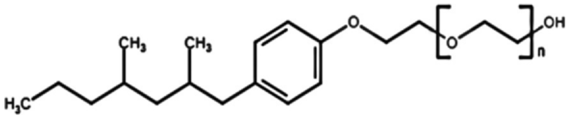
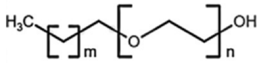
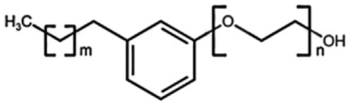
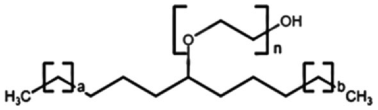
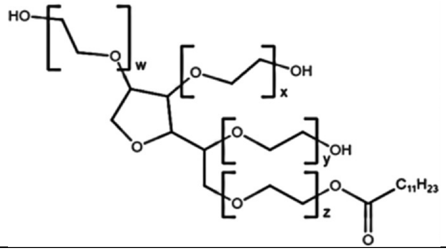
As seen in Table 5, the number of hydrophobic alkyl groups and hydrophilic ethylene oxide groups in the structure of Synperonic® N and the potential replacement Tween® 20 are quite different. The increased molecular weight (MW) and branched chain structure of Tween® 20 could be changing the shape and size of the micelles.

In addition, polysorbates such as Tween® 20 are pH sensitive. Solutions with pH values less than three or greater than nine can cause the surfactant to break down into fatty acid chains and ethylene oxide chains over time. Fatty acid chains may have been causing the observed turbidity in Tween® 20 working solutions, as a consequence of reduced micelle formation. The progressive breakdown of the surfactant structure may also explain why solutions based on this surfactant become more effective over time, possibly reaching a stage where the molecules present are optimum for formation of micelles of a type suited for fingermark development.

The criteria developed for selection of alternative surfactants were therefore:

- Similar HLB to Synperonic® N.
- Lower MW than Tween® 20.
- Similar number of alkyl and ethylene oxide groups to Synperonic® N.
- Resistant to the low pH (≈3) of the PD working solution.

Table 5
Chemical structures of the non-ionic surfactants investigated in PD stock detergent solutions.

Non-ionic surfactant	Chemical structure
Synperonic® N (n = 7)	
Brij® C10 (m = 14, n = 10) Brij® L23 (m = 10, n = 23) Brij® S10 (m = 16, n = 10) DGME (m = 10, n = 10) Polyoxyethylene (10) tridecyl ether(m = 9–12, n = 10) Igepal® CO-360 (m = 7, n = 9–10)	 
Tergitol™ 15-S-9 (a + b = 2–6, n = 9)	
Tween® 20 (w + x + y + z = 20)	

A number of surfactants meeting at least one of the criteria above were obtained and are included in Tables 5 and 6. Some of the relevant properties have not yet been determined and this is denoted by n/k (not known).

The unexplored surfactants in Tables 5 and 6 were selected as they have HLB values ranging from 12 to 13 and/or a similar ratio of ethylene oxide/alkyl groups to Synperonic® N. Brij® L23 was included as it has a similar HLB to Tween® 20. Surfactants with cloud points above 50°C were preferred as they are more stable if subjected to heating (e.g. if the non-ionic surfactant needs to be warmed in order to fully dissolve).

The next step in this experiment was to observe how the unexplored surfactants in Tables 5 and 6 behaved when substituted for Synperonic® N in PD stock detergent solutions. If the surfactant emulsified the nDDAA as anticipated then its respective stock detergent solution would be further investigated in a PD working solution. The stock detergent solutions were prepared using 2.8 g of non-ionic surfactant in combination with 2.8 g of the cationic detergent nDDAA. Observations on the clarity and precipitation levels of the solutions were recorded (Table 8) and, after five days, the cloudy solutions were discarded. It should be noted that decaethylene glycol monododecyl ether (DGME) was not available at this time, but instead similar and more detailed investigations were carried out on this detergent in Experiment 3.

A planted mark study was performed using the most transparent PD working solution based on an unexplored surfactant (Brij® C10) compared to PD working solutions incorporating Synperonic® N and Tween® 20.

Twelve donors and the following six porous substrates were used:

- Banner plain white paper.
- Wilkinson plain white paper.
- Xerox plain white paper.
- Owl Brand plain brown envelope.
- Pukka Pad lined white paper.
- Ryman lined yellow paper.

Table 6
Properties of the surfactants investigated in PD stock detergent solutions [12,36–50].

Surfactant	Average/estimated molecular weight (g/mol)	Critical micelle Conc. (mMol/L)	Cloud point (°C)	Hydrophilic-lipophilic balance (HLB)
n-DDAA	245.40	0.52	n/k	≈12
Synperonic® N	590	0.085	n/k	12.3
Brij® C10	683	0.002	74	12.9
Brij® L23	1198.0	0.06–0.091	>100	16.9
Brij® S10	711	0.003	68	12.4
DGME	626.86	n/k	n/k	n/k
Polyoxyethylene (10) tridecyl ether	n/k	n/k	n/k	n/k
Igepal® CO-360	617	n/k	n/k	13
Tergitol™ 15-S-9	584–596	0.0958	60	13.3
Tween® 20	1228	0.059	76	16.7

Fingermarks were deposited as a six mark depletion series and were aged for one week before processing. For each paper type the following comparisons were carried out:

- Brij® C10-based PD working solution (three days old) vs. Synperonic® N-based PD working solution (three days old).
- Brij® C10-based PD working solution (five days old) vs. Tween® 20-based PD working solution (five days old).

The age of the working solution was selected in accordance with previous observations on stability and effectiveness. Synperonic® N-based working solutions perform more effectively when used less than five days old, and Tween® 20 solutions perform better once aged for approximately one week. Data from a previous experiment is also included in the results due to the difficulties with completing a batch of items using the unstable Tween® 20-based PD working solution. This data comprised the same experimental format, with the differences being only three of the paper types were processed (Xerox, Banner and Owl) and different ages of solution were used (two day old Brij® C10 and seven/eight day old Tween® 20-based PD working solutions).

2.6. Experiment 3 Identification of DGME and Optimisation of Formulation

In order to identify further candidates for alternative surfactants, several theoretical molecular structures with characteristics matching those of a Synperonic® N replacement were outlined. Of the structures proposed, DGME was found to be the only one commercially available. DGME was not available during the early stages of the study but was believed to meet many of the criteria required for a replacement for Synperonic® N. Preliminary trials using a DGME-based PD proved promising as a clear working solution was produced and it was capable of developing marks in a small comparison experiment with Brij® C10. Experiments 1 and 2 had identified limitations with both Tween® 20 and Brij® C10 formulations so it was decided to focus further work on developing a DGME-based PD formulation.

Table 7
Experimental formulations with varying nDDAA:DGME molar ratios.

Detergent formulation	Quantity of nDDAA in detergent solution g/L	Moles of nDDAA in the PD working solution	Quantity of DGME in detergent solution g/L	Moles of DGME in the PD working solution	nDDAA: DGME molar ratio
A	2.00	4.07×10^{-4}	2.00	1.60×10^{-4}	2.55:1
B	1.50	3.06×10^{-4}	1.50	1.20×10^{-4}	2.55:1
C	2.50	5.09×10^{-4}	2.00	1.60×10^{-4}	3.19:1
D	1.25	2.55×10^{-4}	1.00	7.98×10^{-5}	3.19:1
E	1.50	3.06×10^{-4}	1.25	9.97×10^{-5}	3.07:1
F	1.25	2.55×10^{-4}	1.25	9.97×10^{-5}	2.55:1
G	1.00	2.04×10^{-4}	1.00	7.98×10^{-5}	2.55:1

DGME, nDDAA and Synperonic® N have different molecular weights (626.86 g/mol, 245.40 g/mol and 590 g/mol respectively). This detail was taken into consideration when determining the concentration of DGME required in this experiment. Initial work focussed on assessing the solution stability based on the visual clarity and amount of precipitate (such as white detergent deposits or silver flakes) in the various formulations over a period of five days. 28 different stock detergent solutions were produced to give DGME concentrations of 3.0 g/L or below, combined with nDDAA concentrations in the range of 1.0–3.5 g/L. This created stock detergent solutions with various molar ratios of nDDAA:DGME ranging from 1.02 to 17.91. Stock detergent solutions were kept at room temperature after manufacture, which was maintained above 15 °C. PD working solutions were prepared (at or above 20 °C) from their respective stock detergent solutions over 24 h later. The quantity of stock detergent solution used was 50 mL, an increase from the 40 mL of Synperonic® N-based detergent solution used in the existing formulation in order to create a one litre working solution. This has a very minor effect on the concentration of silver present (10.0 g/dm^3 from 10.1 g/dm^3) and no adverse effects were noted as the mark contrast was visually comparable to the Synperonic® N formulation.

Seven of the DGME-based PD working solutions were also explored on a microscopic level using dynamic light scattering (DLS). The formulations in Table 7 were selected for this assessment based on the early results from Experiment 3, where the molar ratio of 2.55–3.19 was identified as the optimum range for stable DGME-based PD working solutions.

A Malvern Zetasizer Nano S was used to measure the particle size of the colloids within the PD working solution. Each solution was placed into a low volume disposable cuvette and kept at a consistent temperature of 25 °C. Each working solution was tested for a duration of 21 s during which it was subjected to seven light scattering measurements, leading to an accurate calculation of particle size and particle distribution.

2.7. Experiment 4 Planted Mark Studies of Stable DGME Formulations

Planted mark studies were conducted using the five most promising DGME-based PD working solutions determined from Experiment 3, see Table 7; formulations A-E. These solutions were selected due to their ability to produce clear, precipitate-free stock detergent and PD working solutions.

Two separate three-way studies were executed comparing A–C and C–E, using six donors and the following five porous substrates:

- Blake plain brown envelope.
- NCR thermal paper.
- Pukka Pad lined white paper.
- Ryman lined yellow paper.
- Xerox plain white paper.

The most effective DGME-based PD formulations were compared to the current Synperonic® N-based PD formulation in a further trial. For this comparison, 12 donors and the following three porous substrates were used:

- Xerox plain white paper.
- Blake plain brown envelope.
- 3M yellow Post-it® note.

Fingermarks were deposited as a six mark depletion series and aged for one week before processing. In order to include marks aged for varying lengths of time, a subsequent experiment was performed using the most effective DGME-based PD formulation. This experiment used six donors, the following three porous substrates and was repeated to gather more marks:

- Xerox plain white paper.
- Blake plain brown envelope.
- Purely Everyday plain white envelope.

Fingermarks were deposited as a six mark depletion series and aged for three, 14 or 35 days.

3. Results and discussion

3.1. Experiment 1 Stability Assessment of a Tween® 20-based PD Formulation

The first observation from this experiment was that the refrigerated Tween® 20-based PD solutions exhibited rapid precipitation after 48 h, supporting previous observations with Synperonic® N [16] that PD working solutions need to be prepared and stored at room temperature.

The two month old solution contained a large amount of precipitate consisting of flakes of silver, and further precipitation occurred during processing. Therefore, the experiment using this solution was terminated and no further work was conducted on solutions older than two months.

The mark development using the two week old working solution was compared with the one month old working solution; summarised in Fig. 3.

The number of marks developed to a high quality was low (less than one-quarter of all 216 marks were grade three and four), which makes drawing firm conclusions difficult. This is often found during research into PD [27,35] because it has not been conclusively established what constituents are being targeted and what a ‘good’ donor would be depositing [21,51]. There were minor differences between paper types however, the one month old solution appears to be slightly less effective overall. No statistical analysis was performed due to the ordinal data and small sample size creating less than ten marks for some of the grades [52]. Repeat experiments would be required to confirm whether this trend is reproducible.

The principal observation from Experiment 1 was the difficulty in establishing whether the Tween® 20-based working solutions were stable and if they were likely to be consistently effective when applied to fingermark development. Although the Tween® 20-based detergent solution was clear on production, it would appear cloudy only a few days later and remained cloudy in the following months, which in turn, affected the appearance of the working solution, see Fig. 4. The degree of opacity varied with solution age but it did not become transparent with time and this suggests that the reagents were not forming a homogenous solution. In conversations with operational users of Tween® 20-based PD, it would seem that some cloudiness was to be expected [32]. However, this is in contrast to the Synperonic® N-based PD working solution, which has a clear appearance when prepared correctly, whereas a cloudy solution indicates that the effectiveness will be compromised [31].

The effect of heat on the cloudy solutions was explored and it was found that the solutions became clear between 29 and 35 °C. One working solution was incubated at 30 °C for a week in order to keep the surfactant dissolved in the solution. However, when this incubated solution was used to process articles, flecks of silver were visible and a fine coating of powder was observed on the bottom of the vessel.

Duplicate solutions using alternative suppliers of nDDAA and an alternative batch of Tween® 20 produced the same appearance displaying a fine precipitate of powder on the bottom of the vessel. It was considered that the surfactant may be in excess in the solution or the quantity used is causing instability, so a parallel study was conducted using differing quantities of Tween® 20 (1.4–5.6 g) and nDDAA (1.5–2.8 g). However, these investigations were unsuccessful as cloudy solutions and poor mark development were still observed [53].

These observations gave rise to concerns that Tween® 20-based PD working solutions could not be reliably produced as clear, stable reagents under typical UK laboratory environmental conditions. The presence of cloudiness in a working solution did not necessarily mean that it would be ineffective, but it was not possible to easily distinguish this from a solution where cloudiness indicated a drop in performance (in contrast to the Synperonic® N formulation). There was also the additional concern that the solution is less effective if used fresh and this may cause an issue for laboratories that would therefore need to prepare the detergent at least two weeks before use. Based on this, it was decided to conduct research into alternative surfactants to Tween® 20 that could be implemented in the UK.

3.2. Experiment 2 Identification of Alternative Surfactants

A summary of the observations recorded for the stock detergent and PD working solutions made with alternative surfactants is shown in Table 8. It should be noted that it was necessary to heat the Brij® C10 stock detergent solution to 39 °C in order to dissolve the reagent, whereas the other surfactants did not require this step.

Although Brij® L23 has similar chemical properties to Tween® 20 it differs in that it produced a clear detergent solution even after storage for two months. However, Brij® L23 was not progressed further due to the numerous other alternatives that also produced clear detergent solutions. Brij® C10 and Brij® S10 detergent solutions were also diluted by a factor of ten to observe the impact on stability but the silver precipitation was more rapid when these were incorporated in working solutions. In order to narrow the field of detergents to test in more depth, working solutions that were not transparent were discarded from further studies due to commonality with Tween® 20 formulations described in Experiment 1. These alternative detergents may have been effective when used to process PD marks however it was decided to focus on the homogenous,

Table 8
Observations on the clarity and stability of stock detergent and working solutions made with different non-ionic surfactants.

Non-ionic surfactant used	Detergent solution observations		Working solution observations	
	Production	*2 months old*	*Production*	*Time taken for significant precipitation to occur*
Brij® C10	Clear	Clear	Clear	5 days
Brij® L23	Clear	Clear	Not prepared	N/A
Brij® S10	Slightly cloudy	Cloudy	Cloudy	48 h
Igepal® CO-630	Clear	Clear	Cloudy	24 h
Polyoxyethylene (10) tridecyl ether	Clear	Clear	Cloudy	3 days
Tergitol™ 15-S-9	Clear	Clear	Cloudy	48 h

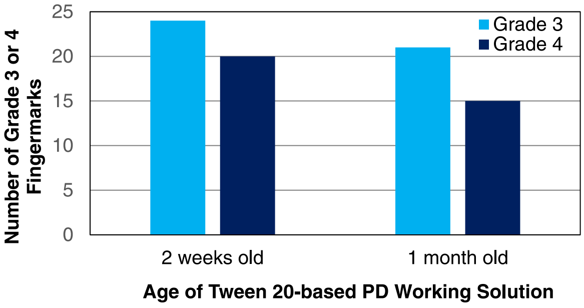


Fig. 3. The number of marks graded three or four developed on different paper types for Tween® 20-based PD working solutions of different ages.

longer lasting solution formed using Brij® C10 as this detergent appeared more promising from the outset. The period of stability (~five days) is similar to the current Synperonic® N formulation so its use would not require a change to current practices.

The results of the comparison between the Synperonic® N and Brij® C10-based PD working solutions are summarised in Fig. 5.

From a total of 432 fingermarks, the relative number of marks that are developed to a high quality is low. Only one age of fingermarks was used in the experiment so this limitation may have been a factor in the poor mark development. From the data obtained, there appears to be little discernible difference between the performances of the two solutions. This can be seen in Fig. 6, which shows a representative mark developed to grade four by both working solutions.

However, it was noted that the typical development time required in the Brij® C10 solution was longer (30–40 min) than that in the Synperonic® N working solution (20–30 min) at the same temperature.

The Tween® 20-based PD working solution was inspected after one week and it was noted that precipitation was present. Further precipitation occurred during the comparison study with Brij® C10-based PD working solutions, thereby reinforcing the concerns over the stability of Tween® 20 formulations. As a consequence, only one paper type (Wilkinson white paper) comprising 72 fingermarks was processed using both solutions. The results of this comparison are shown in Fig. 7.

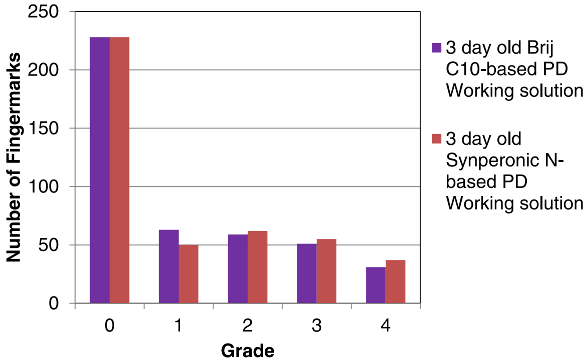


Fig. 5. The number of marks of different grades produced across all six different paper types processed with PD working solutions using Synperonic® N or Brij® C10 in the stock detergent.

From the comparison on this substrate alone, it appears that Brij® C10 is developing less high quality marks than the Tween® 20 working solution. However, the Tween® 20 solution has essentially failed under our desired parameters because of its rapid precipitation during processing. To show how the trends may read across to other types of paper, results from a similar previous in-house study are shown in Fig. 8. The graph shows the combined results of 216 graded fingermarks from Banner white paper, Xerox white paper and Owl Brand brown envelopes.

With the same caution relating to the low numbers of high quality marks developed, there does not seem to be a consistent

Fig. 4. Photographs of cloudy solutions; Tween® 20 stock detergent (left) and Tween® 20-based PD working solution (middle), and a clear PD working solution using Synperonic® N (right).

Fig. 6. A typical split fingermark developed using Synperonic® N-based PD working solution (left) and Brij® C10-based PD working solution (right).

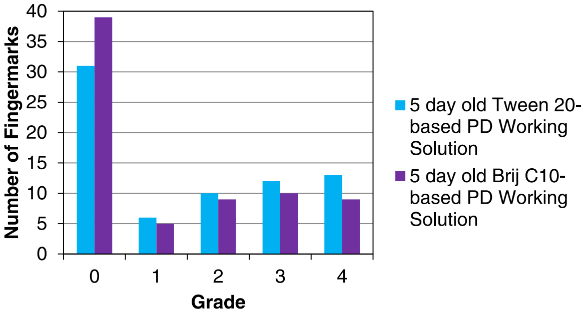


Fig. 7. The number of marks of different grades developed on Wilkinson white paper by PD working solutions using Tween® 20 or Brij® C10 in the stock detergent.

trend in Brij® C10 solutions outperforming Tween® 20 solutions or vice versa, and their performance may be roughly comparable. However, in general Brij® C10 solutions were clearer and more stable than those based on Tween® 20, see Fig. 9.

Although PD solutions based on Brij® C10 have exceptional clarity and appear to be able to detect similar numbers of fingermarks as Tween® 20 and Synperonic® N, the development time is longer than Synperonic® N-based PD solutions. This is not acceptable for many operational laboratories as a reduced processing speed would negatively affect the number of crimes investigated. It may be that the micelles formed by this surfactant are too stable in solution, contributing to the reduced rate and quantity of silver deposition. Another disadvantage with the operational use of Brij® C10 is that the stock detergent solution requires heating to over 30 °C in order for all of the surfactants to dissolve, which is an additional preparation step. Brij® C10 may be a usable alternative to Synperonic® N if the concentration was altered. Further work on this surfactant was halted in favour of investigations into an alternative (DGME), which did not have to be heated to dissolve.

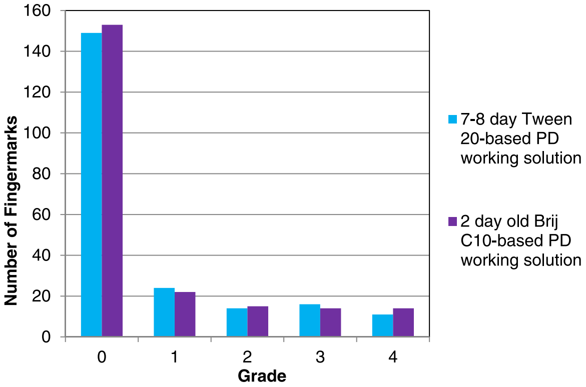


Fig. 8. The number of marks developed across all paper types by Tween® 20 and Brij® C10 working solutions.

3.3. *Experiment 3 Identification of DGME and Optimisation of Formulation*

Observation of the 28 different nDDAA:DGME stock detergent solutions indicated that only formulations with molar ratios in the range 2.55–5.12 produced clear solutions with minimal detergent precipitate.

Dynamic light scattering results provide further understanding of how the nDDAA-DGME surfactant combination is interacting with the silver particles. The nDDAA- Synperonic® N-based PD working solution has been previously assessed to have a Z-average diameter of 700–800 µm [12]. The Z-average is the intensity-weighted mean diameter. Z-average is used in DLS analysis as a polydisperse solution can have numerous peaks for the various constituents, illustrated by Fig. 10, so the intensity of the peaks needs to be considered. It is postulated that the silver micellar particles are the largest component within the solutions, and therefore the most intense peak in the example below.

Z-Average diameter (µm) and Polydispersity Index (PdI) were calculated from the seven measurements per solution. PdI is a measurement of the broadness of size distribution. A PdI over 0.7 is deemed a very broad distribution of particles and the solution may not be suitable for DLS. Fig. 11 shows the Z-Average diameter (µm) per PD working solution containing each detergent formulation.

All Z-Average diameters were generally consistent, at ~300–500 µm, apart from detergent formulation F (DDAA:DGME mass 1.25 g:1.25 g, molar ratio 2.55:1). PdI's were measured at ~0.3–0.5, which is expected from a PD solution, the exception again being detergent formulation F. This detergent formulation showed some instability within solution at a macroscopic level and this has been confirmed by the DLS measurements. It is the assumed that the surfactants are not forming stable micelles which prevent aggregation, resulting in large silver accumulation within the solution, shown by the Z-Average Diameter of 1002 µm. The PdI for detergent formulation F is 0.789 which suggests that the solution is too polydisperse for an accurate DLS measurement. Aggregations were forming in detergent formulation F even when the working solution was freshly prepared, demonstrating the inefficiency of the detergent formulation for maintaining solution stability.

Five of the detergent solutions in the range 2.55–3.19 were investigated further in Experiment 4 as they produced PD working solutions that had the least amount of DGME deposits and were the most transparent in appearance (A-E).

3.4. *Experiment 4 Planted Mark Studies of Stable DGME Formulations*

From the 28 DGME solutions investigated in Experiment 3, five stock detergent solutions (Table 7; solutions A-E) were progressed to comparative tests on a range of paper types.

The relative performance of these five formulations were assessed in two separate three-way comparisons (A vs B, B vs C, C vs A, and C vs D, D vs E, E vs C) both consisting of 540 fingermarks. Formulation C was included in both test sets to give some degree of read across between the different experiments. The results of these trials are summarised in Fig. 12.

From analysing the results from the two comparisons separately, it appears the working solution based on formulation B develops the most high quality marks in the first study, and formulation E gives the best results in the second study. Formulation C did not develop

Fig. 9. Freshly prepared Brij® C10-based PD working solution showing a clear appearance (left) and Tween® 20-based PD working solution showing slight cloudiness (right).

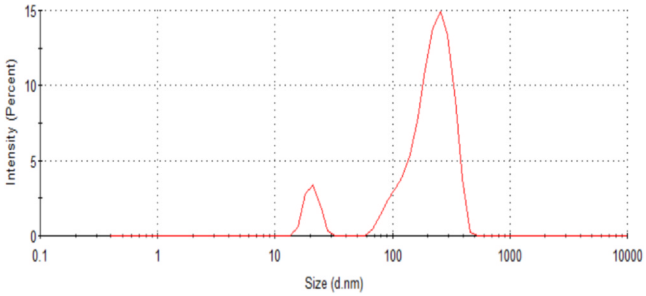


Fig. 10. Example of a size distribution by intensity graph for the working solution incorporating detergent formulation E.

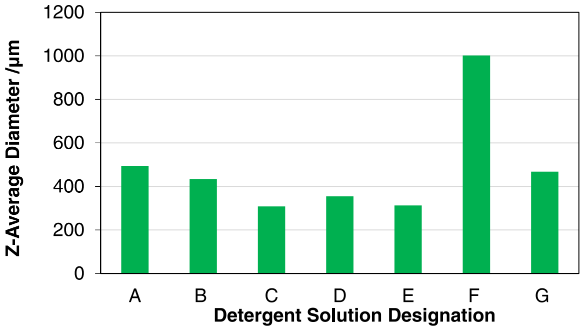


Fig. 11. Z-Average diameter based on the detergent formulation used in PD working solutions.

any marks of a quality high enough to be graded three or four in the second study. This highlights the variability in fingerprint deposits between different donors and days of deposition, resulting in the need to perform larger or multiple experiments upon which to base conclusions. If the use of formulation C is considered as a means of providing a constant across the two experiments, it may be expected that formulations D and E would both outperform formulation B. Stock detergent solutions containing higher quantities of detergent (i.e. A and C) were the least effective in these comparative experiments.

It was decided to progress the best performing solutions in each individual study (formulations B and E) into the comparative trial with Synperonic® N. The results of this further three-way comparison consisting of 648 fingermarks are shown in Fig. 13.

These moderately small scale comparisons have indicated that the performance of the DGME-based PD working solutions was equivalent to, if not better than, the existing Synperonic® N-based PD formulation. Solution E was subsequently used on marks of varying ages ranging from three, 14, and 35 days and it was found to be effective at developing these marks (78% of marks deposited were developed to a grade three or four criterion).

It is difficult to draw firm conclusions due to the relatively low proportion of good quality marks developed during each planted mark experiment, and the processing time required when using PD makes data collection time consuming. A further limitation of the work is that typically only one age of fingermark was used for each experiment due to the numerous other variables to be included. It should therefore be considered that the age of mark used may not have been optimum for the development of high quality PD marks and ideally a range of fingermark ages should be included to test the effectiveness of different formulations fully. Based on these challenges, a large-scale pseudo-operational trial was determined the most informative way to compare the performance of the DGME-based PD formulation with the existing Synperonic® N-based PD formulation. This subsequent work progressed formulation E (1.25 g/L DGME and 1.5 g/L nDDAA) from these trials as the most promising alternative to Synperonic® N. This formulation gave a successful combination of solution stability and sensitivity, although it is noted that it may be possible to further optimise alternative formulations. The validation of formulation E has now been completed and it is intended that the results will be described in a subsequent paper [23].

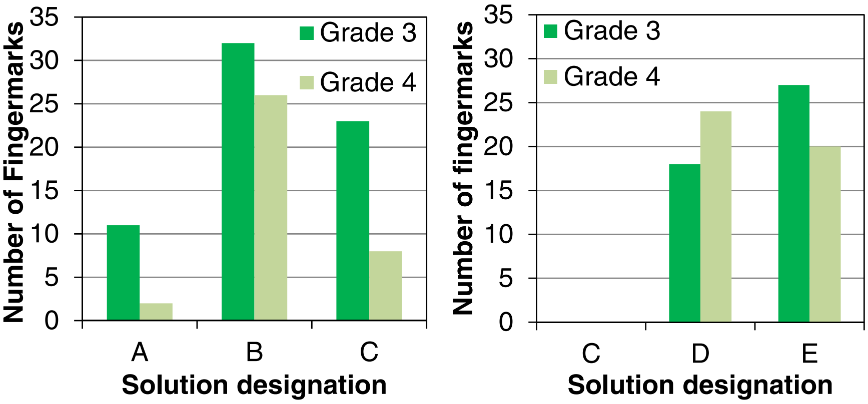


Fig. 12. The number of marks of grades three and four developed across all paper types by different DGME-based PD working solutions, a) first comparison, and b) second comparison.

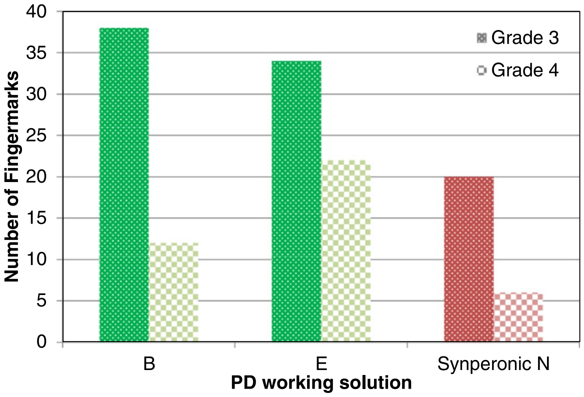


Fig. 13. The number of marks of grades three and four developed across all paper types by DGME-based PD working solutions (formulations B and E) and the Synperonic® N-based PD working solution.

Table 9
Proposed new formulation of PD requiring further validation.

Physical Developer Working Solution
900 mL PD Redox Solution
50 mL PD Stock Detergent Solution
50 mL Silver Nitrate Solution
Physical Developer Stock Detergent Solution
1.25 g Decaethylene glycol mono-dodecyl ether
1.5 g n-Dodecylamine acetate
1 L Water
Physical Developer Redox Solution
30 g Iron (III) nitrate nonahydrate
80 g Ammonium iron (II) sulphate hexahydrate
20 g Citric acid anhydrous
900 mL Water
Silver Nitrate Solution
10 g Silver nitrate
50 mL Water
Maleic Acid Pre-Wash Solution
25 g Maleic acid
1 L Water

4. Conclusions

The aim of this work was to find an alternative detergent to Synperonic® N and this was achieved through a series of planted mark studies. The decision was taken to omit any solutions with a cloudy appearance to limit the number of detergents taken forward for more detailed investigation. These alternatives may have been successful if they were progressed further and different concentrations used. The authors recognise that it is not possible to draw solid conclusions from each individual experiment due to insufficient data and the variabilities associated with using fingermarks. The resource required to explore each avenue in depth would have been impractical in a sensible timeframe so a rationalised approach to finding a suitable formulation was undertaken. However, the most promising formulation will be subjected to more vigorous testing via a pseudo-operational trial (to be published in a subsequent paper [23]).

It was found that PD formulations produced using Tween® 20 in combination with nDDAA often exhibited a cloudy appearance. This immiscibility sometimes resulted in the solution rapidly precipitating before or during use but this did not always correlate to poor fingermark development. It was decided not to implement a revised formulation based on Tween® 20 due to the operational impact of solution instability, as well as the requirement to age the solution for at least two weeks to improve fingermark development.

Brij® L23, Brij® S10, Igepal® CO-630, Polyoxyethylene (10) tridecyl ether and Tergitol™ 15-S-9 were alternative detergents also explored in this study but deemed unsuitable due to the formation of cloudy solutions or inappropriate detergent properties, i.e. HLB value.

PD formulations produced using Brij® C10 in combination with nDDAA were transparent in appearance but were also considered impractical for operational use. The solutions were too stable causing longer exhibit processing times and an additional preparation stage was necessary to dissolve the stock detergent solution.

The most promising substitute for Synperonic® N in PD solutions was DGME. The PD formulation selected for further validation work was solution E. Solution E contained 50 mL of the stock detergent and the stock detergent comprised 1.25 g of DGME and 1.5 g of nDDAA in 1 litre of deionised water, see Table 9.

DGME satisfied the structural criteria required to give similar results to Synperonic® N and planted mark comparative testing demonstrated this to be the case. Molar ratios of nDDAA:DGME in the range 2.55–3.19:1 offered clear and stable PD formulations, with the exception of solution F (1.25 g of both DGME and nDDAA), which did not contain sufficient detergent.

Depletion series experiments suggest that a range of DGME and nDDAA detergent quantities were effective at developing marks but solution E (9.97×10^{-5} moles of DGME and 3.06×10^{-4} moles of nDDAA) was selected as the most sensitive. It should be noted that alternative detergents may also be deemed a suitable replacement for Synperonic® N if further work is applied to the optimisation of the formulation.

The results from these experiments showed mixed success in the number of grade three and four marks developed with PD due to the variability in fingerprint deposits (such as between different donors and the same donor on a different day). This highlights why care must be taken when comparing across two different experiments and results in the need to perform larger or multiple experiments upon which to base conclusions of fingermark visualisation processes. The study is also limited by the use of one age of fingermarks per experiment and therefore it was not possible to determine if the changing fingermark composition with age had an impact on the mark development or formulation effectiveness. However, a suitable operational PD formulation needs to be effective on a range of fingermark ages, and although this was not included in the scoping experiments due to the number of other variables under consideration, it was incorporated when testing the final formulation (Solution E).

A subsequent publication will report additional trials on DGME including work to establish the critical parameters of the component solutions as well as the performance of DGME compared to Synperonic® N in a pseudo-operational trial and on wetted items [23].

Brij®, Tween® and Synperonic® are registered trademarks of Croda International PLC. Tergitol™ is a registered trademark of Union Carbide. Igepal® is a registered trademark of Rhodia Operations [37].

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CRediT authorship contribution statement

A. Thomas-Wilson: Formal analysis, Investigation, Visualisation; **Z. Y. Guo:** Formal analysis, Investigation, Visualisation; **R. Luck:** Formal analysis, Investigation; **L. J. Hussey:** Writing - original draft, Supervision; **M. Harmsworth:** Conceptualisation, Investigation; **J. L. Coulston:** Conceptualisation, Investigation; **A. R. Hillman:** Conceptualisation, Methodology, Writing - review & editing, Supervision; **V. G. Sears:** Conceptualisation, Methodology, Writing - review & editing, Supervision, Project administration.

Declarations of interest

None.

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