

TECHNICAL NOTE

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Modifications to the Silver Physical Developer

ABSTRACT: The silver physical developer is currently the most successful reagent used for visualizing the water-insoluble components (e.g., lipids) of latent prints on porous surfaces. It is normally used after the amino acid visualizing reagents (e.g., ninhydrin and DFO) are used. This work found that the performance of the current formulation of silver physical developer is strongly reduced when the water used is changed from the usual distilled water to the more purified reverse osmosis/deionized (RO/DI) water. Based on numerous experiments involving the systematic variation of the component concentrations, the performance was restored and even improved by reducing the concentration of all the components (except that of the ferric salt) and by including malic acid in the formulation. These modifications resulted in a new silver physical developer formulation that performs as well as or better than the current formulation and is less expensive to make.

KEYWORDS: forensic science, silver physical developer, PD, fingerprints

The theory and operation of the silver physical developer in the development of latent prints on porous surfaces has been discussed by Cantu (1) and Cantu and Johnson (2). In brief, the currently used silver physical developer is a reagent borrowed from photographic chemistry. It consists of an aqueous solution of silver nitrate, a ferrous/ferric redox couple containing citric acid, and a cationic and nonionic surfactant. In photography, the silver physical developer selectively deposits silver particles on photo-exposed silver bromide crystals. In developing latent prints on paper, the silver physical developer selectively deposits silver particles on the water-insoluble components (e.g., lipids) of latent print residue. An important step usually taken prior to submerging paper items in the silver physical developer solution is to neutralize the paper (most of which is alkaline today) by immersing it in an acid prewash for about 10 min. The most common acid prewash solutions used are maleic acid (2.5% w/v), malic acid (2.5% w/v), and dilute nitric acid (1% v/v).

This work began when the U.S. Secret Service forensic laboratory was considering replacing distilled water with deionized water that is processed using reverse osmosis. The latter is referred to as reverse osmosis/deionized or RO/DI water. One of the present authors (DB), while a 2001 summer intern, was assigned the task of evaluating the performance of the silver physical developer made with RO/DI water. In the United Kingdom, the Police Scientific Development Branch (PSDB) in Sandridge made this change in the mid-1990s. They found that the amount of detergent used could be

reduced due to the higher purity of the water. After discussions with Dr. John Brennan from the Forensic Science Services (FSS) in London (UK), the U.S. Secret Service Forensic Services Division (USSS-FSD) began the evaluation using RO/DI water processed using an Elga Purelab Option (Model 0S015XXM1) RO/DI unit.

Like PSDB, we also found that the concentration of detergents can be reduced when RO/DI water is used. However, we also found that the level of silver nitrate can be reduced. These were among some of the modifications made in an effort to optimize the formulation. During the academic year 2001–2002, David Burow (DB) tried the following experiment at his university (University of Southern Mississippi, Hattiesburg, MS): he treated the paper items in a given volume of malic acid prewash, and after the items were neutralized he added an equal volume of the silver physical developer to the acid prewash (with the paper items in it) and obtained development. This led to the consideration of adding malic acid to the already-modified formulation. As a 2002 summer intern, DB worked on testing and optimizing the formulation. What we present here shows that the formulation to date develops prints as good or better than the traditional formulation and is less expensive to make. A brief technical note describing this formulation was submitted (by DB) for publication in the *Journal of Forensic Identification* (3).

Material and Method

The current silver physical developer is made using distilled water according to the published procedure (4,5). In the new formulation, the RO/DI water used in all the changes made to the current formulation is from an Elga unit described above (Purelab Option—Model 0S015XXM1). The resulting new formulation of the silver physical developer involves two major changes: it uses RO/DI water and contains malic acid. It also uses less silver, detergents, ferrous salt, and citric acid. It is made according to the procedure outlined in Appendix 1.

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Comparison of the Traditional and New Formulation for the Silver Physical Developer

Note that in making the working solution of the new formulation, one first adds 640 mL of the ferrous/ferric redox solution to 260 mL of the malic acid stock solution. This provides 900 mL of what we may call a “dual acid” ferrous/ferric redox solution. The corresponding current formulation contains 900 mL of a “single acid” ferrous/ferric redox solution. This is summarized in Table 1. Here both formulations contain 990 mL. It is readily seen that the new formulation uses 65% less detergents, 25% less citric acid, 20% less silver, and 12.5% less ferrous salt.

Testing Method

The three types of paper that were used in all tests performed were blue photocopy paper, loose-leaf paper, and brown office envelope paper. In each of these, fingerprints were placed and marked using a pencil to trace around the finger. These papers were cut in half with one half designated for processing with the current physical developer and the other half designated for processing with modifications of the current formulation.

For each comparison experiment, five samples were processed for each paper type. Each half of a print was labeled with the solution used to process that half. In order to remove a “left side-right side” bias, the left side of the print was processed with one solution, and on the next trial the same solution was used to process the right side of the print. All comparisons were done at the same time for the same length of time. All solutions tested were of the same age.

Changes to the Current Formulation

Several experiments were done to determine how well the silver physical developer performed when a particular parameter of its current formulation was changed. These experiments determined the effect of changing the following parameters:

1. The quality of water (from distilled to RO/DI).
2. The concentration of the detergent stock solution (from 0.4 to 0.2 to 0.14%).
3. The concentration of malic acid stock solution (from no malic acid to 2.5 to 5%).
4. The concentration of the silver nitrate stock solution (from 20 to 16%).
5. The type of acid (malic to maleic).
6. The amount of citric acid.
7. The amount of ferrous ions.

Also, the effect of the age of the reagent and of the latent print was considered.

In all cases, components of the three *stock solutions* were changed, but not the proportions in which they are used to make the working solution of the silver physical developer: 900 mL (redox stock solution) + 40 mL (detergent stock solution) + 50 mL (silver nitrate stock solution).

Results and Discussion

Effect of Changing the Quality of Water (from Distilled to RO/DI)

When the current formulation of the silver physical developer is made with RO/DI water instead of the usual distilled water, the effect this has on latent print development is quite noticeable, reproducible, and occurred on all paper substrates tested. It gives inferior development, as can be seen in Fig. 1. Here the paper substrate used was copy paper. Both halves were processed with the current formulation, but the formulation used on the left side of the print was made with RO/DI water.

The components in the developer that are most affected by the change in water quality are the two surfactants. Since the RO/DI water is less ionic than the distilled water, less detergent is needed to form the necessary micelles. This is why the PSDB (UK) changed their surfactant concentration when they changed to RO/DI water. They now use a 2.8% detergent stock solution instead of the 4% (6).

Effect of Changing the Concentration of the Detergent Stock Solution (from 0.4 to 0.2 to 0.14%)

When the current formulation of the silver physical developer is made with RO/DI water instead of the usual distilled water and the concentration of detergent stock solution is reduced from 0.4 to 0.2%, the resulting formulation develops prints in a similar way as the current formulation (see Fig. 2). Here the paper substrate is brown office envelope paper (other papers also gave the same results). Both formulations give comparable results. When the silver nitrate concentration was decreased (this is discussed below), it was found that the detergent concentration could be reduced to 0.14%.

The quality of water depends on what it contains. Ultra pure water is free of any dissolved or suspended organic and inorganic materials. Dissolved inorganic solids include all ions other than the hydrogen and hydroxyl ions in equilibrium with water. A measure of the ionic character of water is its resistivity (or its inverse conductivity). Ultra pure water has a resistivity of 18.2 megaohms/cm. As ions are introduced, the resistivity decreases. The distilled water

TABLE 1—Comparison of the current and the new formulation of the silver physical developer.

Component	Mol. Wt. (g/mole)	Current Formulation (with distilled water)	New Formulation (with RO/DI water)
Malic acid	134.09	0 g	13 g (96.95 mmol)
Ferric nitrate nonahydrate	403.87	30 g (74.28 mmol)	30 g (74.28 mmol)
Ferrous ammonium sulfate hexahydrate	392.05	80 g (204.06 mmol)	70 g (178.55 mmol)
Citric acid	192.12	20 g (104.10 mmol)	15 g (78.08 mmol)
Surfactants			
Cationic: <i>N</i> -dodecylamine acetate	259	0.16 g (617 μmol)	0.056 g (216.2 μmol)
Nonionic: Synperonic- <i>N</i> *	572	0.16 mL (285.3 μmol)	0.056 mL (99.9 μmol)
Silver nitrate	169.89	10 g (58.86 mmol)	8 g (47.09 mmol)

*density = 1.02 g/mL.



FIG. 1—Left side of print (labeled DI) was developed with the current formulation (with RO/DI water). Right side of print (labeled dist) was developed with current formulation (with distilled water).

generated at the United States Secret Service (USSS) laboratory has a resistivity of about 0.118 megaohms/cm. The Elga RO/DI unit produces water with an average resistivity of 16 megaohms/cm. These measurements were made using a resistivity/conductivity meter by Myron L. Company, model EP (Carlsbad, CA). The change from distilled water to RO/DI water on surfactants is quite dramatic, as the following account shows. Take two 1-L bottles and add about 0.9 L RO/DI water to one and 0.9 L distilled water to the other. Add to each of these the same amount (ca. 40 mL) of detergent from the detergent stock solution. Shake both bottles equally for the same amount of time. Suds form at the top of the bottles. Over the course of the day, the bottle with distilled water loses all of its suds, while the bottle with RO/DI water still has suds over halfway up to the top of the bottle. This observation clearly supports the hypothesis that reducing the detergent concentration in the RO/DI water should make it behave like distilled water with detergent.

Effect of Changing the Concentration of the Malic Acid Stock Solution (from no Malic Acid to 2.5 to 5%)

When malic acid is included in the working solution of the new formulation and the solution is stored in an amber bottle, silver fall-

out (precipitation) is noticed within 30 min and then it stops. This fallout does not hinder the development of latent prints. The inclusion of malic acid also increases the deposition of silver particles on the latent print residue, as shown in Fig. 3. Here the 5% malic acid stock solution was used. This was observed regardless of the paper substrate.

If one decreases the malic acid stock solution concentration from 5 to 2.5%, one still gets about the same amount of silver fallout; however, there is a noticeable decrease in the amount of silver particles that deposit on the latent print residue, as can be seen in Fig. 4. Again, this occurred regardless of the paper.

If one uses a malic acid stock solution concentration above 5%, there is no change in the initial silver fallout and there is no increase in silver particle deposition on the latent print residue.

Malic acid, like citric acid, binds to ferric ions (7,8). This probably plays an important role in explaining the effect observed. From data compiled by Sillen and Martell (7,8), the binding constants can be shown to be:

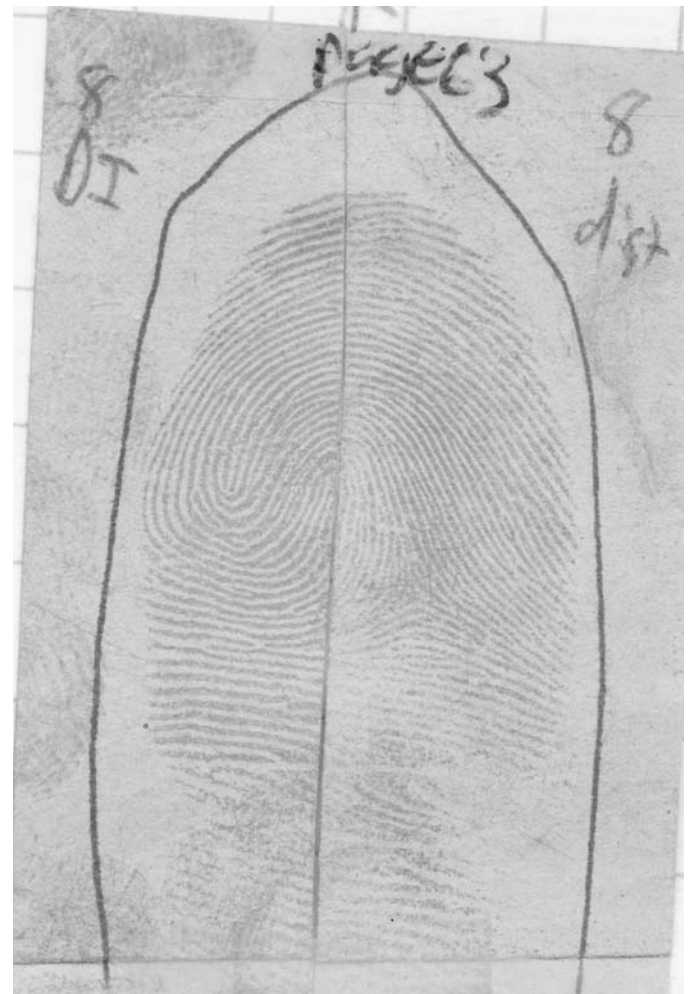


FIG. 2—Left side of print (labeled DI) was developed with the current formulation (with RO/DI water) and a detergent stock solution concentration 0.2% (reduced from 0.4%). Right side of print (labeled dist) was developed with the current formulation.

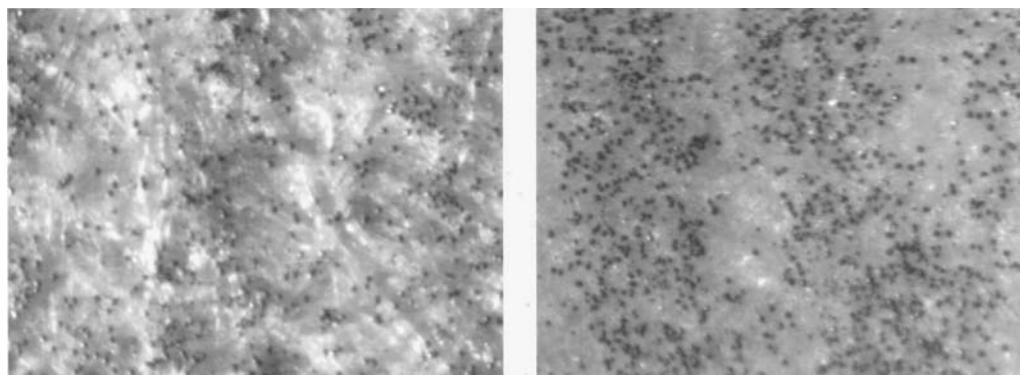


FIG. 3—Magnified portion of friction skin ridges developed with the new formulation without malic acid (left) and with the new formulation made with a 5% malic acid stock solution (right).

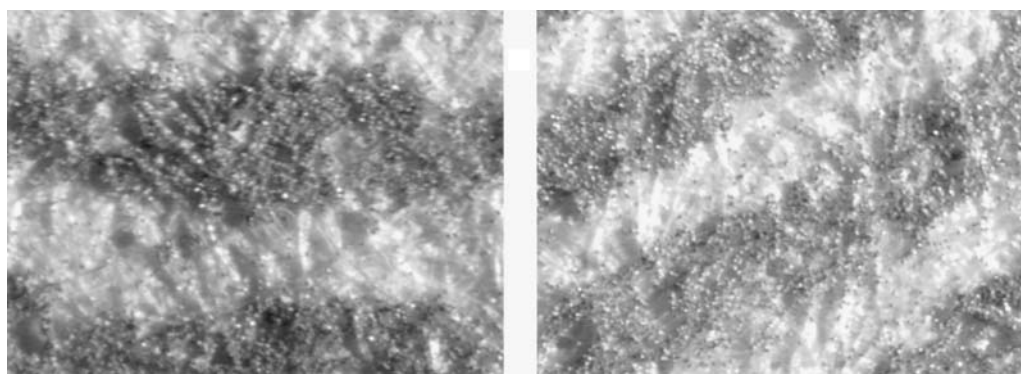
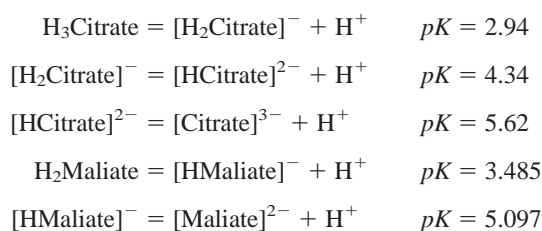


FIG. 4—Magnified portion of friction skin ridges developed with the new formulation using 5% malic acid stock solution (left) and with new formulation using 2.5% malic acid stock solution (right).

This clearly shows that malic acid binds ferric ions, though not as strongly as citric acid. The pK values for these acids are also given by Sillen and Martell (7,8):



This shows two things. The first ionization of each acid is the main contributor to the acidity of the solution and a citric acid solution is more acidic than a malic acid solution of the same molar concentration.

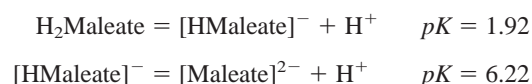
Effect of Changing the Concentration of the Silver Nitrate Stock Solution (from 20 to 16%)

Silver nitrate is the most expensive component of the silver physical developer. When the surfactant concentration was reduced as a result of using RO/DI water and the malic acid was introduced, it was thought that perhaps the silver concentration could also be reduced and still have the developer perform well. This was tried and we found that reducing the concentration of the stock solution to 16% gave comparable and sometimes better results to the current formulation. Reducing the concentration below 16% began to give inferior results.

Effect of Changing the Type of Acid (Malic to Maleic)

Adding maleic acid (a common acid used in the acid pretreatment) instead of malic acid to the formulation eliminated the initial silver fallout noticed; however, print development is greatly reduced, as can be seen in Fig. 5. This is representative of all papers tried.

At this stage it is important to compare malic, maleic, and citric acid. The binding constants of citric and malic acid with ferric ions are given above as well as their pK values. At present, there are no binding constants given for maleic acid with ferric ions. The pK values for maleic acid are given by Sillen and Martell (7,8) to be:



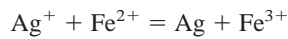
This shows that the acidity of the solution comes mostly from the first ionization and that, compared to malic and citric acid, it is the most acidic on a molar basis.

Effect of Changing the Amount of Citric Acid and of Ferrous Ions

Other changes between the new and current formulations are the reduction of the citric acid and the reduction of ferrous ammonium sulfate in the new formulation. The reduction of citric acid results in less amount of the initial fallout of silver. The reduction of ferrous ammonium sulfate yields darker development than the current

formulation, as shown in Fig. 6. This was seen for all paper substrates tried.

The electrochemical behavior of the silver physical developer is governed by the equation



The Nernst equation (1,2) for this reaction provides the energetics of the physical development process. It is given by

$$\Delta E_{\text{cell}} = \Delta E_{\text{cell}}^{\circ} - 59 \log Q \text{ in millivolts (mV)}$$

where $\Delta E_{\text{cell}}^{\circ} = 28.6 \text{ mV}$ and $Q = [\text{Fe}^{3+}]/[\text{Ag}^+][\text{Fe}^{2+}]$. Here $[\text{Fe}^{3+}]$ is the concentration of *free* ferric ions, that is, *after complexation* with citric acid has occurred. An elementary explanation of what may be happening is that the *free* ferric ion concentration is reduced in three ways—by reducing its concentration, by binding with the citric acid (to form ferric citrate), and by binding with malic acid (to form ferric maliate ions). To compensate for this (i.e., in order to keep the same Q value), the product of the silver ion concentration, $[\text{Ag}^+]$, and the ferrous ion concentration, $[\text{Fe}^{2+}]$, should be reduced. At present we have no explanation for obtaining “darker” prints by reducing the ferric ion concentration.

Developing Older Prints

The prints tested up to this point were no more than two weeks old. Most cases processed can contain evidence that is over a year



FIG. 5—Left side of print (labeled MA) was developed with the new formulation using 5% malic acid stock solution. Right side of print (labeled ME) was developed with the new formulation using 5% maleic acid stock solution.



FIG. 6—Left side of print was developed with the new formulation made with 75 g ferrous ammonium sulfate hexahydrate. Right side of print was developed with the new formulation made with 70 g (right) ferrous ammonium sulfate hexahydrate.

old. So, a test was run that contained various substrates that had intentionally placed prints that were over one year old. The new formulation was compared with the current formulation and gave excellent results, regardless of the paper substrate (see Fig. 7).

New Formulation—Cost Reduction

The reduction of some of the chemicals in the new formulation also brings a reduction in price. Working with the actual cost of chemicals, Burow (3) showed that there is a net reduction in cost of 15.6%, that is, to make 3.96 L, the cost of the current formulation is \$23.84 while that of the new formulation is \$20.12. In a fiscal year, the USSS spends \$11,868.36 on chemicals for the current formulation of the silver physical developer. With the new formulation the cost would be \$1851.46 less, or \$10,017.36.

Conclusions

By using RO/DI water and making several modifications to the currently used silver physical developer, a formulation was arrived at that performs as well as or better than the current formulation and is less expensive. Though it is “better and cheaper” than the current



FIG. 7—Latent print placed on newspaper on 6/22/01 and processed on 7/10/02 with the current formulation (left) and with the new formulation (right). Both solutions were made on 7/3/02 (seven days old).

formulation, it is by no means optimized. There are several questions that still need to be answered.

Questions Regarding the Present (New) Formulation—Does the stability of the redox solution change when the malic acid is added? What if the detergent solution is added to this “dual acid” redox solution? Can one make the silver physical developer by mixing two solutions—the “dual acid” redox solution with detergent and the silver nitrate solution? What is the ΔE_{cell} of an electrochemical cell made with this binary system? What is the pH of the working solution? What causes the initial silver fallout?

Questions Regarding Other Modifications—Can the nonionic surfactant be removed completely? What effect will other organic acids have? Is there a single organic acid that can replace the combination of citric and malic acid?

We hope to eventually answer these and other questions and perhaps in doing so we will come up with an even better formulation. Up to now, there was no better reagent than the currently used silver physical developer for visualizing the water-insoluble fraction of latent prints on porous surfaces. The formulation presented here is a step in improving this.

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APPENDIX 1

The Silver Physical Developer (New Formulation)

Stock Solutions

Malic Acid Stock Solution (5.0% w/v Malic Acid)

1. Measure out 1-L of RO/DI water and add to a 2-L beaker.
2. Add 50 g malic acid to the beaker and stir with a magnetic stirrer until all the crystals are completely dissolved.
3. Store in a glass bottle.

Ferrous/Ferric Redox Stock Solution

1. Measure out 900 mL of RO/DI water and add to 2-L beaker.
2. Add 30 g of ferric nitrate nonahydrate to the beaker and stir with a magnetic stirrer until crystals are completely dissolved.
3. After this, add 70 g of ferrous ammonium sulfate hexahydrate to the beaker and stir with a magnetic stirrer until all the crystals are completely dissolved.
4. Finally, add 15 g of citric acid to the beaker and stir with a magnetic stirrer until all the crystals are completely dissolved.
5. Store in a glass bottle.

Make sure the chemicals are added in the order indicated and each chemical is completely dissolved before adding the next chemical.

Detergent Stock Solution (0.14% in Each Detergent)

1. Measure out 1-L of RO/DI water and add to a 2-L beaker.
2. Add 1.4 g *n*-dodecylamine acetate and stir with a magnetic stirrer until it is completely dissolved.
3. After this, add 1.4 mL of synperonic-*N* and stir with a magnetic stirrer until it is completely dissolved.
4. When the solution is clear, add to a glass bottle and store.

Silver Nitrate Stock Solution (16% w/v in AgNO_3)

1. Measure out 1-L of RO/DI water and add to a 2-L beaker.
2. Add 160 g of silver nitrate to the RO/DI water and stir with a magnetic stirrer until all the crystals are completely dissolved.
3. The solution should be clear. Store this in an amber bottle to keep out light.

Working Solution

Silver Physical Developer Working Solution (990 mL)

1. Add 260 mL of the malic acid stock solution to a 2-L beaker.
2. Add 640 mL of the ferrous/ferric redox stock solution and stir with a magnetic stirrer for about 1 min.
3. Add 40 mL of the detergent stock solution and stir with a magnetic stirrer for about 2 mins.
4. Add 50 mL of the silver nitrate solution (slowly) and stir.
5. Store in an amber bottle to keep out light.

Note that the first two steps provide 900 mL of a “dual acid” redox solution, i.e., it has both citric and malic acid. Both of these acids are chelates and form complexes with ferric ions.

During the first 30 min after making the working solution, some silver precipitation (fallout) occurs and then stops. This does not affect the performance of the formulation. This working solution has a shelf life of at least nine days. Processing with this working solution is done in the same way as with the working solution of the current silver physical developer (see Appendix 2).

APPENDIX 2

The Silver Physical Development Process

If paper evidence is soiled or extensively stained (inherently or from the initial DFO or ninhydrin treatment), it becomes necessary to wash away the soil, grime, and stains. This is done with a *water wash pretreatment* as follows:

- Place the evidence in a plastic/glass tray.
- Place enough distilled water or RO/DI water to cover the evidence.
- Place the tray on an orbital shaker and agitate for about 10 min or until the traces of the previous processes are gone.

Once this is done, continue with the acid wash pretreatment and then with the silver physical developer treatment. All this can all be done using the *same* glass/plastic tray. However, it is important to not use metal trays (this will cause the silver to fall out of solution). Also, do not process evidence that has staples or other metal objects as these also cause the silver to fall out of solution (thus, all staples should be removed before processing). The *acid wash pretreatment* involves the following steps:

- Remove the (prewash) water from the tray.
- Add enough malic acid prewash solution to cover the evidence and agitate for about 5 to 10 min.

Note, if there is no soil, debris, or heavy stains (e.g., from the ninhydrin or DFO treatment) on the evidence, one can start with the malic acid prewash.

After this, the *silver physical developer treatment* is done in the same tray as follows:

- Remove the malic acid solution.
- Place enough working silver physical developer solution to cover the evidence (in this and in all the above treatments make sure that the surfaces of all the pieces of evidence are exposed to the treatment).
- Agitate for 10 min or until satisfactory results are obtained with the development (it may take longer or shorter than 10 min).
- Discard the working solution.
- (*Water Wash Post-Treatment*) Rinse the evidence three times with tap water in order to stop the development and remove all excess silver physical developer.
- Dry by either air-drying or other methods.

Please note that when working with these solutions, dispose of them in a manner that is within your jurisdiction’s environmental disposal guidelines.