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Examination of the Steps Leading up to the Physical Developer Process for Developing Fingerprints

ABSTRACT: This is a systematic study that examines several acid prewashes and water rinses on paper bearing latent prints before its treatment with a silver physical developer. Specimens or items processed with this method are usually pretreated with an acid wash to neutralize calcium carbonate from the paper before the treatment with a physical developer. Two different acids at varying concentrations were tested on fingerprints. Many different types of paper were examined in order to determine which acid prewash was the most beneficial. Various wash times as well as the addition of a water rinse step before the development were also examined. A pH study was included that monitored the acidity of the solution during the wash step. Scanning electron microscopy was used to verify surface calcium levels for the paper samples throughout the experiment. Malic acid at a concentration of 2.5% proved to be an ideal acid for most papers, providing good fingerprint development with minimal background development. Water rinses were deemed unnecessary before physical development.

KEYWORDS: forensic science, physical developer, fingerprint, fingerprint development, SEM, SEM-EDS, acid wash, water rinse, malic acid, nitric acid

Silver physical development usually follows the ninhydrin development in the visualization of latent prints on paper (1,2). Ninhydrin develops the water-soluble amino acid fraction of the latent print residue while the silver physical developer (PD) develops the remaining water-insoluble fraction of the latent print residue. DFO, a fluorogenic reagent that reacts with amino acids to give a fluorescent product, sometimes precedes the ninhydrin development. The water-insoluble fraction that the silver PD develops contains lipids, which are sometimes referred to as the "oils" of latent print residue. The sweat pores in the palm of the hand do not excrete lipids; hands become contaminated with lipids by touching the face, which contains sebum-secreting sebaceous glands, hair, which acquire its lipids from its roots, or lipid-based items such as certain foods and cosmetics.

The main components of a silver PD are silver ions (Ag^+) and ferrous ions (Fe^{2+}) that end up reducing the silver ions to silver metal.

$$Ag^+ + Fe^{2+} \rightleftharpoons Ag + Fe^{3+} \quad (1)$$

This reduction occurs on triggering or nucleating sites, apparently contained in the water-insoluble fraction of latent print residue on paper (1,2). Interestingly, the silver deposition does not occur on latent print residue that is on nonporous surfaces; this indicates that the large surface area that the residue acquires when it penetrates paper plays a role. The components in the developer that keep the system stable (i.e., keep the silver ions from being reduced by the ferrous ions) include ferric ions (these form a "redox couple" with ferrous ions, allowing reversibility in the reaction), citric acid (its citrate ions binds with ferric ions to form ferric citrate), a cationic surfactant (this keeps any in-solution reduced silver from growing), and a nonionic surfactant (this helps solubilize the cationic surfactant). The delicate balance among the silver, ferrous, ferric, and citrate ions suppresses the in-solution reduction of silver.

If a paper is basic ($pH > 7$), it is usually because it contains a calcium carbonate ($CaCO_3$) filler. Before treating it with the silver PD, it must be neutralized, for otherwise the silver ions in the developer will react with it, forming silver oxide (Ag_2O). The Ag_2O essentially turns the paper black. Thus, acid neutralization is necessary for clear visualization of the latent prints. Additionally, the acid must not contain chloride ions (Cl^-) as these ions usually remain in the paper and they combine with the silver ions from the developer to form silver chloride, which eventually turns to silver, making the paper black. Historically, maleic acid was recommended (3). However, dilute nitric acid (1,2) or even acetic acid works (personal communication with Inlow V. and Ramotowski R. from the United States Secret Service, 1998), although the latter leaves an odor. Malic acid was recently introduced by the FBI as a replacement of maleic acid. All of these acids make the paper-containing $CaCO_3$ effervesce, releasing carbon dioxide (2,4).

$$2H^+ + CaCO_3 \rightleftharpoons Ca^{2+} + H_2CO_3 \rightarrow Ca^{2+} + H_2O + CO_2 \uparrow \quad (2)$$

The purpose of this study was to examine the interactions of the pretreatment that precede the PD process. The first part of the study was to examine the difference between the use of malic acid and nitric in the acid wash step. The accepted acid for washing a paper at the United States Secret Service is malic acid. It has been shown to have properties similar to maleic acid and is less expensive (personal communication with Ramotowski R. from the United States Secret Service, 2004). Other labs use a dilute nitric acid solution for the acid wash step. This initial experiment was to determine whether there was any advantage to using one acid over the other for both fingerprint and background development on paper. An examiner wants to develop a process that not

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only provides a print with good ridge detail but also a print with a background that does not develop. Overdeveloped backgrounds lead to less contrast between the paper and the fingerprint.

The next part of the study was to determine the concentration level of acid that gave reliable and reproducible results for the process. As the accepted concentrations for the malic and nitric acids are different, an experiment was developed that examined different concentration levels for both acids. Concentrations were chosen that allowed the acids to be compared with nearly equal pH values.

After the acid concentration experiment, it was found to be instructive to determine the pH level of the acid solutions to gain further insights into the acid-washing process. Different acid concentrations were monitored during the additions of paper.

The fourth part of the study examined the use of water to rinse the paper between acid washes and before the addition of PD. It was hypothesized that a water rinse between the acid wash and the addition of PD would aid in the further removal of $CaCO_3$, thus giving the paper less background development.

The final study used scanning electron microscopy energy-dispersive X-ray spectroscopy (SEM-EDS: SEM-EDXA) to examine paper samples from previous experiments to monitor the levels of calcium in the papers. This allowed direct comparisons to be made between samples based on their calcium levels remaining on the paper surface. This addresses the question of whether or not the neutralization of $CaCO_3$ also removes the resulting calcium salt formed. These salts are calcium malate when malic acid is used and calcium nitrate when nitric acid is used. It appears obvious that calcium nitrate could be removed as it is highly soluble in water, provided, of course, that none remains in the interior of the paper. Its solubility is 121.2 g in 100 mL of water at 18°C (5). However, the solubility of calcium malate is 0.321 g in 100 mL of water at 0°C for the *d,l*-calcium malate salt (5), for example.

Materials and Methods

Part I

The types of paper used in this experiment were prepared using cloth gloves to prevent sample contamination. A pencil was used to draw finger-size arches where subjects were to place their prints on the paper. Each subject left 10 prints on each type of paper. A list of the 13 papers used in this experiment can be found in Table 1.

Subjects consisted of three men and two women of various ages. Each subject was instructed to rub their face to acquire sebaceous oil on their fingers. Then they touched a substrate several times, pausing a couple of seconds between each touch to ensure that the fingers got "recharged" with eccrine moisture. No set time limits or pressures were given to the subjects for pressing their prints on the paper, thus allowing different types of contact to be made.

The prints were allowed to age for 5 days at room temperature. After aging, the prints from each subject were cut in half vertically. The left and right halves were placed into two different groups, alternating their placement in case a subject tended to place more pressure on one side of a print versus the other.

Each paper type was processed separately with fresh solutions. One set of the paper halves was washed with 2.5% malic acid for 10 min. The samples were processed with the PD solution for 12 min. The preparation protocol for the PD solution can be found in the "Appendix A" of this paper. A final 1-min wash with tap water was performed before letting the samples dry. The second set of paper halves was washed with 3.4% nitric acid solution for 10 min. The acid solution was removed and the PD was immediately added. The prints were allowed to develop for 12 min. A 1-min wash with water was performed before letting the samples dry. All washes were facilitated with an orbital shaker. After the samples were dry, the halves were reconnected with tape so that side-by-side comparisons could be made.

Part II

Ten fingerprints from two different donors (male and female) were placed on three types of paper (copy, 100% cotton, and coated paper). These papers were chosen because they are common and represent three types of paper that would typically have varying levels of $CaCO_3$. The prints were placed on the paper in a similar manner as the prints in "Part I" of this experiment. The prints were allowed to age for 5 days and were then split in half as before.

All split fingerprint samples were washed with acid (varying concentration for this part of the experiment) for 10 min. The concentrations prepared were as follows:

Malic acid	2.5 g in 100 mL of water	2.5%	pH ~ 2.0
	Saturated (55.0 g in 100 mL of water)	55.0%	pH ~ 1.0
Nitric acid *c*. 60%	0.6 mL HNO_3 in 1000 mL of water	0.036%	pH ~ 2.0
	4.0 mL HNO_3 in 1000 mL of water	0.24%	pH ~ 1.2
	15.7 mL HNO_3 in 1000 mL of water	0.94%	pH ~ 0.6

TABLE 1—*Fingerprint and background development on various papers with physical developer after an acid prewash with either malic or nitric acid.*

	Malic			Nitric			Background Development
Paper	Developed Prints	Total Prints	% Developed	Developed Prints	Total Prints	% Developed	Favored
Copy paper	38	50	76	26	49	53	Nitric
White-lined paper	37	50	74	23	50	46	Even
Yellow-lined paper	27	48	56	19	50	38	Nitric
100% wood paper	26	50	52	11	46	24	Even
100% cotton paper	39	50	78	7	50	14	Nitric
Yellow envelope	26	48	54	2	50	4	Even
Manila folder	15	48	31	16	50	32	Nitric
Magazine paper	44	49	90	42	49	86	Even
Kraft paper	2	50	4	1	50	2	Even
Routing paper	6	46	13	15	46	33	Even
Acid free	46	50	92	20	48	42	Nitric
Hammermill coated	41	50	82	18	50	36	Even
Newspaper	16	50	32	10	48	21	Nitric

The PD solution was then used on the samples for 12 min. The samples were rinsed with water and allowed to dry. A direct comparison was made between the acids by piecing the print halves together and comparing print detail and background development.

Part III

An apparatus was set up that allowed an IQ Scientific Instruments Inc. pH meter (model IQ150) to be placed into a glass tray on an orbital shaker. Pieces of paper could be added to an acid solution and the pH could be measured over time. For all experiments in this section, 700 mL of acid was prepared and placed in the orbital shaker. Sheets of 8.5 in. × 11 in. copy paper were added throughout the experiment. The pH meter was calibrated before each part of this experiment.

Malic Acid—Three experiments were set up to monitor the pH level of malic acid. The first experiment monitored the successive addition of paper to 2.5% malic acid. A piece of paper was placed in the tray and a pH measurement was made every 30 sec. After 15 min, paper was removed and a second sheet was added and monitored over 15 min. Finally, a third sheet was added and monitored after the second was removed.

The second part of the experiment was conducted by adding three sheets of copy paper to 2.5% malic acid all at one time. The acid was agitated for 15 min and measured every 30 sec.

The last part of the experiment was like the first; however, a 55% malic acid solution (saturated) was used.

Nitric Acid—The nitric acid part of this experiment was similar to the malic acid part. Instead of using 2.5% malic acid, a 0.036% solution of nitric acid was prepared. This had a pH value that was close to the malic acid. Like the first experiment, a piece of copy paper was added and the pH was monitored over 15 min. Two more pieces of copy paper were eventually added and monitored.

The second part of this experiment mirrored the second part of the malic acid experiment with the addition of three pieces of copy paper all at one time. The acid used was the 0.036% solution of nitric acid.

The last part of this experiment monitored the successive addition of copy paper every 15 min to a 0.24% nitric acid solution. This solution proved to be a suitable concentration for developing fingerprints in "Part II" of this experiment.

Part IV

Ten fingerprints from two different donors (male and female) were placed on three types of paper (copy, 100% cotton, and coated paper). The prints were placed on the paper in a manner similar to the prints in Part I of this experiment. The prints were allowed to age for 5 days and were then split in half for comparison after development.

Two different acids were prepared for this study. The ideal concentrations of malic (2.5%) and nitric (0.24%), taken from earlier experiments, were used to wash the prints for 10 min. Rinse steps were added between the acid washes and the PD steps. The three comparisons made were between prints that had a 1-min water rinse, two 1-min water rinses, and no water rinses. The water used was reverse osmosis deionized water (RODI) in a glass tray on an orbital shaker. After development with PD, the prints were allowed to dry and pieced back together for comparisons.

Part V

Three different types of paper were used in the SEM-EDS study: Xerox copy, Southworth 100% cotton, and Hammermill-coated paper. The papers were chosen because they were used in previous studies in this paper and they were expected to have varying levels of calcium. All papers used measured 8.5 in. × 11 in.

The washing solutions used included RODI water, 2.5% malic acid (pH $\sim$ 2), saturated malic acid (pH $\sim$ 1), 0.036% nitric acid (pH $\sim$ 2), and 0.24% nitric acid (pH $\sim$ 1). For each wash, 500 mL of the solution was placed in a glass tray on an orbital shaker. The paper was submersed in the solution for either 3 or 10 min. The paper was then removed, placed on polyethylene wrap, and allowed to dry for at least a week before SEM-EDS sampling.

After the paper samples were dried, small sections were cut from the center and mounted on SEM-EDS stubs. The stub was placed in a Hitachi S-3500N VP SEM equipped with an EDXA detecting unit, and an elemental profile was obtained. The instrument was used with a magnification of × 120 (25 kV, 30 mm working distance, and 75 mA ionization current).

Results and Discussion

Part I

The fingerprints from the first part of this experiment were reconnected and compared in order to determine the advantages of malic or nitric acid used in washes. The results for all 13 paper types can be found in Table 1. A fingerprint was considered developed if any fingerprint detail could be distinguished. For each type of paper, a percentage of fingerprints that were developed was calculated by dividing the number of developed prints by all prints. The lack of background development was also important in this study, and a determination was made for each paper highlighting the paper with less background development. Some samples had equal background development and were labeled as even.

The malic acid washed fingerprints were found to have better development for 11 of the 13 papers. An example is shown in Fig. 1. The advantages of using malic acid for quality of print development were probably most noticeable on cotton, coated, and news print papers.

Nitric acid did not develop the background to the extent that malic acid did in six of the 11 papers. An image showing the reduced background development can be found in Fig. 2. The other five had similar background development, indicating that malic

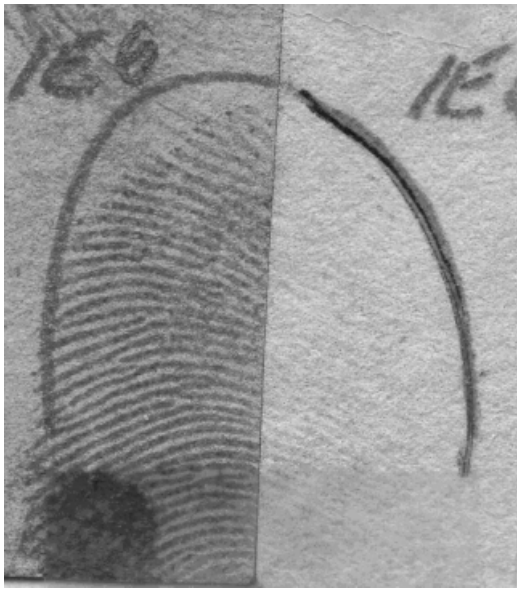

FIG. 1—*This fingerprint was made on 100% cotton paper. The left side of the fingerprint was washed with malic acid and the right side with nitric acid. The malic acid-washed side displayed better ridge detail.*

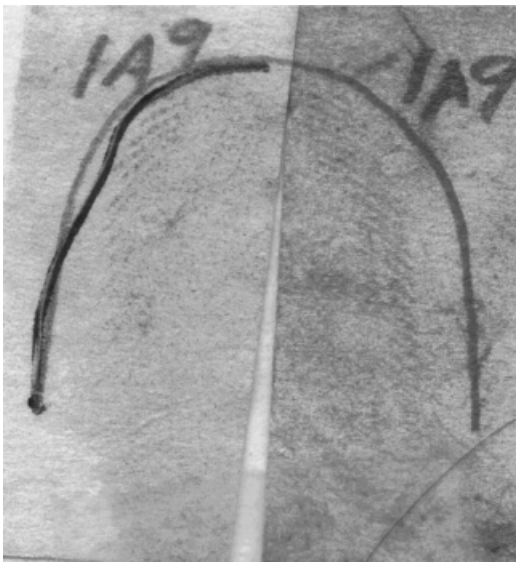

FIG. 2—*This fingerprint was made on copy paper. The left side of the print was washed with nitric acid and the right side with malic acid. Slight ridge detail is noticeable in each print; however, the background development is less on the nitric acid side.*

acid did not outperform nitric acid for any type of paper when looking at the level in which the background develops.

There were two fingerprint donors that left better prints than the other donors. Sex did not seem to be a factor; however, one female donor had very good prints for many of the papers. This could be due to possible contaminants in the prints such as makeup. Other possible reasons why some donors left better prints could be that some people are better secretors than others, the amount of time the fingers were allowed to recharge, the amount of time the prints were in contact with the paper, and the amount of pressure that was applied. These factors were not controlled, as they will vary with people in general as they leave prints.

Part II

Malic and nitric acid solutions were made that had similar pH values for comparison. Three different concentrations of nitric acid were prepared that had pH values that ranged from 0.6 to 2.0. For comparison, two malic acid concentrations were made at similar values. The lowest pH value achieved for malic acid was about 1.0 in a saturated solution. All concentrations were compared against each other for three different types of paper in order to indicate whether one acid concentration was superior to another.

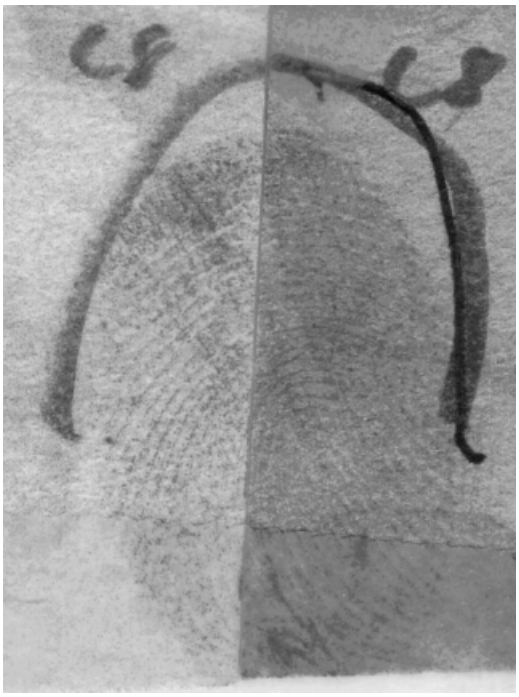

FIG. 4—*The fingerprint was made on copy paper and washed with malic acid at pH levels of ~ 1.0 and 2.0 (left and right, respectively). The right side had good print development similar to nitric acid samples, but the left side had a weaker print development despite the higher acid concentration.*

Fingerprint Development—Fingerprint development followed a trend that the stronger the acid concentration for both acids, the better the fingerprint development was for copy and coated paper. The development of prints for pH values of 0.6 and 1.2 nitric acid was nearly identical; however, the solution with a pH of 2 did not lead to good fingerprint development (Fig. 3). The concentration

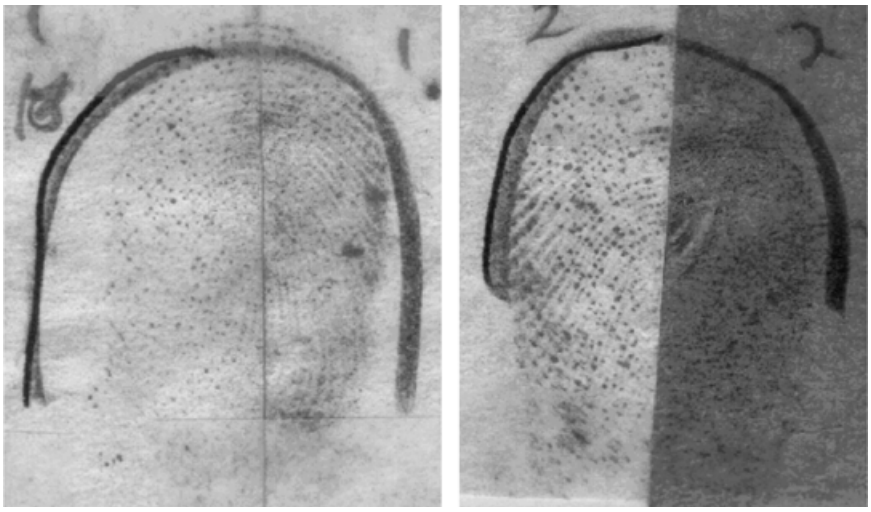

FIG. 3—*These fingerprints on copy paper were washed with nitric acid at different pH levels. The print on the left shows little difference in print quality between the left- and right-hand sides (pH 0.6 and 1.2, respectively). The print on the right compares nitric acid strengths of 1.2 and 2.0 (left and right sides, respectively).*

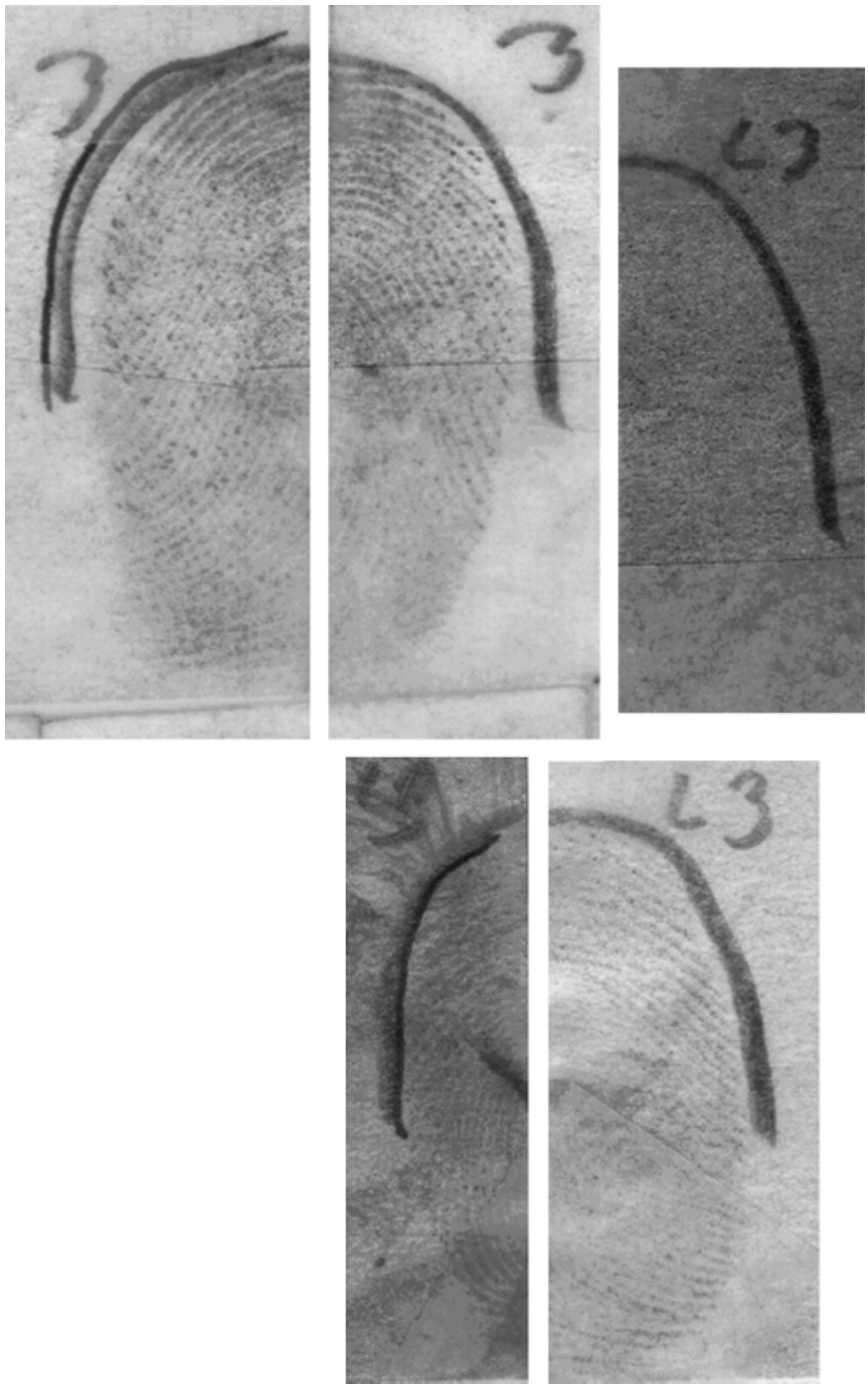

FIG. 5—*These fingerprints show the difference in background development on copy paper between the two acids at various concentrations. The top row is nitric acid at pH values of ~ 0.6, 1.2, and 2.0, respectively. The bottom row is malic acid at pH values of ~ 1.0 and 2.0. The development increases with increased pH concentrations. For unknown reasons, a strong malic acid concentration (i.e., pH ~ 1.0) showed typically more background development than weaker acid (i.e., pH ~ 2.0).*

of acid did not affect cotton paper as greatly, probably due to low levels of calcium in the paper.

The malic acid solution with a pH value of 2.0 did develop prints similar to the nitric acid values of 0.6 and 1.2; however, malic acid at pH 1.0 (saturated) showed poorer development as shown in Fig. 4. It remained unknown why the saturated solution with a low pH did not have similar development as nitric acid at the same pH.

Background Development—The background development increased with higher pH values (Fig. 5). This was expected as the weaker acids failed to neutralize completely the $CaCO_3$ in the papers before the addition of PD. The pH levels of 2.0 for both acids caused the papers to have extreme background development, which masked fingerprint detail. Another interesting observation was that the saturated solution of malic acid caused more background development in paper, even though it had a lower pH value than the other malic acid solution. The reason is unknown.

Overall, the pH level of the nitric acid used in the wash should be *c*. 1.0. When the pH value increases to 2.0, the fingerprint detail diminishes. The background will also overdevelop as the pH 2.0

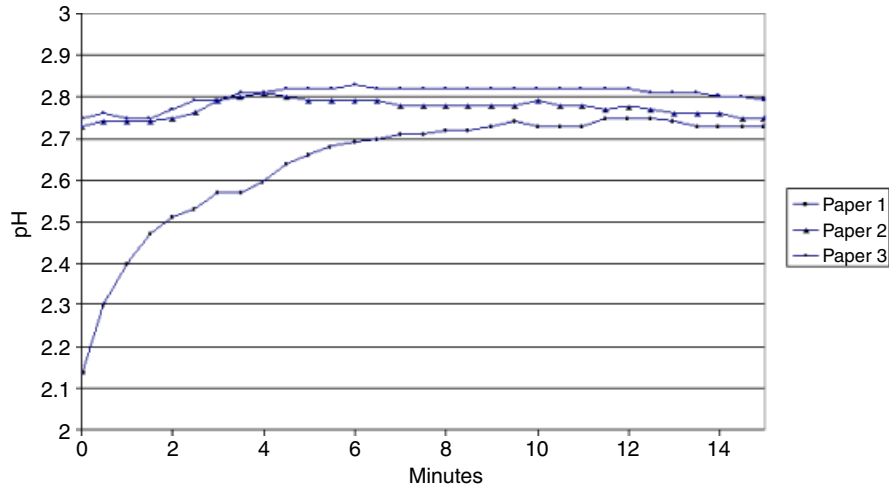

FIG. 6—*Successive additions of copy paper to malic acid pH ~ 2.06.*

solution fails to neutralize the paper completely. It was also shown that malic acid with a pH of 2.0 is preferred to stronger concentrations, which cause the background to overdevelop. It must be noted that the wash times were 10 min for all samples for direct comparisons. A longer wash time for some samples may have led to a further neutralization of $CaCO_3$ and less background development in the PD.

Part III

The first part of this experiment monitored the pH level of a 2.5% malic acid solution with the addition of copy paper. The results can be found in Fig. 6. The pH value of the system starts around 2.1 and increases over the first 15 min to 2.7. After this paper was removed and a second sheet was added, the pH did not increase significantly. The same result was also seen with the third sheet of paper.

The second part of the experiment monitored the same solution with the addition of three sheets of copy paper all at the same time. Like the first results, the solution started off with a pH close to 2.2 and climbed to 2.6 over 15 min.

The successive addition of three sheets of paper to a 55% solution of malic acid was monitored in the last part of this experiment. The pH level started close to 1.0 and only climbed to 1.3 after the addition of all three papers. This can be seen in Fig. 7.

Each of the malic acid experiments demonstrated that the malic acid pH climbs slightly with the addition of copy paper but will remain at a level that is strong enough to dissolve $CaCO_3$ in the paper. Eventually, one would expect this level to climb to a pH value that would not totally neutralize the $CaCO_3$ from paper; however, it appears that this would occur only after an addition of many pieces of paper.

The successive addition of copy paper to a 0.036% nitric acid was performed for comparison with malic acid at a similar starting pH value. The results can be found in Fig. 8. The nitric acid pH level started close to 2.5 and climbed with the addition of the first sheet of paper to 4.0. The solution continued to become less acidic with the second and third sheets of paper. The levels were 7.0 and 8.0, respectively.

Three sheets of copy paper were added all at once for the second part of this study to the same 0.036% starting solution. The pH value climbed from 2.5 to close to 6.5 over 15 min.

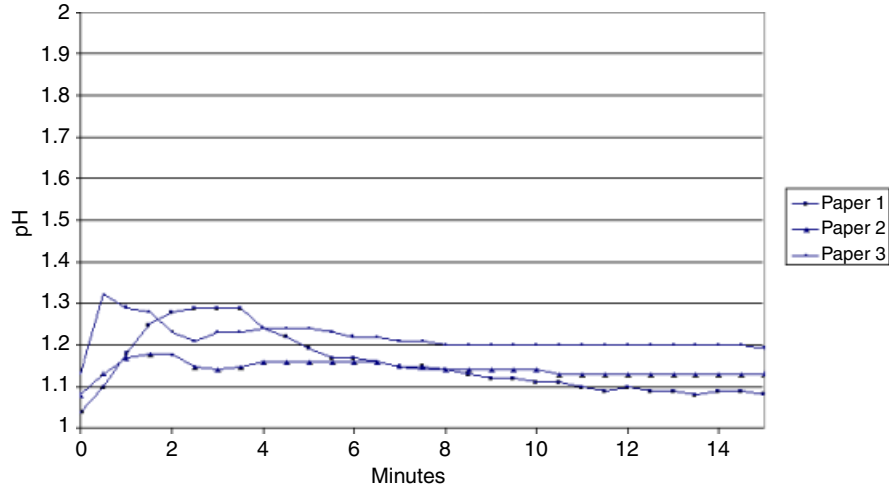

FIG. 7—*Successive additions of copy paper to malic acid pH ~ 1.04.*

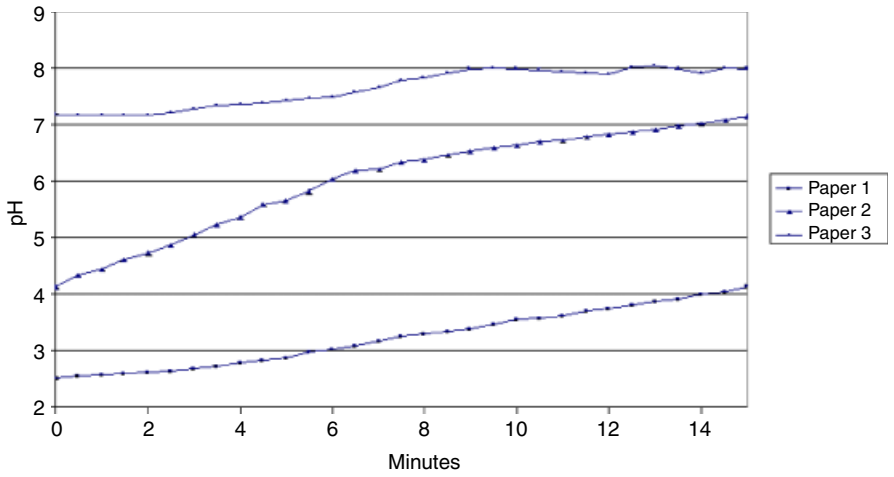

FIG. 8—*Successive additions of copy paper to nitric acid pH ~ 2.52.*

The successive addition of three sheets of paper to a 0.24% nitric acid solution was monitored with the pH meter. This solution was shown to be ideal for the nitric acid wash step. The pH level did not increase significantly with the addition of the copy paper. It increased slightly from 1 to 1.1. This can be seen in Fig. 9.

These experiments were conducted to monitor the pH levels of the acids used for washing papers to neutralize them. Malic acid was able to hold a low pH value with the addition of several pieces of paper, making it a good acid for washing many pieces of paper. Nitric acid was similar only at concentrated levels (0.24%). A nitric acid solution with the same pH as malic (2.0) would steadily increase with the addition of paper. The ability of this solution to neutralize basic paper decreased when the levels reached higher pH values. This occurred with the addition of only three pieces of paper. These results may be attributed to the buffering effect of weak acids in general.

Part IV

The water rinse steps between the acid wash and the PD did not prove to be advantageous for either acid (Fig. 10). Malic acid used on copy and cotton paper and rinsed did not have any difference in fingerprint detail than those samples that were not rinsed. Cotton paper had slightly better detail with either of the rinses compared with no rinse. Background development, however, does increase with the addition of the rinse steps. Therefore, an examiner generally would not want to use a rinse step due to a noticeable increase in background development.

Samples washed with nitric acid and rinsed were similar to those of malic acid. The fingerprint detail did not change for any of the papers between the rinsed samples and the nonrinsed ones. The background development did not increase as much as with the malic acid samples.

The hypothesis that adding a water rinse between the acid wash and the PD steps will help further remove $CaCO_3$ was disproved. Generally, fingerprint detail did not increase with the addition of rinse steps. If malic acid is being used, an examiner may develop the background greater than desired using the rinses. For unknown reasons, the nitric acid followed by rinses did not produce this effect.

Part V

The individual conditions and results from the SEM-EDS experiment can be found in Table 2. First, the data support that

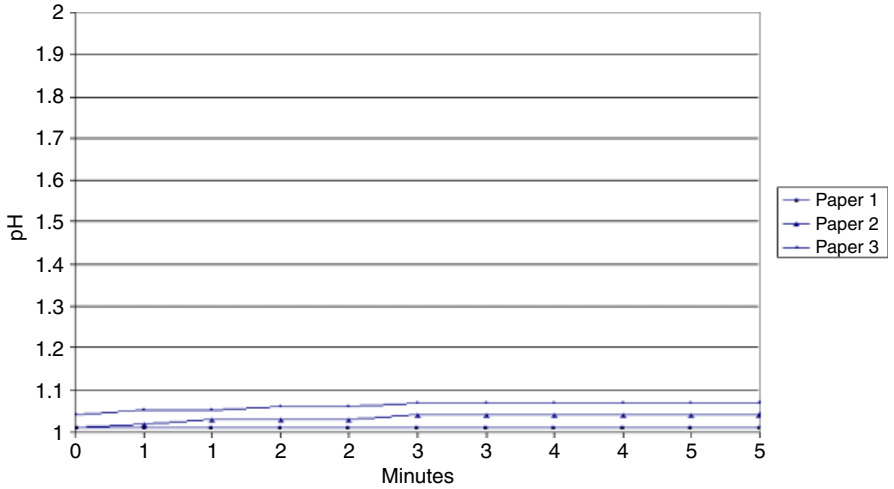

FIG. 9—*Successive additions of copy paper to nitric acid pH ~ 1.01.*

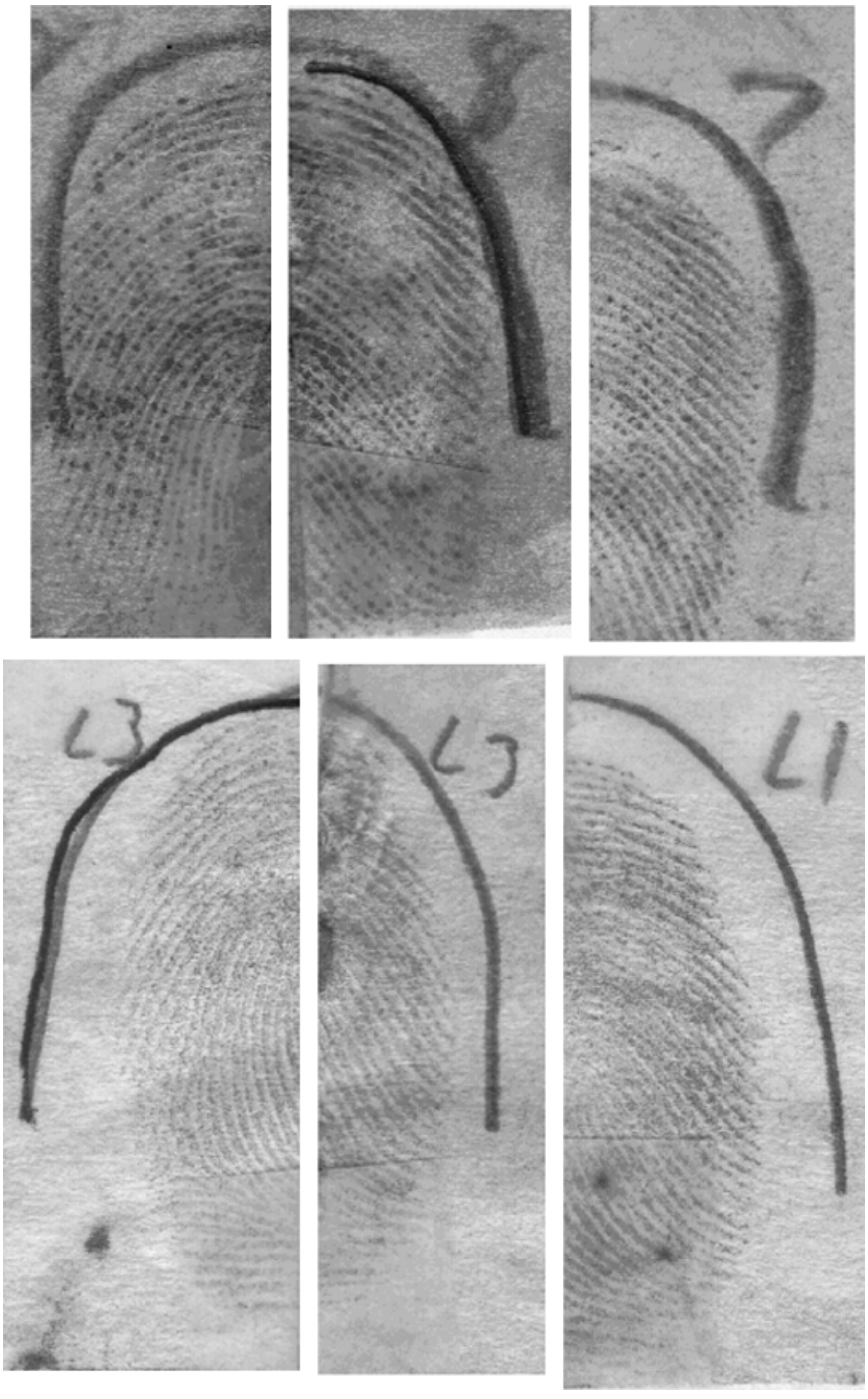

FIG. 10—*These fingerprints on copy paper show that there was no beneficial effect in using a water rinse between the acid-wash step and the physical developer step. The top row of prints compares prints washed with malic acid. The left sides of both prints did not have any rinse steps. The right side of the first print had a 1-min rinse and the second print had two 1-min washes. The same comparison is made in the bottom row, except that the acid used was nitric. Notice that there were no differences in print development due to the addition of a rinse step.*

neutralization of $CaCO_3$ led to the removal of calcium from the paper, at least from its surface. However, as the paper samples used in the SEM-EDS study were thin, we shall assume that the results also represent the calcium content in the interior of the paper. Thus, the data support that neutralization removes the aqueous calcium nitrate or the calcium malate salts formed. Consequently, the absence of calcium indicates the absence of $CaCO_3$, and the detection of a calcium peak relates to the amount of background development. It was known that the acid wash step neutralizes the $CaCO_3$ in the paper, and using the above reasoning, it depletes the calcium from the paper. However, the time, acid, and acid concentration necessary were not known.

It is noted that the SEM-EDS data for the papers represent semiquantitative comparisons based on the relative peak heights of their elemental constituents, as the spectra were collected under identical instrumental conditions as described above. The qualitative and relative ratios of the constituents would be expected to remain reliable indicators of the elemental profiles of the paper.

TABLE 2—*Scanning electron microscopy energy-dispersive X-ray spectroscopy (SEM-EDS) calcium detection in papers after various acid prewashes and water rinses.*

Paper	Acid	pH ~	Wash Time (min)	Rinses	Calcium Peak Size
Copy	No acid	—	No wash	No rinse	Large
	Water	—	10	No rinse	Large
	Malic	2	10	No rinse	Trace
	Malic	2	10	1 min	None
	Malic	2	10	2–1 min	None
	Malic	2	3	No rinse	Trace
	Malic	2	3	1 min	None
	Malic	2	3	2–1 min	None
	Malic	1	10	No rinse	Small
	Nitric	2	10	No rinse	Large
	Nitric	2	10	1 min	Large
	Nitric	2	10	2–1 min	Large
	Nitric	2	3	No rinse	Large
	Nitric	2	3	1 min	Large
	Nitric	2	3	2–1 min	Large
	Nitric	1	10	No rinse	Trace
	Nitric	1	10	1 min	None
	Nitric	1	10	2–1 min	None
	Nitric	1	3	No Rinse	Small
	Nitric	1	3	1 min	Small
	Nitric	1	3	2–1 min	Small
Cotton	No acid	—	No wash	No rinse	None
	Water	—	10	No rinse	None
	Malic	2	10	No rinse	None
	Malic	2	3	No rinse	None
	Nitric	2	10	No rinse	None
	Nitric	2	3	No rinse	None
	Nitric	1	10	No rinse	None
	Nitric	1	3	No rinse	None
Coated	No Acid	—	No Wash	No rinse	Large
	Water	—	10	No rinse	Large
	Malic	2	10	No rinse	Medium
	Malic	2	10	1 min	Small
	Malic	2	3	No rinse	Medium
	Nitric	2	10	No rinse	Large
	Nitric	2	10	1 min	Large
	Nitric	2	3	No rinse	Large
	Nitric	1	10	No rinse	Medium
	Nitric	1	10	1 min	Medium
	Nitric	1	3	No rinse	Medium

Copy paper was initially measured without any washing or rinse steps. A sample of copy paper was also washed with water as a control. Both of these samples contained a large calcium peak and would become very dark in a PD solution. Malic acid of two different concentrations (2.5% and saturated) was used to wash the paper. Both concentrations proved strong enough to deplete the $CaCO_3$ in the paper, with the 2.5% solution working slightly better. The two different wash times were used with no significant difference noticed. It appeared that even though the water rinse removed residual calcium, it caused slight background spotting to appear during PD development.

Copy paper washed with a nitric acid solution had slightly different results than the malic acid. The stronger nitric acid solution (0.24%) removed the calcium sufficiently at all wash times and with all different types of rinses. A 10-min wash time removed more of the calcium than the 3-min wash. The weaker nitric acid concentrations (0.036%) could not remove the calcium from the copy paper at all.

The 100% cotton paper contained very little, if any, calcium initially. Calcium was not represented in the paper blank. The paper samples were still washed at different times in different concentrations of acid for completeness. Calcium was not found in any of the cotton paper samples.

Coated paper contained the largest peak of calcium initially and also proved to be the most difficult of the papers to remove the calcium. The 2.5% malic acid failed to remove the calcium completely for both the 3- and 10-min washes. Similar results were observed in the strong nitric acid solution. The weaker nitric acid solution did not remove calcium at all from the coated paper. The result of a medium peak of calcium remaining in the paper after the wash results in partial background development, which can be seen throughout samples in this study.

Overall, the SEM-EDS study reinforced the assumptions that residual calcium after acid exposure results in background development during the PD process. This study shows that a water rinse is not necessary as the calcium level will not change with the rinses. It also shows that papers like copy and coated can have the levels of calcium reduced with different acids at proper strengths. Malic acid at a pH of 2 can remove calcium, whereas nitric acid at the same pH cannot. This study also shows how different papers may need shorter or longer times with an acid wash depending on the composition. Cotton paper may not need an acid prewash at all, but a coated paper may need 10 min or more to deplete enough calcium from the sample so the background does not overdevelop.

Conclusions

Malic acid washes were shown to have better fingerprint development than nitric acid washes for nearly all the paper types examined. These results were seen across different ages and sexes of donors. Low background development was better for nitric acid washes for about half of the papers tested.

The concentration of the acid washes should be about 2.5% for malic acid or at least 0.24% nitric acid. Stronger malic acid concentrations can lead to overdevelopment of the background. The same results are found with weaker levels of nitric acid washes.

A pH monitoring study was conducted and indicated that malic and nitric acids have different abilities in neutralizing $CaCO_3$ in paper. At similar starting pH values around 2.0, malic acid has the ability to remain at a stable pH with the consecutive addition of paper. Nitric acid will have increased pH values with these additions to a level where $CaCO_3$ is not neutralized. However, a stronger starting concentration of nitric acid will behave similarly to malic acid.

Rinse steps between the acid wash and the PD steps are not needed. The fingerprint detail does not increase, but there may be a greater development in the background. The acid wash step alone appears sufficient to neutralize the paper.

The SEM-EDS study provided an elemental profile of samples to compare with similar work throughout this paper. It indicated that an acid at a proper strength needs to be used in a prewash in order to neutralize $CaCO_3$. The study demonstrated how the $CaCO_3$ in some papers, like coated, are not greatly affected by the acid over a period of time and may need a stronger acid or a longer wash time. It also showed that water rinse steps are not necessary before PD.

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Appendix A

Physical developer preparation.

Redox solution	Add and mix 900 g of ferric nitrate to 27,000 mL deionized water Add 2400 g of ferrous ammonium sulfate, mix Add 600 g of citric acid, mix
Detergent solution	Add 12 g of N-dodecylamine acetate to 4000 mL of deionized water Add 12 mL of Tween 20 and mix
Silver nitrate solution	Add 400 g of silver nitrate to 2000 mL of deionized water, mix
Working solution	Add 160 mL of detergent solution to 3600 mL of redox solution, mix Add 200 mL of silver nitrate solution, mix Store in amber bottle