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Fingermark visualisation with iron oxide powder suspension: the variable effectiveness of iron (II/III) oxide powders, and Tween® 20 as an alternative to Triton™ X-100

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Highlights

- Powder suspension performance varied between batches of Fisher iron oxide I/1100/53
- A greater number of particles <1 µm was measured in the more effective powder batch
- Tween® 20 was shown to offer contingency if Triton™ X-100 becomes unavailable
- The effectiveness of some iron oxides may vary between surfactant systems
- A new Tween® 20 / iron oxide nanopowder (Sigma Aldrich) formulation is demonstrated

Abstract

The effectiveness of the current UK iron oxide powder suspension formulation, 'C-IOPS-09' (Triton X-100 based), for fingermark or latent fingerprint visualization is shown to be affected by variations between batches of the recommended iron oxide powder from Fisher Scientific (I/1100/53). When incorporated into the C-IOPS-09 formulation, a 2015 powder batch resulted in the detection of ~19% fewer fingermarks, of broadly reduced contrast, when compared to powder suspension prepared with a 2008 batch of the same product. Furthermore, the 2015 powder batch was found to be unsuitable in experimental reduced-surfactant concentration powder suspension, because it caused surface-wide or background staining. The studies in this paper also investigated the use of Tween 20 surfactant as an alternative to the currently utilised Triton X-100, in preparation for the potential unavailability of Triton X-100 in the future. Powder suspensions prepared with Tween 20 surfactant solutions of 4% and 40% were shown to offer similar effectiveness to the currently recommended C-IOPS-09 formulation, when compared using the same batch of Fisher Scientific iron oxide powder (2008 or 2015). The difference between the 2008 and 2015 iron oxide batches was hence also evident with these alternative surfactant solutions. Particle size distribution analysis of the iron oxide powders in Tween 20 and Triton X-100 based surfactant solutions show that the more effective powder exhibits a higher sub-micrometre particle population than the less effective powder. This work leads to an improved specification for powder suspension formulations. This is demonstrated with an example powder suspension formulation which uses a 10% Tween 20 surfactant solution and iron oxide nanopowder (50 – 100 nm) from Sigma Aldrich, which was shown to visualise 27% more fingermarks than the C-IOPS-09 formulation prepared with the 2015 Fisher Scientific powder batch, in a comparative study.

1. Introduction

The physico-chemical fingermark visualisation process 'powder suspension' is effective for use on non-porous and semi-porous surfaces in general [1, 2], and provides capability for fingermark detection on evidential items that have been exposed to water [1-3]. The process is encountered under other names in the field, including 'wet powders' [2], 'sticky-side powder' and 'thick powder suspension' [4]. It is treated as a separate process to small particle reagent (SPR) in the Home Office Fingermark Visualisation Manual (FVM) [2].

The black iron (II/III) oxide powder suspension formulation published by the Home Office Centre for Applied Science and Technology (CAST) in 2009 [5] is currently recommended in the UK for treating light, non-adhesive surfaces [2]. The components of this formulation ('C-IOPS-09' - Appendix), which include iron (II/III) oxide powder and an aqueous 'surfactant solution' of Triton™ X-100 and ethylene glycol, were the subject of recent studies [6, 7]. It was demonstrated that the effectiveness of the formulation is strongly dependent on the iron (II/III) oxide powder product utilised [6].

The Fisher Scientific iron (II/III) oxide powder 'I/1100/53' (a general purpose material [8]) has been an effective powder for C-IOPS-09 [3, 6, 7, 9]. Scanning Electron Microscopy (SEM) analyses of fingermarks developed with iron oxide powder suspension prepared with this material showed that the particles adhering to the ridges ranged in size from a few hundred nanometres to one micrometre in diameter [10]. This information formed the basis for subsequent specifications for effective particle size for the process [3, 6]. An example SEM image highlighting the range of particle sizes on a fingermark developed with Fisher Scientific iron oxide (I/1100/53) powder suspension is shown in Figure 1. Other iron oxide particle parameters such as surface texture, coating and agglomeration behaviour have not been studied in relation to the efficacy of iron oxide powder suspension (C-IOPS-09 or similar formulations), but have been shown to be important in other micro-sized powder, and powder suspension formulations [11, 12].

[Please place Fig. 1 here: single column size]

Effective powder suspension formulations should selectively deposit powder on fingermark ridges and not the backgrounds of the surfaces to which they are applied. General ‘background staining’, caused by surface-wide powder deposition, is undesirable as it may reduce the contrast of visualised fingermark ridges [13, 14] and render fainter marks difficult to observe. Recently, the ‘fingermark selectivity’ exhibited by the C-IOPS-09 formulation was shown to relate to the concentration of the surfactant Triton™ X-100 [7]. C-IOPS-09 is prepared from a surfactant solution with a Triton™ X-100 concentration of > 400 times the critical micelle concentration (c.m.c.) [7]. A powder suspension prepared using surfactant solution with Triton™ X-100 reduced to approximately the c.m.c. was shown to deposit iron oxide over the entire treated surface area of samples [7], whereas at ~2 × c.m.c., powder suspension did not cause background deposition in the study [7]. Triton™ X-100 micelle structures form spontaneously at or above the c.m.c. [15], and hence the presence of micelles may be essential for visualising fingermark ridges without causing background staining [7]. It was also demonstrated that effective powder suspensions could be prepared with C-IOPS-09 surfactant solution diluted to 10% and 1%, and these formulations were advantageous in their ease of being rinsed off surfaces [7].

It should be noted that additional processes can cause background staining effects to occur when powder suspensions are applied to incompatible surfaces. Known examples include C-IOPS-09 on acrylic-based adhesives such as some parcel tapes [2, 16] and carbon-based powder suspension on surfaces containing titanium dioxide, a common pigment in light coloured polymers [13].

In general, a more detailed understanding of how powder particles interact with surfactant molecules would further our understanding of the powder suspension process [7], which is important for future process optimization and formulation resilience.

The field of chemical fingermark visualisation has a history of formulation revisions driven by economic, environmental, and/or health and safety factors. Examples include the reformulation of ninhydrin working solution [17-19] due to the CFC bans in the mid 1990’s [18]; the replacement of Synperonic N surfactant with Tween® 20 in the U.S. Secret Service physical developer formulation [20, 21] due to the phase-out of nonylphenol ethoxylates [20]; and the development of a less-flammable methoxypropanol-based solvent black 3 formulation for use at crime scenes [22, 23]. Recent work includes replacing HFE formulations for amino acid reagents [24].

Presently there is a risk associated with the C-IOPS-09 formulation, because the Triton™ X-100 surfactant belongs to the group of 4-(1,1,3,3-tetramethylbutyl)phenol ethoxylates residing on the Candidate List of Substances of Very High Concern [25, 26], as defined in article 57 of the REACH Regulation (European Commission) [27]. The concern is associated with the accumulation of 4-(1,1,3,3-tetramethylbutyl)phenol and the shorter chain ethoxylates in the environment, which are potential degradation products of the larger ethoxylates in the group (e.g. Triton™ X-100) [26]. Substances residing on the Candidate List may be placed on the Authorisation List (REACH) [28]. It is therefore possible that Triton™ X-100 will require authorisation in the European Union in the future, which may impact the permissible uses for the surfactant, and its availability. However, there is resilience for powder suspension, as researchers recently suggested an iron oxide powder suspension that is formulated utilising the Tween® 20 surfactant (Appendix) [29], however, the use of this has not been thoroughly assessed.

This paper explores Tween® 20 iron oxide powder suspension formulations, including variation of concentration and comparisons with C-IOPS-09, and changes to the behaviour and effectiveness of different powders with surfactant formulation.

2. Materials and Methods

Experiments 1 and 3 were relatively small-scale and concerned with exploring powder suspension components. These experiments were in line with 'Phase 1' or 'proof of concept work' as defined in the CAST Methodology [30] and the Guidelines for the Assessment of Fingermark Detection Techniques, by the International Fingerprint Research Group [31]. Experiments 2 and 4 compared powder suspension formulations using natural fingermarks and may be categorised as 'Phase 2' work as set out in the methodology papers [30, 31]. Phase 2 work is concerned with technique optimisation and is the phase preceding validation [31].

A selection of locally sourced non-porous substrates (Table 1) were acquired in new condition for these experiments, to challenge the iron oxide powder suspensions with operationally relevant surfaces with differing properties [30, 31]. Not all substrates were used for each experiment due to time and resource constraints, and the limitations associated with donating fingermarks for fair comparisons.

Where substrates were cleaned (as specified), they were washed with warm tap water and detergent using a non-abrasive cloth. This was followed by successive rinsing with warm tap water (20 s), ethanol (5 s) and deionised water (5 s). Substrates were then allowed to air–dry at room temp (15–25°C).

For natural fingermark donation, volunteers did not wash their hands for a minimum of 30 min before deposition and no eccrine or sebaceous loading was conducted [31]. Immediately prior to donation, volunteers rubbed their hands together to evenly distribute sweat and any environmental contaminants across all fingers. 'Multiple donor' and 'depletion series' fingermark collection methodologies were used [30], and are described in more detail by experiment. All fingermarks were aged in a laboratory environment (United Kingdom), out of direct sunlight.

Powder suspensions were prepared fresh (before application) in each experiment, in a 1:1 w/v ratio (powder (g): surfactant solution (ml)) unless specified. Laboratory grade Triton™ X-100 (Sigma Aldrich, X100), ReagentPlus ≥99% ethylene glycol (Sigma Aldrich, 324558), Tween® 20 (Sigma Aldrich, P1379) [32] and deionised water were utilized for the surfactant solutions (specific formulations given by experiment). Details for the iron (II/III) oxide powders investigated, as referenced in each experiment, are provided in Table 2.

All powder suspensions in these studies were used as detailed in the Home Office FVM [2]. This included pre-wetting surfaces with tap water before applying powder suspensions using moistened squirrel-hair brushes, and leaving the suspensions on surfaces for approximately 10 s before rinsing off. Where different powder suspensions were compared in an experiment, separate clean squirrel-hair brushes were used for each.

Visualised fingermarks were graded using a scheme published by the Home Office [30, 31] (see Table 3). All grading was conducted in a laboratory environment under reflected white light conditions, and directly from the substrates by eye. Only grade 3 and 4 fingermarks were considered in the results analyses as they were deemed to be identifiable (although in some cases grade 2 marks may be sufficient for identification or exclusion).

Further details for each individual experiment are provided on the following pages.

2.1 Experiment 1 – factors affecting background staining

This experiment was designed to further explore background staining with iron oxide powder suspension in relation to; the batch of iron oxide powder used; the surfactant solution concentration; and the cleanliness of substrates.

Powder suspensions were produced using three Triton™ X-100–ethylene glycol surfactant solutions with different concentrations (as explored previously [7]) and two different batches of the recommended [9] I/1100/53 iron oxide powder product from Fisher Scientific (see Table 4 for details).

All suspension were prepared form the same stock surfactant solution, with dilutions as shown in table 4.

This experiment utilized a 'spot-testing' methodology: a pair of marked areas (30 x 60 mm) on each substrate (1–7, as per Table 1) was treated with each powder suspension: this size has been shown to be sufficient for analysis of substrate variation [13]. One marked area from each pair had been pre-cleaned on the day of the experiment, whilst the other had not been cleaned. There was no intentional fingermark deposition and visualisation incorporated into this study.

2.2 Experiment 2 – Comparison between C-IOPS-09 and Tween® 20 powder suspension formulations

The aim of this experiment was to compare the performance of the two iron oxide powder batches and compare C-IOPS-09 with iron oxide powder suspensions prepared with Tween® 20 surfactant solutions of different concentrations.

C-IOPS-09 was compared to iron oxide powder suspensions produced with 40% Tween® 20 [29], 4% Tween® 20 and 0.66% Tween® 20 (~100 × c.m.c.) surfactant solutions. With the inclusion of both A and B iron oxides (Table 2), 8 different powder suspensions were compared overall (see Table 5). The 100 × c.m.c. (approx) Tween® 20 surfactant solution was created using volumetric glassware, and the c.m.c. was taken to be 0.06mM as per the manufacturer's information [32] (similar values, e.g. 0.058mM, appear in the literature [35]).

This experiment featured two substrate groups with different donors:

- Group1:
    - Substrates 4, 7 and 9 (Table 1).
    - 7 donors (4 male, 3 female), aged 20–40 (approx).
- Group 2:
    - Substrates 5, 6 and 8 (Table 1).
    - 6 donors (3 male, 3 female), aged 20–50 (approx).

All substrate sheets except HDPE were pre-cleaned as described in section 2. HDPE preparation omitted this step because ethanol was observed to dissolve the printed inks.

Fingermarks were donated on 8 sheets of substrate 4 – to create one sample for each of the 8 powder suspensions in the comparison. Donations were in depletion series of ten marks, and each donor contributed one depletion series per sheet, using a different finger each time. Donors then re-rubbed their hands together, and donated marks to create another set of 8 samples for substrate 7. This was then repeated for substrate 9, and these 24 samples were aged for 7 days before being processed with the powder suspensions. On the same day but at a later time, this fingermark collection strategy was repeated to generate 8 more samples each of substrates 4, 7 and 9. These 24 samples were aged 28 days before being processed.

The above fingermark collection pattern was repeated on a different day for the group 2 substrates, to create further samples for aging 7 and 28 days.

For this experiment, powder suspension preparation and processing were carried out on 4 separate days (representing the 2 substrate groups and 2 aging times). After processing, each sample was coded, and the treatment details were concealed so that pseudo blind grading could be undertaken by the primary experimenter. Half of the samples were re-graded blind by a second assessor who had no knowledge of the details of the comparison.

2.3 Experiment 3 – Scoping study for sub-micrometre iron oxide powders

This experiment was designed to gauge whether iron oxide powders composed of sub-micrometre sized particles (as stated in the product specifications [33, 34]) perform more effectively in powder suspension than iron oxide powder B from Fisher Scientific.

Iron oxides B, C and D (table 2) were compared for use in C-IOPS-09 and powder suspension produced with 4% Tween® 20 surfactant solution (see table 6 for formulations).

The C-IOPS-09 (B), (C) and (D) powder suspensions were prepared from the same stock surfactant solution. The 4% T20 (B), (C) and (D) powder suspensions were also prepared from the same stock surfactant solution (Table 6).

This experiment utilized a multi-donor methodology [30]. On each substrate (3, 5 and 8 (Table 1), all pre-cleaned, three sets of single fingermarks were collected (from 8 male and 8 female donors, in the approximate age range of 21-60 years old) for processing with the C-IOPS-09 (B), (C) and (D) powder suspensions (Table 6). Donors re-rubbed their hands together and repeated this donation pattern to create a set of samples to be processed with the 4% T20 (B), (C) and (D) powder suspensions. The fingermarks were aged for 7 days.

2.4 Experiment 4 – Comparison between Tween 20 / sub-micrometre iron oxide powder suspension and C-IOPS-09

This experiment aimed to gauge the effectiveness of a powder suspension prepared with Tween 20 surfactant solution and sub-micrometre iron oxide (powder C) against the currently recommended C-IOPS-09 [2].

C-IOPS-09 with iron oxide powder B was compared to iron oxide powder suspension produced with 10% Tween 20 surfactant solution and iron oxide powder C (table 7). The ratio for the novel Tween 20 and sub-micrometre iron oxide powder suspension was 1:2 w/v (powder (g): surfactant solution (ml)).

Eighteen volunteers (9 male, 9 female) participated in this experiment, in the approximate age range of 20 to 50 years old. Two sets of samples were created using substrates 6, 7, 8 and 10, with each volunteer donating fingermarks in depletions of 6, using a different finger each time. Donors re-rubed their hands and repeated this donation pattern to produce 2 sets of additional samples with substrates 3, 4, 5 and 9. The fingermarks were aged for seven days. One set of 8 substrate samples were processed with C-IOPS-09 (B) and the other set was processed with 10% T20 (C) (table 7).

2.5 Iron oxide particle size analyses

In support of these studies, iron oxide powders were analysed for particle size using a laser scattering particle sizer. Samples were prepared as an aliquot of dry powder, mixed with 10 ml of 4% Tween® 20 in distilled water or 10 ml of C-IOPS-09 surfactant solution. Samples were vortexed and a drop or series of drops from the prepared solution were analysed within a Malvern Mastersizer 3000E equipped with a small volume dispersion unit. The amount of material added was selected to allow an obscuration within the instrument of 2-15%. The refractive index and density of the samples were assumed to be unvarying across the powders. Each sample was measured for five consecutive 10 s periods and the process repeated. Particles between 0.1 µm and 1000 µm are included in the analysis, grouped into 100 size bins. Figures for each powder are normalized to 100%, and any possible particles outside the detection range are not included in the figures.

2.6 Health and Safety note

Avoid the inhalation of iron oxide dust. Inhalation of particles below 10 µm can have an effect on asthma, other respiratory diseases, cardiovascular disease, and cancer. The effect is stronger with particles below 2.5 µm in size, equivalent to fine particulate air pollution [36]. Additionally, magnetite particles with diameters of <~200 nm can be transported directly into the brain, where they may pose a hazard to human health [37].

The Sigma Aldrich iron oxide product used in this work may be classified as a nanomaterial, and should be used with appropriate control measures. The need for further information regarding the effects of particulate nanomaterials on human health is widely acknowledged [38].

3. Results

3.1 Experiment 1

The results of experiment 1 are represented in Figure 2. Expanded examples of full processed samples are provided in the Electronic Supplementary Information – ESI Fig. 1.

[Please place Fig. 2 here: 1.5 column size]

On ABS, painted steel (red), HDPE, and plastic board (4 of the 7 substrates), only 1% surf sol (B) powder suspension caused background iron oxide deposition, and this was true for both the cleaned and unclean sample areas (Figure 2). However, for the ABS and HDPE, the background deposition was less pronounced on the cleaned sample areas.

The 1% surf sol (B) powder suspension was not the only formulation to cause background staining on uPVC, painted steel (silver), and the wood-effect laminate, however, it caused more continuous and intense staining than the other formulations (Figure 2).

The other iron oxide B powder suspensions – 10% surf sol (B) and 100% surf sol (B) – did not cause background staining, other than some minor deposition on the wood-effect laminate and the uPVC (Figure 2).

The 1% surf sol (A) powder suspension caused patchy deposition on the wood-effect laminate, uPVC and painted steel (silver) sample areas that had not been cleaned, and there was some just noticeable localised staining on the cleaned areas. Similar effects also occurred with the 10% surf sol (A) and 100% surf sol (A) suspensions (Figure 2), however, no iron oxide A powder suspension caused staining as intense or continuous as the 1% surf sol (B) powder suspension.

3.2 Experiment 2:

With the data for all substrates and both ageing periods combined, the results from experiment 2 (Figure 3) show that the iron oxide A powder suspensions recovered between 536 marks (4% T20 (A)) and 580 marks (100×cmc T20 (A)), or 68.7% and 74.4% of the donated marks. The iron oxide B powder suspensions recovered between 338 (40% T20 (B)) and 428 marks (C-IOPS-09 (B)), or 43.3% and 54.9% of the donated marks.

[Please place Fig. 3 here: 1.5 column size]

The appearance of the fingermark development achieved with powder suspensions prepared with iron oxide A was broadly equivalent. However, the 100×cmc T20 (A) powder suspension produced marks with more contrasting ridges for some donors, and occasionally

4% T20 (A) also yielded more contrasting marks for some donors than the C-IOPS-09 (A) and 40% T20 (A) powder suspensions. The appearance of visualised marks was also broadly similar between the iron oxide B powder suspensions C-IOPS-09 (B), 40% T20 (B) and 4% T20 (B). The development achieved using 100×cmc T20 (B), however, was characterised by darker ridges and significant background staining for most samples.

The grouped data for Experiment 2 (Figure 3) indicates that each powder suspension formulation (C-IOPS-09, 40% T20, 4% T20 and 100×cmc T20) visualised more identifiable marks when prepared with iron oxide powder A than with powder B. The iron oxide B powder suspensions generally visualised fingermarks with weaker contrast than the corresponding iron oxide A powder suspensions (examples provided in Figures 4, and 5), although for some surfaces the difference was subtle. This overall trend was also true for each of the four sample sets (processed on the four separate days – Table 8) when assessed independently.

Considering the currently recommended formulation (C-IOPS-09) [2] only, the data shows a difference in fingermark recoverability of 19.2% between powder suspensions prepared with A and B iron oxide powders overall. A more detailed analysis of the difference between the iron oxides is achieved in considering the pairs of samples (the same substrate with a comparable set of fingermarks) processed with powder suspensions with common surfactant solutions. For example, C-IOPS-09 (A) recovered 61 marks, whereas C-IOPS-09 (B) recovered 30 marks on the HDPE samples aged 7 days (see Table 8). Extending this analysis reveals that:

- more fingermarks were detected by iron oxide A powder suspensions on 44/48 of the sample pairs
- more fingermarks were detected by iron oxide A powder suspensions, with a difference of ≥10% of the deposited marks on 36/48 of the sample pairs
- more fingermarks were detected by iron oxide A powder suspensions, with a difference of ≥25% of the deposited marks on 15/48 of the sample pairs

[Please place Fig. 4 here: 2 column size]

[Please place Fig. 5 here: 2 column size]

The secondary assessor's fingermark grade assignments (Electronic Supplementary Information – ESI Table 1) provided trends that were in broad similarity to those generated by the primary experimenter, for both the set 1 sample group (aged 7 days) and the set 2 sample group (aged 28 days) (Figure 6). The trends from both individuals show that iron oxide A powder suspensions performed more effectively than iron oxide B powder suspensions. There is also similarity in the relative bar heights between most of the compared powder suspensions (Figure 6). Verifying trends in this way mitigates against any bias the primary experimenter may have had due to knowledge of the formulations.

[Please place Fig. 6 i here: single column size]
[Please place Fig. 6 ii here: single column size]
[Please place Fig. 6 iii here: single column size]
[Please place Fig. 6 iv here: single column size]

3.3 Experiment 3

On grouping the data for the three substrates, the 4% T20 powder suspensions visualised between 41/48 and 42/48 of the donated marks to grade 3 or 4 quality, and the C-IOPS-09 powder suspensions visualised between 37/48 and 41/48 of the marks to grade 3 or 4 quality (Electronic Supplementary Information – ESI Table 2). This experiment was too small for meaning to be derived from the slight performance difference between the three powders, for both surfactant solutions. Of more interest is the visual appearance of the developed fingermarks.

Processing with the 4% T20 (C) and (D) powder suspensions resulted in more on-mark iron oxide deposition than processing with 4% T20 (B) powder suspension (see Figure 7). For a few donors, the ridge detail was obscured due to both on-ridge and inter-ridge powder deposition following the use of 4% T20 (C) and (D). The 4% T20 (C) powder suspension yielded marks that appeared darker than the marks visualised with other Tween® 20 powder suspensions, and the 4% T20 (D) produced brownish marks (see Figure 7). These trends were true for all three substrates.

Where the C-IOPS-09 surfactant solution was used, there were no noticeable differences observed in terms of amount of powder deposited on the marks between the powder suspensions (B), (C) and (D) (see Figure 7). There was no clear difference in visualised mark contrast between C-IOPS-09 (B) and C-IOPS-09 (C) powder suspensions, and C-IOPS-09 (D) produced brownish marks. These observations were consistent for all three substrates.

[Please place Fig. 7 here: 1.5 column size]

3.4 Experiment 4

On grouping the data for the eight substrates, the 10% T20 (C) powder suspension visualised 599 of the donated marks (69.3%) and the C-IOPS-09 (B) powder suspension visualised 365 of the marks (42.2%), to grade 3 or 4 quality (Table 9). The 10% T20 powder suspension was also more effective on each surface individually (Table 9).

The C-IOPS-09 (B) powder suspension predominantly visualised fingermarks with weaker contrast than the 10% T20 (C) powder suspension (examples provided in Figure 8). This contrast difference was obvious for most surfaces, except for the ceramic tile and HDPE surfaces where it was only apparent on closer examination of the fingermarks. Of the marks visualised with 10% T20 (C), up to 2% appeared over-developed, with some inter-ridge iron oxide deposition.

(i) *[Please place Fig. 8 here: 1.5 column size]*
(ii) *[Please place Fig. 8 here: 1.5 column size]*

3.5 Iron oxide analyses

Particle size results are shown in Figure 9 and cumulative volume fraction is summarised in Table 10. The measured particle size will be reflective of original dry size, expansion in the solution and agglomeration of particles. In 4% Tween® 20 solution iron oxide powder A has the largest fraction of sub-micrometre particles, with 14.4% as opposed to 5.7% for iron oxide powder B and 7.4% for iron oxide C. However, in this detergent iron oxide C has approximately 98% of particles below 5 µm, compared with 79% for iron oxides A and B. In C-IOPS-09 surfactant solution iron oxide A again shows the largest fraction of sub-micrometre particles, with 13.2%, as opposed to 1.8% for iron oxide B and 0.8% for iron oxide C.

The primary particle size for iron oxide A (in 4% Tween® 20 or C-IOPS-09 solution) is 1.7 µm. For iron oxide C in Tween 20 it is 1.9 µm. For iron oxide B the peak of smallest particle size is for particles around 1.8-2.5 µm, but this does not necessarily cover the bulk of the sample, with peaks of particles from 30 µm to a few hundred. In C-IOPS-09 surfactant solution the distribution is bimodal and there is clear distinction between the two size groups of particles giving clear absence of particles between ~5 and ~30 µm. The iron oxide A powder in C-IOPS-09 surfactant solution has 92% of particles below 5 µm, as opposed to 25% for iron oxide B, and the remaining particles are above 100 µm. The biomodality and difference between powders is less evident in Tween® 20 solution where there are long tails from the distribution peaks.

4. Discussion

In previous work [7], it was shown that the surfactant solution for C-IOPS-09 could be diluted to 10% and 1% without reducing the effectiveness of the resultant powder suspension, when prepared with Fisher Scientific iron oxide powder batch 0760600 (2008) [7]. This included no undesirable iron oxide background deposition when used to visualise donated fingermarks on cleaned surfaces [7]. The results from Experiment 1 in this paper indicate that the previous findings may have also related to the properties of the particular iron oxide batch used. In Experiment 1 (this paper), continuous background staining occurred on most of the cleaned surface areas treated with 1% surf sol (B) powder suspension (which used Fisher Scientific iron oxide lot 1409138, 2015) whereas minimal if any background staining was observed when cleaned areas were processed with 1% surf sol (A) powder suspension (which used the same powder batch as the previous work [7]: Fisher Scientific iron oxide 0760600, 2008). Most of the other powder suspensions in experiment 1 with higher surfactant concentrations did not cause background staining on the cleaned sample areas, and where they did, it was mostly minimal and discontinuous.

Experiment 1 has therefore indicated that significant surface staining relates mainly to the use of a powder suspension composed of lot number 1409138 Fisher Scientific iron oxide powder (2015) and low concentration surfactant solution (C-IOPS-09 surfactant solution diluted to 1%). Surface cleanliness was also an influencing factor, since some powder suspensions caused greater staining on sample areas that had not been cleaned. Earlier works demonstrated the importance of the substrate properties in fingermark visualisation [10, 13], and Experiment 1 further highlights this, as the intensity of background staining caused by 1% surf sol (B) powder suspension also varied between materials (Figure 2).

In Experiment 2, Tween® 20 surfactant solutions of a range of concentrations were demonstrated to offer similar capability to C-IOPS-09 surfactant solution for use in powder suspension when the same iron oxide powder batch was used, in terms of the number of identifiable marks visualised. The 100×cmc T20 powder suspension may be the least ideal formulation to take forward, because it caused background deposition with iron oxide powder B and thus may be a less stable formulation. The 40% T20 and 4% T20 powder suspensions were similar in effectiveness, although the 40% T20 powder suspension was more difficult to apply and rinse off.

The trends generated in Experiment 2 suggest that the differences between the powder batches (iron oxides A and B) had a greater impact on powder suspension effectiveness than the differences between the four surfactant solutions tested (Figures 3 and 6). The reduced numbers of identifiable fingermarks recovered by iron oxide B powder suspensions likely relates to the observed reduction in the contrast of visualised marks, when compared to corresponding marks visualised by iron oxide A powder suspensions. The particle size distribution analysis shows that the percentage of sub-micrometre particles in suspension was less with iron oxide B (5.7%) than for iron oxide A (14.4%) in 4% Tween® 20, and a similar trend was observed in C-IOPS-09. It is particles of this size that have been shown to be responsible for ridge visualisation in previous work [10] therefore the greater number of these particles in iron oxide A is likely to lead to increased deposition of particles on the fingermark ridge. This will lead to increased contrast and the observed increased mark quality, with development of 68.7% of marks at high quality (grade 3 or 4) with iron oxide A in 4% Tween® 20 compared to 47.1% for iron oxide B, as shown in Figure 3. The larger particles are likely to be washed off in the mark development protocol, or in some cases may contribute to the background staining, the degree of which is likely to be substrate and surfactant dependent [10, 13].

The difference in effectiveness between the two Fisher Scientific I/1100/53 iron oxide batches (powders A and B) shown in this paper was not observed by Downham et al. [6]. However, that study concentrated on a comparison to considerably less effective iron oxides, restricted the surfactant to C-IOPS-09 and was overall limited-scale.

The variation in behaviour between the batches of Fisher Scientific iron oxide I/1100/53 observed in these studies suggests that this product may lead to inconsistent C-IOPS-09 performance in the operational setting. In experiment 2, powder B was demonstrated to be less effective than powder A in the currently recommended powder suspension formulation (C-IOPS-09) by approximately 19%, in terms of the recovery of identifiable fingermarks. The requirement for a more refined iron (II/III) oxide powder was hence considered.

Experiment 3 provided an indication that 50-100 nm iron oxide nanopowder from Sigma Aldrich (powder C) and micronized Bayferrox 318M from Lanxess (powder D) provided greater on-ridge deposition than Fisher Scientific iron oxide (powder B) when incorporated into powder suspension prepared with 4% Tween® 20 solution. No difference in on-ridge deposition was observed between these powders when the C-IOPS-09 surfactant solution was used, which demonstrates that the fingermark visualisation potential of some iron oxides in powder suspension is dependent on the surfactant. The observed variation in fingermark enhancement between iron oxides B and C in 4% T20 powder suspension, and their performance similarity in C-IOPS-09 powder suspension appear to be reflected in the particle size distribution data. In 4% Tween 20 surfactant solution, the percentage of iron oxide C sub-micrometre particles (7.4%) and sub 2 micrometre particles (59.8%) were shown to be greater than for iron oxide B (5.7% and 38.4% respectively), whereas in C-IOPS-09 surfactant solution, the percentage of iron oxide C sub-micrometre particles (0.8%) and sub 2 micrometre particles (11.4%) were both similar to the values for iron oxide B.

Iron oxides C and D in 4% Tween® 20 solution visualised some fingermarks with obscured detail in experiment 3. This may be because a 1:1 w/v powder suspension is excessive in powder when using iron oxides with higher percentages of fine particles. Of further interest is the brown colour of the fingermarks visualised with powder suspensions produced using iron oxide D. This colour difference, relative to the marks visualised with B and C iron oxide powder suspensions, may relate to other structural or chemical differences between the iron oxides not investigated in these studies.

The final study in this paper tested a 10% Tween 20 powder suspension with iron oxide powder C (1:2 w/v) against the C-IOPS-09 formulation prepared with the less effective Fisher Scientific powder (B). The 10% T20 (C) formulation visualised ~27% more fingermarks to identifiable quality (grade 3 or 4) than C-IOPS-09 (B). The use of Tween 20 at 10% dilution and half the usual load of iron oxide resulted in a powder suspension that was relatively easy to rinse off surfaces, and caused very few fingermarks (<2%) to be over-developed. Iron oxide C is a finer grade material than Fisher Scientific I/1100/53, as the product specification quotes a particle size range of 50-100 nm (SEM) [33]. It is anticipated that this product is less likely to present inter-batch variability issues, such as those demonstrated for the Fisher Scientific product in this work. This formulation, 10% T20 (C), hence represents a potential replacement for C-IOPS-09 with Fisher Scientific iron oxide I/1100/53. This formulation will need to be tested further before it can be recommended for operational use.

6. Conclusion

The studies in this paper show that two different batches of the recommended Fisher Scientific iron (II/III) oxide powder (from 2008 and 2015) perform differently in powder suspension. Initially it was determined that the 2015 batch of powder was unsuitable for use in the 1% C-IOPS-09 powder suspension formulation [7] due to resultant background staining. Furthermore, this batch was demonstrated to be less effective in the higher surfactant concentration C-IOPS-09 formulation (the iron oxide powder suspension currently recommended for operational use in the UK), because it visualised ~19% fewer fingermarks than powder suspension prepared with the 2008 powder in a comparative investigation. This difference in effectiveness is demonstrated to relate to the size distribution of the particles, particularly the quantity of particles between 0.5 µm and 1 µm, which are responsible for development of the fingermarks. The volume fraction of particles in this size range was shown to be 14.4% for the 2008 batch and 5.7% for the 2015 batch. This type of inter-batch variability may cause inconsistent iron oxide powder suspension performance in the operational setting.

The recently proposed 40% Tween® 20 surfactant solution [29] was demonstrated to be similarly effective to C-IOPS-09 surfactant solution when compared with the same batch of Fisher Scientific iron (II/III) oxide powder (2008 or 2015). However, a 4% Tween® 20 surfactant was found to be equally effective and has advantages in ease of application. Thus, Tween® 20 offers contingency for the iron (II/III) oxide powder suspension process in the event that Triton™ X-100 becomes restricted for use in the near future.

Reflecting the findings of importance of concentration of particle size below 1 micron and potential for use of Tween 20, a new powder suspension formulation using 10% Tween 20 surfactant solution and a Sigma Aldrich iron oxide nanopowder (50-100 nm), in the ratio of 1:2 w/v, was demonstrated to be 27% more effective than C-IOPS-09 prepared with the 2015 batch of Fisher Scientific iron oxide. The iron oxide nanopowder incorporated into this new formulation is anticipated to be more consistent between batches than the Fisher Scientific material, however more extensive testing is required. Further exploration of alternative surfactant solutions are to be encouraged and optimum concentration may have to be tuned to the specific iron oxide powder product in use.

Declarations of interest: none

Declarations

Declarations of interest: none

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Appendix

2009 CAST Iron Oxide Powder Suspension (‘C-IOPS-09’) [5]
- 20 g iron (II/III) oxide (precipitated)
- 20 mL stock detergent (surfactant) sol. (% by volume):
  - 25% Triton™ X-100
  - 35% ethylene glycol
  - 40% deionized water

Australian Iron Oxide Powder Suspension [29]
- 20 g iron (II/III) oxide (precipitated)
- 20 mL stock detergent (surfactant) sol. (% by volume):
  - 40% Tween® 20
  - 60% deionized water

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Figure 1 SEM image showing iron oxide particles on the ridge of a powder suspension-visualised fingermark, ranging from c.300 nm to 1 µm in diameter (with one particle above 1 µm).

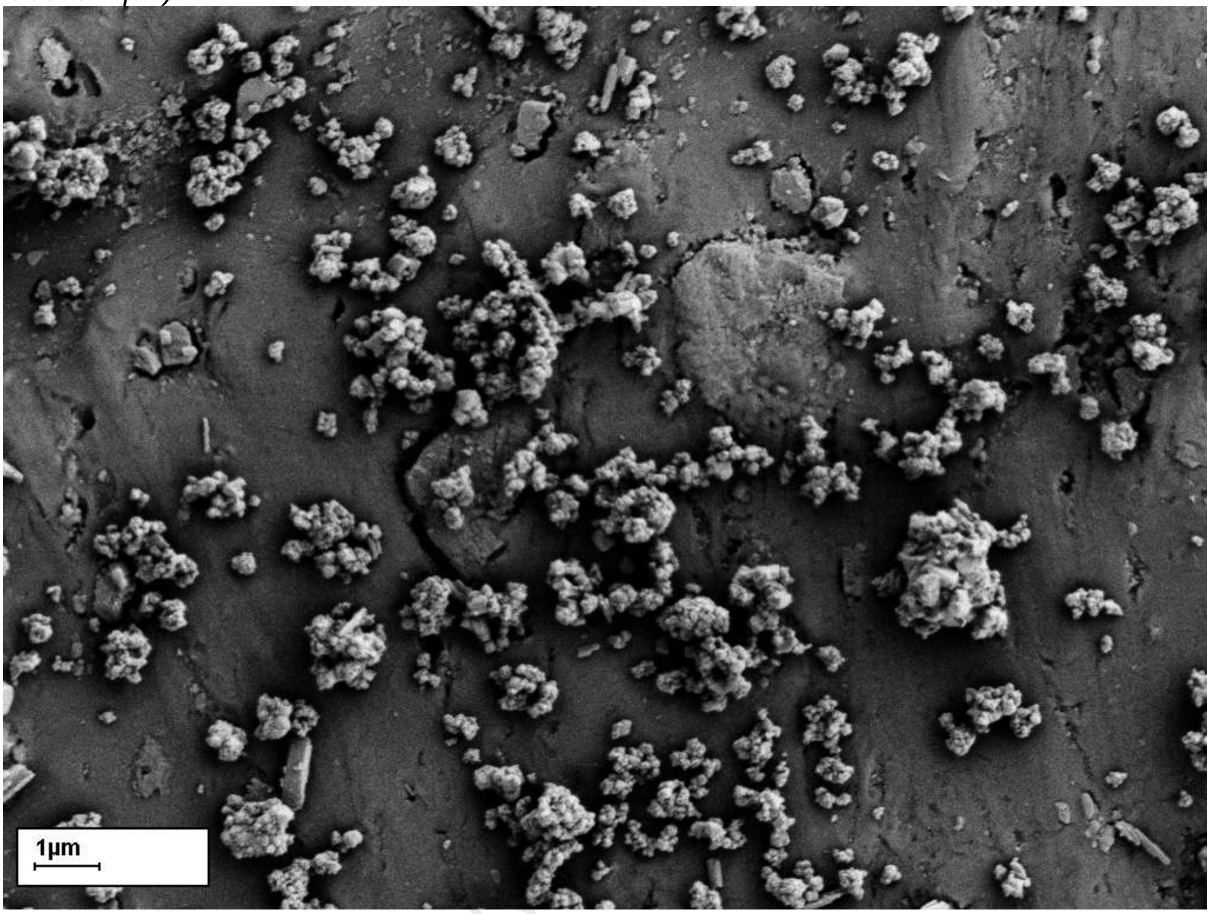


Figure 2 Relative surface staining of powder suspensions – experiment 1 overview

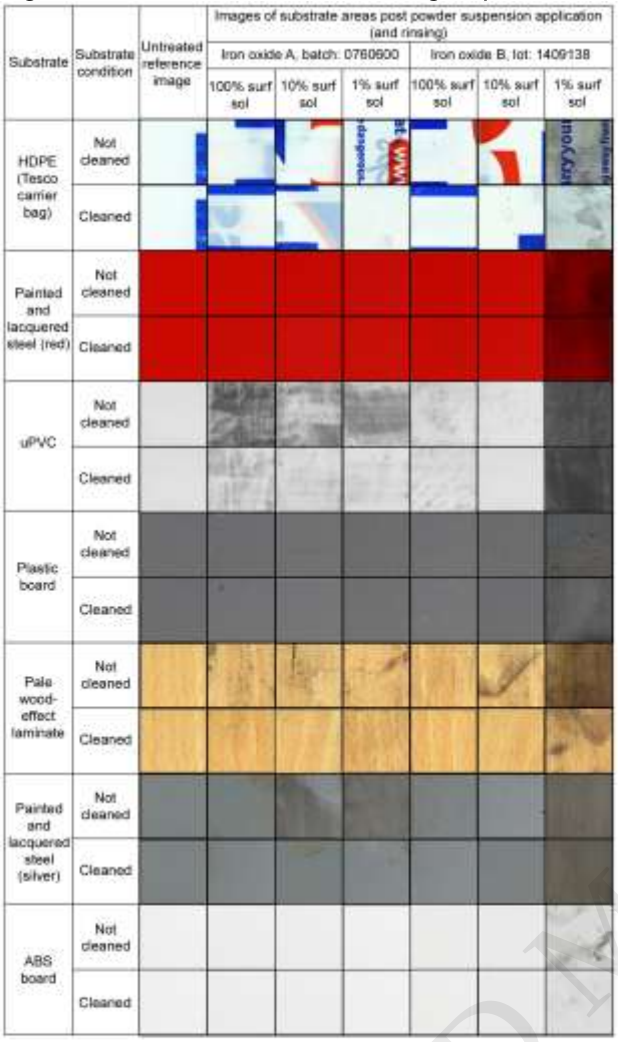


Figure 3 Combined data for Experiment 2 (all surfaces, both fingermark ages), primary experimenter's grades

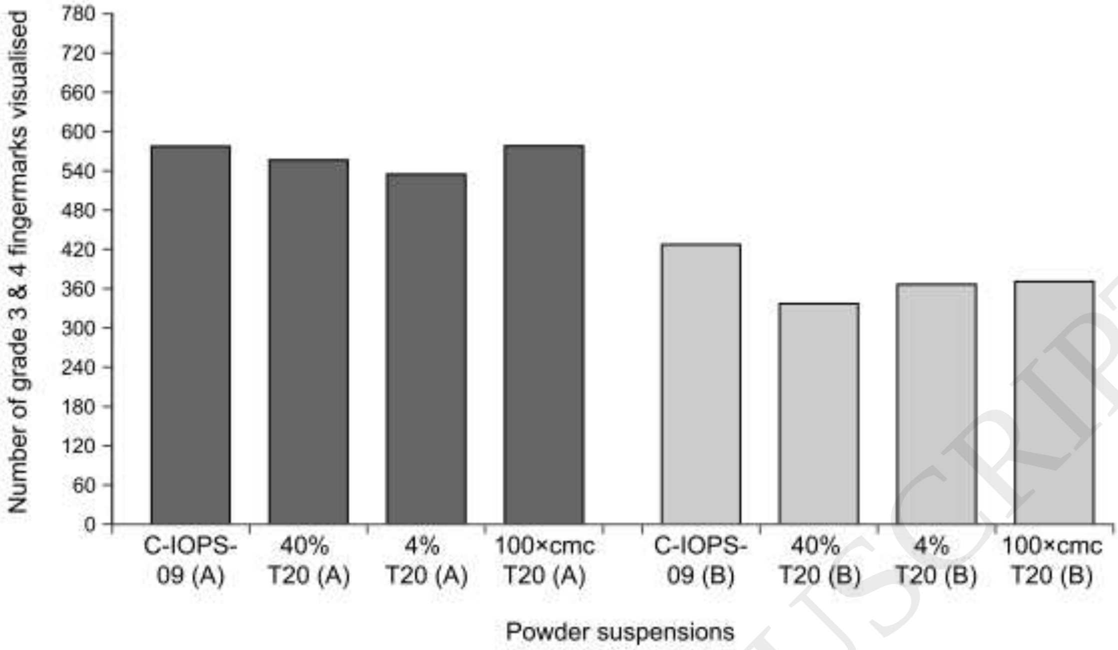


Figure 4 Overviews of ceramic tile and glass samples (7-day-old marks, first 5 depletions) processed with C-IOPS-09 and 4% T20 powder suspensions. The iron oxide powder A formulations yielded more contrasting marks.

Figure 5 Comparable processed 28-day-old fingermarks on glass (same donor and depletion number) from Experiment 2. Fingermarks on the top row were visualsied with powder suspensions produced with powder A: (i) C-IOPS-09 (A), (ii) 40% T20 (A), (iii) 4% T20 (A), (iv) 100×cmc T20 (A). Fingermarks on the bottom row were visualised with powder suspensions produced with powder B: (v) C-IOPS-09 (B), (vi) 40% T20 (B), (vii) 4% T20 (B), (viii) 100×cmc T20 (B).

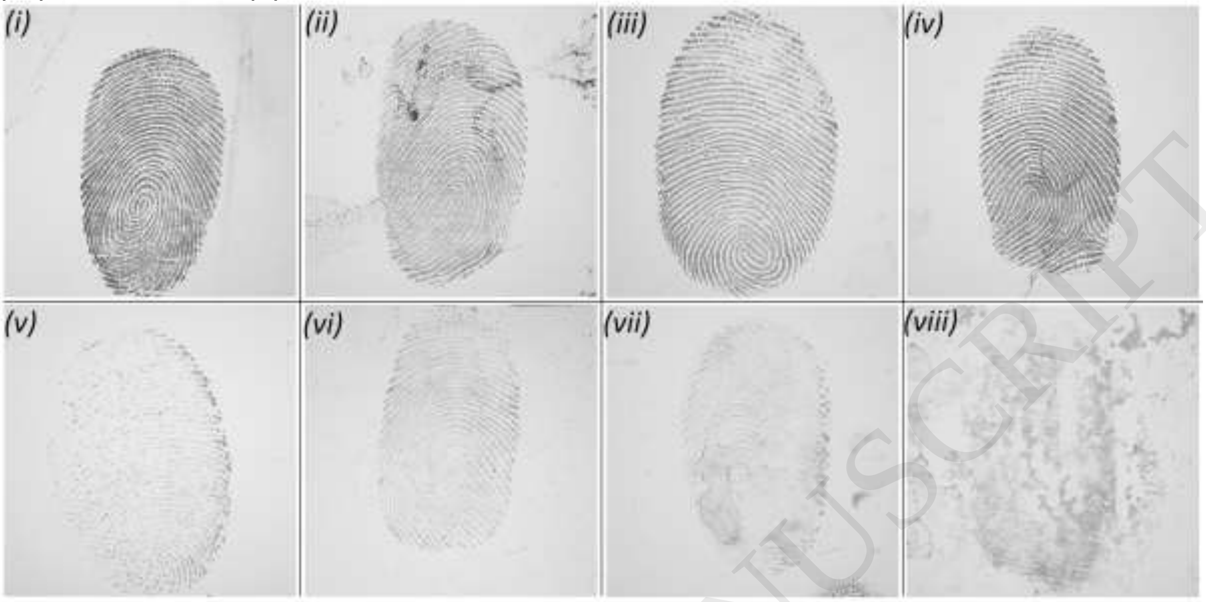
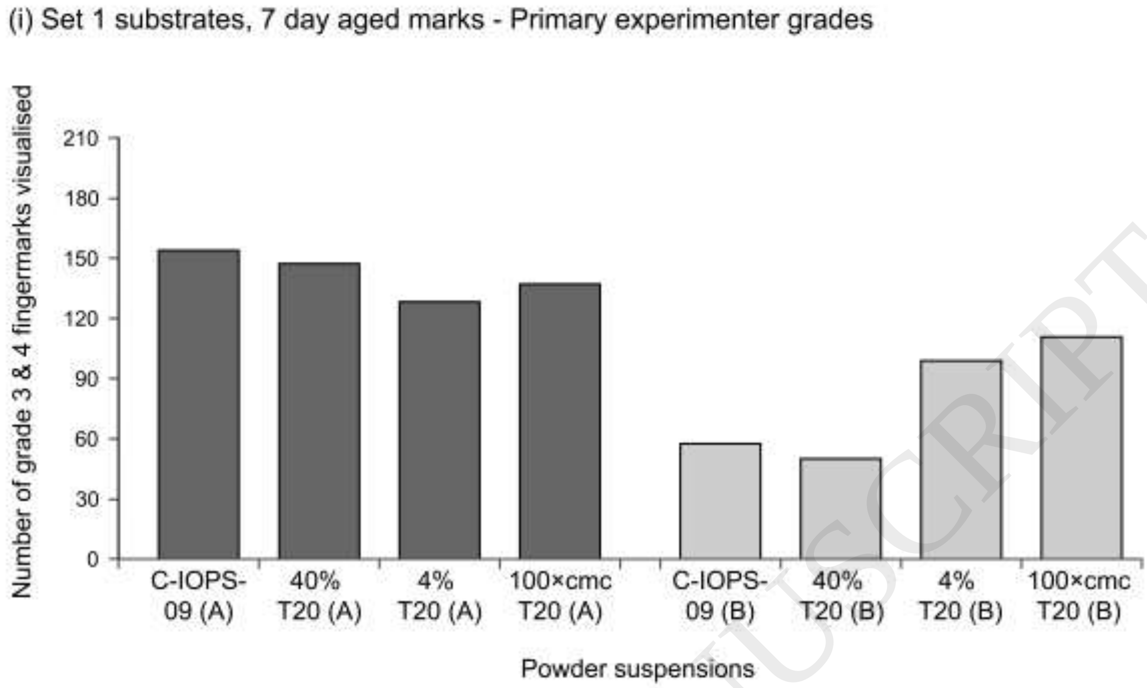
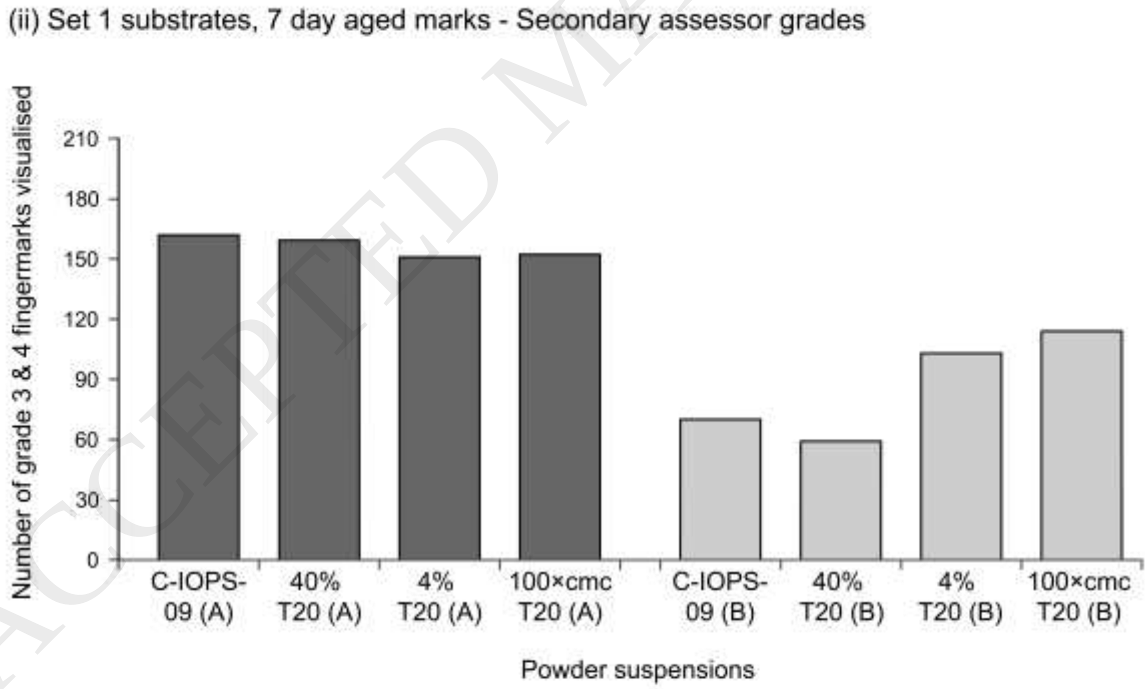
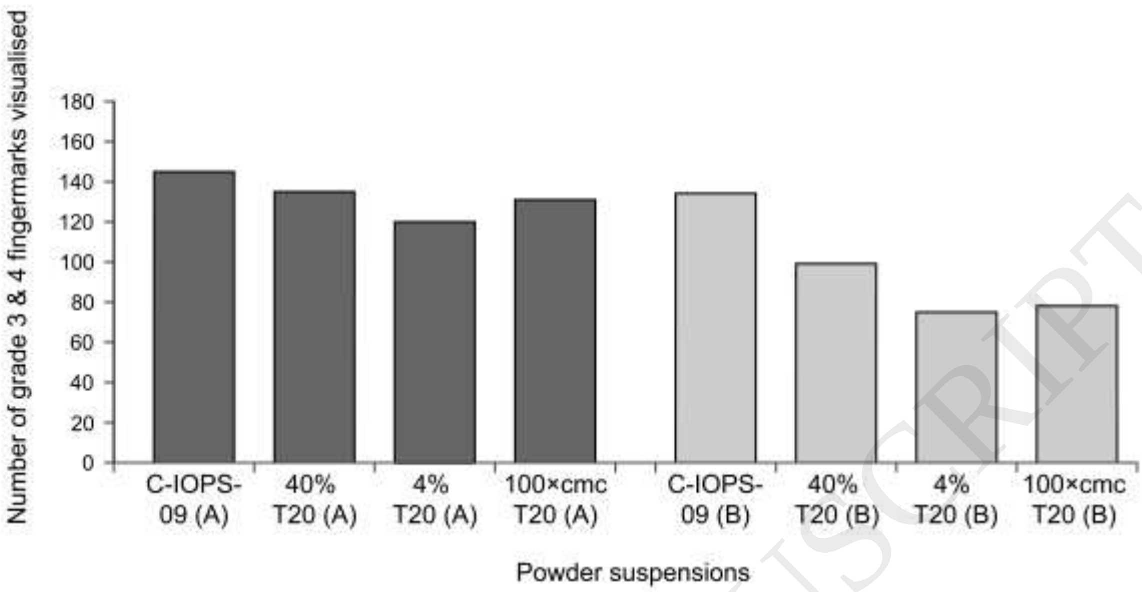


Figure 6 Trend comparison between the primary experimenter and secondary assessor for the set 1 sample group ((i) and (ii)) and the set 2 sample group ((iii) and (iv)).





(iii) Set 2 substrates, 28 day aged marks - Primary experimenter grades



(iv) Set 2 substrates, 28 day aged marks - Secondary assessor grades

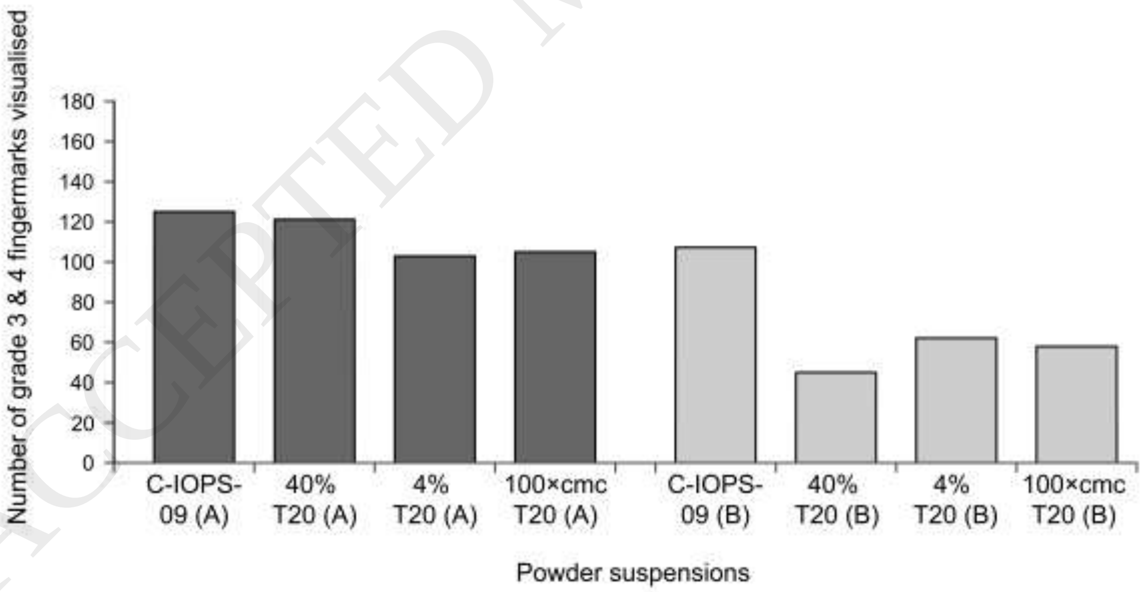


Figure 7 Comparison of different iron oxides (B, C and D – see Table 2) in C-IOPS-09 and 4% T20 powder suspensions on (i) ceramic tile and on (ii) painted steel (red).

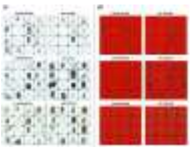
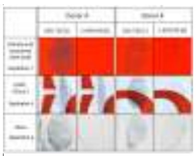


Figure 8 Examples of fingermarks visualised by 10% T20 (C) powder suspension and corresponding fingermarks visualised with C-IOPS-09 (B), drawing upon different substrates and depletion numbers. (i) Donors A and R, (ii) donors E and Q



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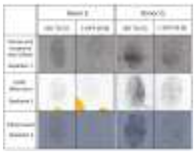

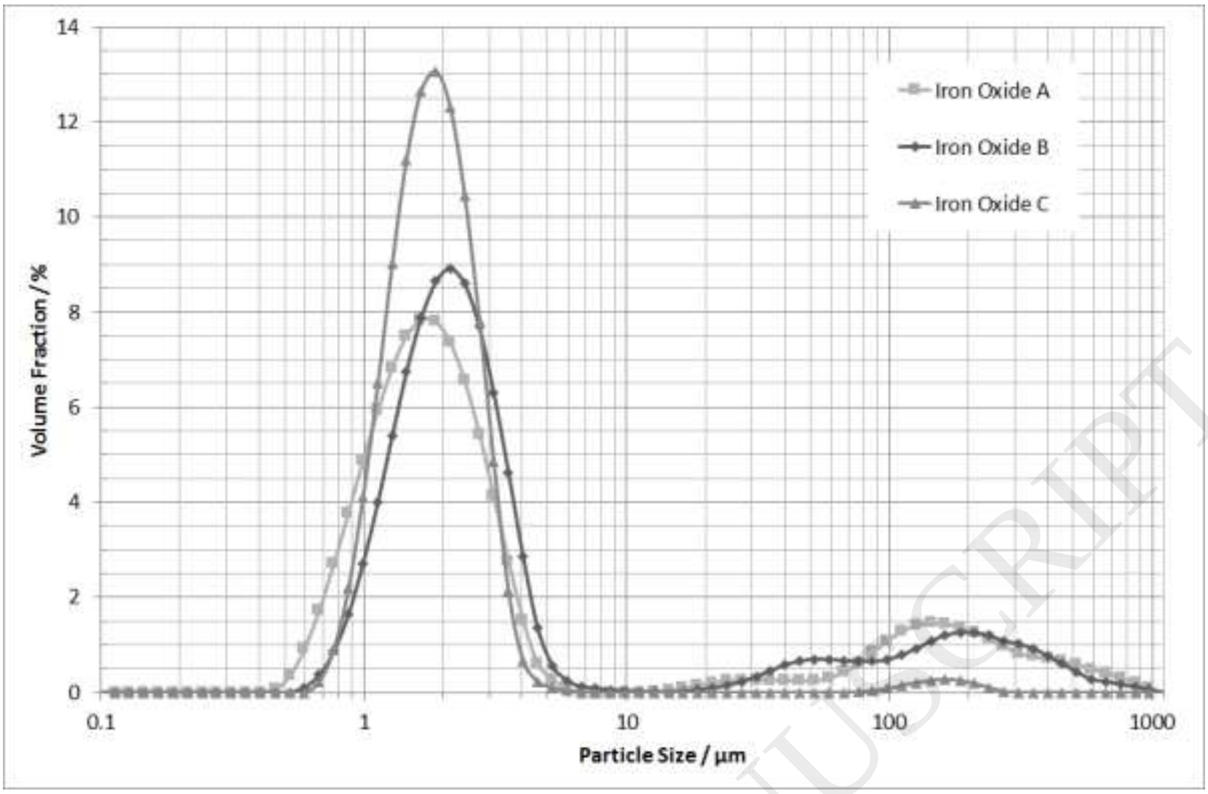

Figure 9
Mean measured particle size from powder samples in 4% Tween® 20 solution showing volume fraction of the material as a function of particle size.

Table 1
Substrate reference table.

Designation	Substrate	Colour	Experiment numbers involving this substrate
Substrate 1	Acrylonitrile butadiene styrene (ABS) board	White	1
Substrate 2	Pale wood-effect laminate ('Japanese beech')	Light brown	1
Substrate 3	Painted and lacquered steel	Red	1, 3, 4
Substrate 4	High density polyethylene (HDPE) Tesco carrier bag	White with blue and red print	1, 2, 4
Substrate 5	Unplasticized polyvinyl chloride (uPVC)	White	1, 2, 3, 4
Substrate 6	Painted and lacquered steel	Silver	1, 2, 4
Substrate 7	Plastic board	Grey	1, 2, 4
Substrate 8	Ceramic tile (gloss finish)	White	2, 3, 4
Substrate 9	Glass (clear, 'pro tough')	Colourless	2, 4
Substrate 10	HDPE Morrisons carrier bag	White with green print	4

Table 2
Iron oxide powder product details. The same container of each material was used throughout the experiments.

Powder Reference	Powder Product Name	Manufacturer / Supplier	CAS Number	Additional Details
A	Iron oxide, pure, magnetic, precipitated	Fisher Scientific	1317-61-9	Product code: I/1100/53 Packing date: 14/08/2008 Batch number: 0760600
B	Iron oxide, pure, magnetic, precipitated	Fisher Scientific	1317-61-9	Product code: 10385990 Manufacturer part number/code: I/1100/53 Packing date: 09/03/2015 Lot: 1409138
C	Iron (II/III) oxide, 50–100nm	Sigma Aldrich	1317-61-9	Product number: 637106 Product code: 1002164693 Particle size: 50–100 nm [33] Purchased: 2017 Lot: MKBT3736V
D	Bayferrox 318M	Lanxess / Bayferrox	1317-61-9	Synthetic, predominant particle size ~0.2µm [34] Sample provided: 2017

Table 3
Fingermark grading scheme.

Score	Level of detail
0	No evidence of fingermark
1	Evidence of contact but no fingermark ridge details
2	Less than 1/3 of the fingermark ridge detail is present
3	1/3 to 2/3 of the fingermark ridge detail is present
4	Over 2/3 of the fingermark ridge detail is present

Table 4
Powder suspension formulation details for Experiment 1 (surf sol = surfactant solution).

Powder Suspension Reference	Iron Oxide Powder (as per Table 2)	Surfactant Solution
100% surf sol (A)	A	C-IOPS-09 stock sol. (Appendix)
100% surf sol (B)	B	
10% surf sol (A)	A	10 ml C-IOPS-09 stock sol. 90 ml deionised water
10% surf sol (B)	B	
1% surf sol (A)	A	1 ml C-IOPS-09 stock sol. 99 ml deionised water
1% surf sol (B)	B	

Table 5
Powder suspension formulation details for Experiment 2.

Powder Suspension Reference	Iron Oxide Powder (as per Table 2)	Surfactant Solution
C-IOPS-09 (A)	A	C-IOPS-09 stock sol. (Appendix)
C-IOPS-09 (B)	B	
40% T20 (A)	A	40 ml Tween® 20 60 ml deionised water
40% T20 (B)	B	
4% T20 (A)	A	4 ml Tween® 20 96 ml deionised water
4% T20 (B)	B	
100×cmc T20 (A)	A	100 ml solution of 0.737g Tween® 20 in deionised water
100×cmc T20 (B)	B	

Table 6
Powder suspension formulation details for Experiment 3.

Powder Suspension Reference	Iron Oxide Powder (as per Table 2)	Surfactant Solution
C-IOPS-09 (B)	B	C-IOPS-09 stock sol. (Appendix)
C-IOPS-09 (C)	C	
C-IOPS-09 (D)	D	
4% T20 (B)	B	4 ml Tween® 20 96 ml deionised water
4% T20 (C)	C	
4% T20 (D)	D	

Table 7
Powder suspension formulation details for Experiment 4.

Powder Suspension Reference	**Iron Oxide Powder (as per Table 2)**	**Surfactant Solution**
C-IOPS-09 (B)	B	C-IOPS-09 stock sol. (Appendix)
10% T20 (C)	C	10 ml Tween® 20 90 ml deionised water

Table 8
The number of grade 3 and 4 fingermarks visualised by each powder suspension in Experiment 2, by substrate and ageing period, graded by the primary experimenter.

Substrate group	**Fingermark aging period**	**Substrate**	**Powder suspensions (iron oxides A and B, Table 2)**							
			C-IOPS-09		40% T20		4% T20		100×cmc T20	
			A	B	A	B	A	B	A	B
1	7 days	HDPE (Tesco)	61	30	52	22	41	45	47	50
		Plastic board	62	0	29	6	45	15	42	30
		Glass	31	28	66	22	42	39	48	31
	28 days	HDPE (Tesco)	55	38	43	30	53	37	56	28
		Plastic board	35	31	64	13	53	9	54	10
		Glass	60	52	49	40	44	38	65	48
2	7 days	uPVC	52	40	43	35	51	45	51	24
		Painted steel (silver)	40	35	35	40	48	38	50	37
		Ceramic tile	37	40	40	31	39	26	36	34
	28 days	uPVC	49	46	50	39	41	25	43	20
		Painted steel (silver)	40	39	39	25	39	30	38	19
		Ceramic tile	56	49	46	35	40	20	50	39

Table 8
The number of grade 3 and 4 fingermarks visualised by each powder suspension in Experiment 2, by substrate and ageing period, graded by the primary experimenter.

Substrate group	**Fingermark aging period**	**Substrate**	**Powder suspensions (iron oxides A and B, Table 2)**							
			C-IOPS-09		40% T20		4% T20		100×cmc T20	
			A	B	A	B	A	B	A	B
1	7 days	HDPE (Tesco)	61	30	52	22	41	45	47	50
		Plastic board	62	0	29	6	45	15	42	30
		Glass	31	28	66	22	42	39	48	31
	28 days	HDPE (Tesco)	55	38	43	30	53	37	56	28
		Plastic board	35	31	64	13	53	9	54	10
		Glass	60	52	49	40	44	38	65	48
2	7 days	uPVC	52	40	43	35	51	45	51	24
		Painted steel (silver)	40	35	35	40	48	38	50	37
		Ceramic tile	37	40	40	31	39	26	36	34
	28 days	uPVC	49	46	50	39	41	25	43	20
		Painted steel (silver)	40	39	39	25	39	30	38	19
		Ceramic tile	56	49	46	35	40	20	50	39

Table 9
The number of grade 3 and 4 fingermarks visualised by both powder suspensions in Experiment 4, by substrate.

Substrate	**Number of grade 3&4 fingermarks**	
	10% T20 (C)	C-IOPS-09 (B)
Painted steel (red)	77	38
HDPE (Tesco)	75	27
Upvc	48	33
Painted steel (silver)	84	51
Plastic board	64	40
Ceramic tile	72	47
Glass	94	71
HDPE (Morrisons)	85	58

Table 10

Mean volume fraction (%) of binned cumulative particle sizes of three powder formulations (A, B and C – see Table 2) in C-IOPS-09 and 4% Tween 20 solutions with standard error.

Particle size	C-IOPS-09 solution									4% Tween® 20 solution								
	A			B			C			A			B			C		
<1 µm	13.2	±	1.8	1.8	±	0.3	0.8	±	0.2	14.4	±	2.5	5.7	±	1.2	7.4	±	0.8
<2 µm	68.8	±	6.4	15.3	±	0.7	11.4	±	2.1	50.3	±	7.7	38.4	±	5.9	59.8	±	3.3
<5 µm	91.7	±	8.3	25.5	±	1.0	22.5	±	3.8	78.7	±	11.3	78.8	±	10.4	98.3	±	1.7
<10 µm	91.7	±	8.3	25.5	±	1.0	22.5	±	3.8	79.1	±	11.3	79.9	±	10.5	98.4	±	1.6
<20 µm	91.7	±	8.3	25.5	±	1.0	22.5	±	3.8	79.4	±	11.2	80.0	±	10.5	98.4	±	1.6
<50 µm	91.7	±	8.3	25.5	±	1.0	22.6	±	3.8	81.1	±	10.9	82.5	±	9.6	98.4	±	1.6
<100 µm	91.7	±	8.3	27.6	±	0.9	44.0	±	5.4	84.6	±	9.8	86.6	±	8.6	98.5	±	1.5
<200 µm	92.0	±	8.0	55.4	±	1.1	72.0	±	9.3	91.6	±	6.7	91.8	±	6.1	99.7	±	0.3
<500 µm	96.8	±	3.2	89.3	±	2.5	89.6	±	3.7	97.9	±	2.0	98.7	±	1.2	100.0	±	0.0
>500 µm	3.1	±	3.2	10.6	±	2.5	10.4	±	3.7	2.1	±	2.0	1.3	±	1.2	0.0	±	0.0