Recent Advances in the Use of Physical Developer

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Background
Background

- The PD we use today is based on the classical silver-based physical developers used to develop film.
- The classic developers selectively deposited silver on photo-exposed silver bromide (AgBr).
- Chemical developers selectively change photo-exposed AgBr to silver.
- Photo-exposed AgBr has specks of Ag⁰ and Ag₂S on its surface (these are “triggering sites”).
Background

- The triggering sites are catalytic sites for the reduction of silver by the reducing agent
- Each silver atom that deposits is in turn a catalytic site for further silver deposition
- The development is therefore autocatalytic
Jonker, et al. worked in the 1960s to improve the stability of classic photographic physical developers.

Their primary contribution was to include a cationic (i.e., positively charged) surfactant to the developer.

This extended the half life of the developer from a few minutes to hours (or even months for developers used for photo-fabricating micro-electronic components.)
Morris, et al.

- UK Home Office PSDB
- Morris modified the Jonkers “Philips Research Laboratories PD photographic process” to develop LP on wet surfaces in 1975
- Morris, et al. took advantage of observation that prints left inadvertently on photographic plates were made visible by the photographic PD solution
- Morris’ colleagues had previously used classical PD to amplify faint metal prints developed using VMD
Susan Morton

- Formerly employed by the U.S. Postal Service, Western Region Laboratory (CA)
- Introduced PD to the US law enforcement community in the early 1980s after observing the process at a conference in England
- She was first person in the US to routinely use PD on casework
- She provided assistance to the FBI in a high profile homicide investigation (Jacqueline H Lard case) in 1986
- They requested assistance in processing wet paper items for FP and shoe prints
Susan Morton

- Fifty (50) pieces of evidence were processed and 15 prints of value were developed (11 of which were not developed by previous treatments)
- Fourteen (14) were elimination prints; 1 remained unidentified
- Morton also observed that footwear impressions could also be developed by PD.
- During a robbery of a post office in Arizona, the suspect vaulted over the counter and landed on a white paper desk cover from a post office
- Noted that PD had sensitivity to rubber glove impressions so a decision was made to try to develop rubber shoe impressions on the paper
PHOTOGRAPH "A"
Green-filtered high contrast photograph of barely-visible dusty shoe print.

PHOTOGRAPH "B"
Photograph of shoe print developed with 'Physical Developer'.
Physical Developer
Mechanism
Oxidation-Reduction (Redox)

- A redox reaction is one in which substances exchange electrons (and undergo changes in oxidation number)
- In the PD reaction, iron (Fe) and silver (Ag) change oxidation states (note superscripts below)
- The main reaction that occurs in physical developer may be generalized as follows:

\[ \text{Fe}^{2+} + \text{Ag}^+ \rightarrow \text{Fe}^{3+} + \text{Ag}^0 \]

- This redox reaction produces the metallic silver particles that interact with the latent print deposit
- This is the engine that drives the PD reaction
Oxidation-Reduction (Redox)

- The overall cell potential for the PD reaction:
  \[
  \begin{align*}
  \text{Ag}^+ + e^- & \rightleftharpoons \text{Ag}^0 & \mathcal{E}_0^0 &= 799.6 \text{ mV} \\
  \text{Fe}^{+2} & \rightleftharpoons \text{Fe}^{+3} + e^- & \mathcal{E}_0^0 &= -771.0 \text{ mV} \\
  \text{Ag}^+ + \text{Fe}^{+2} & \rightleftharpoons \text{Ag}^0 + \text{Fe}^{+3} & \mathcal{E}_{\text{cell}}^0 &= 28.6 \text{ mV}
  \end{align*}
  \]

- The standard cell potential for this system is positive (28.6 mV) so the reaction is thermodynamically feasible.

- The small value for \( \mathcal{E}_{\text{cell}}^0 \) was achieved as a compromise by Jonker et al. by adjusting the concentrations of the ferrous, ferric, and silver ions to make the reaction proceed slowly (thus suppressing the spontaneous formation of silver particles) and in a stable fashion.
PD Working Solution (Current SOP)

**Redox Solution**
- 30 g ferric nitrate
- 80 g ferrous ammonium sulfate
- 20 g citric acid
- 900 mL RO/DI water

**Detergent Solution**
- 3 g n-dodecylamine acetate
- 3 mL Tween 20
- 1 L RO/DI water

**Silver Nitrate Solution**
- 10 g silver nitrate
- 50 mL RO/DI water

**Malic Acid Solution**
- 25 g malic acid
- 1 L RO/DI water

**PD Working Solution**
- 900 mL Redox Solution
- 40 mL Detergent Solution
- 50 mL Silver Nitrate Solution
Role of Different Components

- **ferric nitrate** – Fe(NO₃)₃ • 9H₂O
  - Provides the ferric (Fe⁺³) ions that are one component of the redox reaction

- **ferrous ammonium sulfate** – Fe(NH₃)₂SO₄ • 6H₂O
  - Provides the (Fe⁺²) ions that are the other half of the redox reaction

- **silver nitrate** – AgNO₃
  - The source of the silver colloidal particles (reduced by the iron redox system) that ultimately interact with the latent print residue on the surface
Role of Different Components

\[
\frac{[\text{Ag}^+]/[\text{Ag}^+]_{\text{fresh}}}{[\text{Fe}^{2+}]/[\text{Fe}^{2+}]_{\text{fresh}}}
\]

- Good Quality Marks
- Development Time \(\leq 20\) min
- No Marks Developed
- Poor Quality Marks
- Development Time \(\geq 20\) min

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Role of Different Components

- **Citric acid – C₆H₈O₇**
  - Adjusts the pH and provides citrate ions (HL³⁻) that surround the nascent silver colloid particle and changes the charge from positive to negative to prevent aggregation.
Role of Different Components

- n-dodecylamine acetate/ Synperonic N/Tween 20
  - n-dodecylamine acetate (cationic surfactant) forms a micelle around the negatively charged colloid (protecting it)
  - Synperonic N or Tween 20 (non-ionic surfactants) help keep n-dodecylamine acetate soluble (act as protecting groups)
Role of Different Components

negatively charged silver colloid

cationic surfactant

positively charged micelle encapsulating (negatively charged) silver colloid
(cationic surfactant molecules stacked in staggered form)
Role of Different Components

- maleic/malic acid – $\text{C}_4\text{H}_4\text{O}_4/\text{C}_4\text{H}_6\text{O}_5$
  - Acid is needed to eliminate the calcium carbonate present in the paper
  - Failure to do this results in the entire paper surface turning black from spontaneous silver deposition
  - Any acid that does not contain chlorine will work
  - Examples include nitric, acetic, malic, maleic

![Chemical structures of maleic and malic acids]
Role of Different Components
Role of Different Components

- Purified water
  - Purified water is needed for making, rinsing, and processing with PD because traces of chlorine present in regular tap water will react with the silver nitrate present in the PD
  - Although deionized water can be used, most often distilled water is sufficient for processing with PD
  - To determine if the treated water is adequate, place a few crystals of silver nitrate into a small beaker filled with the water*
  - If the solution turns cloudy, the water is not usable

Role of Different Components

![Two beakers with different volumes of liquid.](image)
Role of Different Components
Role of Different Components

- **Bleach intensifier**
  - In some cases the use of a dilute solution of household bleach will help intensify weakly developed PD prints.
  - Bleach may oxidize any “stubborn” ninhydrin stains and will also darken the PD development.
  - The mechanism of this intensification was suggested by Ms. Susan Morton, (formerly of the Postal Crime Laboratory, St. Bruno, CA. The overall reaction is:

\[
2\text{Ag}(s) + \text{ClO}^- \rightleftharpoons \text{Ag}_2\text{O}(s) + \text{Cl}^- \quad E^0_{\text{cell}} = 470 \text{ mV}
\]

(gray) \hspace{1cm} (black)
Role of Different Components

- **Potassium iodide (KI)**
  - Introduced by Dr. George Saunders in the 1990s
  - Developed by Dr. George Saunders (Los Alamos NL) - essentially the PD print is lightened while the background is darkened
  - A solution of redox and KI is used to convert the silver PD print (dark gray) to silver iodide (white)
  - The paper substrate is darkened by the reaction of KI with starch present in the paper (NOTE: paper must have starch)

\[
\begin{align*}
2e^- + 2Fe^{3+} & \rightleftharpoons 2Fe^{2+} & \varepsilon^0 &= 771 \text{ mV} \\
3I^- & \rightleftharpoons I_3^- + 2e^- & \varepsilon^0 &= -536 \text{ mV} \\
3I^- + 2Fe^{3+} & \rightleftharpoons I_3^- + 2Fe^{2+} & \varepsilon^0_{\text{cell}} &= 235 \text{ mV}
\end{align*}
\]
2I\(^{-}\) + 2FeCit + starch ⇌ 2Fe\(^{2+}\) + 2Cit\(^{3-}\) + starch:iodine “complex” (blue-violet)

Ag\(_2\)O + 2H\(^{+}\) + 2I\(^{-}\) = H\(_2\)O + 2AgI (yellow-white)

Ag\(_2\)O-PD print on printed background

Image of the bleached Ag\(_2\)O print (light print & dark background)
Ag$_2$O-PD print on printed background

Reverse color image of the bleached Ag$_2$O print
Temperature Considerations

- Experiments performed by Dr. John Brennan (Forensic Science Service) and presented at the 1999 meeting of the International Fingerprint Research Group in Ottawa, Canada
  - >35°C (95°F) caused the background development to increase
  - <20°C (68°F) resulted in too rapid development time
  - Optimum temperature range was found to be 25 – 30°C (77 – 86°F)
  - Clear and identifiable 15 year old prints were developed at 30°C in about 85 seconds
Temperature Considerations

Source: Dr. John Brennan, Senior Chemist, FSS SL&R Unit, London
(from the 1999 IFRG Meeting, Ottawa, Canada)
Effect of LP Age

- PSDB tested old checks and some bills and receipts found at a house
- The bills dated between 1946-48
- DFO did not develop any ridge detail on the 50 year old samples
- Ninhydrin developed some faint ridges
- PD was the most successful – yielding 7 identifiable prints
Effect of LP Age

Physical Developer on an electricity bill
Physical Developer
Particle Formation
PD Particles

Source: Pacific Northwest National Laboratory
PD Particles

Source: Pacific Northwest National Laboratory
PD Particles

Source: Pacific Northwest National Laboratory
PD Particles

Source: Pacific Northwest National Laboratory
PD Particles

Source: Pacific Northwest National Laboratory
Synperonic N Replacement
Synperonic N Replacement – USSS

- Back in the early 2000s, our source for purchasing Synperonic N had considered no longer selling the product in small quantities.
- Pending ban/phase-out of Synperonic N by the European Union by 2000.
- Three new surfactants were chosen for evaluation: Tween 20, Tween 80, and Nonidet P40 (also known as Triton-X 100 and Tergitol NP 9, it was recommended by the Synperonic N manufacturer, Brenntag).
- Tests began in 2003 with 11 donors, 5 paper types, and prints aged for five days (a total of 117 prints were evaluated).
Synperonic N Replacement – USSS

Figure 1. Figures 1a through 1c are examples of prints that have been processed with PD containing Tween 20 and regular PD.
Synperonic N Replacement – USSS

Figure 2. Figures 2a and 2b are examples of prints treated with regular PD and a PD solution containing P40 Nonidet. Figure 2c is an example of a print treated with regular PD and a PD solution containing Tween 80.
U.S. Secret Service Conclusions

- Of the 13 evaluators (some were certified Fingerprint Specialists and others were laypersons with no formal training), 10 chose Tween 20 as the best replacement.

- Three evaluators chose the Nonidet P40; none chose Tween 80.
Synperonic N Replacement – HOSDB

- The EU banned sales of nonylphenol ethoxylates for industrial uses beginning in 2000
- HOSDB evaluated the following for possible substitution for Snyperonic N: Tween 20, Tween 80, Synperonic 91/5, Synperonic 91/6, Synperonic 13/6.5, and Caflon-N
HOSDB Conclusions

- The results indicate that Tween 20 was the closest to match Synperonic N (average difference of 2)

- Other compounds included (in decreasing order of effectiveness): Synperonic 91/6 (5); Tween 80 (6); Caflon-N (8); Synperonic 91/5 (11.5); and Synperonic 13/6.5

- An interesting observation regarding PD and temperature was made – if the temperature of the PD solution fell below 17°C, silver would begin to fall out of the solution (Brennan noted that the optimum temperature for the PD reaction was ~30°C, which is slightly higher than room temperature)

- Since none of the other compounds worked as well as Synperonic N, no recommendation was made for a Synperonic N substitute
Longevity of PD
Working Solutions
Introduction

- In October 2008, a large batch of PD working solutions were made but not used due to a decrease in casework caused by the presidential campaign.

- In November 2008, Dr. Marcel de Puit, Netherlands Forensic Institute (NFI) visited our laboratory and we observed that a 1-month old PD solution still worked and did not have any precipitates.

- In December 2008, Dr. Steven Bleay, Home Office Centre for Applied Science and Technology (CAST – formerly HOSDB) visited our laboratory and we observed that the same PD solution (now 2 months old) still worked and did not have any precipitates.
This article gave evidence that the non-ionic surfactant's role in PD was more than to just help to dissolve n-dodecylamine acetate.

The physical adsorption of Tween 20 onto the surface of the silver colloid stabilizes them against aggregation because the oligo (ethylene glycol) moieties of the surfactant provide steric stabilization.
Background

- The adsorption of Tween 20 on the colloidal gold particles mentioned in this article took 20 minutes to reach 95% saturation.

- However, with a PD working solution, as the n-dodecylamine acetate begins to envelop the colloid particle, the negative charge is reduced, making the particle susceptible to agglomeration.

- The large, branched structure of Tween 20 prevents this from happening due to steric hindrances.
Background

- Interestingly, Tween 20 has a critical micelle concentration of 0.06-0.07% in water at room temperature.
- The concentration of Tween 20 in the current physical developer formulation used by the U.S. Secret Service is approximately 0.012%.
- Thus, the amount of Tween 20 in the PD solution is too low to spontaneously form micelles (consisting of pure Tween 20) but apparently high enough to adequately protect the nascent silver colloids via steric hindrance.
Background

- Tween 20 appears to be larger than Synperonic N and provides better steric protection for the silver colloid.
- Tween 20 also appears to be more soluble in water than Synperonic N, which can improve stability.
- Detailed solubility data for these two compounds could not be found.
Synperonic N

- Previously known as Lissapol, Synperonic N had a wide range of applications in the conservation of antiquities.
- It is a 27% v/v solution of the nonylphenol ethoxylate, Synperonic NP8 (made by ICI’s Uniqema subdivision until 1999).
- Degradation of nonylphenol ethoxylates occurs by progressive shortening of the polyoxyethylene hydrophilic chains.
- This makes the compound progressively less soluble in water and more likely to aggregate with other suspended solids.

Source: http://aic.stanford.edu/jaic/articles/jaic43-01-005_1.html
Tween 20

- Also known as Polysorbate 20, Tween 20 is a polyoxyethylene derivative of sorbitan monolaurate.
- Related compounds have some applications in the food industry (e.g., ice cream).
- Generally recognized as safe (GRAS).
PD Longevity Tests

- A formal study was initiated to investigate the differences in longevity between PD working solutions made with Synperonic N and Tween 20
- More than 1000 prints from 6 donors were deposited on three paper types (two copier papers and blue lined notebook paper)
- Initially, two 4 L batches of each working solution were prepared
- As these solutions aged, new ones would be made and compared to the aging ones
PD Longevity Tests

- Initial results were somewhat unexpected – when the first bottle had been used up and the other 4 L batch used, the results obtained at the beginning of tests using the second bottle were better than at the end of the first batch.

- It was assumed that since the bottle had been sealed from the atmosphere and not opened until the first bottle had been used up, the contents of the second bottle had been protected from oxidative degradation (e.g., conversion of Fe$^{+2}$ to Fe$^{+3}$ and breakdown of surfactants).

- A new procedure which took equal amounts from each bottle at the same time resolved this issue.
PD Longevity Tests

- Results indicate that for physical developer working solutions using Synperonic N, the range for stability is between 7-15 days.
- For physical developer working solutions using Tween 20, the range for stability was found to exceed 2 months.
PD Longevity Tests – Synperonic N

NOTE: The symbol “(F)” denotes a freshly made solution
PD Longevity Tests – Synperonic N

- PD working solutions incorporating Synperonic N in the detergent solution lasted between 7-15 days
- Noticeable degradation occurred after 7-9 days
- No reactions were observed after ~15 days
PD Longevity Tests – Tween 20

NOTE: The symbol “(F)” denotes a freshly made solution
PD Longevity Tests – Tween 20

- PD working solutions incorporating Tween 20 in the detergent solution lasted for more than 2 months
- Fresh Tween 20 solutions did not work as well as ones that were several days old
- After a few days the solutions appeared to stabilize and then plateau off (with regard to performance)
- Experiment may be repeated with 3 – 5 day old PD working solutions to see if this makes a difference in the comparisons (this had no effect on determining whether older PD solutions could still develop prints)
Reliability Testing
Why Perform Reliability Tests?
Reliability Tests

- How do you know that your reagent was mixed properly?
- Did someone forget to add silver nitrate?
- If so, how could you tell?
- How do you know that your reagent is working properly?
- Did the item you processed really have not latent prints on it or was the reagent made wrong?

Reliability testing of reagents is considered *essential* by accreditation boards like ASCLD-LAB and ASCLD-LAB International.
The Test Strip Idea

- Prior to our laboratory achieving accreditation in 1997 by ASCLD/LAB, a series of spot tests were adopted for latent print visualization reagents.


- Gold chloride selected for the PD spot test.
The Test Strip Idea

- Test strip must react rapidly (ideally in seconds rather than minutes and must be stable for long periods of time)
- Test strip must give some information about the “health” of the PD solution
- Qualitative rather than quantitative measurements
- Planted prints not found to be sufficient (donor variation)
- Artificial sweat (shelf-life/storage conditions issues)
The Test Strip Reaction

- Initial step: Formation of gold particles (these become nucleation sites for Ag physical development)

\[ \text{AuCl}_4^- + 3e^- \rightleftharpoons \text{Au}^0 + 4\text{Cl}^- \quad \mathcal{E}^0 = 1002 \text{ mV} \]

\[ \text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+} + e^- \quad \mathcal{E}^0 = -771 \text{ mV} \]

\[ \text{AuCl}_4^- + 3\text{Fe}^{2+} \rightleftharpoons 2\text{Au}^0 + 3\text{Fe}^{3+} + 4\text{Cl}^- \quad \mathcal{E}_\text{cell}^0 = 231 \text{ mV} \]
The Test Strip Reaction

- Final step: nucleation of silver particles
  \[ \text{Ag}^+ + \text{Fe}^{2+} \xrightleftharpoons[\text{Au}^0]{\text{Ag}^0 + \text{Fe}^{3+}} \]

- The overall cell potential (231 mV) is positive and therefore the reaction is thermodynamically favorable

- This reaction governs the silver deposition (development power) and the rate of silver deposition (development speed)
Test Strip Preparation

- Gold chloride test solution is prepared by taking 10 μl of the 10% w/v stock gold chloride solution from MMD and diluting that in 50 mL of RO/DI water
- A 10 μl spot is placed on a piece of Whatman paper
- Spot test reaction takes < 10 seconds
Test Strip Usage

- The speed of the reaction and the intensity of the spot color are two qualitative measures of PD reagent “health”

- Several batches of PD have failed this test and were subsequently found to have not been made according to the SOP
Stability of Test Strips

- Problems were observed in 2009 with the stability of the tetrachloroauric acid (gold chloride) reagent as well as the spot test strip itself.
- Freshly made PD solutions were not reacting as quickly as expected with the spot test strip and the color was not as intense.
- Within only a few months, the tetrachloroauric acid reagent appeared to deteriorate.
EDTA

- PD was first noted to react with tetra-sodium EDTA by Morris in 1975
- Forensic Science Service (under contract with DoD TSWG) developed a PD test strip based on tetra-sodium EDTA in 2005
- In 2009, the USSS began to experiment with replacing the current gold chloride spot tests with EDTA
- EDTA test strips worked very well and were more stable than gold chloride ones [JFI, 2011, 61(6):640-651]
Other Systems

- The Bundeskriminalamt (BKA) used four different concentrations of ascorbic acid and a single concentration of oleic acid printed with an inkjet printer (HP 550C/HP 51626a cartridge)
- Four-way arrow and fingerprint ridge detail pattern used
- Positive results are indicated if the first three fields of ascorbic acid and the one oleic acid field are dark
- Negative results are indicated if fields 3 and 4 or field 5 are not visible
Other Systems

Strips 1 and 2 are positive results and 3-5 are negative
Limitations

- Test strips v. real operational prints
- Average performance of reagent over time
- This will not tell you if newly prepared reagent will work properly
- Test strip tells operator that the reagent will work within a given set of tolerances
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