<u>WARMING UP TO COLD MERCURY</u>

Author: John R. Hurlock

Introduction

Ten years ago I resumed making Daguerreotypes, after a nearly 40 year hiatus. I started with the Becquerel method of development. I found that getting the right color during the fuming process was a frustrating experience. The exposure times also appeared to be much longer than I had previously experienced with hot mercury development. I was frequently disappointed when a fog veil appeared at the end of the development process. After successfully making a neutral-toned Becquerel plate, I found that the appearance did not satisfy me.

I decided to try mercury development again. However, after reading Kenneth Nelson's article on the serious dangers of mercury poisoning [1], I understood that I could not safely practice hot mercury development in my family house. Lacking a barn or other outbuilding, I could work outdoors, or I could install a fume hood in my basement. It occurred to me that if it were possible to develop with cold mercury, it would be easier to contain the poisonous fumes.

History of Cold Mercury Development

Some photographic histories have reported that, in his research, Louis Daguerre accidentally stumbled on cold mercury development. In their biography of Daguerre, Helmut and Allison Gernsheim[2] relate the "classic legend" which they now find suspect that the inventor had placed an under exposed plate in his chemical cabinet one night intending to recycle the plate. The next morning, when he opened the cabinet, he saw that the latent image had become visible. After several abortive attempts to repeat the result, he finally determined that the development was caused by some mercury that had been left in the cabinet.

The French daguerreotypist, Antoine F. Claudet[3] is known to have experimented with low temperature development. Claudet reported that "placing the plate in the vacuum of an air-pump containing a small amount of mercury" caused development to occur in as little as 10 minutes at 45^{0}F. Such a development scenario, implausible as it may sound, does have a certain appeal. Is cold mercury a practical method for developing daguerreotypes?

The Mercury Development Process

In *The Daguerreotype. Nineteenth-Century Technology and Modern Science,* the mechanics of mercury development is described by authors Susan Barger and William White to be an example of a chemical vapor deposition process.[5.] In this type of process, mobile atoms of a vapor, like mercury vapor, settle on a surface such as the Daguerreotype plate. A common example would be the water vapor from your shower condenses on your bathroom mirror.

The concentration of mercury on the plate surface increases when we heat the mercury. Once adsorbed onto the surface of the daguerreotype plate, the mercury atoms migrate towards defects on the plate surface such as the silver atoms of the latent image. After migrating to the latent image on the plate, these tiny nuclei of mercury amalgam begin to grow. The growth rate and the size and shape of the resulting aggregates depend on the mercury concentration, the temperature and the development time.

Daguerreotypes Developed in Cold Mercury

Daguerreotypes fumed with cold mercury develop very slowly (I.e., 36 hours) and have very small image particles. Barger and White[5] reported those daguerreotype images developed with cold mercury, consist of tiny snow-like particle of silver amalgam that are only a few nanometers in diameter.[6.] These particles are so small that only blue light is reflected by the image.

Daguerreotypes Developed in Hot Mercury

When mercury id heated in the developing box, it becomes more volatile. This volatility increases the concentration of mercury vapor on the surface of the daguerreotype plate. The increased mercury concentration increases the rate of image particle growth. The morphology of the daguerreotype image particle changes from tiny, snow-like particles to larger platelets and crystals. With heated mercury image particles in the highlights are approximately half a micron in size, whereas image particles in the shadow areas are 5 to 10 microns in diameter[8.] These particles reflect a broader spectrum of visible light, giving the daguerreotype image a warmer tone.

Effects of Pressure on Evaporation

If you when to the mountains on vacation and you boil water for cooking, you might observe that your “three minute egg” would now take 4 minutes to cook. The reason for this is that at higher elevations, water boils at a lower temperature because the lower air pressure offers less resistance to evaporation. There are fewer air molecules to get in the way of the evaporating water molecules.

The vaporization of mercury, like the evaporation of water, can also be increased by decreasing the pressure above it. The concentration of mercury molecules in the air will increase because there are fewer molecules of air around to prevent mercury evaporation. This suggests that we should be able to develop Daguerreotypes at room temperature, if we reduce the pressure sufficiently. The object of my research was to find out how low the air pressure needs to be, at room temperature, to achieve the same image particle sizes as those obtained for daguerreotypes developed at a mercury temperature of say 80°C (176°F).

Hot Mercury Evaporation

In the development of daguerreotype plates, modern Daguerreotypists typically heat the mercury to 80° C (176° F) in the developing box. The resulting vapor pressure of the mercury is only one ten thousandths of atmospheric pressure. The ratio of mercury's vapor pressure to the air pressure in the developing box is approximately 0.000117. We will hereafter refer to this ratio as the partial pressure of mercury vapor.

At 80 °C (176 °F), the concentration of mercury in the air is approximately 100 molecules for each million molecules of air. Despite this low concentration, mercury vapor atoms will condense on the surface of the exposed daguerreotype plate where they can begin the development process.

Vacuum Mercury Development

If we reduce the air pressure above the mercury in the developing box from 760 mm Hg down to 25 mm Hg, the vapor pressure of mercury does not change. However, the partial pressure of mercury vapor increases to approximately 100 parts per million. Note that this is approximately the same partial pressure that results when we heat mercury to 80C. At this concentration, mercury vapor atoms will condense on the surface of an exposed daguerreotype.

Proportionally, if we reduce the air pressure above the mercury to 150 mm Hg, the partial pressure (or molar ratio) of mercury in the air increases to eighteen parts per million. This is approximately the same molar ratio that results when we heat mercury to 50C at atmospheric pressure.

We now have two methods to increase the ratio of mercury vapor to air in the developing box. We may heat the mercury to 50C to 80C or we may reduce the pressure of the air to between 25mm Hg and 150mm Hg.

The intriguing possibility of developing daguerreotype plates at room temperatures contained within a partial vacuum appears to offer the daguerreotypist a novel and potentially safer alternative to hot mercury development. However, until now, no one had answered the critical question: Can it be done? To find out I designed a series of experiments to determine if daguerreotype plates developed using mercury under reduced pressure had a satisfactory image-particle structure.

Vacuum Mercury Techniques

After a series of false starts, I was able to arrive at a combination of fuming and development techniques that produced a visible daguerreotype image using vacuum mercury development.

My original technique was as follows:

(1) Fume the plate over Iodine for thirty seconds until a yellow-rose color.

(2) Inspect the plate under subdued light (i.e., 1 lumen/sq.ft).

(3) Fume the plate over Bromine for thirty seconds until a steel blue.

(4) Inspect the plate under subdued light once more.

(5) Fume the plate over Iodine for thirty seconds under a red light.

(6) Expose the plate in the camera for thirty seconds @ f/8 EV=14.

(7) Place the plate in a vacuum desiccator (illustrated in Appendix II) with a dish of mercury in the bottom and evacuate to a twenty-five25 inch vacuum.

(8) Allow the plate to develop for up to twenty-four hours.

(9) Release the vacuum slowly, remove the developed plate, fix and gild if required.

When using this technique I made the following observations;
If the development time was 3 hours or less, or the vacuum was less than 15 inches of Hg, the plates had blue images. The appearance of blue image tones appeared to be associated with underdevelopment due to insufficient time or vacuum.
When the development times and/or vacuums were increased, the images became stronger and the highlights became whiter. Plates developed at 20-30°C under vacuums of twenty-three to twenty-seven inches of Hg produced what we might consider “normal” daguerreotype images.

The following are examples of images developed in cold mercury:

Figure 1

The image in Figure 1 is an example of a daguerreotype that has been fuming in subdued light and developed for 18 hours over cold mercury under a twenty-five in vacuum. It exhibits a rich range of warm tones in both the highlight and shadow areas of the image.

Figure 2

The image in Figure 2 is a pale blue in color and is almost invisible under normal viewing conditions. In this example the daguerreotype has been fumed in total darkness and then developed over cold mercury. Blue images have also been obtained when the development time was too short and/or the vacuum was insufficient. Both images above have been gilded.

The images in Figure 1 and 2 were examined under the scanning electron microscope at 2000x magnification. The image structure in the highlights of the daguerreotype in Figure 1 consists of a nearly uniform mixture of spherical particles approximately 1 micron in diameter (Fig 3). The image structure of the daguerreotype in Figure 2 consists of uniformly small particles less than 0.1 microns in diameter. (Fig 4)

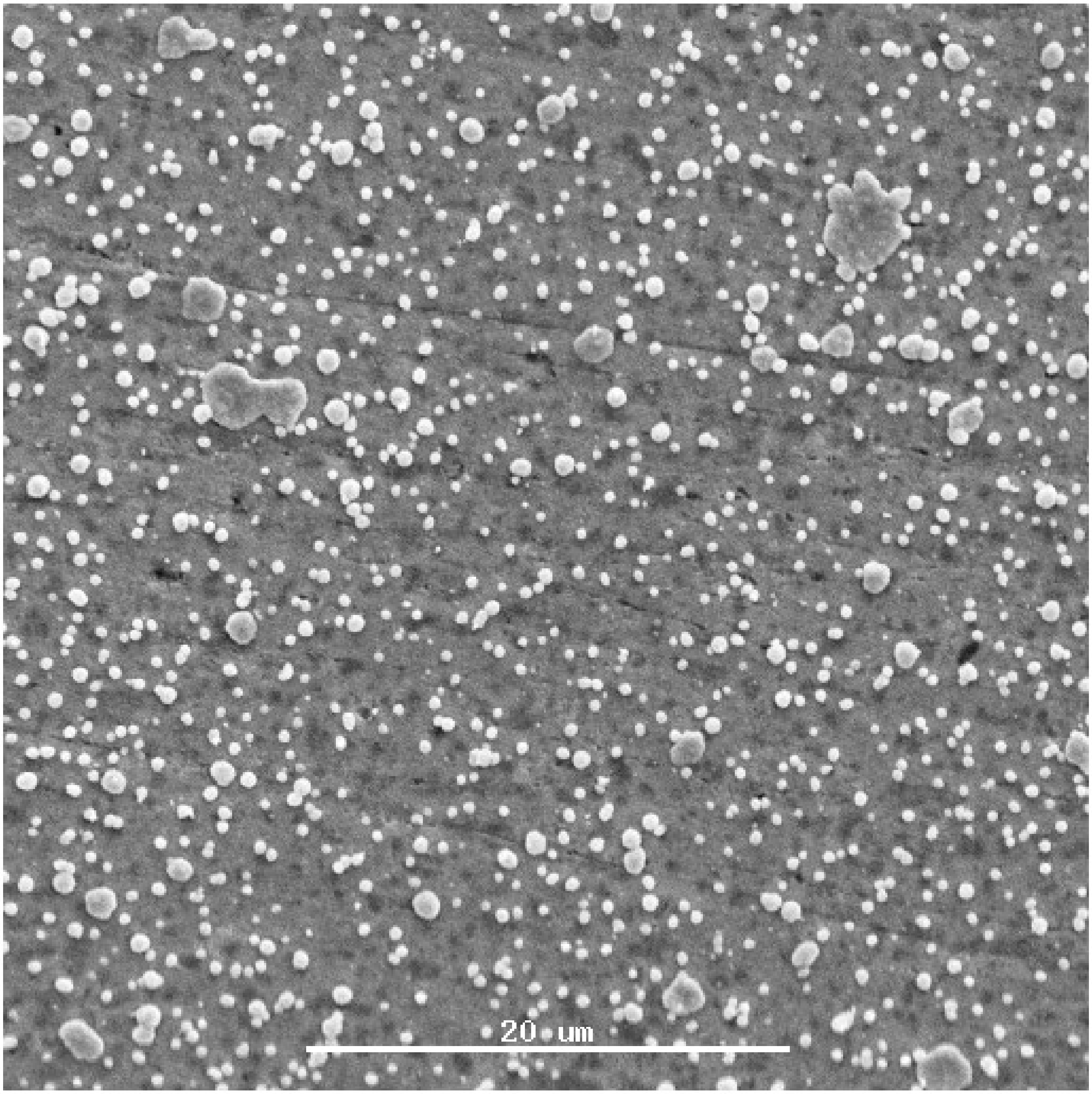

Figure 3

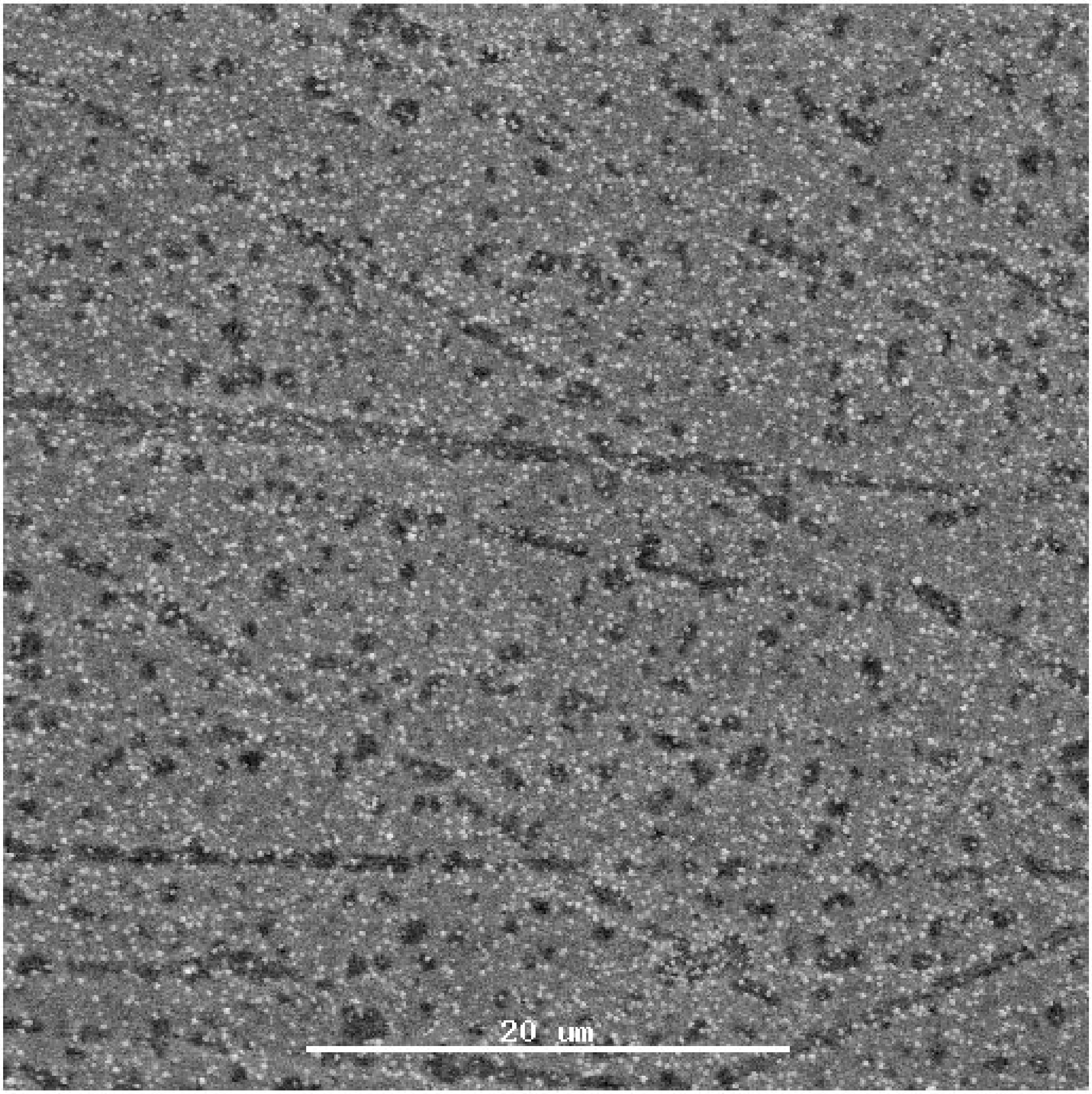

Figure 4

The color of cold mercury images appears to be affected by several factors that determine image particle growth. Increasing light exposure during fuming will increase the number of random photolytic silver atoms in the silver halide coating. Barger and White reported that exposure to subdued light had a major effect upon the speed of the daguerreotype plate[9]. It also appears to affect the size of the image particles and the color of the image.

Cold-Mercury/Vacuum Development Procedure

I have found several exposed plates can be developed at one time. This will minimize the Daguerreotypist's mercury exposure by reducing the number of times the desiccator must be opened. In my apparatus the plates were mounted vertically on a slotted wooden or plastic rack, which is then placed in the desiccator. The incidence of mercury spot formation appears to be reduced if the plates are canted upwards rather than downwards in the rack as this reduces the possibility of splashing if the desiccator is moved. A water aspirator can be used to evacuate the desiccator to a twenty-three to twenty-seven inch vacuum. Since no mercury vapor can escape through the walls of the desiccator, it can be safely handled safely in the darkroom, where the development of the plate may be visually monitored under a yellow light.

The evacuated desiccator should kept in the dark, in a warm place (20C-30C) for up to 24 hours. Longer development times will cause some misting over of the image. I have experimented with placing the desiccator in a black box out in the summer sun. I have achieved temperatures of 40C (104°F) this way, but I did not observe any increase in the rate of development.

Higher vacuums definitely speed up the development process. I have obtained images after only 2 hours under a twenty-eight inch vacuum but they appeared slightly blue. Longer development times (e.g., four to ten hours) in vacuums of twenty-five to twenty-seven inches of mercury appear to build stronger, more neutral images. The following table provides some guidelines for development under various vacuum conditions.

DEVELOPMENT TIMES versus VACUUMS CONDITIONS

VACUUM inches of mercury	DEVELOPMENT TIME @ 20 C HOURS	IMAGE APPEARANCE
23	20.0	BROWNISH
25	10.0	WARM
26	6.0	NEUTRAL
27	4.0	NEUTRAL
28	2.0	BLUISH

Unlike a hot mercury developing pot, the cold vacuum desiccator is almost free of mercury vapor when it is first evacuated. Therefore more time is required to restore the mercury vapor atmosphere in the desiccator after the vacuum is pulled.

Increasing the ratio of the surface area of the mercury reservoir to the desiccator volume will increase the rate of mercury evaporation and thus shorten the development time.

If you insert the largest flat dish that will fit in the bottom of the desiccator, it will minimize the time required for the mercury vapor concentration to reach equilibrium after evacuation. Conversely, if you use a smaller mercury reservoir in a larger desiccator, it will increase development time, especially when multiple plates are developed in the same desiccator.

When the image development is complete, slowly restore atmospheric pressure by bleeding air back into the desiccator. Rapid bleeding can result deposits of mercury or silicone grease on the plate. The possibility of deposits can reduced further if the image surface of the plate faces away from the air inlet of the desiccator. Afterwards, remove the plate(s), fix, dry and gild in the usual way.

I have found for best image quality the plates should be developed as soon as possible after exposure. However if the humidity and temperature are low, development can be delayed for two to four hours after exposure with only a slight deterioration in image quality. This allows a series of plates to be taken in succession and then developed all at one time.

Exposure times

The speed of cold mercury developed plates compares favorably with hot mercury techniques. Exposures of only five to ten seconds at f/11 are required for light with an EV value of 14 (ISO 100). As development time was increased, the speed appeared to increase and highlight tones changed from blue to brown and then white. The daguerreotypes illustrated in Figures 5a-5c were contact printed from an Extachrome transparency. The exposure times were varied from twenty to sixty seconds after which they were developed at 20C under a twenty-five inch vacuum for periods varying from three hours up to ten hours.

COLD MERCURY/VACUUM DEVELOPMENT—EXPOSURE TIMES VS DEVELOPMENT TIMES

Figure 5a
Exposure time 60 seconds
Development time 3 hours

Figure 5b
Exposure time 40 seconds
Development time 6 hours

Figure 5c
Exposure time 30 seconds
Development time 8 hours

EXPOSURE TIMES versus DEVELOPMENT TIMES

EXPOSURE TIME SEC	DEVELOPMENT TIME @ 20 C HOURS	IMAGE APPEARANCE
60	3.0	DARK BLUE
40	6.0	BLUE-BROWN
30	8.0	LT BLUE-TAN

Conclusion

If you are very concerned about the dangers of hot mercury development, I urge you to try vacuum cold mercury development of your daguerreotype plates. Some experimenting with your halogen fuming technique may be necessary to obtain the image tone that you prefer, but the results will surprise you.

ACKNOWLEDGEMENTS

The author would like to thank Charlie Schreiner and Irving Pobboravsky for the many hours they spent proofreading this paper. With his vast knowledge of daguerreotype history, Irv was able to dig up the reference to Claudets' early experiments with vacuum mercury development that was unknown to this author when he set about rediscovering this invention. The author would also like to thank Kenneth Nelson for his advice on modern daguerreotype techniques that greatly simplified relearning the process. Scanning Electron Micrographs (SEMS) were prepared by Dr. Richard W. Cloud, the microscopist at NALCO Chemical Company.

ABOUT THE AUTHOR:

John R. Hurlock and his spouse, Elsa have lived in Hickory Hills Illinois for 38 years. They have three children, Michael, Amy, and John. The author received his BS in Chemical Engineering from Northwestern University in 1961. He retired from Nalco Chemical Company in 2001 where he had been engaged in polymer chemistry research. As a teenager, the author experimented with the daguerreotype and wet collodion processes from 1955 to 1960.

<u>A PORTFOLIO OF IMAGES PRODUCED USING COLD-MERCURY/VACUUM DEVELOPMENT</u>

Plate 1
Vignoles Grapes
Quarter plate cold mercury Daguerreotype

Plate 2
Buffalo Skull
Quarter plate cold mercury Daguerreotype

A PORTFOLIO OF IMAGES PRODUCED USING COLD-MERCURY/VACUUM DEVELOPMENT

Plate 3
Illinois-Michigan Canal Lock
Quarter plate cold mercury Daguerreotype

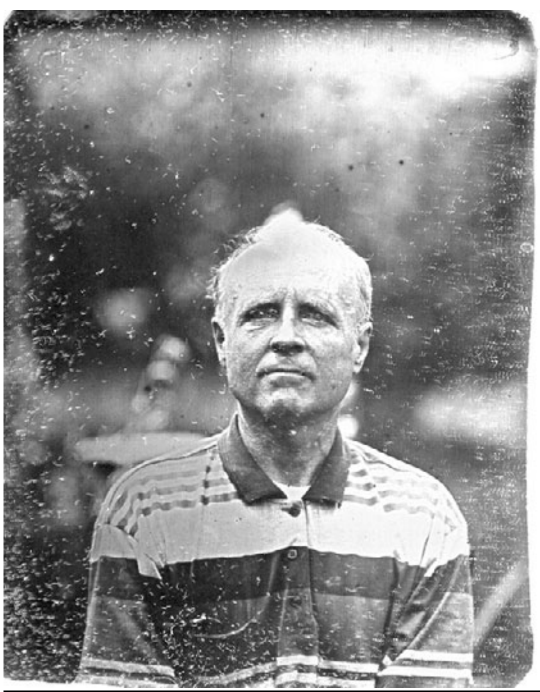

Plate 4
Self_Portrait
Quarter plate
cold mercury Daguerreotype

A PORTFOLIO OF IMAGES PRODUCED USING COLD-MERCURY/VACUUM DEVELOPMENT

Plate 5
Lake Katherine Falls
Quarter plate cold mercury Daguerreotype

NOTES

1. Gerard Meegan, "Becquerel Development 'In a New Light'" The Daguerreian Annual 1991, pp 114-122. The Daguerreian Society 1991.

2 Kenneth Nelson, "Mercury and the Daguerreotypist: A Modern Assessment" The Daguerreian Annual 1994 pp 118-143 The Daguerreian Society 1994.

3 Helmut and Alison Gernsheim, (1956) "L.J.M.Daguerre" Reprinted New York NY, Dover Publications, 1968 pp71-72.

4 Claudet, M. (1845) "The Progress and Present State of the Daguerreotype Art", Journal of the Franklin Society, Philadelphia April 10, 1845.

5 M. Susan Barger and William B. White, "The Daguerreotype--- Nineteenth Century Technology and Modern Science". Washington & London, Smithsonian Institute Press, 1991 p152. Hereafter referred to as Barger and White, *Technology.*

6 Barger and White, *Technology,* pp 147-148

7 Barger and White, *Technology,* p153

8 Barger and White, *Technology,* p143

9 Barger and White, *Technology,* p155

10 Lange's Handbook of Chemistry, New York,NY. McGraw-Hill 1973-

11 VWR Scientific Products, PO Box 5229 Buffalo Grove, Il 60089. Telephone 1-(800) 727-4368. There are other local outlets. You may want to check the internet or the Yellow Pages of your nearest major city.

12 Bel-Art Products, Pequannock, NJ 07440-1962 telephone 1-(800) 423-5278.

13 Rio Grande, 7500 Blue water Road NW, Albuquerque, NM 87121telephone 1-(800) 548=6566.

APPENDIX I

PARTIAL PRESSURE

In a mixture of "ideal gases" the partial pressure (P^I) of each gas component is equal to the molecular fraction (N) of that gas multiplied by the total pressure (P). The partial pressure of mercury vapor in air, a mixture of oxygen, nitrogen, and argon is approximated by the following equation.

$$P_{hg} = P \times \frac{(\text{Mol of Hg})}{(\text{Mol of air + Hg})}$$

Daltons' law of additive pressures' states that the total pressure is equal to the sum of all the partial pressures of the components of a mixture.

$$p = p_{Ox} + p_{N} + p_{Hg}$$

In a container of liquid mercury, the space above the mercury soon becomes saturated with mercury vapor, much as humid air can become saturated with water vapor. The partial pressure of this mercury vapor increases when the total pressure of the mixture is reduced by removing most of the air.

EQUIVALENT MERCURY PARTIAL PRESSURES vs. TEMPERATURE AND PRESSURE

TEMPERATURE CELSIUS	Mercury Vapor Pressure as mm Hg	Partial Pressure @760mm Hg	Partial Pressure @150mm Hg	Partial Pressure @25mm Hg
30	.0028	.0000037	.0000184	.0001119
50	.0127	.0000167	.0000844	.0005068
80	.0888	.0001168	.0005920	

APPENDIX II

Cold Mercury Developing Equipment

Relatively inexpensive equipment can be used to develop daguerreotypes under a vacuum. All of the examples shown here were developed in a glass vacuum desiccator that was protected from light. Vacuum desiccators can be purchased at any chemical supply house such as VWR Scientific Products.[11] The cost of glass desiccators ranges from $180 to $360 depending upon the size. A tube of high vacuum silicone grease (Dow Corning) will also be required.

A suitable polycarbonate desiccator, such as those by Bel-Art[12], capable of holding a twenty-nine inch vacuum for up to twenty-four hours can be purchased for about $50. (Fig 6). Silicone grease is optional for this type of desiccator. According to the manufacturer, polycarbonate desiccators should not be evacuated at temperatures above 49C.

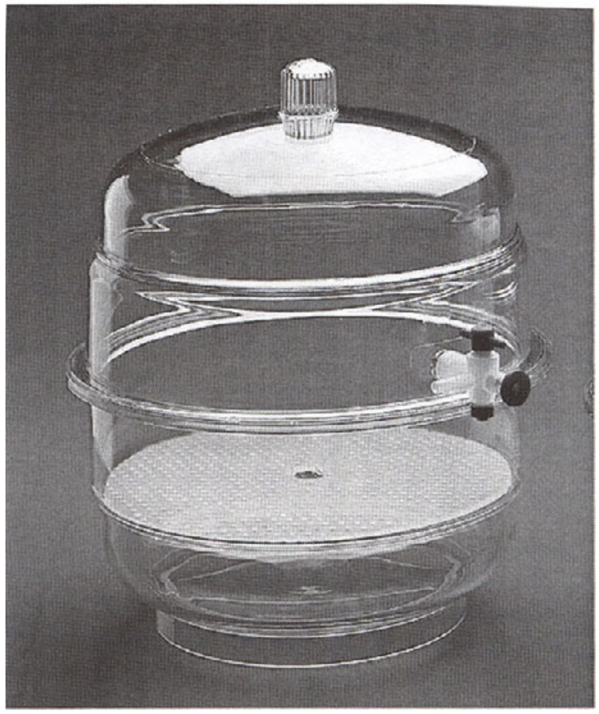

Figure 6

Plastic water aspirators, capable of evacuation down to the vapor pressure of the tap water can be purchased for less than $10 at chemical supply houses. The maximum vacuum that can be obtained is equal to the vapor pressure of the water. This depends on the water temperature and will vary seasonally.

Approximately 5 minutes will be required to reach maximum vacuum in the desiccator using a water flow rate of 5 gallons per minute. The concentration of mercury vapor in air @ $20^{0}C$ is 14 mg/m^3. For the medium size Bel-Art desiccator, approximately six liters of air containing one ten of a milligram of mercury will also be removed during the evacuation. This would result in a maximum of one ppb (part per billion) of mercury in the water discharged from the aspirator. However, if the air from the desiccator is first passed through a length of small diameter copper tubing, most of this mercury will be contained.

Alternate methods of evacuation such as a vacuum pump can also be used. Some provision for venting of the pump discharge may be needed depending on the pump location. Suitable electric vacuum pumps, capable of pulling a 29 inch vacuum, can be purchased at Rio Grande (Albuquerque, NM) for $300 to $500. Hand actuated Vacuum pumps designed for testing automobile vacuum systems can be purchased at many auto supply stores. A vacuum gauge, which is required to indicate when you have the correct vacuum, is also available there. Heavy walled rubber vacuum tubing can be purchased at some hardware and auto supply stores.

SAFE OPPERATION OF VACUUM DESICCATORS

A box or other protective shield should always be used around evacuated glass containers in the event that an implosion should occur. Wrapping the desiccator with electrical tape will also help to minimize any damage due to flying glass. Glass desiccators must be carefully handled. They need to be routinely inspected for cracks or chips. In the event that the desiccator is damaged, it should <u>not</u> be evacuated. Damaged desiccators may still be used without evacuation, to keep plates or apparatus dry over a desiccant such as silica gel.

OPENING A GLASS DESICCATOR

The lids of glass desiccators frequently stick after long periods of use. To loosen a stuck lid on a glass desiccator, place the desiccator on a secure surface and clamp it tightly to prevent it from moving. Then using a rubber mallet or a wooden block and a regular hammer, apply several sharp sideways blows to the edge of the lid. The lid should then slide off easily. To minimize future slicking, and to insure a good vacuum, smooth out the film grease on the ground glass seal of the desiccator before each use, applying additional grease when necessary.