3.4 Ninhydrin

1. History

1.1 Ninhydrin was first synthesised by Ruhemann in 1910, and soon after this the development of a purple (‘dark blue’) reaction product was observed between the new compound and amino acids and proteins [1]. This reaction was further investigated by Adberhalden and Schmidt [2]; they tested a large number of compounds, both singly and in combination, in terms of the reaction products formed with ninhydrin. The purple reaction product was observed to form with proteins and polypeptides. Adberhalden and Schmidt also investigated the reactions with amino acids and different types of body fluid, noting that purple reaction products could be formed with sweat [3], and this could contaminate analyses unless it was ensured that reaction vessels, stirrers, etc. were clean.

1.2 The sensitivity of ninhydrin for proteins and amino acids resulted in its use for detection of amino acids by chromatography techniques and for quantitative measurements of amino acid contents. The first published suggestion that ninhydrin could be used for fingerprint detection was made by Oden and von Hofsten in 1954 [4] based on observations of fingerprints accidentally developed on paper items. They proposed a solution of ninhydrin dissolved in acetone and tested it on fingerprints deposited on a range of different types of paper. Oden later patented a refined formulation [5] that also included acetic acid and this soon became adopted worldwide as an alternative to the iodine and silver nitrate techniques then in use for detection of fingerprints on paper.

1.3 In 1969 Crown [6] proposed an alternative ninhydrin formulation based on petroleum ether solvent in place of acetone, with minor additions of methanol. Diethyl ether was also investigated as a solvent, but this was regarded as too volatile for spraying on documents because of the flammable atmospheres created. The reason for using these non-polar solvents was to minimise ink run on the documents being treated with ninhydrin, thus preserving evidence for subsequent document examination. Crown observed that the reaction could be accelerated by heating, but did not recommend temperatures in excess of 100ºC because this caused unwanted background reactions that could obscure prints. Crown also reported improved results when placing bowls of water in treatment ovens to produce more humid atmospheres.

1.4 Lesk [7] reported the use of both acetone and petroleum ether-based formulations in combination, with petroleum ether being used in most cases to minimise ink running. However, it was also observed that occasionally additional marks could be developed by retreatment of the article in the acetone-based formulation.

1.5 In the early 1970s the Police Scientific Development Branch (PSDB) contracted researchers at the Atomic Weapons Research Establishment

(AWRE) at Aldermaston to investigate improvements to chemical reagents then in use for fingerprint development. Ninhydrin was investigated as part of this contract. An initial observation was that the formulation developed by Crown [6] could be improved in sensitivity by the addition of acetic acid. In 1971/2 a police officer from the Kent constabulary contacted PSDB and asked whether one of the chlorofluorocarbon (CFC) solvents such as 1,1,2-trifluorotrichloroethane (CFC113) could be used as a safe solvent for ninhydrin. His idea was passed on to the AWRE team and as a result the so-called non-flammable, or new formulation, ninhydrin (NFN) was developed by Morris and Goode [8]. This solvent had the additional benefits that it minimised ink running when used to treat documents [8].

1.6 At about the same time Linde [9] observed that processing exhibits treated with ninhydrin in a high humidity oven at 60ºC gave superior results to dry treatment at 100ºC. At first this was not universally accepted. In comparisons of oven processing and treatment with a steam iron, Morris and Gray [10] noted that oven treatment was superior and specifically stated that the steam setting of the iron should not be used during processing. Despite this advice, and although not approved of by PSDB, a number of police forces, in particular Avon and Somerset, regularly used steam irons to speed up the ninhydrin reaction. The recommended procedure at the time was to put treated articles in a brown envelope and wait for three weeks, and the use of a steam iron gave results in a significantly shorter time. Jones and Pounds [11] reinforced the earlier work of Linde, presenting the beneficial effects of steaming exhibits for 10–15 seconds prior to heating in an oven at 80ºC for 3 minutes. Subsequent work by PSDB confirmed the importance of humidity for the optimum development of marks and found the optimum to be around 65% relative humidity [12]. PSDB worked with Gallenkamp around 1980/81 to modify one of their production humidity cabinets to provide rapid humidification for the ninhydrin process. Subsequently these were installed in all UK police forces.

1.7 Ways of adapting the ninhydrin reaction product began to be considered. The contrast between the developed mark and the background could be improved by using coloured filters, and green filters to enhance the purple mark were in common use by police photographers in the 1970s. Contrast between the fingerprint and the background could be improved by other means, and Morris found that post-treatment of the purple reaction product with different metal salts resulted in the formation of complexes with different colours, including blue, red, pink and orange [13]. The best results were obtained with the salts of zinc, cadmium and lead.

1.8 It was also found that marks developed using ninhydrin could be enhanced by illuminating the exhibit using light of a wavelength where the Ruhemann's purple product absorbed and the background fluoresced [14]. This was followed by the discovery that some of the coloured reaction products produced by treating purple ninhydrin marks using metal salts were fluorescent [15] and could be revealed using an argon ion laser [15] or an appropriately filtered xenon arc lamp [16]. It was also shown that the intensity of this fluorescence could be increased by cooling the exhibit to low temperatures using liquid nitrogen [16]. Subsequent researchers also investigated a wider range of metal compounds for complexation [17, 18] and concluded that zinc and cadmium gave products with the optimum fluorescence. It was also suggested that moisture and elevated temperature during processing were necessary to achieve the optimum fluorescence from the reaction products [19,20]. Rare earth elements were also proposed for metal complexation with ninhydrin, the long fluorescence decay time for toning elements such as Europium offering potential for use with techniques such as time-resolved imaging to reduce background fluorescence [21].

1.9 Researchers also began to synthesise analogues of ninhydrin, either to change the colour of the principal reaction product with amino acids, e.g. benzo(f)ninhydrin [11,22], or to give reaction products that gave greater fluorescence intensity when treated with metal salts, e.g. 5-methoxyninhydrin. Some of these analogues are covered in greater detail in Chapter 5.8, Ninhydrin analogues, but at the present time (2011) none have displaced ninhydrin in regular operational use.

1.10 The principal driver for further changes to the ninhydrin formulation arose as a consequence of the Montreal Protocols in 1987 banning the use of ozone depleting solvents, including CFCs. Researchers worldwide began investigating alternatives to the non-flammable ninhydrin formulation. In 1992 Jungbluth [23] proposed the use of a mixture of hydrochlorofluorocarbon (HCFC) and hydrochlorocarbon (HCC) solvents as a substitute to CFC113 in both ninhydrin and 1,8-diazafluoren-9-one (DFO) formulations. Lennard and Mazella [24] proposed reverting to a formulation based on petroleum ether with additions of methanol, acetic acid and ethyl acetate and reported that it gave superior performance to the CFC113 formulation. Watling and Smith [25] suggested using heptane as the primary solvent. However, both formulations presented the issue of solvent flammability and ideally a non-flammable formulation with equivalent (or better) performance to the CFC113-based system was required.

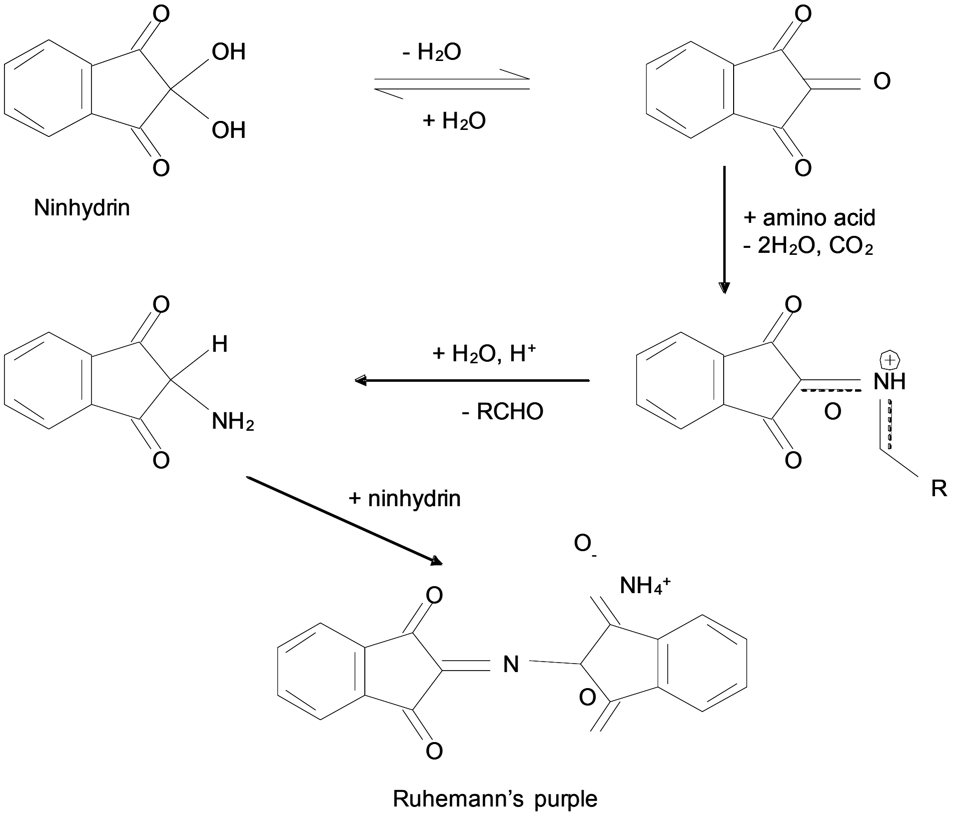
1.11 PSDB alerted the UK police forces to the potential issues that would be caused by phasing out CFCs, and began a comprehensive programme to identify replacement solvent systems. PSDB also investigated a range of alternative, solvent-less carrier systems including supercritical carbon dioxide (CO_2) [26]. The extensive CFC solvent replacement programme was conducted over 3 years and evaluated approximately 300 formulations to an initial stage, with several formulations taken through substantial operational trials. This programme considered the previously published formulations based on heptane and HCFC solvents, refining these formulations and comparing them with CFC113 [27]. A heptane-based formulation giving good results for fingerprint development was produced but was not considered safe to use because of the flammable atmospheres generated around articles that were apparently dry, and the large quantities of solvent that would need to be evaporated from ninhydrin-treated articles. Adoption of the heptane-based formulation would have required specially adapted cabinets and laboratories for safe working, and this was considered impractical. HCFC-based formulations caused excessive ink running and were not considered further.

1.12 The next classes of solvents investigated were hydrofluorocarbons (HFCs) and hydrofluoroethers (HFEs) and it was found that excellent results could be obtained from formulations based on two solvents, 2,3-dihydrodecafluoropentane (HFC4310mee) and 1-methoxynonafluorobutane (HFE7100) [28]. These out-performed the CFC113-based formulation in laboratory trials and therefore the evaluation proceeded to a full operational trial of all three formulations [29]. The results of this two-month study indicated that the HFE7100-based formulation gave the best results overall and this was recommended for operational use in the UK. Petruncio [30] independently reported results of a comparative study between HFC4310mee-, HFE7100- and petroleum ether-based formulations and found the HFC- and HFE-based systems gave better results in terms of the number of marks developed and reductions in ink run damage caused to treated documents.

1.13 As a consequence of this development work, the HFE7100-based formulation is currently (2011) the only one recommended for operational use by CAST, although work to investigate possible alternative solvents is ongoing.

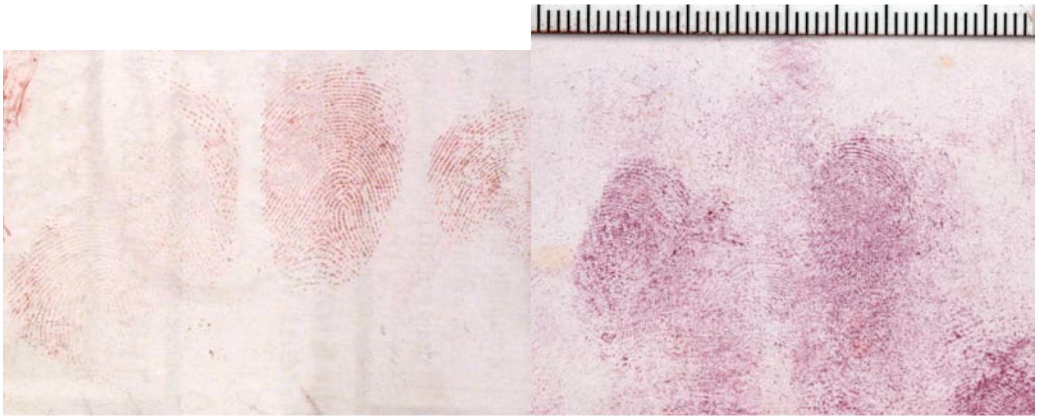
2. Theory

2.1 Many comprehensive studies of the reaction mechanisms, colour formation and kinetics of reaction have been carried out and published for the formation of Ruhemann's purple by reactions of ninhydrin with amino acids. These include the studies by McCaldin in 1960 [31]; Friedman and Sigel in 1966; Friedman and Williams (1974 [32,33]; Yuferov in 1971; [34] and most recently by Joullie *et al.*in 1991 [35]. Some of these papers propose detailed reaction mechanisms for ninhydrin with individual amino acids under different conditions, and seek to identify all intermediate forms that arise during the reaction. The reaction mechanism outlined below is typical of the generally accepted reaction pathway between ninhydrin and amino acids. For amino acids it is the amine group that ninhydrin is reacting with to form Ruhemann's purple, whereas the anomalous reactions that occur with other compounds do not proceed all the way to the formation of the purple product.

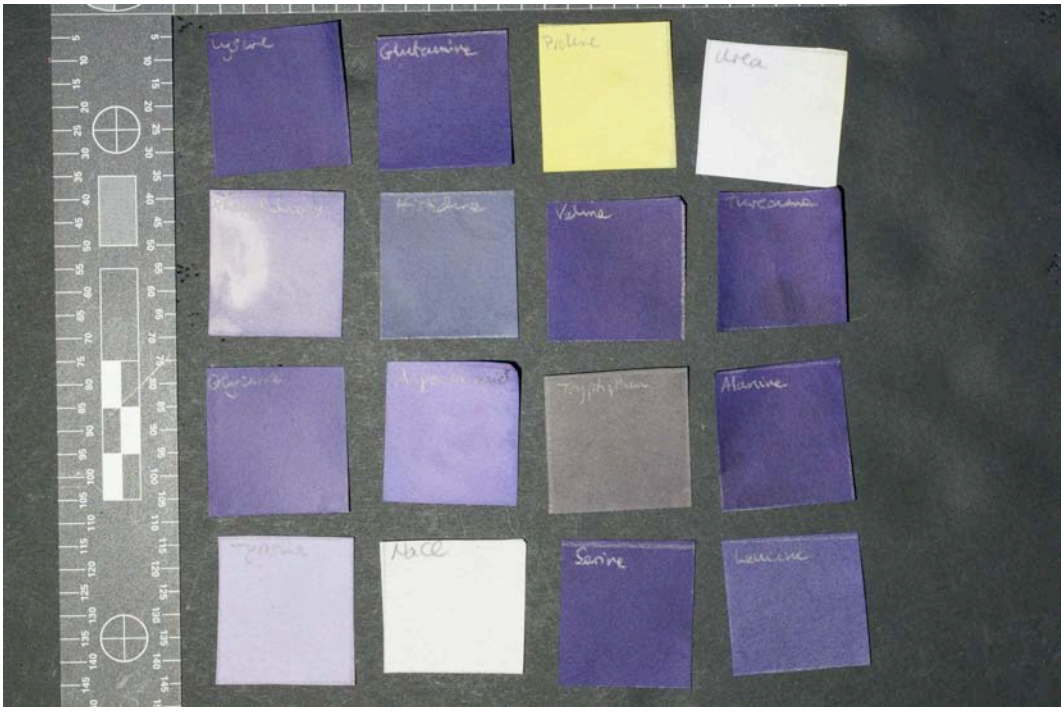


Generally accepted reaction pathway between ninhydrin and amino acids to form Ruhemann's purple.

2.2 The reaction products formed between ninhydrin and different amino acids are not all purple and the colour of the developed fingerprint can vary from nearly red to deep violet, depending on the composition of the fingerprint. Some examples are shown below. Another contributing factor to this difference in colour may be that the reaction above may not have proceeded to completion. There is a coloured intermediate (an imine or an aldimine) in the full ninhydrin reaction scheme that is also coloured, and the reaction may stop at this point if the acidity (pH) is not high enough. A pH of less than five is required for the reaction to proceed past the intermediate product, although if the pH is less than two the reaction proceeds to formation of the colourless hydrindantin product instead of to Ruhemann's purple. The colour of the intermediate imine compound is dependent on the R groups attached to the active species.

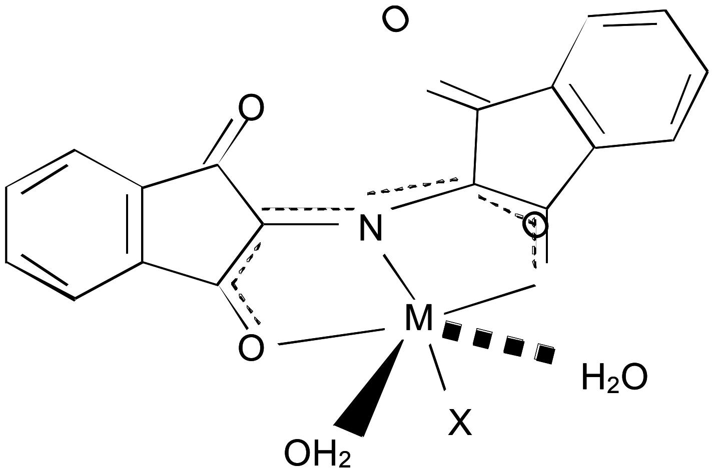


Fingerprints of differing colours developed by treatment using ninhydrin.



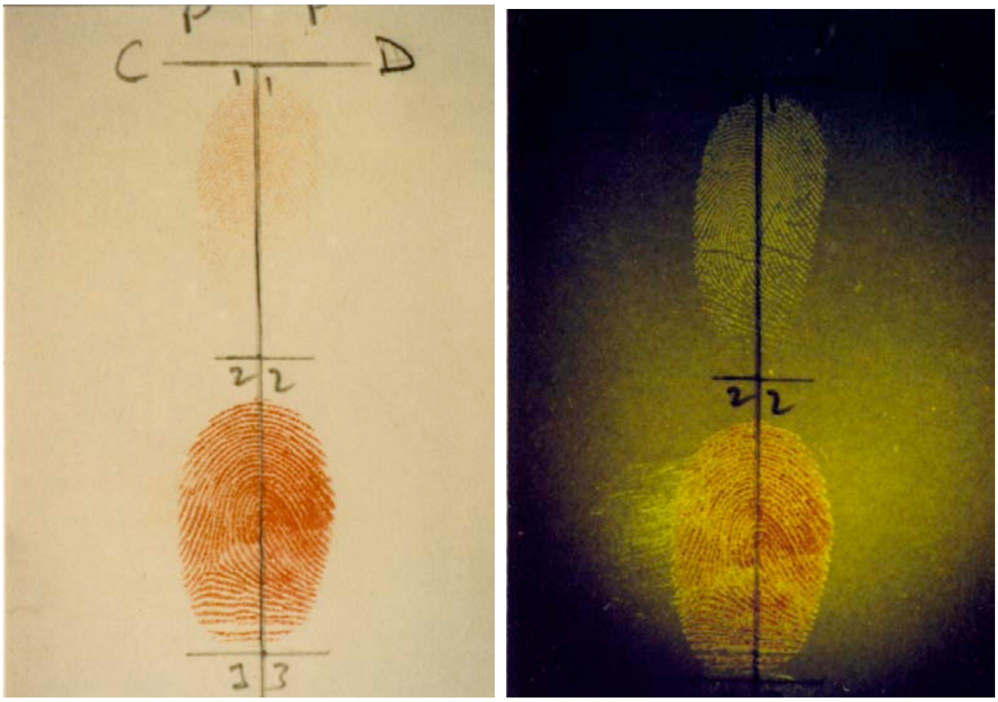
Reaction products formed between ninhydrin and 0.1M solutions of amino acids and other fingerprint constituents.

2.3 Studies have also shown that the subsequent complexation reaction with metal salts gives a complex of the generic structure below.



Complex formed between metal salt and Ruhemann's purple, in some cases giving rise to colour changes and fluorescence.

2.4 In the case of zinc and cadmium, the complexes formed are fluorescent in nature. The pictures below illustrate the visible appearance of marks treated with zinc chloride toning solution and the same marks when viewed using fluorescence examination. Studies by Australian researchers [20] identified two different coloured zinc/Ruhemann's purple complexes, one appearing orange and the other magenta/pink. The magenta/pink complex was found to be more fluorescent than the orange one, the differences being attributed to the amount of water bound into the complex. The importance of water in the formation of the more fluorescent complex makes humidification an important stage in the toning process.



a) b)

Ninhydrin marks toned with zinc chloride solution a) viewed under room lighting and b) viewed using fluorescence examination.

2.5 It should also be noted that ninhydrin does not only react with amino acids. A wide range of coloured reaction products can also be obtained from different amine-containing substances. Dent [36] carried out an extensive study in 1947 of 60 different compounds that reacted with ninhydrin, recording both colour of the reaction product and their natural occurrence. Although these substances react with ninhydrin the reactions cannot proceed to the Ruhemann's purple product because they do not have the structure to react beyond the coloured intermediate compounds. Cashman *et al.* [37] and Dutt and Poh [38] also report the use of ninhydrin for the detection of phenethylamines and other basic drugs, and some of these substances or their metabolites may occur in fingerprint residues. As a consequence, the reaction mechanism given above may not be the only one operating and ninhydrin may detect additional fingerprints that do not contain amino acids.

3. CAST processes

3.1 The process currently (2011) recommended by HOSDB involves the initial preparation of a concentrated solution, followed by the preparation of a working solution when required. This is because the working solution only has a limited stability in air before precipitation occurs.

3.2 The concentrated solution is produced by weighing 25g of ninhydrin and stirring 225mL of absolute ethanol into it to form a slurry. To this should be added 10mL of ethyl acetate and 25mL of acetic acid to form a clear yellow concentrated solution, which should be stored in a cupboard.

3.3 To produce the working solution, 52mL of concentrated solution should be measured out and 1 litre of HFE7100 added to it. This solution is then poured into a shallow tray and exhibits either pulled through it with forceps or immersed for a maximum of five seconds. Treated articles are then allowed to dry on a sheet of cardboard before being placed into a humidity-controlled oven at 80ºC and 65% relative humidity for a time that will depend on the particular conditions during loading of the oven, but that will typically be between five and seven minutes. Developed fingerprints can be photographed immediately but further marks will continue for up to 2 weeks (although additional marks have still been observed to develop after 13 weeks in some cases) during which exhibits should ideally be kept in the dark. The time marks take to develop is dependent on the surface and may be related to the pH because more acidic papers, such as cheques, generally develop more marks.

3.4 The role of the constituents in the CAST formulation can be identified as follows.

3.5 Ninhydrin is the principal active component and reveals fingerprints by means of the (primarily) purple product formed in its reactions with amino acids and proteins. It has limited solubility in the main carrier solvent and is present in as high a concentration as possible without making the working solution rapidly unstable.

3.6 Ethanol is required to ensure solubility of ninhydrin in the carrier solvent.

3.7 Ethyl acetate is added as a co-solvent to inhibit the esterification reaction by shifting its equilibrium towards formation of ethanol and acetic acid, thus preventing water droplet production during processing, which may diffuse fingerprint ridges.

3.8 Acetic acid and water are required to catalyse the reaction of ninhydrin with amino acids, the water being supplied in a controlled manner in the humidity oven. The acetic acid content is kept as low as possible to minimise any ink diffusion on documents being treated, but there is also a balance to be achieved in having sufficient acid present to ensure the reaction proceeds to the formation of Ruhemann's purple. This is of particular relevance for alkaline paper types, such as magazine pages, which have high filler contents and may remove the hydrogen ions provided by the acetic acid [27].

3.9 HFE7100 is the main carrier solvent for ninhydrin and meets the criteria of being non-toxic, non-flammable and causing minimal damage to documentary evidence. It is, however, expensive and the use of specially designed shallow dipping trays is recommended to minimise the volumes of solution required.

3.10 Heating accelerates the reaction and the development of fingerprints, but temperatures in excess of 100ºC may cause unwanted background reactions and possibly damage to the paper.

3.11 PSDB carried out studies into the effect of humidity on processing in the late 1980s/early 1990s [12] which indicated that settings producing 65% relative humidity in the treatment areas of the oven gave the best results. These results are summarised in section 8 below.

3.12 If toning is to be carried out after development of marks, CAST recommends the use of a zinc chloride-based toning solution, produced by mixing 50mL of ethanol, 10mL of propan-2-ol, 10mL of acetic acid and then stirring in 6g of zinc chloride. To this is added 200mL of HFE7100 (used as a direct replacement for the CFC113 in the original formulation), stirring to produce a clear solution. This solution is then sprayed lightly over the marks and they are retreated in the humidity oven at 80ºC and 65% relative humidity.

Zinc chloride solution being applied to an exhibit.

3.13 PSDB also carried out studies into the effectiveness of zinc toning [39] and confirmed the observation that humidity was required to accelerate the complexation reaction with the metal salt [20]. The approximate times for the formation of the orange complex are given below.

Relative humidity	42	47	56	57	60	78	83
Development time	> 1 hr	> 1 hr	< 5 mins	< 5 mins	< 5 mins	< 1 min	< 1 min

Approximate development times for different treatment temperatures.

3.14 Zinc chloride is preferred over cadmium salts for producing fluorescent marks because of the toxicity issues associated with the use of cadmium.

4. Critical issues

4.1 In common with many of the chemical development processes there are several important issues to consider when using ninhydrin.

4.2 The reaction will proceed under conditions of room temperature and humidity, but will be considerably accelerated and enhanced by the use of elevated temperature (80°C) and humidity (65%). Treatment at temperatures over 100°C may cause excessive background development. Design of the humidity oven is critical. Since the exposure time required is relatively brief, about 3 minutes, it is essential that the humidification system provides a substantial quantity of water vapour immediately after the door is closed otherwise the true exposure time will be unknown. Many humidity cabinet designs are constructed for long term environmental testing and do not have this required rapid umidity and temperature recovery time.

4.3 Marks developed using ninhydrin may begin to fade and should be imaged as soon as possible after development. Conversely, marks may continue to develop on items treated using ninhydrin for several days afterwards, and items should be re-examined after two weeks.

4.4 Cloudy solutions or solutions that have separated into oily droplets should not be used to treat articles and must be discarded.

4.5 Ninhydrin cannot be used to treat articles known to have been wetted because the amino acids targeted by the reagent will have been washed away.

5. Application

5.1 Suitable surfaces: Ninhydrin is suitable for use on all porous surfaces including paper, cardboard, raw wood and matt painted walls.

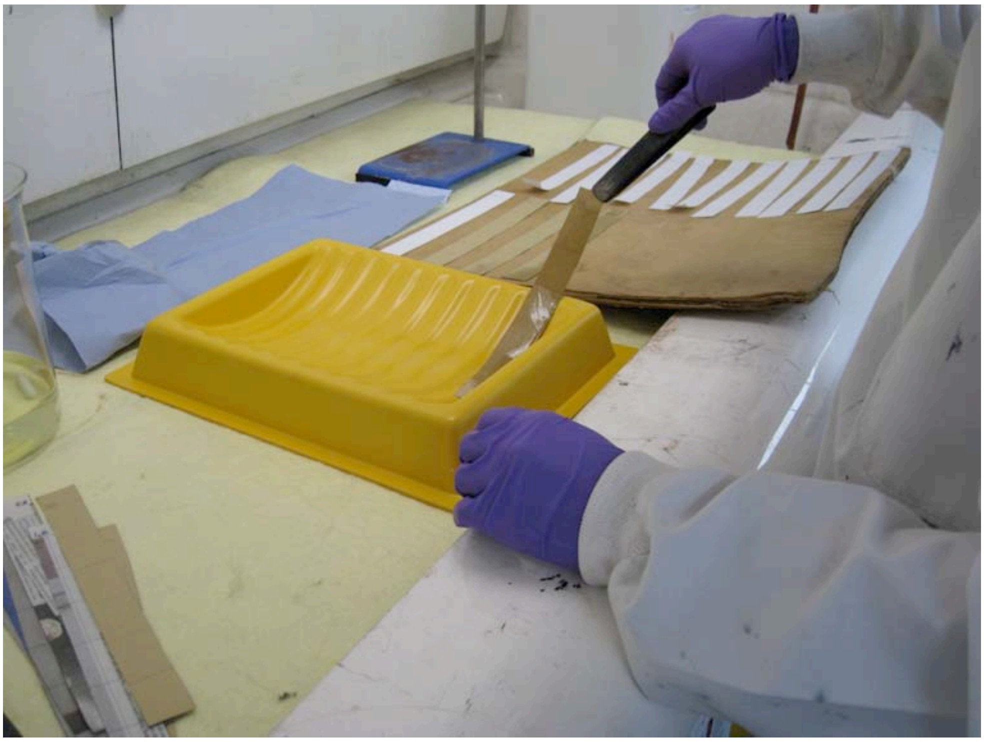
5.2 Ninhydrin is the most widely used process around the world for the development of fingerprints on porous surfaces. This is not because it is the most effective process – DFO and 1,2 indandione will develop higher numbers of marks overall [40,41], but the reason ninhydrin is so widely used is because it develops visible marks that can be quickly and easily captured using a range of equipment (e.g. cameras, scanners, photocopiers). It is thus well suited to applications in volume crime, where it is necessary to process large numbers of exhibits rapidly and it is considered that DFO treatment and subsequent fluorescence examination is too time-consuming. However, caution should be exercised if ninhydrin is to be used in this way because a) it is less effective than other processes and b) marks continue to develop up to two weeks after treatment. Potentially identifiable marks will missed for these reasons if ninhydrin is used as the sole process.

5.3 Ninhydrin is best suited to be used as part of a sequential processing regime for porous exhibits. Although it is not as effective as DFO, it will regularly develop additional marks if used sequentially after it because the DFO reaction with amino acids does not proceed to completion and some residue will be left to react with ninhydrin. In addition, ninhydrin may react with some non-amino acid compounds that may be present in fingerprints, which are not targeted by DFO. Use of ninhydrin does not preclude subsequent treatment of the exhibit with physical developer.

5.4 Ninhydrin will also react with proteins and can be used for the enhancement of marks in blood on porous surfaces. It will not be possible to determine whether a mark is actually in blood by this method alone, but ninhydrin can be used as a sensitive enhancement reagent if blood is known to be present. The application of ninhydrin for the enhancement of marks in blood has not been found to be detrimental to the subsequent recovery of DNA [42, 43].

5.5 If ninhydrin has been applied, it is not possible to go back and retreat an exhibit using DFO so if a mark has been developed on a surface where it may subsequently benefit by converting the mark to a fluorescent product the zinc toning process can be applied. Examples where this may be relevant are banknotes treated by ninhydrin, where parts of the developed mark are obscured by patterned backgrounds. However, previous work by CAST [39] indicates that zinc toning is only truly effective on predominantly white backgrounds that do not fluoresce. Cooling the marks to liquid nitrogen temperatures was sometimes also required to optimise the fluorescence viewed.

5.6 Ninhydrin is a versatile process and can be applied both in a laboratory and at scenes of crime. In a laboratory thin paper exhibits can be drawn through a shallow tray and allowed to dry before processing in a humidity-controlled oven. A recommended specification for a humidity oven suitable for developing marks on articles treated with ninhydrin is given in the *Manual of Fingerprint Development Techniques* [44].



Use of a shallow dipping tray for treatment of paper items with ninhydrin.

5.7 Small paper items should be placed into the oven and treated on sheets of cardboard. This minimises the time taken to load the oven and also avoids direct contact with any condensation that may have formed on the shelves. Treatment time for exhibits will vary according to the time taken for the oven to recover the temperature and humidity levels once the door is opened to insert exhibits and then closed. This can be recorded for a particular oven, and the treatment time used will be the recovery time plus two minutes. This typically results in a treatment time of between four and seven minutes. It is recommended that the oven parameters are regularly checked to ensure that the temperature and humidity values are being displayed accurately, and that the wick in the oven is checked before each run to ensure that it is moist.

5.8 For larger articles that can be fitted into the humidity oven but cannot be drawn through the dip bath, the ninhydrin solution can be applied with a soft brush and the exhibit allowed to dry before treating it in the oven. If articles are particularly dense (e.g. cardboard, wood or plasterboard), they should be heated before being placed in the humidity oven to ensure that the entire exhibit reaches the required reaction temperature and to prevent a thin layer of condensation forming on the surface. The formation of such a layer may have the detrimental effect of diffusing the amino acids in the latent fingerprints. A pre-heating stage in a dry oven at 80°C for 1 hour is recommended.

5.9 Ninhydrin solution can be used at scenes, again using a soft brush to apply it to the surface being treated. The marks produced in this way may require time (up to two weeks) to develop. Development rate can be increased by raising the temperature in the room and increasing humidity if possible. Ninhydrin should never be spray applied at scenes; spray application is less effective and the solvent, although not toxic or flammable, may rapidly displace oxygen if used in this way.

5.10 Ninhydrin solution will keep for 12 months if stored at room temperature, although any solution appearing cloudy should be discarded. Precipitation of ninhydrin from the working solution will occur with time after exposure to air. This is attributed to the fact that as the HFE7100 evaporates it lowers the temperature of the solution to a point where ninhydrin precipitates. As a consequence, the solution should only be poured out immediately before treating the articles. The ninhydrin working solution should be discarded after use.

5.11 Articles to be treated with ninhydrin should not be stored in high humidity environments (e.g. in non-porous bags with other damp articles) as this will cause diffusion of amino acids. After treatment articles should be kept in the dark because developed marks may fade on exposure to light. For this reason developed marks should be photographed as soon as possible after treatment, but because additional marks may continue to develop the article should be re-examined after ten days.

6. Alternative formulations and processes

6.1 Formulations for standard papers

6.1.1 Many other ninhydrin formulations have been proposed since its first reported use for fingerprint development in 1954. The formulation first used by Oden and von Hofsten [4] in1954 consisted of a 0.4% solution of ninhydrin in acetone. Oden (1957) patented a revised formulation consisting of 0.2% ninhydrin and 4% acetic acid in acetone or diethyl ether. These formulations would not be recommended by CAST because of the ink running that would potentially be caused by the solvents, combined with their high flammability.

6.1.2 The formulation proposed by Crown in 1969 [6] consisted of 7.5g ninhydrin in 40mL methanol, then the addition of 960mL of petroleum ether. The main purpose of this formulation was to reduce the damage caused to documents by the acetone solvent. The formulation satisfied these criteria, but again is based on a highly flammable solvent and would not be recommended by CAST. The absence of acidity in the formulation would also reduce effectiveness.

6.1.3 The non-flammable ninhydrin (NFN) formulation developed by AWRE under contract to CAST in the early 1970s consisted of 25g ninhydrin, 50mL acetic acid, and 100mLethanol mixed to form a stock solution. Subsequently, 30mL of stock solution was added to 1 litre of CFC113 to give a working solution. This equates to 5g ninhydrin, 10mL acetic acid, 20mL ethanol, and 1 litre CFC113 in the working solution. This was the formulation published in the first edition of the *Manual of Fingerprint Development Techniques* [45] and continued to be recommended until 2002, when it was replaced by the HFE7100 formulation. It would not now be used because the use of CFC113 is banned under the Montreal Protocol.

6.1.4 Studies by PSDB indicated that supercritical CO_2 could be used as a solvent for ninhydrin [26], with the advantage that the solvent caused minimal damage to the document being treated. However, specially built reactors were required to produce the supercritical CO_2 and it was considered unlikely that these would produce sufficient material for the processing of large numbers of exhibits.

6.1.5 Another formulation that is in operational use is the formulation based on petroleum ether solvent proposed by Lennard and Mazella [24]. This is formulated by dissolving 4g of ninhydrin in 20mL methanol, adding 10mL of acetic acid and 70mL of ethyl acetate, then adding 900mL of petroleum ether. CAST would not recommend this formulation because of the flammability of the solvent, but other researchers have indicated that similar ninhydrin formulations based on petroleum ether also give inferior results in terms of fingerprints developed and the effect on the documents being treated.

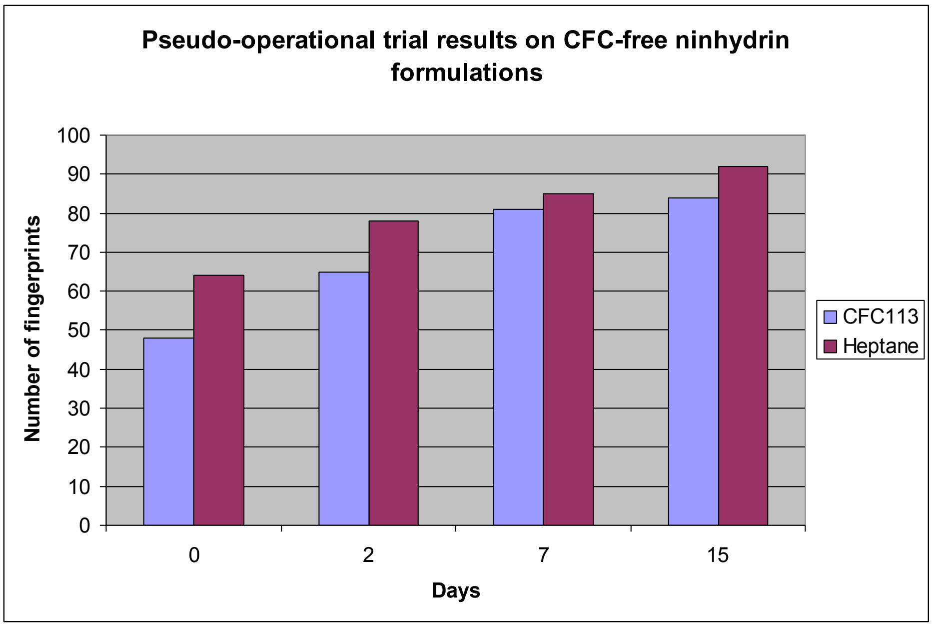
6.1.6 In the comparative study carried out by Petruncio [30], a ninhydrin formulation consisting of 5g ninhydrin, 20mL methanol, 10mL acetic acid and 1 litre petroleum ether was trialled against the PSDB formulations based on HFE7100 and HFC4310mee. The study compared ink run and contrast and clarity of latent prints, and produced the results below.

	HFE7100 better	Equal	Pet. ether better
Latent print quality	47.8%	45.6%	6.7%
Ink run	33.3%	66.7%	0%

	HFC4310 better	Equal	Pet. ether better
Latent print quality	48.9%	45.6%	5.6%
Ink run	41.7%	58.3%	0%

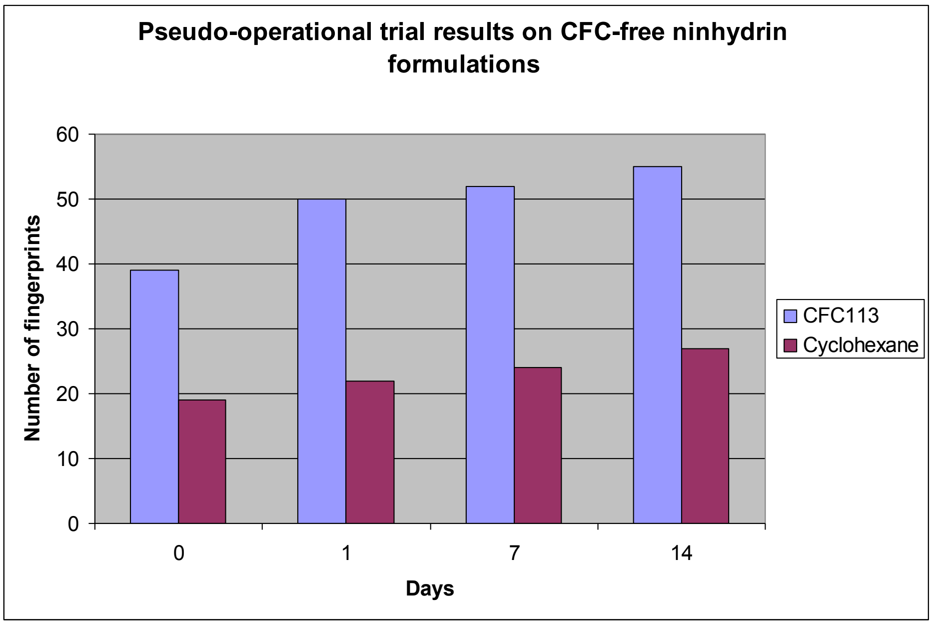
Comparison of the effectiveness of HFE, HFC and petroleum ether-based ninhydrin formulations.

6.1.7 Other comparative trials conducted by PSDB in the search for a CFC113 replacement used the heptane-based formulation proposed by Watling [25] as a starting point for an optimised heptane system [27]. This comprised 5g ninhydrin, 75mL ethanol, 25mL ethyl acetate, 3mL acetic acid and 1 litre heptane, and performed well against the CFC113 formulation. However, at the time it was not recommended by PSDB because of its high flammability.



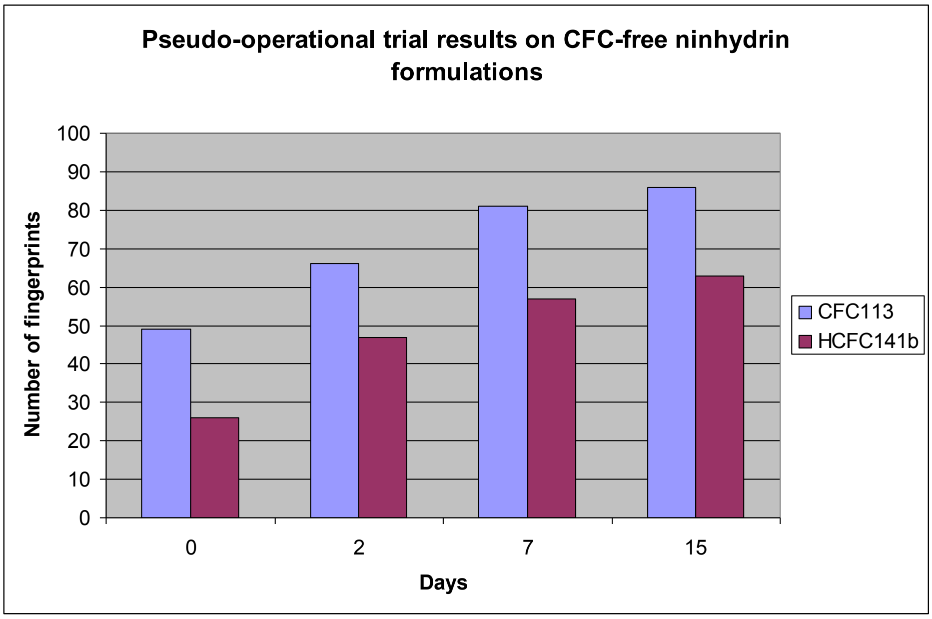
Comparative test results on batches of 75 cheques for different ninhydrin formulations.

6.1.8A cyclohexane-based solution was also developed, containing 5g ninhydrin, 20mL ethanol, 10mL propan-2-ol, 10mL acetic acid and 1 litre cyclohexane. In trials, this was significantly worse than the CFC113 formulation and was not recommended.



Comparative test results on batches of 75 cheques for different ninhydrin formulations.

6.1.9The final class of solvents assessed in the initial phase of solvent replacement studies were the HCFCs [27] and the following formulation was identified for trial: 5g ninhydrin, 15mL ethanol, 5mL ethyl acetate, 10mL acetic acid, 1 litre of HCFC141b. In comparative trials this did not perform as well as the CFC113 system, caused more ink running and there were concerns at the time that HCFCs would also ultimately be banned. As a result, the formulation was not pursued further.



Comparative test results on batches of 75 cheques for different ninhydrin formulations.

6.1.10Although effective, the cost of the HFE7100 solvent makes the volume use of ninhydrin expensive and if cheaper, similarly effective, alternatives were to be identified this would assist police forces in cost savings. CAST has recently been assisting in research conducted by police laboratory staff to evaluate novel, cheaper solvent systems and further work is anticipated. The system showing most promise to date is Asahiklin AE-3000, produced by the Asahi Glass Company in Japan [46]. This was originally projected to be priced around 30% less than HFE7100, but more recent estimates by the supplier indicate that there will be little, if any, cost savings.

6.2 Formulations for thermal papers

6.2.1A modified formulation has been proposed by CAST for the treatment of thermal receipts [47]. When thermal receipts are treated with ninhydrin they blacken due to reaction between acetic acid and the thermal ink layer. Blackening also occurs due to the heat applied to the exhibit in the oven used to develop marks. To counteract this, CAST carried out trials and devised a formulation with an additional 45mL of ethanol added per litre. This dissolves away the thermal ink layer and significantly reduces subsequent blackening. The thermal paper is retained in the dip bath until all the black deposit is removed from the surface of the paper, then placed into the oven. In practice, this did reduce the problems associated with blackening of thermal receipts but as ink compositions changed it did not prove possible to remove all of the ink layer easily in this way. Pre-dipping the receipt in ethanol until all the text is removed and then allowing it to dry prior to dipping in a solution of the standard formulation has proved more effective [48].

6.2.2 Two other ninhydrin formulations have been proposed for the development of fingerprints on thermal papers. In the ‘Nin-Dry’ process proposed by McMahon [49], 30–50g of ninhydrin is dissolved in 1.5 litres of acetone and this solution is used to impregnate sheets of paper by soaking the paper and then letting it dry in a vented fume cupboard. The document to be treated is placed between two impregnated sheets of paper in a sealed plastic bag and left for three to seven days. If faster development is required, the sandwich of document and impregnated paper sheets can be covered in a moist towel and an iron used to apply gentle heat and humidity.

6.2.3 The final process is the commercially available ‘ThermaNin’ product marketed by BVDA, which consists of a hemiketal of ninhydrin with the water molecule exchanged for an alcohol. On contact with the water present in paper (or in the atmosphere) ThermaNin converts to ninhydrin The combination of alcohol and the ninhydrin then becomes available for reaction with the fingerprint residues. The working solution suggested by BVDA consists of 4–5g ThermaNin, 5mL propan-2-ol, 15mL ethyl acetate and 980mL of HFE7100 (petroleum ether or heptane may be used as alternatives). Fingerprints are developed by dipping the exhibit in the solution and leaving the exhibit overnight at elevated humidity (~80% relative humidity), at room temperature in the dark. Thermal papers treated in this way retain all printed text while developing the characteristic purple fingerprints. CAST has initiated a comparative trial between ThermaNin and other techniques capable of developing fingerprints and leaving printed text intact [50]. The results of this exercise are summarised in Chapter 5.2, 4-Dimethylaminocinnamaldehyde (DMAC), but ThermaNin performed well, giving results closely equivalent to physical developer. No direct comparison has been conducted between ThermaNin and the standard ninhydrin formulation.

7. Post-treatments

7.1 Post-treatments for ninhydrin can be divided into two main categories: optical techniques that increase the contrast between the ninhydrin mark; and the background and chemical treatments that change the colour and/or fluorescence properties of the mark.

7.2 Marks developed using ninhydrin are non-fluorescent over broad regions of the visible spectrum, and this can be used to make the marks appear dark against a light background where appropriate light sources are used to produce background fluorescence [14].

7.3 The spectral reflectance curve of ninhydrin exhibits two minima in the region of 410nm and 535nm, which may be utilised to enhance the contrast of the mark. By either illuminating the marks with monochromatic light of these wavelengths [51] or using narrow bandpass filters passing these wavelengths in front of the imaging system significantly enhanced the contrast of the ridges that can be obtained. A green (~535 nm) bandpass camera filter is most commonly used for the capture of marks developed using ninhydrin. Alternatively, modern digital imaging systems and processing tools allow digital filtering of the red, blue and green channels to achieve a similar end product.

7.4 The use of metal salt spray treatments to form metal complexes with Ruhemann's purple has been described in sections 2.3, 2.4, 3.12 and 3.13. Originally this was investigated as a means of producing a colour change in the mark although in most cases the colour change was only slight, typically from purple to red, orange or pink, and insufficient to significantly enhance the mark. However, the observation that some of these complexes are also fluorescent has proved more useful as a post-treatment, with the complexes produced using zinc and cadmium giving the most intense fluorescence. For safe, practical purposes, zinc toning is the only chemical post-treatment for ninhydrin recommended by CAST. Cooling of the exhibit enhances the intensity of fluorescence produced and ideally zinc toning should be combined with fluorescence examination with the exhibit cooled to liquid nitrogen temperatures. Fluorescence examination should be carried out using the 468–526 excitation band of a Quaser and a 529nm cut-on long-pass viewing filter.

8. Validation and operational experience

8.1 Laboratory trials

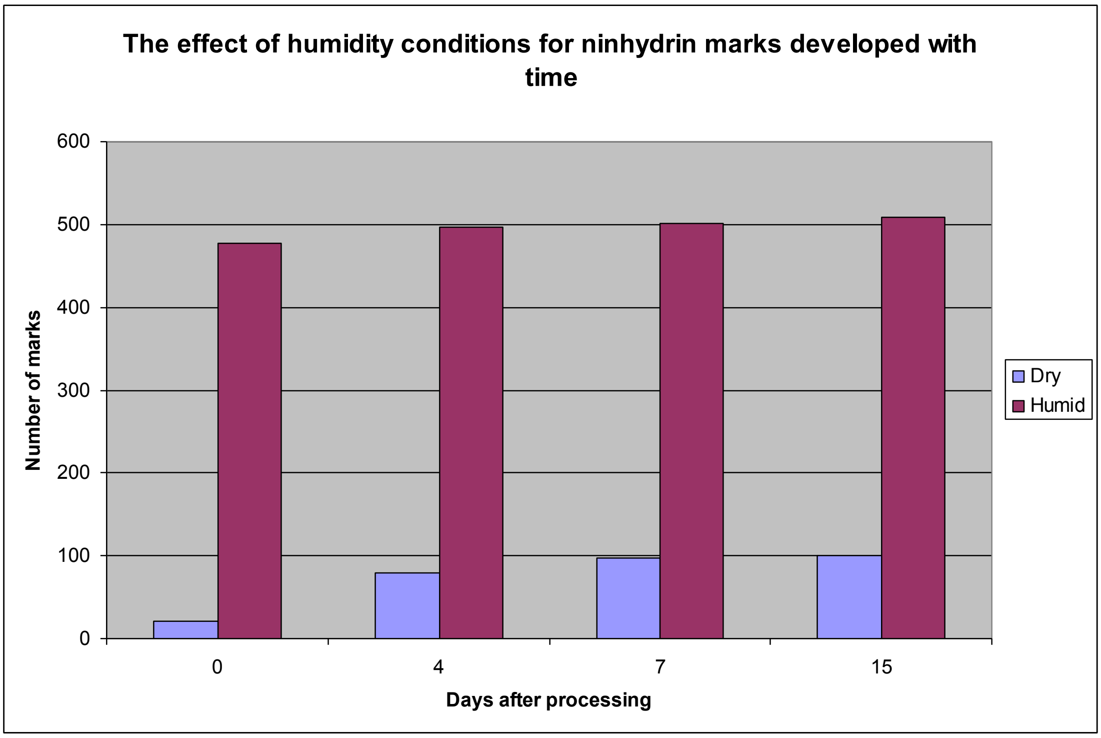
8.1.1 Although laboratory trials were conducted during the initial development of ninhydrin formulations in the mid-1970s, these results are no longer available. It has been found from experience that planted prints rarely give operationally representative results in such trials, typically performing worse than seen on casework [52]. This is possibly because perpetrators of crimes may be under increased stress and sweat more, giving more eccrine prints than seen in the laboratory. As a consequence, development of revised formulations at CAST is usually carried out using small-scale comparative tests until best performing formulations are identified, after which testing proceeds to pseudo-operational trials using realistic items such as bundles of cheques, as can be seen in many of the results reported in this section.

8.1.2 A recent exception to this is precursor work carried out to evaluate possible alternative solvents to HFE7100, which carried out tests on split depletion series deposited on a range of different paper substrates [53]. The two solvents investigated in this study were Asahiklin AE-3000 (1,1,2,2-tetrafluoroethyl-2[2,2-trifluoroethyl ether]) and Lenium (75%

1,1,1,3,3-Pentafluorobutane + 25% 1,1,1,2,2,3,4,5,5,5-Decafluoropentane). The results showed no significant difference between the performance of the three solvents when used for fingerprint development, although the Lenium solvent did cause more ink running on treated documents. Lenium ultimately became unavailable and subsequent pseudo-operational trials focused on the AE-3000 solvent [46].

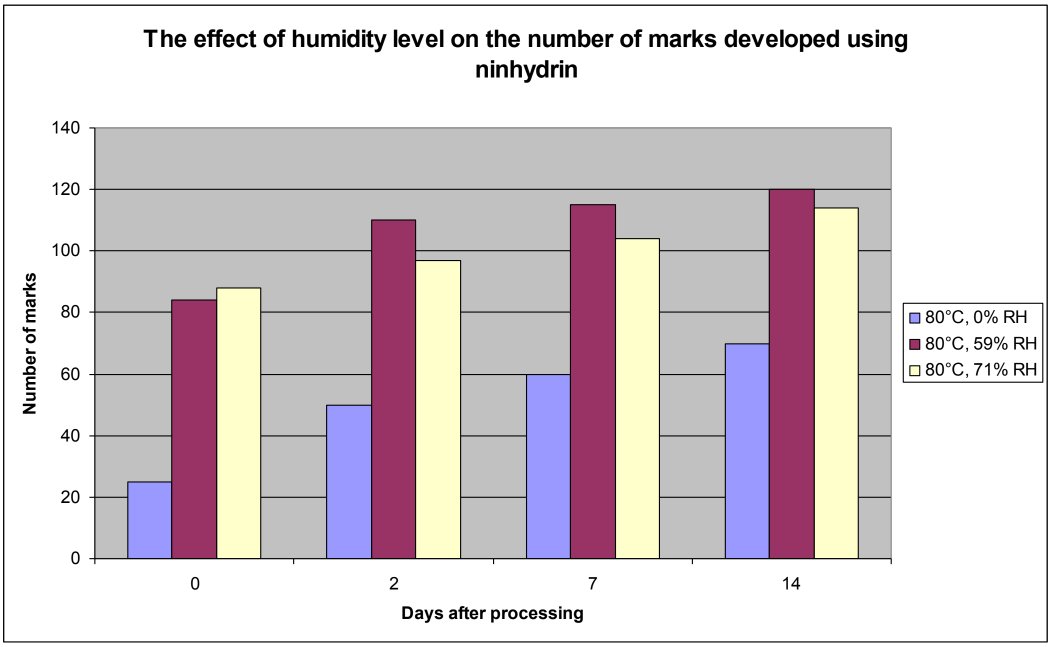
8.2 Pseudo-operational trials and operational experience

8.2.1 An important element in optimising the ninhydrin process was to establish the role of humidity in fingerprint development. Work to investigate this was conducted by HO SRDB, later PSDB in the late-1980s/early-1990s [12]. Initial trials carried out by counting fingerprints developed on 250 cheques representing 77 separate cases clearly demonstrated that humid processing conditions produced up to 5 times more marks, and that these marks developed more quickly.



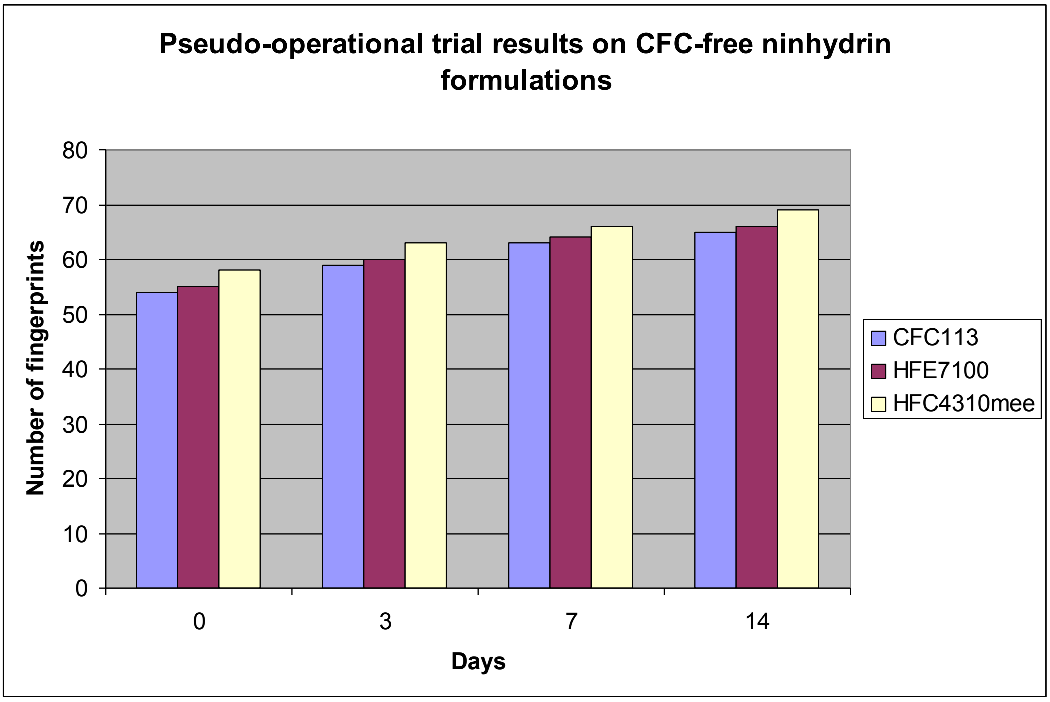
Results of trials carried out on cheques to establish the effect of humidifying exhibits treated with ninhydrin during processing.

8.2.2 Later trials in 1992 refined the humidity conditions required and tests on batches of 100 cheques, 25 from each of 4 banks, indicated that an oven humidity setting of 59% relative humidity gave the best results. This setting actually equates to a higher humidity (65%) in the region where the exhibits are treated, but means that the oven should be set to 59% relative humidity to achieve optimum development, which avoids issues associated with ‘overshoot’ in the humidification system. This is described in the *Manual of Fingerprint Development Techniques* [44].



Results of trial to refine the optimum humidity level required for development of marks using ninhydrin

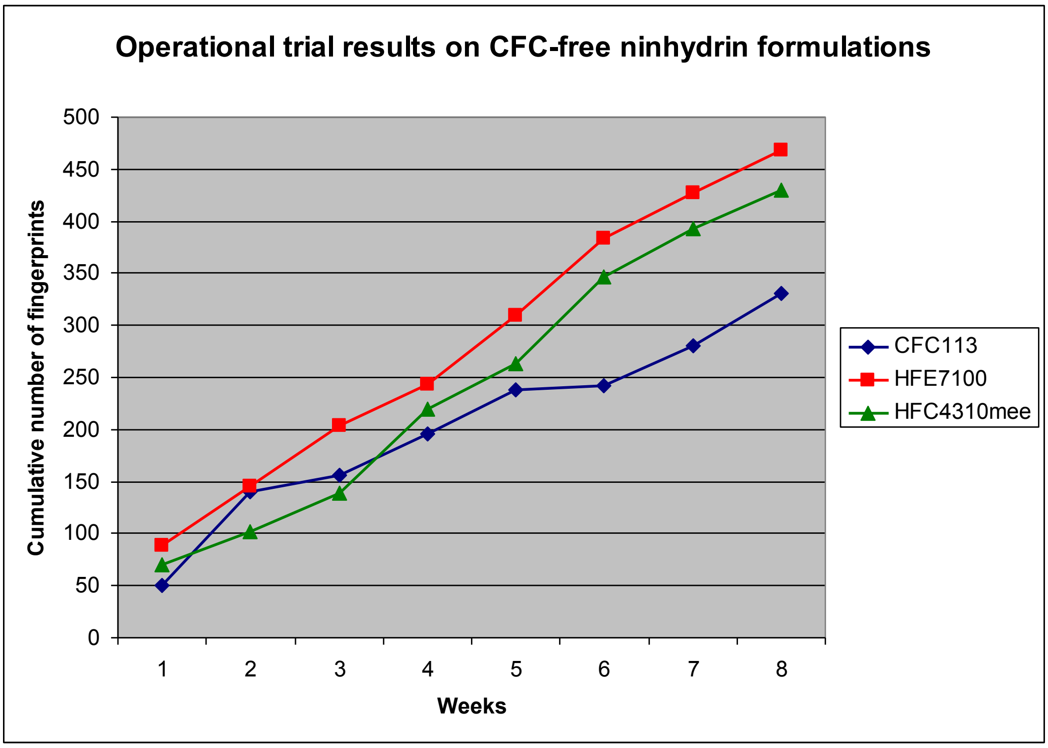
8.2.3 The HFE7100-based formulation now recommended in the CAST *Manual of Fingerprint Development Techniques* [44] has been trialled under UK conditions and found to be superior in performance to the CFC113-based formulation previously used. As part of the programme to find a suitable CFC-free ninhydrin formulation, Hewlett and Sears first tested a number of CFC-free formulations against the CFC113 formulation then in use. Some of these early studies are reported under section 6 'Alternative formulations and processes' above. A pseudo-operational trial, counting numbers of fingerprints with >8 minutiae developed using each technique on batches of 75 fraudulently passed cheques, gave the following result for the most promising HFC and HFE compounds.



Pseudo-operational trial results obtained on batches of fraudulently passed cheques.

8.2.4 These results indicated that both formulations had the potential to give equivalent, if not better, performance compared with the CFC113 formulation and fingerprints were developed over a similar timescale. As a consequence, both formulations were carried forward to a full operational trial carried out over a period of eight weeks at Essex Police. Articles suitable for ninhydrin treatment were separated into three batches, one treated with the CFC113 formulation, one based on HFE7100 solvent and the other based on HFC4310mee solvent. The number of fingerprints with > 8 minutiae was recorded, with exhibits being examined for fingerprints after 2 days and again after 2 weeks. Over the 8 weeks, 110 cases were treated by each process with an equivalent number of articles treated by each process overall. The results are tabulated and displayed graphically below.

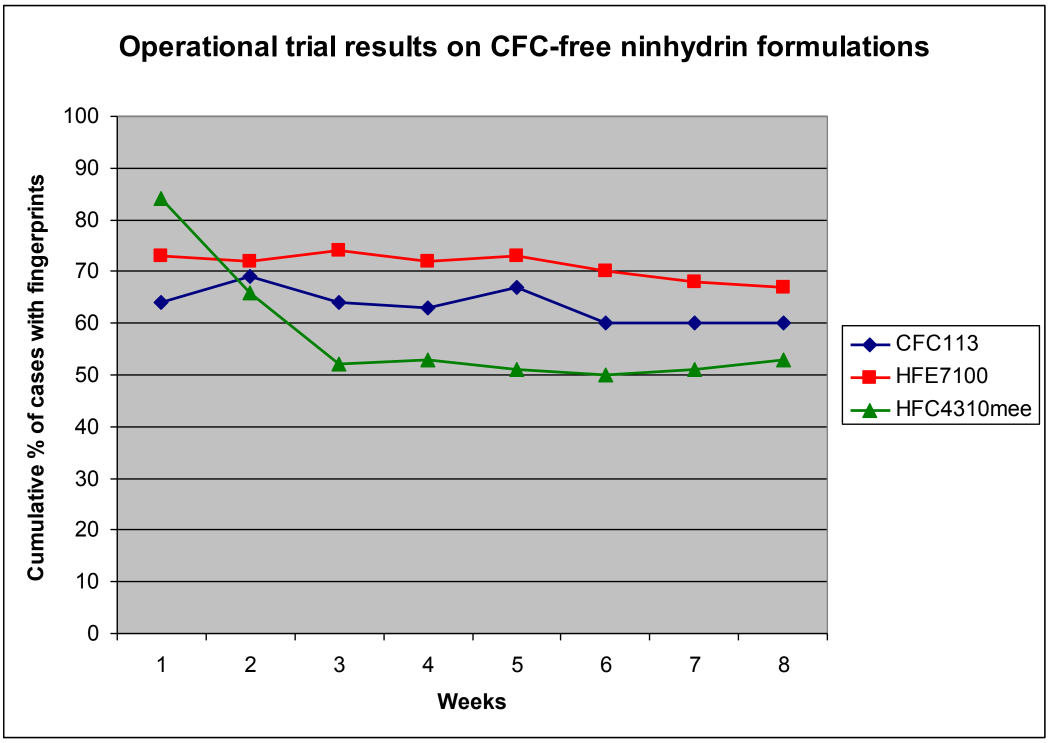
Week	**Cumulative figures**					
	CFC113		**HFE7100**		**HFC4310mee**	
	Cases	F'prints	Cases	F'prints	Cases	F'prints
1	14	50	15	89	12	70
2	29	140	32	146	29	102
3	39	156	42	204	42	139
4	54	196	54	243	55	220
5	69	238	66	309	68	263
6	80	242	83	384	79	347
7	102	280	102	427	102	393
8	110	331	110	468	110	430



Number of fingerprints developed in operational trial on chlorofluorocarbon-free ninhydrin formulations.

8.2.5 Although this analysis shows HFE7100 and HFC4310mee to perform better than CFC113 it was considered that these results may be misleading because single cases could yield disproportionate numbers of fingerprints; one-sixth of all fingerprints developed using HFC4310mee coming from a single case. It is statistically good practice to remove 'outliers' (i.e. the largest and smallest figures) from such analyses for the reason given above. The data were therefore also analysed in terms of the proportion of cases where fingerprints were developed, and these results are given below.

Week	**Cumulative figures**					
	CFC113		**HFE7100**		**HFC4310mee**	
	Cases	% with f'prints	Cases	% with f'prints	Cases	% with f'prints
1	14	64	15	73	12	84
2	29	69	32	72	29	66
3	39	64	42	74	42	52
4	54	63	54	72	55	53
5	69	67	66	73	68	51
6	80	60	83	70	79	50
7	102	60	102	68	102	51
8	110	60	110	67	110	53



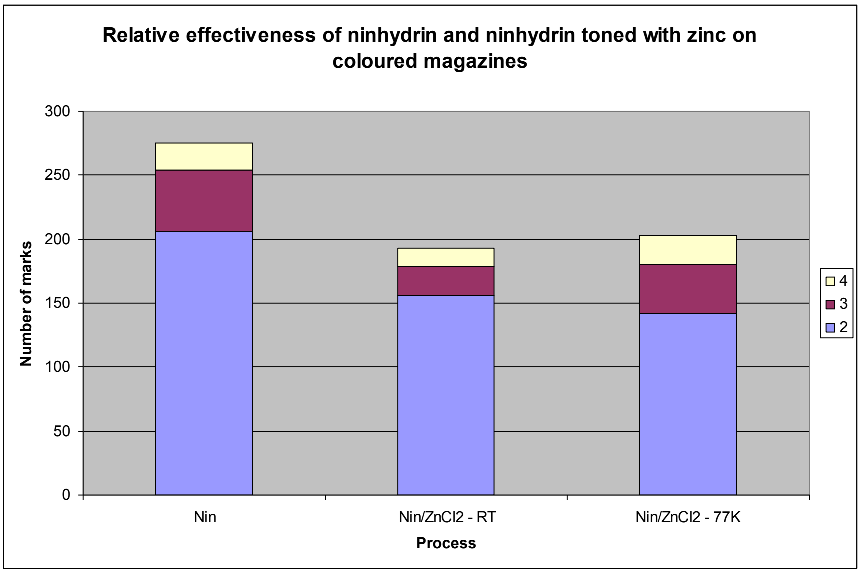
Proportion of cases yielding fingerprints in operational trial on chlorofluorocarbon-free ninhydrin formulations.

8.2.6 Under this analysis it appeared that the HFE7100-based formulation was the most effective, having the dual advantage of being non-ozone depleting and more effective than CFC113-based ninhydrin on operational work. This formulation was therefore recommended for operational use. It was also observed that the HFC-based formulation became less effective as the solution used became older, indicating that there may have been additional interaction between the HFC4310mee solvent and other constituents. The reasons for this were not explored further.

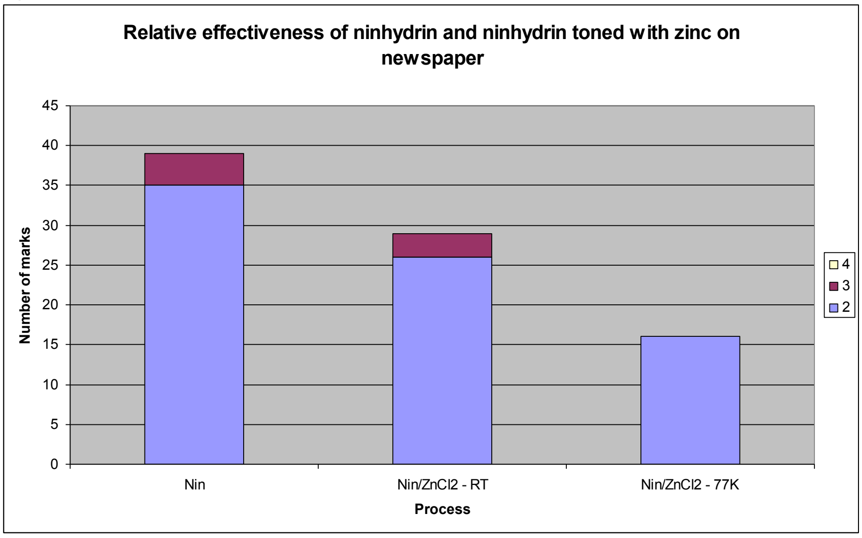
8.2.7 This study only refers to the use of ninhydrin as a single treatment, where in practice it may be used in sequence after DFO. Studies reported in Chapter 3.3 1,8-Diazafluoren-9-one (DFO) demonstrate that as a single process ninhydrin is less effective than DFO, but if used sequentially after DFO, ninhydrin will develop additional marks.

8.2.8 Results reported in Chapter 3.5 Physical developer also indicate that the application of ninhydrin is not detrimental to subsequent physical developer treatment and that physical developer can develop additional marks after ninhydrin. The recommended sequence of DFO-ninhydrin-physical developer for porous exhibits continues to be used successfully in the UK.

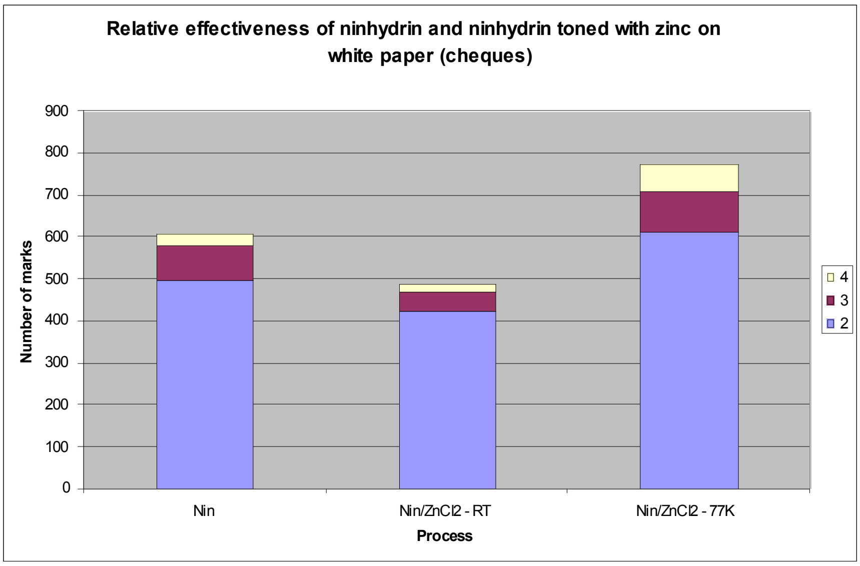
8.2.9 The effectiveness of zinc toning was also investigated in a pseudo-operational trial in the late-1980s, looking at marks deposited on cheques, coloured magazines and newspaper. The results of this trial indicated that results were poor on newspaper and obscured by background fluorescence on coloured magazines, but on cheques (based on white, non-fluorescing paper) zinc toning and fluorescence examination increased the number of marks recovered if the paper was chilled to liquid nitrogen temperature.



a)



b)



c)

Psuedo-operational trial results (marks graded 2, 3 and 4) on naturally handled items treated with ninhydrin and subsequently toned with zinc.

8.2.10 The most recent assessment of ninhydrin has been a pseudo-operational trial to compare the effectiveness of the HFE7100-based formulation with a revised formulation based on the alternative solvent AE-3000 [46, 53]. This trial utilised items representative of casework, including envelopes, receipts from retail shops, newspapers and letters. The items were divided into 8 experimental batches of 50 exhibits and 4 control batches of 10 exhibits, the types of exhibits being evenly distributed among the groups. These exhibits were then processed using the standard ninhydrin conditions, comparing the effectiveness of the two formulations and gathering additional information about long-term stability. The results were analysed in several different ways: using the basic CAST grading scheme; using a grading scheme taking into account additional factors, such as ridge continuity and background development developed at Staffordshire University; and also by running the developed marks on an Automated Fingerprint Identification System (AFIS) system. The results were analysed statistically using several different models, and all results indicated that there was no statistical difference between the effectiveness of the HFE7100 and AE-3000-based formulations.

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3.5 Physical developer

1. History

1.1 Physical developer solutions had been in use for many years in the photographic industry for the development of film. These worked with exposure to light causing silver bromide or silver iodide crystals in the film to reduce to specks of silver, these specks becoming sites for the subsequent deposition of silver from solution. In 1969, Jonker *et al.* at the Philips Research Laboratory in Eindhoven published a series of papers on physical developers when investigating methods for making printed circuit boards. These began with a review of classic physical developer solutions [1] but most importantly also included the description of a stabilised physical developer formulation [2,3] with the addition of surfactants and ferrous ions to suppress spontaneous deposition of silver from solution.

1.2 In common with many processes, the potential for fingerprint development was recognised when fingerprints were accidentally developed during the processing of photographic plates. Work to evaluate the technique as a fingerprint development process began at the Atomic Weapons Research Establishment (AWRE) Aldermaston in the early 1970s [4,5], with Morris and Goode recognising that although the process could develop marks on both non-porous and porous surfaces, it was most effective on porous items. The process was assessed against ninhydrin and osmium tetroxide on paper, both in the dry condition and after wetting. It was found that although the performance was not as good as ninhydrin or osmium tetroxide on dry paper, physical developer was the only process to develop marks on wetted paper and it was concluded that further trials should be conducted by the Police Scientific Development Branch (PSDB).

1.3 These studies included background research on the electrochemical characteristics of the formulation, together with investigations of alternative metals to silver [6]. This work primarily focused on taking the existing formulation towards operational use. Laboratory trials were conducted across a range of different paper types, both fully wetted and exposed to high humidity environments [7]. Rigorous testing, leaving paper samples in cages in the Thames, indicated that fingerprint ridge detail was still detected on paper samples which were close to physival disintegration.

1.4 The use of a radioactive toner based on ^{35}S for the revelation of developed marks on patterned backgrounds was also proposed, using autoradiography of the radioactive toned item to separate the mark from the background. The recommendation of the original study was to proceed to a one-year operational trial for both the basic process and the toning technique This commenced at Sussex Police and the Metropolitan Police in 1976, with HOSDB staff processing the exhibits in police laboratories [8]. The operational trial confirmed the laboratory observations; additional marks were developed using physical developer after ninhydrin treatment, marks were developed on items known to have been wetted, and the radioactive toning process was successfully used to reveal marks on patterned backgrounds. The trial was continued without HOSDB involvement, using trained police staff to process exhibits [9] and it was shown that similar results could be achieved. However, during the early stages of this phase of the work it was observed that the physical developer solutions were unstable, resulting in rapid 'fogging' of the entire exhibit. Work was carried out by PSDB to establish the reason for this [10] which concluded that the principal cause was excessive exposure of the solution to light. With elimination of this factor, results improved significantly. It was also discovered that water quality was crucial for the production of stable solutions, so there was a move to use only distilled, not deionised water. After further testing, PSDB progressed with the operational implementation of the process across the UK at the beginning of the 1980s [11].

1.5 Although the technique had been introduced into operational use, the fingerprint constituents responsible for influencing development were still not firmly established. Early work by Morris [5] had suggested that cholesterol esters, hydrocarbons or triglycerides may trigger deposition but in later tests by Gray [12] using a range of model compounds it was not possible to identify clearly which were actively promoting deposition and it may be that combinations of substances are responsible rather than any constituent in isolation.

1.6 A problem sometimes observed during operational use of physical developer was that background interference could occur. In some cases this was seen as light greying, which did not affect visualisation of the developed mark, but in other cases dark grey/black patching occurred, which could obscure marks. Investigations at PSDB established that this was caused by the calcium carbonate filler present in many papers, which made them alkaline in nature. This caused silver hydroxide to be formed, which was subsequently converted to the brown/black compound silver oxide (Ag_2O). The proposed solution was to neutralise the paper before the application of physical developer and a range of acids were tested in this role, with maleic acid ultimately being selected by PSDB (dilute nitric acid being recommended as an alternative by the Home Office (HO) Forensic Science Service (FSS) laboratory at Aldermaston). Another refinement to the formulation made by PSDB (now renamed HO SRDB) in the mid-1980s was the reduction in the concentration of surfactants used, made possible by the availability of higher purity surfactant grades.

1.7 The technique began to be used worldwide, with published papers promoting the benefits of the technique and giving case studies where success had been obtained on wetted items [13, 14] and on items over 30 years old [14]. The importance of using an acid pre-wash to neutralise alkali fillers in most commercial papers was emphasised [15]. As discussed above, without this pre-wash a reaction occurred that caused the paper to darken, obscuring developed marks and inhibiting more widespread use of the technique. A range of commercially produced, pre-mixed physical developers were evaluated by the same researcher [16], none of which supplied, or commented on, the need for a pre-wash. All were capable of giving reasonable performance if a pre-wash was used, but the researcher expressed concern that the lack of this advice may cast doubt on the effectiveness of the process. Few commercially produced packs explicitly state the constituents used, and CAST encourages UK police forces to make their own solutions for operational work to optimise performance.

1.8 The basic formulation recommended for operational use by CAST is little modified from that originally described by Jonker *et al.* in 1969 and has continued in use to the present day. Research into alternative formulations has been predominantly carried out in the USA, with the objectives of reducing cost, simplifying the process, reducing the time taken to process exhibits and to improve visualisation of the developed marks. Saunders experimented with a range of different physical developer solutions at different dilutions [17], starting to process exhibits with dilute solutions and if development did not occur silver nitrate was progressively added until success was obtained.

1.9 Other adaptations investigated included:

- copper-based physical developers [18]
- toning of marks to make them fluorescent [18]
- bleaching of marks to make them more visible on darker backgrounds [19].

1.10 A revised formulation was published by the US Secret Service in 2003, incorporating malic (as opposed to maleic) acid in the solution and reductions in the amount of silver, surfactants, ferrous salt and citric acid [20, 21]. Split comparisons with the established process suggested that the revised formulation gave equivalent, if not better, development. A comprehensive review of the physical developer process and alternative formulations investigated has been produced by Cantu [22].

1.11 More recently, acid-free formulations have been suggested for the development of marks on porous and non-porous surfaces [23] but other researchers have not been able to recreate these results. There has also been concern about the continued availability of Synperonic N, one of the surfactants used in the formulation, and work has been carried out both in the USA and by HOSDB in the UK [24] to assess possible alternatives. None of those investigated has yet proved to be as effective as Synperonic N.

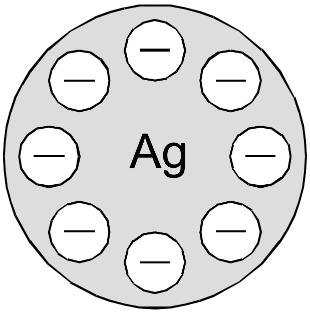
1.12 Physical developer remains an important reagent for fingerprint development on porous surfaces. It appears to target different fingerprint constituents to the amino acid reagents 1,8-diazafluoren-9-one (DFO) and ninhydrin, and will regularly develop additional marks if used sequentially after them. It has also been shown to develop marks on exhibits exposed to some of the harshest environments, including long periods of water immersion, charring [25], gamma ray irradiation [26] and on paper nearly 60 years old [27].

1.13 More recently there have been published papers demonstrating that Oil Red O can also develop fingerprints on wetted surfaces and in some situations may be more effective than physical developer. This debate is more fully addressed in Chapter 5.12 Oil Red O, but the CAST position is that physical developer remains more effective under typical operational conditions and should continue to be the technique of choice for use on wetted paper. Many of the studies on Oil Red O have used freshly deposited, ‘groomed’ marks and this is not representative of marks encountered operationally.

1.14 A number of workers overseas have indicated that they have problems implementing the physical developer process, in particular the development of high backgrounds. A team from PSDB carried out trials during a visit to Israel in the late 1990s and concluded that local differences in paper manufacture, possibly including the nature of the inorganic fillers used, can affect the levels of background development. Similar problems have been reported in China and in Taiwan. Some of these issues may arise from water quality but others may result from differences in paper manufacture.

2. Theory

2.1 In conventional physical developer solutions, spontaneous, homogeneous nucleation of silver nuclei occurs by reduction of silver ions. These nuclei carry a negative charge, and grow by progressive silver deposition from solution, the negative charge being maintained throughout their growth.



Negatively charged silver nuclei.

2.2 In stabilised physical developer solutions, several other chemicals are added to suppress the reduction of silver ions to elemental silver unless a suitable initiation site is present. In the case of the physical developer solution used for fingerprint development, the initiation sites are the fingerprint ridges (although as mentioned above it is not fully clear which constituents actually initiate deposition).

2.3 The physical developer solution contains both ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions, setting up a ferrous/ferric couple reaction that acts as a reducing agent for the silver ions. The reversible reaction below is set up:

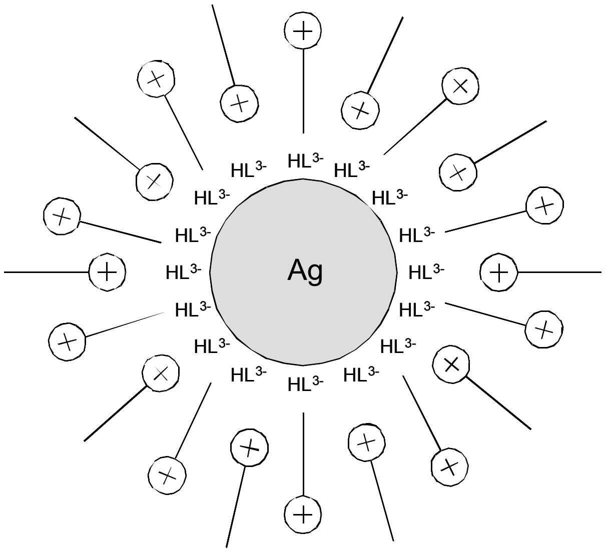
$$Ag^{+} + Fe^{2+} \leftrightarrow Ag + Fe^{3+}$$

2.4 Addition of citric acid reduces the ferric ion concentration by the formation of ferric citrate, which releases three protons and essentially drives the overall reaction in the direction of suppressing elemental silver deposition.

$$Ag^{+} + Fe^{2+} + H_3Cit \leftrightarrow Ag + FeCit + 3H^{+}$$

2.5 By adjusting the relative concentrations of each component, the reduction reaction can be balanced so that it only occurs on fingerprint ridges (or other sites where initiators are present) rather than in solution. However, once a silver nucleus has formed, it acts as a site for further silver deposition and this will result in depletion of silver ions from the solution unless the initiation capability of the nucleus is suppressed.

2.6 Surfactants are added to the formulation in order to inhibit the growth of the colloidal silver particles. As stated above, the silver nuclei formed in solution are negatively charged, attributed to the adsorption of the negatively charged citrate anions on the surface. A cationic surfactant is therefore added to suppress particle growth, with the molecules of the surfactant arranging around the silver particle in a staggered fashion to form a micelle.

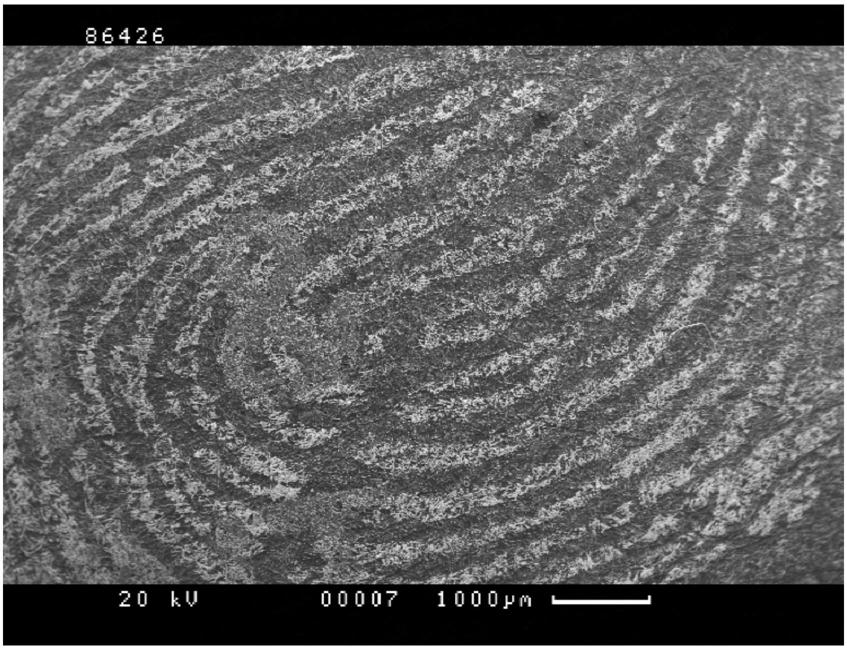


Micelle formed around silver particle by cationic surfactant molecules interacting with citrate anions (HL^{3-}).

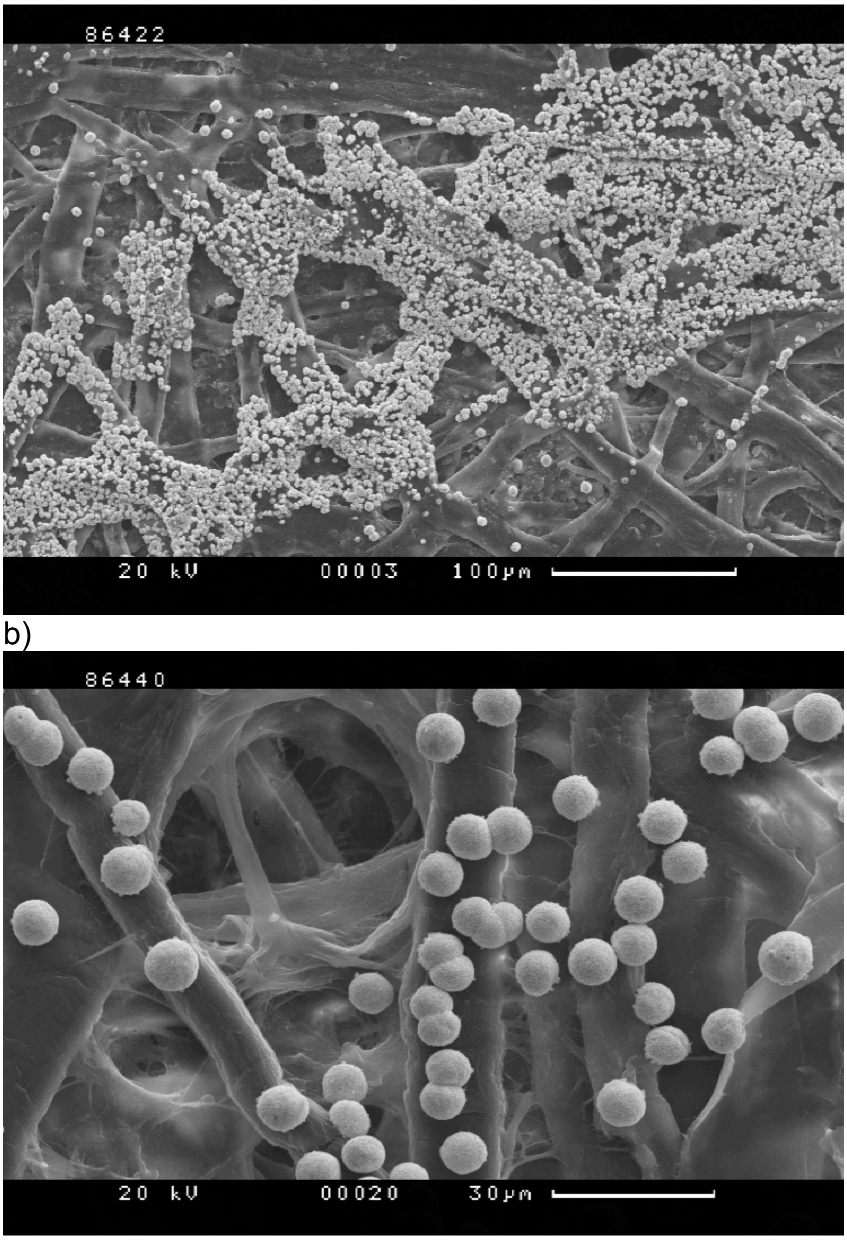
2.7 A further non-ionic surfactant is added to prevent the cationic surfactant being precipitated out of solution.

2.8 Despite several studies failing to identify conclusively individual fingerprint constituents responsible for triggering nucleation, it is thought that the essential element in the selective deposition of silver on fingerprint ridges is that the fingerprint residue becomes positively charged when exposed to the acidic (pH < 3) conditions of the physical developer solution. This may be due to protonation of the amine groups of proteins held within the emulsion of the fingerprint deposit, or by olefins in the residue acquiring a positive charge. A brief study by Wright [24] showed that physical developer gave weak positive development with an amino acid mixture, a strong development with a lipid mixture and the strongest reaction with a mixture of lipids and amino acids. The mixed chemical environment within the fingerprint residue may create a better environment for protonation and subsequent deposition to occur.

2.9 As described above, any silver nuclei formed in the solution will be negatively charged. It is likely to be enveloped by the cationic surfactant molecules, but close to the fingerprint ridges there is competition from the positively charged components of the residue. In this environment the micelle may be destabilised and the silver nucleus deposited on the ridge, where it becomes neutralised. Once a metallic silver particle has formed it can grow autocatalytically, resulting in a series of silver particles 10–40μm in diameter deposited along the length of the fingerprint ridge.



a)



b)

c)

Scanning electron micrographs of a fingerprint treated with physical developer a) low magnification, showing fingerprint structure b) medium magnification showing fingerprint ridge and c) high magnification showing individual particles.

3. CAST processes

3.1 The process recommended by CAST consists of three stages. In the first stage, the exhibit is exposed to an acid pre-wash to ensure that the substrate is neutralised and that darkening of the background will not occur. In the second stage the exhibit is placed in the physical developer working solution and agitated until it is considered that optimum development has occurred. In the final stage, the exhibit is taken through a series of water wash baths, removing all traces of the physical developer solution and stopping the reaction. It is recommended that the glassware used for all these treatment baths is kept scrupulously clean to prevent silver depositing on residual impurities such as dust particles.

3.2 The acid solution used for the pre-wash is a 2.5% w/v solution of maleic acid, prepared by dissolving 25g of maleic acid in 1 litre of de-ionised water. The role of the maleic acid is to neutralise the calcium carbonate filler found in many papers. Maleic acid reacts with calcium carbonate to form calcium maleate, releasing bubbles of carbon dioxide. The reaction is considered to be complete when bubbles are no longer seen forming on the surface of the paper.

3.3 The physical developer working solution is produced by adding a pre-mixed stock detergent solution and a pre-mixed silver nitrate solution to a further solution containing the ferrous and ferric ions and citric acid.

3.4 The stock detergent solution is produced by adding 2.8g of n-dodecylamine acetate to 1 litre of distilled water then stirring. Once it has dissolved, 2.8g of Synperonic N is added and stirred for 24 hours, with the container being covered in clingfilm to prevent ingress of foreign particles. The role of n-dodecylamine acetate is to act as the cationic surfactant, forming micelles around any silver nuclei forming in the physical developer working solution. Synperonic N is the non-ionic surfactant, primarily added to prevent precipitation of the cationic surfactant from solution although it is thought that it may have other functions in the development reactions. It is known that without the non-ionic surfactant being present, physical developer solutions do not work. It is essential that the resultant working solution is clear at this stage for optimum performance, cloudy solutions giving poor results. Cloudy solutions may arise if the temperature in the laboratory is too low (<20°C) or from contamination in one of the components; both causes should be investigated if this issue begins to arise.

3.5 Silver nitrate solution is produced by dissolving 10g of silver nitrate in 50mL of distilled water, then storing it in a dark cupboard until required. Silver nitrate is the source of the silver ions (Ag^+) in the redox reaction leading to silver deposition.

3.6 To prepare the working solution, 900mL of distilled water is measured out and then, in order, the following chemicals are stirred into solution: 30g iron (III) nitrate, 80g ammonium iron (II) sulphate, 20g citric acid. To this are then added 40mL of the stock detergent solution and all of the silver nitrate solution. The iron (III) nitrate is the source of the ferric (Fe^{3+}) ions for the redox reaction, and ammonium iron (II) sulphate provides the ferrous (Fe^{2+}) ions. Citric acid acts as a buffer for the reaction, reducing pH to below three and suppressing formation of elemental silver.

3.7 The concentrations of each component have been selected such that the redox reaction is balanced in favour of silver deposition on initiation sites among the fingerprint residue, and not in solution.

3.8 It is possible to reduce the time taken for the washing stage of physical developer by introducing a fixing bath after treatment with physical developer [28]. A commercial photographic fixing agent can be used for this purpose, following the manufacturer's instructions. This has the advantage of reducing the overall treatment time but means that it will not be possible to retreat the exhibit with physical developer if faint marks are present that could have benefited from a longer development time.

4. Critical issues

4.1 There are several critical issues relating to the successful implementation of the physical developer process.

4.2 An acid pre-wash is essential for paper items so that the alkali fillers present in most papers are neutralised. If this stage is omitted heavy background development may occur, which obscures marks.

4.3 The glassware used to carry out the process must be kept scrupulously clean because scratches and impurities may act as preferential nucleation sites and cause silver to precipitate out of the solution.

4.4 Distilled, rather than deionised, water should be used to make the solutions because this has been shown to improve performance.

4.5 The presence of a non-ionic surfactant in the formulation is essential for development to occur. The process is critically dependant on the surfactants used and their purity. The early work conducted at AWRE used a stock of dodecylamine acetate which was subsequently found to be of low purity but produced excellent results. A subsequent purchase of dodecylamine acetate, believed to be of higher purity, produced acceptable results but the concentration recommended in the formulation was revised downwards from 4g to 2.8g per litre for this batch. There are still some questions over the performance of current sources of dodecylamine acetate and no definitive comparisons have been reported.

4.6 The process should be carried out at temperatures above 20°C to avoid the formation of cloudy solutions, which are less effective in developing marks.

5. Application

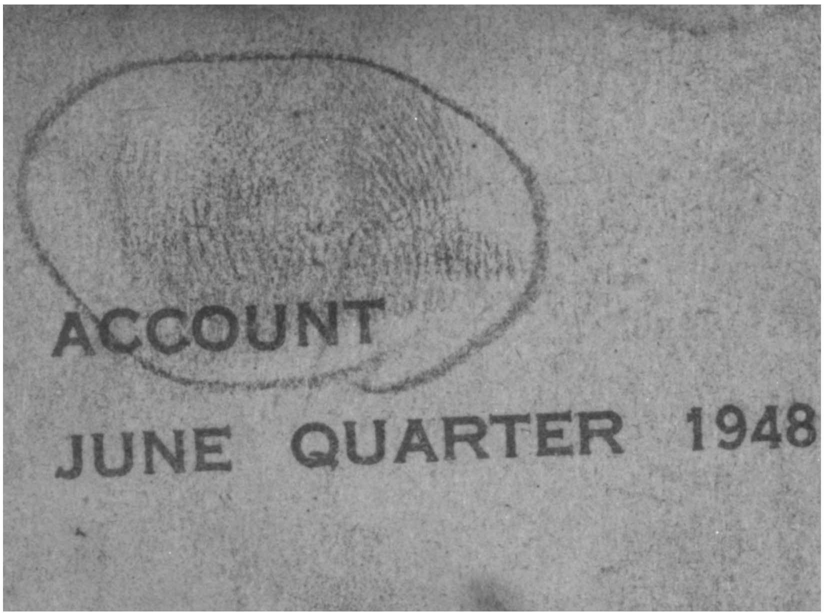
5.1 Suitable surfaces: physical developer is suitable for use on all porous surfaces, including paper, cardboard and raw wood.

5.2 The principal application of physical developer is the final stage in any sequential treatment process for porous items. It has been repeatedly demonstrated that physical developer targets different components within fingerprint deposits than DFO and ninhydrin, and will frequently develop additional marks if used sequentially after them. It should not be used before DFO and ninhydrin in a sequence because on its own it is less effective than either reagent and the aqueous solutions used will dissolve the amino acids targeted by these processes.

5.3 Physical developer is also the reagent of choice when it is known a porous item has been wetted. Because it targets insoluble components of the fingerprint residue (or soluble components retained within an emulsion of insoluble components) it is capable of developing fingerprints after long periods of immersion in water. Operationally, fingerprints have been developed on exhibits immersed for over three months [13].

5.4 Physical developer has also been shown to develop marks on exhibits exposed to temperatures in excess of 200ºC [25], providing evidence that the components targeted by the process are resilient to adverse conditions. Supporting this are other results obtained during treatment of articles known to be nearly 60 years old [27], where physical developer produced several identifiable marks. It is therefore a process that can be applied when it is known that an exhibit has been exposed to extreme conditions.

a)



b)

Photographs of marks developed on articles exposed to extreme conditions using physical developer a) marks on charred paper and b) mark on a bill nearly 60 years old.

5.5 In a laboratory, physical developer is applied to articles by processing them through a series of shallow dishes. The paper article is first placed into a dish containing the acid pre-wash, agitating the dish gently until bubbles are no longer formed on the surface. It is then transferred to a dish containing the physical developer working solution, which is rocked gently until optimum development of the marks has been observed. This typically takes 10–15 minutes, but may take longer. Finally, the paper is removed to a series of water wash baths before being allowed to dry in air on an absorbent surface. Once the article is dry and developed marks have been examined, a decision can be made about whether a retreatment with physical developer is required or a post-treatment should be used to improve contrast. It is important to control the temperature during processing, with temperatures below 17ºC inhibiting successful development by destabilising the developer solution [24].

5.6 Physical developer is not a technique suited to application at scenes of crime, although there are occasions where improvisations are known to have been made, such as half-fish tanks pressed against walls and successively filled with each treatment solution in turn.

6. Alternative formulations and processes

6.1 Alternatives have been considered to all elements of the physical developer formulation.

6.2 Several different acids were considered for the pre-wash before maleic acid was selected. More recently nitric acid and malic acid have been studied as possible alternatives, but none of them have given noticeably better performance over maleic acid.

6.3 With regard to the metal component of the formulation, early studies by Fuller and Thomas [6] indicated that solutions based on palladium, rhodium and gold were investigated and although these deposited metal on the surface as expected they did not appear to develop fingerprints. Ramatowski and Cantu [18] reported research into a copper-based physical developer using copper sulphate in place of silver nitrate. Although development was obtained via this route, it has not proved as sensitive as the silver-based system and is not recommended as a replacement for it.

6.4 As part of a drive to reduce the cost of the large quantities of physical developer used by the US Secret Service, revisions to the CAST formula were investigated. These resulted in a revised formulation incorporating malic acid [20,21], with reductions in the concentrations of ammonium iron (II) sulphate, citric acid, both surfactants and silver nitrate. The proposed formulation (based on 1 litre of water for each stage) is given below:

malic acid 13g;

iron (III) nitrate 30g;
ammonium iron (II) sulphate 70g;
citric acid 15g;
n-dodecylamine acetate 0.056g;
Synperonic N 0.056mL;
silver nitrate 8g.

6.5 The results presented suggested that the above formulation was as effective as the CAST formulation, if not more so. However, no comprehensive trial has yet been reported that compares the two formulations either in laboratory tests or on operationally representative exhibits, so it is not yet possible to state whether a revision to current (2011) UK practice is required. An adaptation of this formulation using Tween 20 in place of Synperonic N was developed by the US Secret Service, as a precaution against the possibility of Synperonic N becoming unavailable. This formulation was tested against the CAST formulation in trials of Synperonic N-free systems, and although it gave better results on one-day-old prints it was poorer on prints that were two weeks old. Further details of this trial are given below.

6.6 Another revised formulation omitting the maleic acid pre-wash was issued by Yapping and Yue [23], but attempts by other researchers to reproduce this formulation and the results claimed for it were unsuccessful and at present it is discounted.

6.7 Concerns have been expressed about the environmental issues associated with compounds closely related to Synperonic N. These are becoming banned because they closely mimic oestrogen in structure and as these compounds enter the environment they may lead to reduced sperm count and increases in testicular cancer. Recent research in both the USA and the UK has therefore investigated alternative surfactants to Synperonic N. In the UK study [24], the following alternative compounds were considered.

Surfactant	General description
Tween 20	Polyoxyethylene sorbitan (fatty acid ester)
Tween 80	Polyoxyethylene sorbitan (fatty acid ester)
Synperonic 91/5	Fatty alcohol ethoxylate
Synperonic 91/6	Fatty alcohol ethoxylate
Synperonic 13/6.5	Fatty alcohol ethoxylate
Synperonic 13/8	Fatty alcohol ethoxylate
Caflon-N	Fatty alcohol ethoxylate

Surfactants used in the comparative study.

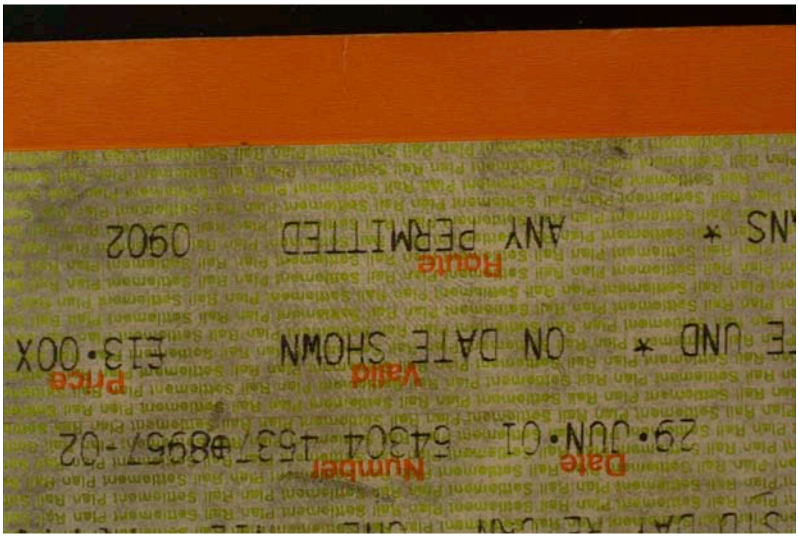
6.8 The solutions containing the different surfactants were compared with the Synperonic N-based solution and applied to split depletions of several thousands of marks deposited on a range of paper types. The results showed that none of the proposed replacements for Synperonic N gave equivalent performance, the nearest being the formulation based on Tween 20 recommended by the US Secret Service from their own internal research. The long-term availability of Synperonic N remains a concern and therefore it is likely that this study will have to be revisited at some point in the future. One observation that has been made subsequently by the US Secret Service is that the Tween 20 formulation benefits from being used after ageing for several days, and that the solution used in the HOSDB comparative studies may have been ‘too fresh’. This is another factor that requires further investigation.

7. Post-treatments

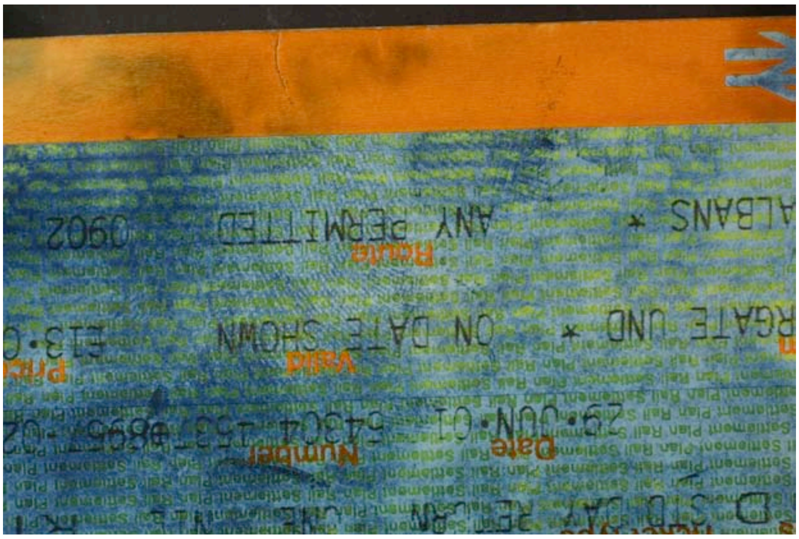
7.1 A range of post-treatments have been proposed for enhancing marks. One of the earliest treatments proposed [6], and still outlined in the CAST *Manual of Fingerprint Development Techniques* [29] is the treatment of developed marks with a radioactive toner, then using autoradiography to capture the marks. The principal application of this technique was to reveal developed marks that would otherwise be obscured by highly coloured or patterned backgrounds. In the radioactive toning process, the exhibit is treated with radioactive sodium sulphide. This converts the silver particles to silver sulphide, resulting in the radioactive sulphur being bound into the fingerprint ridges. The treated exhibit is then sandwiched between sheets of film for several days, during which radiation emitted from the sulphur causes the film to darken in regions where it is present. On development the film will show all the regions of the film that have become radioactive. The fingerprints will only be more useful if the underlying background, ink or contamination, has not taken up the radioactive sulphur. The technique has not been used for many years and will be removed from future editions of the manual.

7.2 Bleaching has also been proposed as a technique for both revealing fingerprints on dark papers or as an initial step in the coloured toning of developed marks [19,22, 30]. Several techniques have been proposed for treating developed marks, the most widely used formulation operating by the conversion of silver to silver iodide by first converting it to Ag_2O then converting Ag_2O to the silver halide. To carry out the process, a stock solution of 20g potassium iodide in 100mL of distilled water is prepared and one part of this solution added to 19 parts of the standard physical developer working solution. The article to be treated is then immersed in the solution until the paper background becomes blue-black (this is thought to be due to the starch in the paper reacting with iodine) and good ridge detail is observed. This may take between 15 minutes and 2 hours. On dark paper or against dark backgrounds, the bleaching process alone can reveal marks. For faint, developed marks on pale backgrounds a weaker concentration of potassium iodide can be used to treat the mark without darkening the background.

7.3 Alternatively, developed marks can be treated with standard photographic colour toning solutions, e.g. Fotospeed Blue Toner (BT20), using the manufacturer’s instructions to change the colour of the mark and enhance its contrast [31]. Any silver deposited on the background will also be toned in this way.



a)



b)

Marks on a rail ticket obtained by using physical developer a) as developed and b) after bleaching and treatment with blue photographic toner.

7.4 A final post-treatment that can be applied to articles treated using physical developer is infra-red (IR) imaging, described in detail in Chapter 4.2 Infrared imaging. The principle used is that the marks produced using physical developer remain visible in the near IR and many printing inks use organic pigments that are IR transparent. If a camera sensitive in the near IR is used in combination with an appropriate light source and a long-pass filter blocking the visible region of the spectrum, it may be possible to suppress the background pattern and reveal the features of the mark.

8. Validation and operational experience

8.1 There have been a limited number of extensive trials carried out on physical developer, primarily because of its position within sequential processing regimes. Physical developer is only going to be used as the first process on items that are known to have been wetted, where until recently it was the only process that could be considered for this role. It is accepted that physical developer is less effective than DFO and ninhydrin, but because it develops additional marks when used after them rather than being considered in place of them, large-scale validation has been considered unnecessary.

8.2 <u>Laboratory trials</u>

8.2.1 The first reported comparative studies of the effectiveness of physical developer were carried out at AWRE Aldermaston in 1975, where it was compared with the non-flammable ninhydrin formulation being developed by the same research group, and to osmium tetroxide [5].

8.2.2 In this study, single fingerprints from two separate fingers from the same donor were used and these were aged for different periods of time. One set of exhibits was then wetted, and the paper processed using the three processes being compared. A basic, non-numeric grading system was used where:

none = no trace of fingerprint;
very poor = traces of fingerprint only;
poor = just sufficient for general classification;
good = sufficient detail for identification;
very good = easily identifiable;
excellent = all ridge detail developed.

The results are summarised below.

Age of mark	**Number of prints**	**Dry**			**Wet**		
		Ninhydrin	**OsO_4**	**PD**	**Ninhydrin**	**OsO_4**	**PD**
1 day	1	Excellent	Excellent	V. good	None	None	V. good
	2	Excellent	Excellent	V. good	None	None	V. good
5 months	1	Good	Good	Good	None	None	V. poor
	2	Fair	Good	Poor	None	None	Poor
6 months	1	V. good	V. good	Good	None	None	Poor
	2	V. good	V. good	Good	None	None	Good
7 months	1	V. good	V. good	Good	None	None	Poor
	2	V. good	V. good	Good	None	None	Poor
8 months	1	Good	V. good	Good	None	None	Good
	2	Good	V. good	Good	None	None	Excellent
10 months	1	Good	Good	Good	None	None	Poor
	2	Good	Good	Good	None	None	None

Results of early comparative trials on both dry and wetted paper articles.

8.2.3 It was evident that physical developer was not as effective as ninhydrin or osmium tetroxide for marks on dry surfaces, but was the only process to develop marks on paper soaked for 24 hours.

8.2.4 Continuation of this work was carried out at HOSDB in 1975 and 1976 and focused on evaluating the effectiveness of physical developer against ninhydrin on paper kept in conditions where the surface became wet [7]. Two trials were conducted, both using split palm prints where one-half were kept indoors under dry conditions and the remainder were exposed to the wet environment.

8.2.5 The first trial exposed palm prints on paper kept exposed to the atmosphere in an outside test rig at PSDB Sandridge over the period November 1975 to January 1976. The grading system below was used.

1 = no reaction;
2 = reaction, no useful ridge structure;

3 = useful, poor contrast;
4 = useful, good contrast;
5 = useful, very good contrast;
6 = excellent.

Week	£5 Banknote		Kraft paper		Glazed paper		Bond paper	
	Control	Test	Control	Test	Control	Test	Control	Test
1	2+	2	3	4	5	4	3+	3
2	5	3+	5	4	4	4	3	4
4	4	5	3	3+	5	4	5	5
9	-	-	3	4	-	-	5+	4+

Ninhydrin comparison

Week	£5 Banknote		Kraft paper		Glazed paper		Bond paper	
	Control	Test	Control	Test	Control	Test	Control	Test
1	3+	1	3+	1	4	1	4	1

Results of early trials on paper items exposed to outside environments.

8.2.6 A follow-on test was carried out holding samples in a water immersion rig in the River Thames. This gave the following results.

Day	£5 Banknote		Kraft paper		Glazed paper		Bond paper	
	Control	Test	Control	Test	Control	Test	Control	Test
1	1	3	3	2	3	4	2	3
2	3	2	3+	4	3	4	3	1
3	4	3	1	1	3	4	5	1
4	3	1	5	3	5	1	5	3

Ninhydrin comparison

Week	£5 Banknote		Kraft paper		Glazed paper		Bond paper	
	Control	Test	Control	Test	Control	Test	Control	Test
1	3+	1	3+	1	3+	1	3+	1

Results of early trials on paper items immersed in the River Thames.

8.2.7 It was evident that for wetted surfaces ninhydrin gave no reaction, and that physical developer should be the development technique of choice.

8.2.8 The most recent laboratory trials conducted by HOSDB focused on comparisons of the existing physical developer formulation with those based on the alternative surfactants identified in the ‘alternative formulations and processes’ section above. The solutions containing the different surfactants were applied to split depletions of several thousands of marks, deposited on a range of paper types consisting of:

- brown envelope;
- white envelope;
- parchment paper;

- magazine;
- newspaper;
- printer paper;
- green card;
- silk finish paper;
- wove paper.

8.2.9 The number of marks scoring three and four (equating to clearly identifiable marks) were recorded for each process on test strips aged for one day and two weeks. The differential between the number of marks graded three and four between the two techniques is recorded below, with negative scores indicating that the surfactant performed worse than Synperonic N.

	One-day differential	**Two-week differential**	**Average differential**
Tween 20 (US Secret Service formulation)	11	-15	-2
Synperonic 91/6	-3	-7	-5
Tween 80	-6	-6	-6
Caflon-N	-7	-9	-8
Synperonic 91/5	-5	-18	-11.5
Synperonic 13/6.5	-22	-18	-20
Tween 20	-33	-40	-36.5

Performance of different surfactants in physical developer solution relative to Synperonic N.

8.2.10 The results show that none of the proposed replacements for Synperonic N gave equivalent performance, the nearest being the formulation based on Tween 20 recommended by the US Secret Service from their own internal research. Production of Synperonic N is being discontinued so it is necessary to implement a revision to the surfactant used, and it is likely to be detrimental to the performance of physical developer for fingerprint development unless a more suitable replacement is identified.

8.3 Pseudo-operational trials and operational experience

8.3.1 The results of the operational trials conducted in 1977 prior to implementation of physical developer throughout the UK [9] are summarised below.

	Number of marks			%		
	New Scotland Yard	Sussex (1–29)	Sussex (30–90)	New Scotland Yard	Sussex (1–29)	Sussex (30–90)
Neither process +ve	11	0	6	28.9	0	10
Ninhydrin +ve PD -ve	6	13	8	15.8	46.4	13.3
Ninhydrin -ve PD +ve	11	0	8	28.9	0	13.3
Both processes +ve	10	15	38	26.4	53.6	63.4
Total cases	38	30	60	-	-	-
Total articles	433	69	234	-	-	-

Operational casework results obtained by applying physical developer after ninhydrin on a range of porous articles.

8.3.2 There were differences between the results obtained at different sites and between different phases of the work at the same site, but in general it was observed that physical developer consistently developed additional marks when used after ninhydrin. In the first phase of the work at Sussex the physical developer solution was degraded by exposure to light and results were poor, in the work at New Scotland Yard exhibits were selected because they were less likely to give positive results using ninhydrin, hence the results obtained in the second phase of the work at Sussex (where all exhibits passing through the laboratory were processed) were probably most representative. In the course of the trial the value of the technique in developing marks on wetted items was confirmed, as was the usefulness of the radioactive toning post-treatment for revealing marks on patterned backgrounds. The subsequent operational recommendations that physical developer should be used sequentially after ninhydrin and as a treatment for wetted paper items were supported by the results above.

8.3.3 This recommendation is still supported by operational results where physical developer continues to develop additional marks as the final stage of sequential treatments and as the sole treatment for wetted items. In some cases the items treated have been over 25 years old and have been immersed in water.

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3.6 Powders

1. History

1.1 The use of powders is one of the oldest reported techniques for development of latent fingerprints. Faulds, in his publication ‘Dactyloscopy, or the study of fingerprints’ of 1912 [1], refers to the experiments conducted by Forgeot in the late 19th century as the first studies into the powdering technique, and also comments on subsequent experiments of his own [2]. By 1912 Faulds [1] was able to describe formulations and application techniques for both black and white powders, and by 1920 many more types of powders had been reported for development of fingerprints, including mercury-chalk (hydrargyrum–cum–creta), graphite, lamp black, ferric oxide, magnesium carbonate, aniline dye stuffs, lycopodium powder-Sudan Red mixture, red lead oxide, lead carbonate, lead iodide and lead acetate [3]. By the end of the decade a further selection of fingerprint development powders had been reported, including the first references to the use of aluminium powder. The purpose of many of these materials was to provide investigators with a range of different coloured powders that could be used to both develop a crime scene mark and provide contrast with coloured backgrounds. Some of these early powders persisted in use for many years. Mercury-chalk was still in use in the UK in the 1970s, and carbon black-based powders remain in use worldwide to the current day (2011).

1.2 Another technique for providing contrast between the developed mark and the substrate and considered relatively early in the history of fingerprint development was fluorescence. Zinc sulphide and anthracene were proposed as fluorescent dusting powders in the 1930s [4], with the developed marks being illuminated with long-wave ultraviolet (UV) radiation to promote phosphorescence and luminescence respectively. Variants of these powders were still being recommended for development of latent fingerprints on multi-coloured surfaces in 1954 [5].

1.3 The range of powders that have been formulated and marketed for fingerprint development in the intervening years far exceeds the number of chemical development techniques, and more enter the market every year. Some examples of powder ‘recipes’ that have been used by police forces in the past [6,7] but that are now predominantly obsolete, are given in the table below.

Colour of powder	Constituents	Wt% of constituent
Black	Lamp black Graphite Gum acacia	70 20 10
	Black magnetic ferric oxide Rosin Lamp black	50 25 25

White	Titanium dioxide	67
	Kaolin	16.5
	French chalk	16.5
	Titanium dioxide	33.3
	Basic lead carbonate	33.3
	Gum arabic	33.3
Grey	Mercury	25
	Chalk	50
	Aluminium powder	25
	Basic lead carbonate	87.5
	Gum arabic	12.5
	Aluminium powder	trace
	Lamp black	trace to give colour
Red/orange	Red lead oxide	33
	Rosin	67
	Lycopodium	90
	Sudan Red III	10
Fluorescent	Anthracene	50
	White tempera	50

Published formulations for various types of early fingerprint powders.

1.4 These early powder formulations do not appear to have been devised by any standardised testing system, nor were any recorded comparative trials carried out to establish which formulations were most effective. Their use was often according to the personal preferences of the person treating the marks at the crime scene rather than any scientific assessment of which powder was most appropriate for a particular type of surface. As a consequence, no single type of powder predominated and many local variations in practice arose worldwide.

1.5 Some of the constituents used in early fingerprint powder formulations were toxic or carcinogenic and their prolonged use could cause health problems. The best documented of these problems is the occurrence of mercury poisoning among officers in UK police forces [8,9], initially reported in the late 1940s and caused by the use of mercury-chalk powder. Although most of these powder formulations have since been withdrawn, it is still recommended that users consult material safety data sheets before employing any new type of powder.

1.6 Many powders used for fingerprint development in the first half of the 20th century were also granular in nature, typically applied with animal hair brushes. Photography of the marks developed by powdering was almost exclusively carried out in situ. Developments in the 1960s meant that alternative types of powders began to become more widely used. The first of these developments was the 'Magna brush' in the early 1960s [10], consisting of a retractable bar magnet within a non-magnetic cover material. When dipped into a pot of magnetic powder, a brush-like head of powder became attracted to the magnet, which could then be drawn across the surface like a hairbrush. A range of magnetic powders were soon developed for use with this brush. The second development was the increasing recognition that aluminium flake powder, already in operational use in the 1950s, had a combination of properties that made it ideally suited for use with lifting media, thus overcoming the need for photography in situ and enabling the separation of the developed mark from backgrounds that may have made photography difficult.

1.7 PSDB has carried out several unpublished surveys of the types of powders in use in police forces around the UK, showing the progressive change in the types of powders used. The use of aluminium flake powder and subsequent lifting of the mark was adopted by the Metropolitan Police around 1971 after observing the practice in the USA. The principal objective of this change in practice was to avoid the transport of exhibits for photography; although it was argued that results were as good as or better than previous procedures. It was widely adopted around the UK over the next 5–10 years, although two forces were still almost exclusively using white and black powders into the late 1980s.

1.8 Since then, aluminium flake and magnetic powders have been increasingly used in place of granular powders and the types of powder currently (2011) in widespread use can be grouped into four main classes, namely:

- metal flake powder (e.g. aluminium and bronze);
- granular powder (black and white);
- magnetic powders;
- fluorescent powders.

1.9 The categories above represent a general classification, the actual number of powder formulations that are available on the world market can be numbered in the hundreds and some formulations actually fall into more than one category. Each of these different powder types have particular types of surface to which they are most suited – there is no one powder that will consistently develop marks of optimal quality on all surfaces. However, despite this recognised performance variation there is very little reported evidence of large-scale comparative studies to demonstrate the relative effectiveness of powders other than the experiments carried out by the Home Office Scientific Development Branch (HOSDB) [11,12,13]. These comparisons were limited to a small number of powders identified as being representative of the general categories by a survey of police force scene of crime units and by preliminary evaluations. By tracing the commercial powders back to source it was established that many differently labelled products were in effect the same powder, and some other less-used powders performed poorly in early trials and were therefore eliminated from subsequent studies. This enabled the large-scale trials to focus on powders that were effective, and/or widely used. A methodology is presented [11] that allows researchers to carry out similar comparative assessments for any new powder system.

1.10 Powdered marks probably account for the largest number of fingerprint identifications worldwide, in the UK alone approximately 50% of the 60,000 fingerprint identifications per annum arise from marks developed using this process. It is therefore evident that even the small proportional improvements that can be achieved by the selection of the optimum powder and brush combination for a particular surface have the potential to provide significant operational benefits, and further study of this area may be required.

2. Theory

2.1 The development of fingermarks by powdering occurs by preferential adhesion of powder particles to the ridges, with the background material having less affinity for the particles. This means that powders should not be used where surfaces are sticky or heavily contaminated because the particles will not be able to discriminate between the constituents in the fingerprint residues and the contaminant, and will adhere across the entire surface.

2.2 The factors that are thought to play a role in promoting powder particles to adhere to fingerprint ridges are:

- particle shape;
- surface chemistry of the powder particle;
- electrostatic charge on the particle;
- adhesion to grease or liquid;
- low(er) adhesion to the substrate.

The overall adhesive effect of a particle to a fingerprint ridge is likely to be a combination of all these factors and therefore no one dominant mechanism can easily be identified.

2.3 In terms of particle shape, it has been suggested that flake powders are more sensitive than granular powders because their shape gives them a higher surface area and hence better contact with the fingerprint deposits.

2.4 With regard to surface chemistry, it is known that the adhesion of a powder particle to a solid surface in air or a gaseous medium is partly due to molecular forces [14]. It is therefore anticipated that changing the molecules on the surface of the powder particle will have an effect on the interaction between that particle and the medium it adheres to. It has been demonstrated that surface coatings do play a role in the effectiveness of metallic flake powders for fingerprint development. Experiments conducted by James *et al.* [15,16] demonstrated that flake powders without stearic acid coatings were poor for fingerprint development, irrespective of flake diameter. Further investigation of stearic acid coating thickness showed that optimum results were obtained for a coating thickness of 70nm.

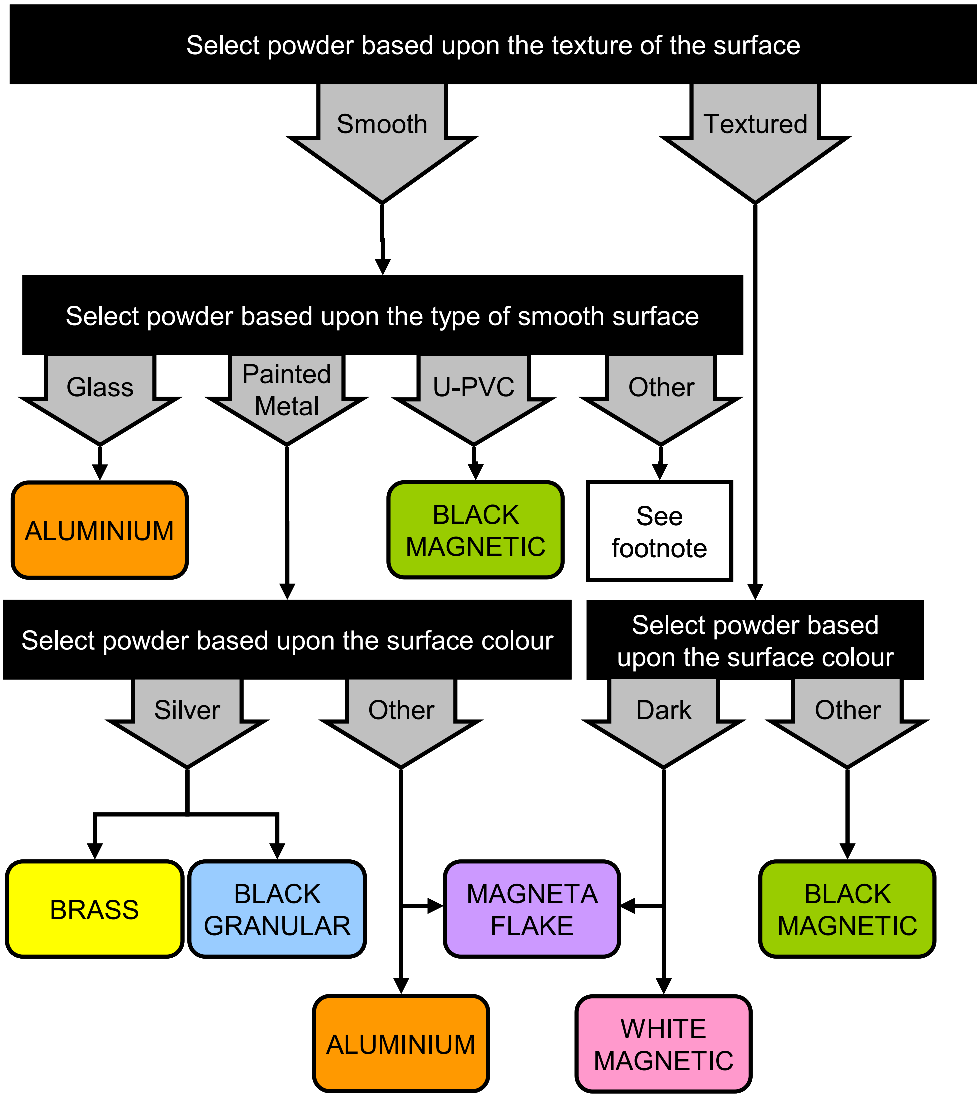
2.5 Electrostatic charge can potentially make large contributions to adhesion. It has been stated [14] that if particles are highly charged, the value of the attractive Coulomb forces exceeds that of other contributions to adhesion. Researchers have investigated various ways of utilising this effect for enhancing fingerprint development using powders, but it is not the major mechanism used in any of the types of powder widely used at crime scenes.

2.6 The presence of liquid or grease in a fingerprint deposit will promote adhesion of the particle to it for two principal reasons. The first is that the liquid is able to wet the surfaces, thus giving a greater contact area for the powder particles. The second is the capillary force of the liquid caused by surface tension. In atmospheres of relative humidity in excess of 70% the increase observed in the adhesion of microscopic particles is due to capillary forces. It has been suggested that in dry climates or for fingerprints that have dried out, ‘huffing’ (blowing warm, humid air or breath over the mark) or rehumidification prior to powdering may improve the quality of the developed print [17].

2.7 Once the initial layer of powder particles have adhered to the fingerprint ridge, the process of auto-adhesion (the interaction between individual powder particles) becomes important. In the case of aluminium powders it is suggested that repeated passes of the brush are used to ‘build up’ the mark, indicating that strong auto-adhesive bonds do exist between aluminium powder particles. For powdering with magnetic flake powders, a single sweep of the applicator is suggested, with further passes thought to ‘fill in’ or reduce the quality of the fingerprint. This indicates that auto-adhesive forces between magnetic flake particles are weak, and there is a possibility that the magnetised particles may repel each other.

3. CAST processes

3.1 CAST recommendations suggest the use of several different generic types of powder, the advice regarding selection being dependent on the type of surface being treated. The current (2011) recommendations are as follows [18]:



Home Office Centre for Applied Science and Technology flowchart for the selection of powders.

3.2 Aluminium flake powder is the most effective powder on glass, but shows similar performance to several alternative powders on other smooth, non-porous surfaces. For these surfaces aluminium may still be the powder of choice as it is easy to apply and develops good contrast marks on most smooth surfaces. The most effective brush for use with aluminium powder is the glass fibre, Zephyr-style. Although monitored trials established that exposure to aluminium dust in normal usage is an order of magnitude lower than allowable exposure limits, dust masks should be used with this powder when used in confined environments.

3.3 Brass (copper/zinc alloys commonly referred to as ‘bronze’ or ‘gold’ due to their colour) flake powders perform similarly to aluminium flake powder, but should only be used on smooth, silver coloured surfaces where aluminium would give low contrast. An appropriate dust mask must be worn when using this type of powder because the exposure limits for this type of powder are lower than those for aluminium flake and can be exceeded during normal use.

3.4 Black granular powder may be used on some smooth surfaces only and can be considered as an alternative to brass flake powder on silver coloured surfaces. Dust masks should be worn when using this powder.

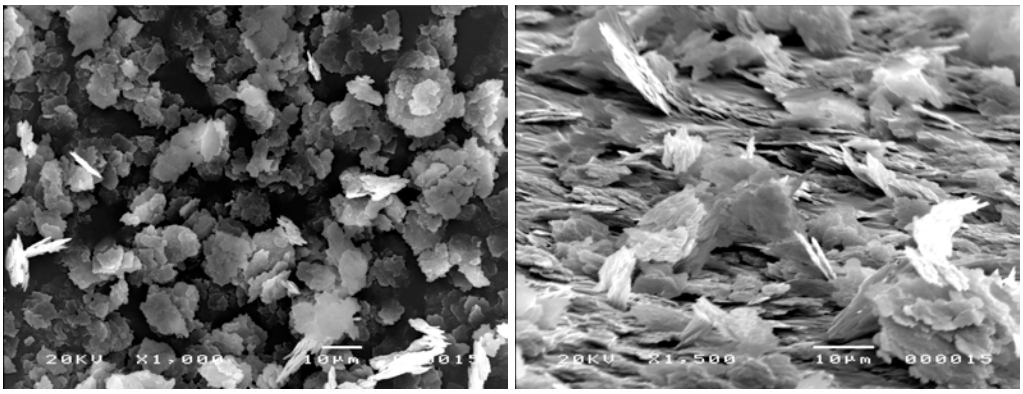
3.5 Black magnetic powder is the most effective powder on textured surfaces and unplasticised poly vinylchloride (uPVC). Similar results were obtained with 'jet black' magnetic powder, but others (grey, silver, etc.) were found to be considerably less sensitive. White magnetic powder, although less sensitive, may be used on dark, textured surfaces when contrast is an issue.

3.6 Magneta Flake powder is slightly less sensitive than black magnetic powder on textured surfaces, but may offer an alternative on dark textured surfaces. It may also be used on most smooth surfaces although application can be difficult and inconsistent.

3.7 Further information on each type of powder is given below.

3.8 Aluminium powder

The aluminium powder that was widely used throughout the UK was either 'Aluminium Super 8000' or 'Offset 901', both supplied by Wolstenholme International Ltd. Wolstenholme has recently been taken over and a closely equivalent powder is now supplied by the new parent company (Eckart Effect Pigments). Small-scale tests and microscopy indicate no significant differences in morphology or performance. They are metal flake powders, with smooth surfaces and jagged edges. The diameter of the particles falls within the range 1–12μm and the thickness is ~0.5μm. The flakes are coated with stearic acid during the milling process to prevent clumping.



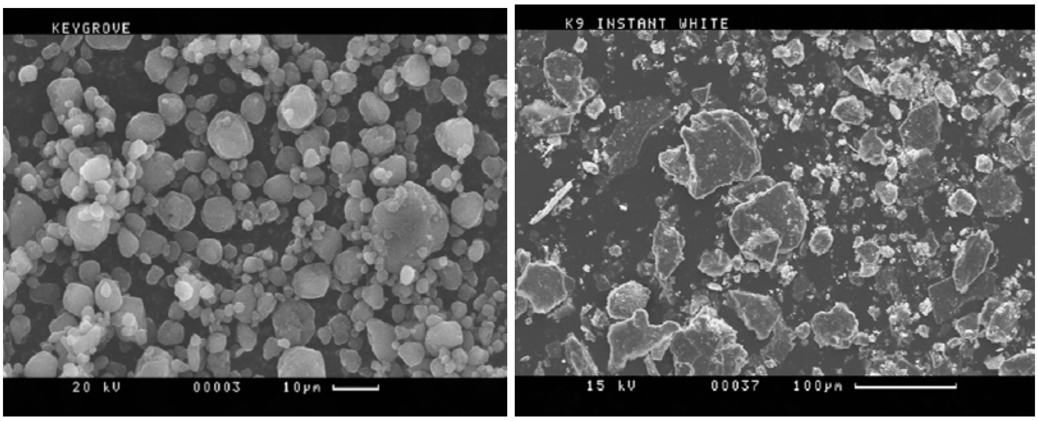
a) b)

Scanning electron micrographs of Wolstenholme Super 8000 aluminium powder showing a) flakes viewed from above and b) flakes viewed from the side.

3.9 Granular powders

Most black granular powders are carbon-based. The main carbon supplier in the UK is Cabot Ltd, which supplies most forensic providers with the Elftex 415 grade of carbon powder. This is an amorphous, elemental carbon with a particle size in the range 5–10µm and a textured, irregular (but smooth) shape.

3.10 White powders may contain more than one particle type. The example shown below consists of large flakes of magnesium silicate (20–100mm in size) with small granules of titanium dioxide (mostly <1µm). The small granules coat the surface of the flakes, suggesting that the flakes act as the carrier for the titanium dioxide granules.



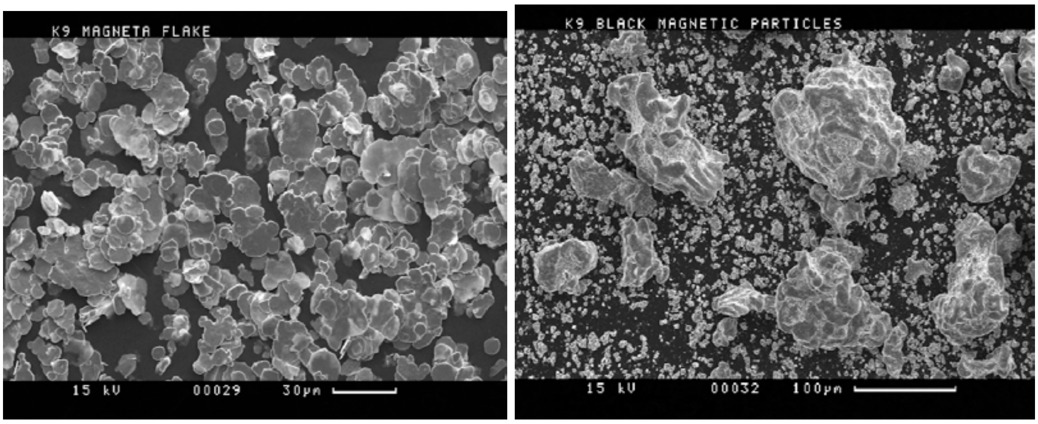
a) b)

Scanning electron micrographs of typical a) black and b) white granular powder.

3.11 Magnetic powder

There are two distinct types of magnetic powder used in the UK, Magneta Flake and black magnetic powder (traditionally called Magna powder). Magneta Flake was developed as part of a joint project between the Home Office and the University of Swansea in the early 1990s [15,16] and is now manufactured and distributed by CSI Equipment Ltd. It is produced by milling spherical carbonyl iron with 3–5% stearic acid in an appropriate solvent to produce a smooth edged flake with particle sizes in the range 10–60µm. Other types of magnetic flake powder are now available from other suppliers.

3.12 Black magnetic powder has a substantially different microstructure, consisting of large magnetic carrier particles of elemental iron (20 – 200µm) and smaller non-magnetic particles of iron oxide (Fe_3O_4) with a particle size in the range 3–12µm. The larger particles act as a carrier medium for the smaller particles, which adhere to the fingerprint ridges and develop the mark.



a) b)

Scanning electron micrographs of magnetic powders a) Magneta Flake and b) black magnetic powder

4. Critical issues

4.1 There are several critical issues to consider before powdering a surface. Before any powder is applied, a search should be made using a white light source to establish whether any visible marks are present. These should be captured before proceeding because not all marks found in this way will subsequently develop using powders.

4.2 An assessment should be made of the surface itself. If the surface is heavily contaminated, highly textured and/or porous, powdering may not be the best technique to use and alternative processes should be considered.

4.3 The type of powder used should be selected according to the nature of the surface, choosing both a powder type known to work well on that surface and a powder colour that gives a good contrast with the background.

4.4 The means of application should be compatible with the powder selected. Aluminium powders are best applied using a glass fibre Zephyr brush, magnetic powders using a magnetic applicator, and granular powders using a soft mop style of brush.

4.5 The decision on whether to lift the mark or to image in situ must be made according to the type of powder used. Aluminium (and brass) flake powders are well suited to lifting, magnetic and granular powders may be better imaged in situ first. However, regardless of the powder used there is always the possibility of damage during lifting and photography of the mark in situ should always be considered as a first option.

4.6 The sequential use of powders should be considered. It is possible that marks will not be developed by one type of powder, but may be subsequently enhanced by use of a different type.

5. Application

5.1 Suitable surfaces: Powders can be used on all non-porous types of surface including glass, plastics, metals, painted and varnished wood and ceramic, although they may not be the most effective process for that surface. In general, as the surface becomes rougher and more porous, the less effective powdering is likely to be.

5.2 The principal application of powders is the development of fingerprints on smooth non-porous surfaces at crime scenes, although recent research has shown them to be a valuable method for finding marks on textured or semi-porous surfaces such as wallpaper. The brush application method allows large areas such as windows, doors and door frames to be speculatively treated without recourse to more messy or time-consuming chemical treatments. The speed and effectiveness of the technique makes powders well-suited to volume crime applications. The fact that other treatments (such as blood dyes, powder suspensions and superglue) can be used sequentially after it also makes it an important first treatment at serious crime scenes.

5.3 In the laboratory, powders can be used on non-porous exhibits where it is suspected there may be a mixture of latent prints and marks in blood. This is because they can develop both types of mark and have no detrimental impact on subsequent treatment with blood dyes (unlike the alternative treatment option, superglue).

5.4 Powders should not be used if it is suspected that a surface is contaminated with any sticky residues (e.g. foodstuffs, oils) because powder will adhere to the entire surface and marks will not be resolved.

5.5 The means by which the powder is applied to the surface can also affect the quality of the mark. It has been recognised [19] that marks may be damaged by poor powdering practice and/or the use of the wrong type of brush. Similarly, brush application may often develop surface texture instead of the mark, and selection of an appropriate applicator may in some cases be more important than selection of the correct powder. HOSDB carried out extensive studies [11,20] to determine the optimum brush for use with aluminium powder and concluded that glass fibre, Zephyr-style brushes gave the optimum combination of ridge detail developed, contrast of the developed mark and minimal brush damage. This is because the glass fibre brush retained the powder well and released it gradually, which is most compatible with the gradual build up of the marks produced with this type of powder. In contrast, squirrel hair, mop style brushes give significantly worse performance in all three respects for aluminium powder, but are the most widely used brush for use with granular powders.

5.6 Magnetic powders (both black magnetic and Magneta Flake) are applied using magnetic wand applicators, where a small magnet in the tip of the wand picks up a ‘brush’ of powder when dipped into the powder container. This powder ‘brush’ is then applied to the surface, thus avoiding any direct contact between the applicator and the surface. Although such powders are relatively easy to apply to horizontal surfaces, application to vertical surfaces is less straightforward and powder may drop off. Ease of application to a particular surface should be taken into consideration when selecting the powder to use.

6. Alternative formulations and processes

6.1 There are many different types of powder being sold for fingerprint development applications and it is not possible to evaluate every product on the market. As a consequence, the advice given in the powder selection flow chart above refers to generic powder types only and not to a specific manufacturer’s products. It is known that several nominally similar products are now available on the market (e.g. ‘Magneta Flake’ and ‘Mag100’) and not all of these have been tested by CAST.

6.2 It is possible that some products may give better performance than those covered in the existing CAST guidance. If the use of a product not currently (as of 2011) within the generic powder types outlined above is proposed, it should be extensively evaluated against the existing powder types in laboratory trials on representative surfaces before being used operationally. The guidance given by CAST originates from tests utilising thousands of developed marks, and any trials recommending changes to that guidance should incorporate an equivalent number.

6.3 PSDB funded work in the mid- to late-1970s to develop an electrostatic powder process for developing fingerprints at scenes of crime [21-25]. The perceived advantages of the technique were that it could develop fingerprints without making any contact with the latent mark, and that the developed mark could be enhanced by removing excess powder without damaging the mark. The concept proposed by Roy 22] was the use of a positively charged high voltage electrode introduced above a quantity of powder within an insulating container to attract a powder coating onto the electrode. Holding the electrode over a surface bearing a fingerprint resulted in the formation of a powder cloud, with charged powder particles moving between powder and surface and some being retained on the fingerprint ridges. Several different powders were studied, the most appropriate for this purpose being found to be the semiconductor calcium tungstate ($CaWO_4$). Work was also carried out to develop a practical apparatus for powder delivery [21] and to explore mechanisms of deposition and cheaper alternative powders to calcium tungstate [23-25]. Ultimately the system did not enter widespread operational use, possibly because of limited benefits over conventional powdering, coupled with the added complexity of the application device compared with brushes.

7. Post-treatments

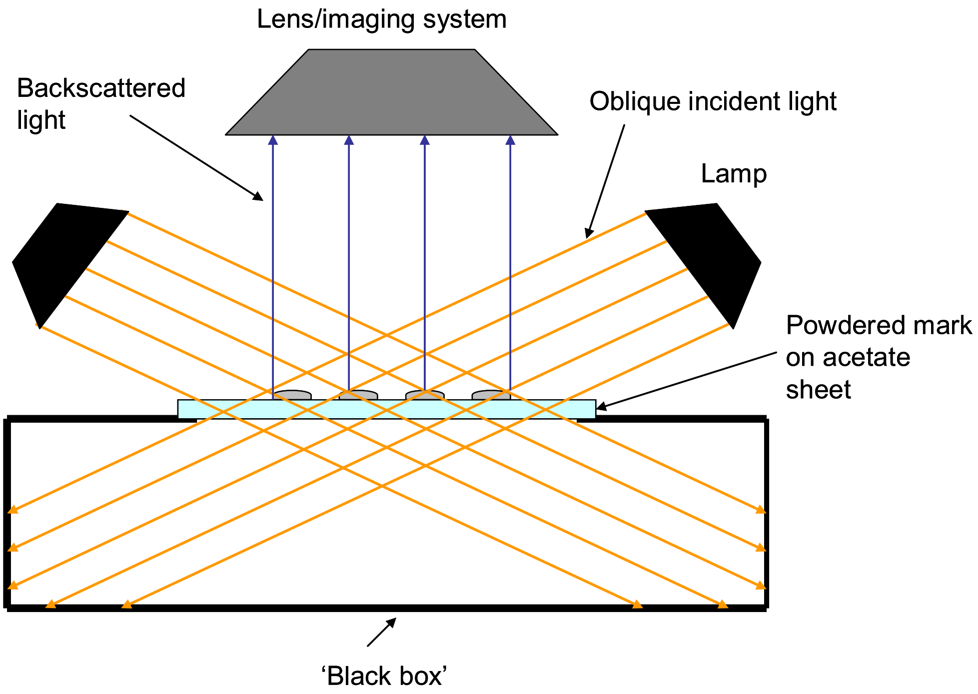
7.1 The main post-treatment for powdered marks is that of lifting. Advantages of this process include the fact that it enables a large number of marks developed using powder to be rapidly collected from a scene, it removes the powdered mark from the background environment it has been developed on and thus makes imaging of the marks in isolation easier, and it removes many issues associated with the level of skill of the crime scene photographer in capturing a good quality image.

7.2 To counter this, some disadvantages are that lifting may remove contextual information about the environment the mark was found in, and the quality of the lifted mark is potentially degraded from the mark developed in situ because some powder remains on the surface while the remainder adheres to the lifting medium. Lifting is most compatible with flake powders, it is less appropriate for granular and magnetic powders and may cause greater degradation to the quality of the lifted mark for these powder types. If it has been decided that the developed mark is to be lifted there are several types of material that can be used as lifting media, including:

- adhesive tapes and sheets;
- gelatine lifts;
- casting compounds.

7.3 In common with powders and brushes, selection of the optimum lifting medium for a particular type of mark may improve the quantity and quality of the marks recovered. However, there are few extensive published studies in this area.

7.4 The lifting process is principally used for aluminium powdered marks, but may be used for marks developed using other types of powder. For marks developed using aluminium flake, clear adhesive tapes are most commonly used as the lifting medium. The lifted mark is stuck to a clear acetate sheet, which is then retained as the exhibit. The contrast between the reflective aluminium powder and the transparent tape and acetate can be utilised to capture images of the lifted mark. Techniques used include contact printing using equipment such as the Camtac (although the advent of digital imaging is leading to this method becoming obsolete), scanning using a glossy black backing sheet, or using a ‘black box’ to enhance the contrast.



'Black box' imaging arrangement used to enhance contrast of aluminium lifts.

7.5 The type of lifting tape used does have an effect on the quality of the mark, and some studies have been carried out to assess this [26]. However, in practice there are few, if any, adhesive tapes produced solely for forensic use and it is difficult to ensure that any particular tape type will perform consistently from roll to roll. For this reason, CAST does not recommend any specific brand of lifting tape. Small-scale tests by CAST indicate that black gelatine lifts may actually be better than adhesive tape in lifting aluminium powdered marks, but this type of lift is more expensive, and more difficult to store and transport than tape lifts and is not routinely used.

7.6 Other recent developments associated with the lifting process include the introduction of wireless transmission of the fingerprint image from the crime scene to the fingerprint bureau. One approach [27] uses a flatbed scanner with a gloss black backing paper to scan the aluminium lift and image compression software to reduce the file size to a level that can transmitted over a mobile phone network in around 30 seconds.

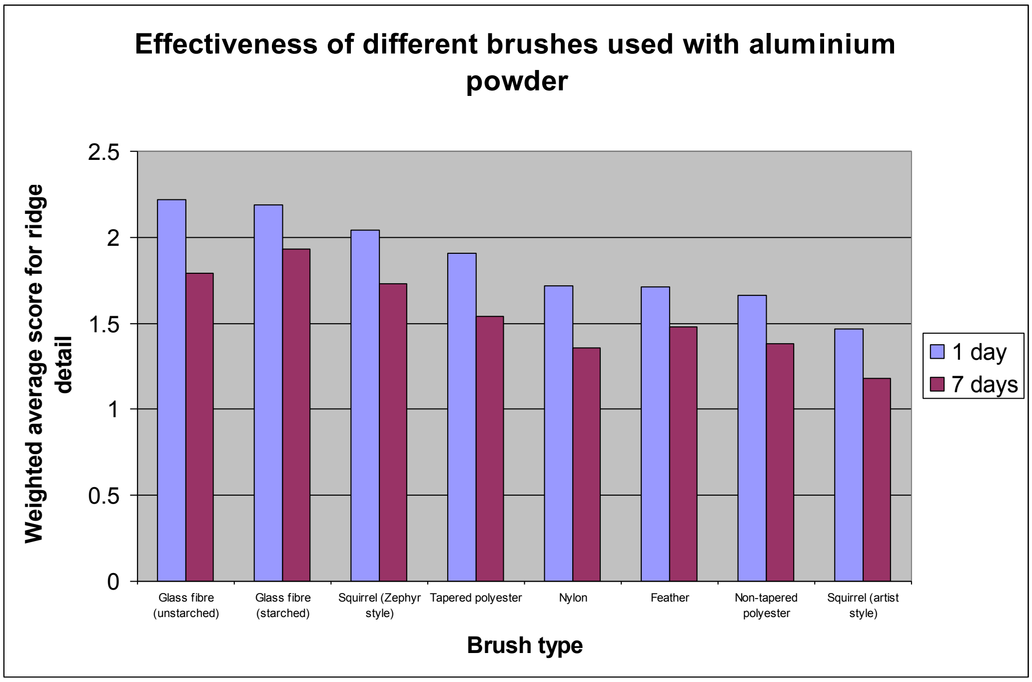
8. Validation and operational experience

8.1 Powdering is a very important process for fingerprint identification, with approximately 50% of fingerprint identifications (in excess of 30,000 per annum) being obtained from marks developed using this technique. As a consequence, any improvement in the effectiveness of powdering or guidance associated with its application has the potential to provide a significant number of additional identifications.

8.2 Laboratory trials

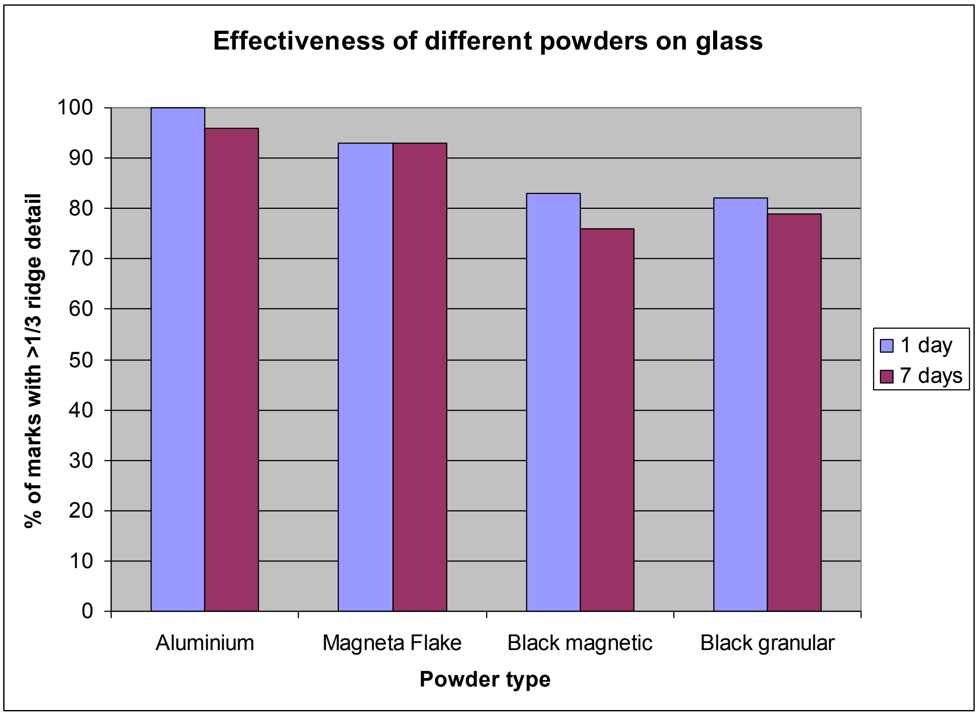
8.2.1 CAST has conducted extensive laboratory trials on both powders and the brushes used to apply them. Each study has involved the development and assessment of approximately 10,000 fingerprints.

8.2.2 Surveys carried out on powdering practice in the UK confirmed that by far the most widely used powder was aluminium, although many different brushes were being used for its application, including glass and polyester Zephyr, feather, and squirrel hair. The initial study [11,20] looked at the most effective brush type for the application of aluminium powder. Trials were carried out on four surfaces identified by a survey of scene of crime officers (SOCOs) as those most representative of those found at crime scenes, namely glass, uPVC, painted wood and painted metal. In all 12,640 marks were powdered and graded in terms of ridge detail developed, contrast and brush damage. The conclusion of this work was that glass fibre, Zephyr-style brushes gave the best results for this type of powder.

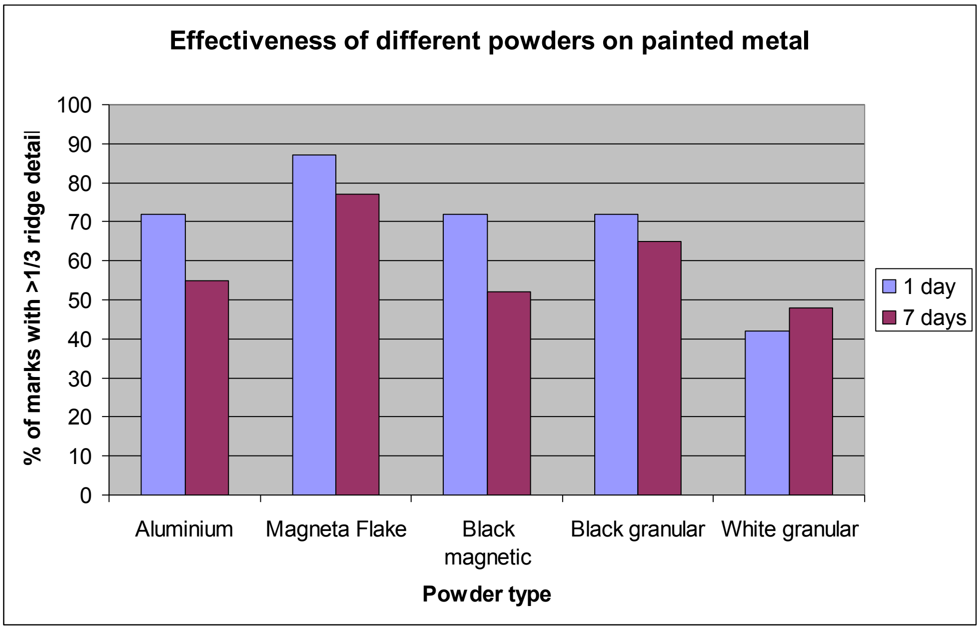


Summary of results obtained comparing the effectiveness of different types of brush used with aluminium powder.

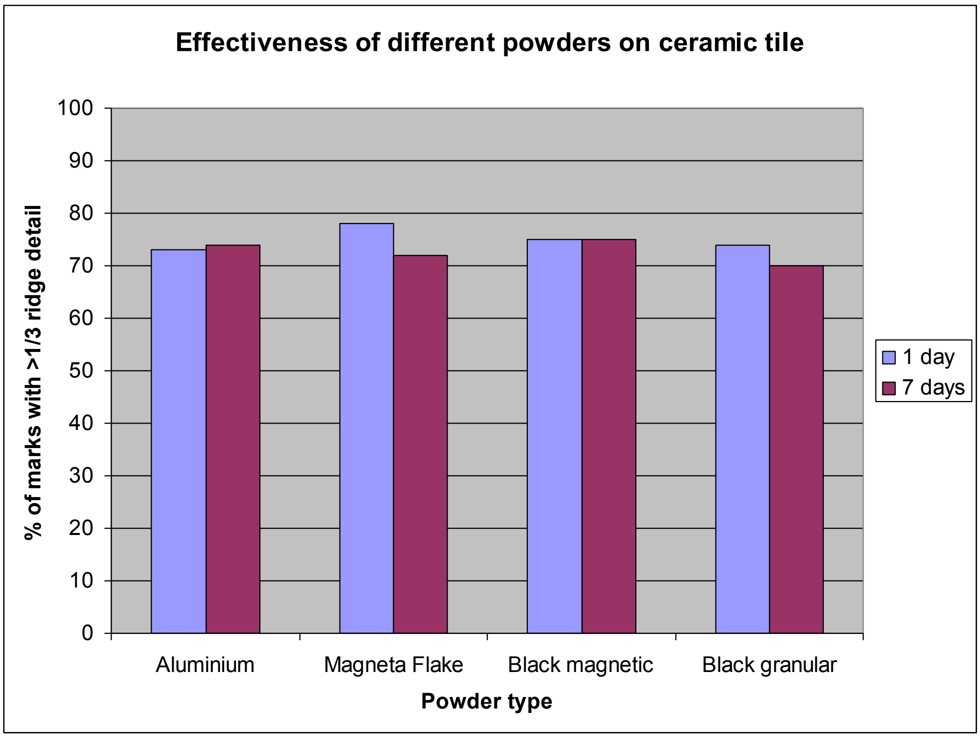
8.2.3 It was recognised that although aluminium is routinely applied to all the surfaces used in the trial summarised above, it may not actually be the best powder to use in all cases. The next stage of the work [12] therefore compared the effectiveness of aluminium against other types of regularly used powder on a series on smooth, non-porous surfaces (glass, painted metal, ceramic and gloss painted wood). Approximately 1,500 marks were developed on glass and approximately 2,500 on the other three surfaces. The results are shown below.



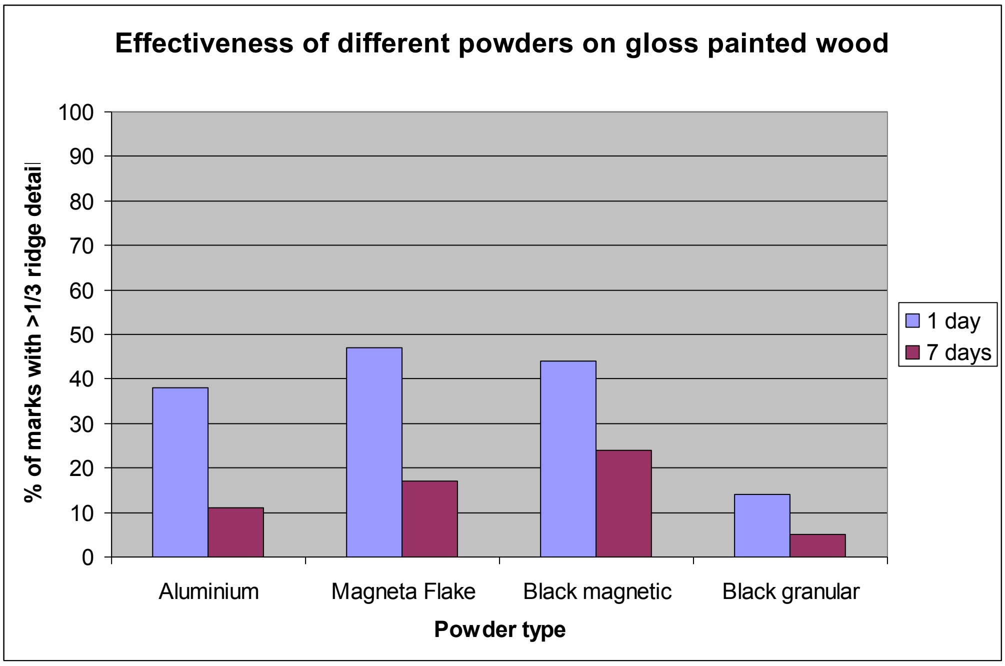
Comparison of different powder types on glass surfaces.



Comparison of different powder types on painted metal surfaces.

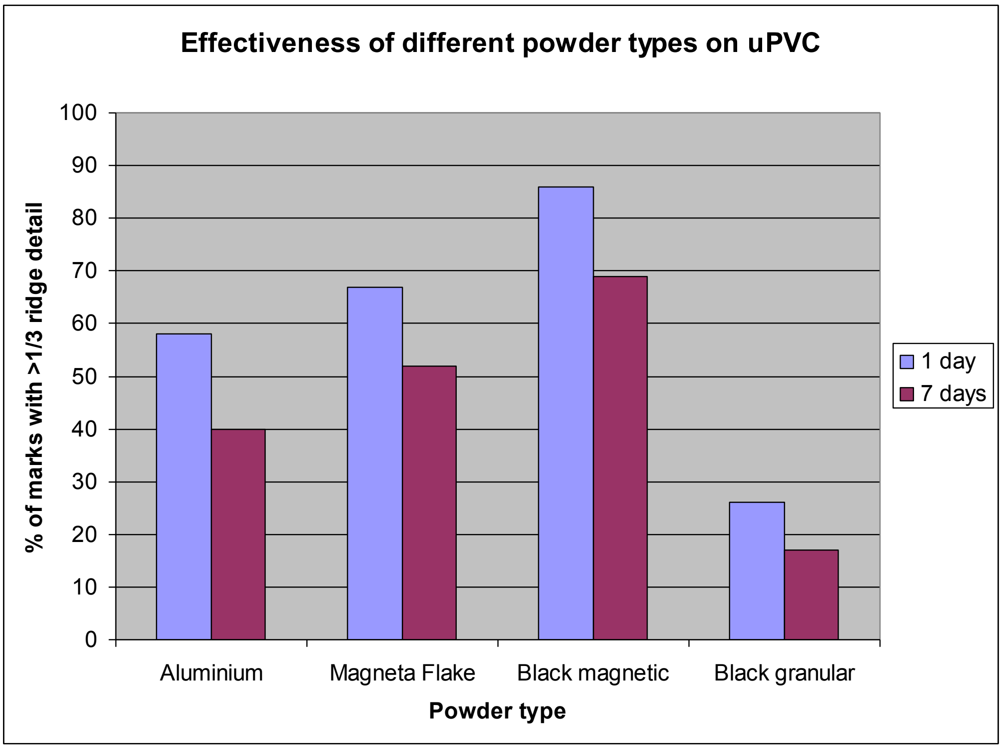


Comparison of different powder types on ceramic tiles.

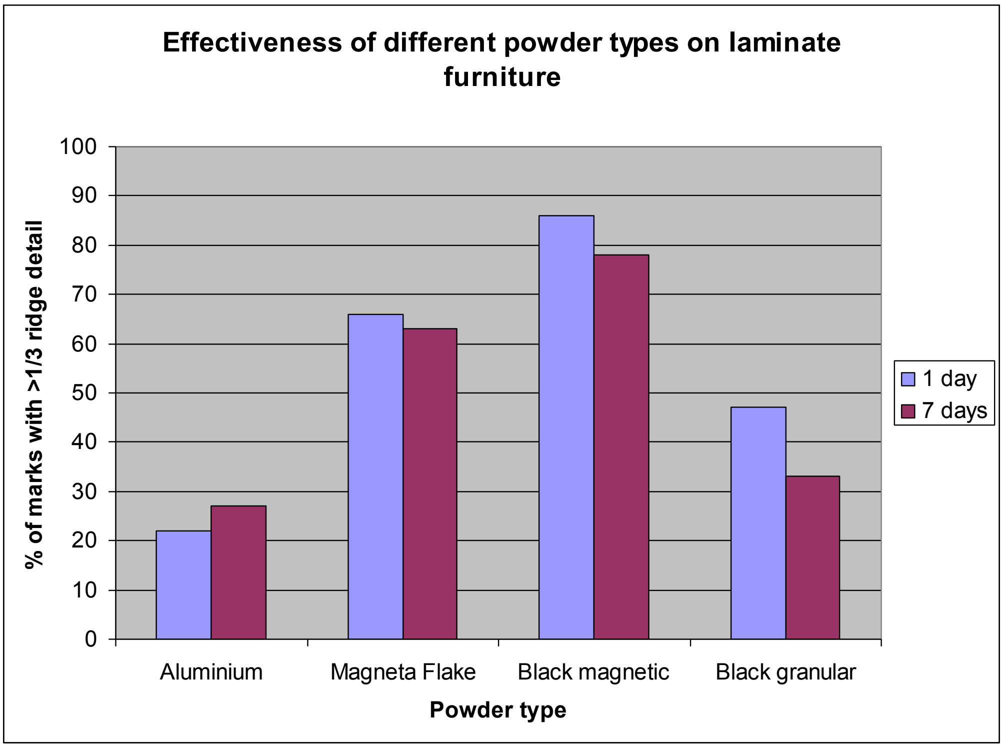


Comparison of different powder types on gloss painted wood.

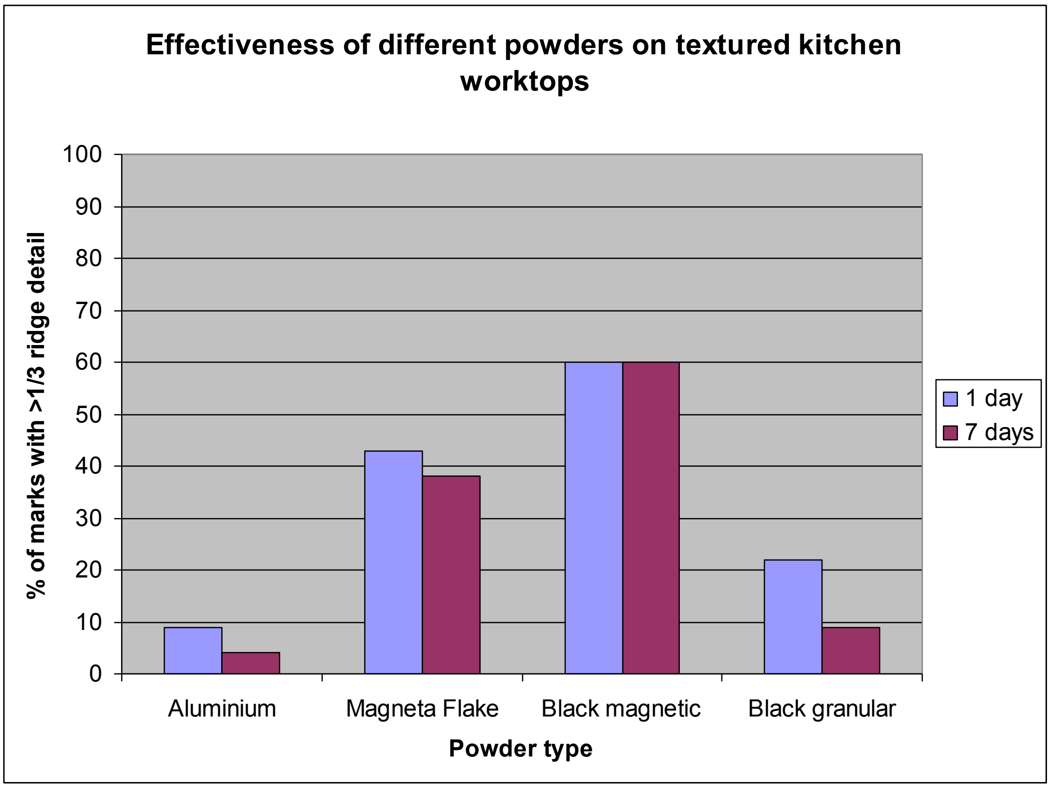
8.2.4 The results indicate that although aluminium powder is the best performing powder on glass, on other smooth surfaces magnetic powders may actually give slightly better performance. As the roughness of the surface increases the effectiveness of aluminium drops off and both types of magnetic powder are more effective. In order to investigate this further, the next trial compared a range of powders on surfaces with different levels of surface texture including uPVC, laminate furniture, kitchen worktops and wood furniture [13,28]. The graphs below show the results of this study, which developed and graded 9,560 marks.



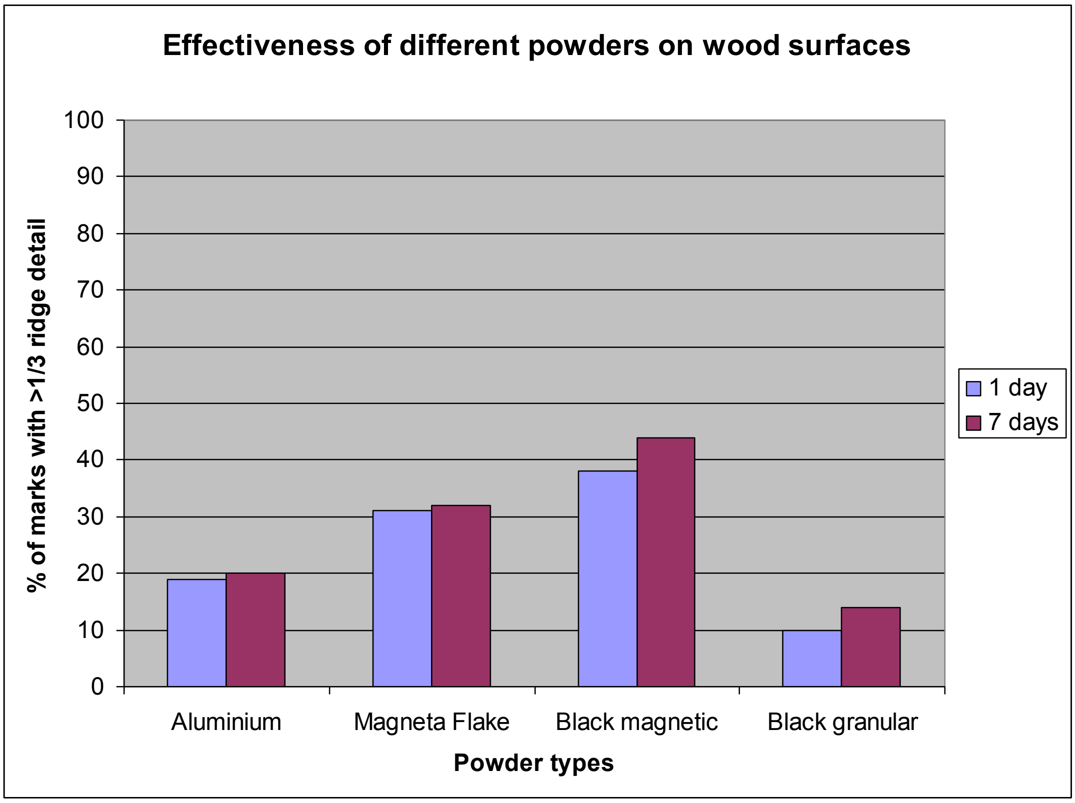
Comparison of different powder types on uPVC.



Comparison of different powder types on laminate furniture.



Comparison of different powder types on textured kitchen worktop material.



Comparison of different powder types on wood furniture.

8.2.5 When considering the results obtained from all surfaces examined, it is evident that as the surface becomes more textured, the effectiveness of both aluminium flake and black granular powder decreases significantly. The effectiveness of both types of magnetic powder also decreases as surface texture increases, but the degradation in performance is not as great and these powders are recommended for use on this type of surface.

8.3 Operational experience

8.3.1 Since the issue of the *Fingerprint Powders Guidelines* [18] in 2007, CAST has supplemented this with several training sessions targeting SOCOs at individual police forces. In some cases there have been reported rises in the use of black magnetic powder at the expense of aluminium flake and an increase in marks developed, but at present (up to 2011) it is difficult to assess whether both trends will be sustained in the long term.

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