

Fig. 1. A seventeenth-century mercury sweat-box for the treatment of syphilis. The patient sat in an atmosphere of warm mercury vapor so it could be absorbed through the skin. (From Goldwater, Mercury; A History of Quicksilver, p. 223.)

Mercury & the Daguerreotypist: A Modern Assessment

by Kenneth E. Nelson

The hottest, the coldest, a true healer, a wicked murderer, a precious medicine, and a deadly poison, a friend that can flatter and lie.

Thus did J. Woodall describe mercury in The Surgeon's Mate, or Military & Domestic Surgery, which he wrote in 1639.1 Man's relationship with the fluid metal has always been tempestuous. Mercury and its compounds have been used freely as desperate medicine for treating desperate illness, and also used freely to end life by suicide or murder, or merely as an antiseptic or fungicide. Desire for mercury gave rise to history's first mandates toward occupational safety and health for the men who mined it, and mercury has been indispensable to many of history's most profound scientific discoveries. In the last two hundred years, though, mercury's value as a therapeutic or antiseptic agent has diminished against its increasingly intolerable toxicity, and its role has shifted almost exclusively to that of chemical tool for agriculture, industry, science, and technology. In the last few decades, even these uses have been assailed, as concentrations of spent mercury compounds released to the environment still find their way into toxic contact with humans. Currently, mercury and its compounds are among the most heavily regulated industrial substances in common use.

The history of the myriad uses (and mis-uses) of mercury has been documented in medical and industrial contexts by many researchers, particularly Leonard J. Goldwater.² The history of mercury exposure in occupational health has been intensely studied toward the establishment of modern guidelines. In the modern age, tight regulations on occupational and casual exposure to mercury mean that further study of the effects of gross acute and chronic mercury exposure in humans is mostly limited to historical documentation and accidental occurrence. Within this context, this author found that one significant area of historical documentation

remains untapped. Despite the scrutiny given the history of mercury in the workplace, none of the medical, historical, scientific, or occupational health sources canvassed in this research mentioned the word "daguerreotype," save those that dealt exclusively with photography or photographic history.

Every reader of photographic history has probably come across accounts of mercury poisoning among daguerreotypists, and as is true with most ailments, there were probably many more cases that were only scantily mentioned or left unreported. The dangers of occupational exposure to mercury vapor were already well known from a number of mercuryconsuming industries by the time of Daguerre's discovery, and exposure to mercury was cautioned in the daguerreian press along with the reports of serious poisonings.3 With more than 2,600 individuals declaring their occupation as daguerreotypist in the U.S. Census of 1860 and several major companies supplying chemicals and materials to daguerreotypists in the amount of twelve million U.S. dollars annually,4 the worldwide daguerreian industry must have been a notable consumer of mercury in the mid-nineteenth century.

Author's note: This paper examines mercury as a critical component of the daguerreotype process. Emphasis is on important information about the characteristics of mercury, precautions for its use in daguerreotypy, its effect on health, and treatment for exposure. This paper is at best an overview. It is incumbent upon each daguerreotypist to assure for him- or herself that his or her techniques for working with mercury are adequate to protect personal safety, the safety of others, and the surrounding environment. Those not willing to take such precaution should not attempt mercury-process daguerreotypy at all.

A Very Brief History of Mercury

The use of mercury compounds goes back to the foundation of image-making. Neolithic-age drawings on cave walls5 and ceremonial applications to human bones were made with cinnabar, naturally occurring mercury sulfide, which is a soft, stable, red-colored mineral containing 80 percent mercury in its pure form. Aristotle gave the western world its first written account of metallic mercury, which he called hydrargyrum ("liquid silver") in the 4th century BC,7 and Pliny the Elder summarized known practical means for its extraction from cinnabar and listed important cinnabar mines at about the time of Christ.8 Over the course of centuries, the mysterious silverywhite metal bore several names and was tried in a bewildering number of applications, some of them brilliant, not all of them successful.

Because of its high grade, cinnabar was the obvious choice for the extraction of mercury from the earth, and as man increasingly sought mercury, the places of highest concentration were mined with increasing intensity. Mercury mines at Almaden, Spain, have been in continuous operation for more than two thousand years and have veins of cinnabar so rich that free mercury oozes from the walls.9

Mercury in Medicine

Almost since its identification, mercury has been perceived to have medicinal properties. Concurrently, mercury has also been identified as a dangerous poison. The balance between the therapeutic and toxic effects of mercury has been blurred throughout history.

At the same time that miners in Almaden were being protected from excessive exposure to mercury vapor via the first occupational safety and health mandates in history, large numbers of people were being treated with massive doses of the same mercury vapor for a scourge called lues venerea, or "The French disease," which we now know as syphilis (fig. 1). The treatment of syphilis with mercury persisted into the twentieth century and finally was displaced by the advent of penicillin in the 1940s (fig. 2). For hundreds of years, mercury in nearly every known form was administered to syphilitics, often with remarkable effects (such as the generation of more than a liter of saliva per day in some individuals). Interestingly, mercury was never clinically proven to have a positive effect in combating the disease.10

Largely on the supposition that mercury cured syphilis (which no other medication could cure, therefore it should have similar effect on other incurables), the medical use of mercury drastically increased in the ninteenth century. According to Maurissen, mercury and its compounds were prescribed for "a wide variety of illnesses . . . such as testicular diseases, hepatic disorders, plague, pleuritis, purpura haemorrhagica, peritoneal inflammation, erysipelas, cholera, chronic diarrhea, amenorrhea, eczema, hydrophobia, chronic diseases of the brain, typhoid fever, amaurosis, and inflammation" and was applied via "solutions, lotions, eyewashes, baths, injections, gargles, ointments, powders, pills, plasters, fumigations, and trochisci."11 It was even used in cosmetics, such as skin-lightening cremes.12 Metallic mercury was swallowed in quantities of up to two pounds or more to clear intestinal blockages by its sheer weight without ill effect, most of the time. Mercuric chloride, on the other hand, was commonly taken by mouth only in infinitesimal doses as a diuretic. For those inclined toward a different outcome, such as death, mercuric chloride taken in doses of as little as 1/2 gram usually was sufficient. The common name for mercuric chloride, "corrosive sublimate," was bestowed to describe the compound's effect on human tissues. Despite the fact that death by corrosive sublimate was slow (sometimes days) and excruciating (destruction of tissue along the whole gastrointestinal tract, with death finally occurring from kidney failure), it is odd to note that corrosive sublimate was a popular choice to effect suicide during the Victorian Era.13

Use of mercury in medicinal and cosmetic capacities continued well into this century before being gradually replaced with products having far less toxic side- or post-effects. As knowledge of the long-term and low-level toxic effects of mercury became known, more and more products containing mercury compounds were withdrawn from the pharmacopoeia. Some of the last to go were mercurycontaining teething compounds given to infants that actually resulted in a form of mercury poisoning known as acrodynia, or "pink disease,"14 skinlightening cremes, and vaginal contraceptive jellies (still on the market in 1970) that contained mercury in concentrations sufficient to raise women's urine mercury levels significantly.15 Compounds such as Mercurochrome TM topical antiseptic can still be purchased over-the-counter at local drug stores, even though the efficacy of mercury-containing

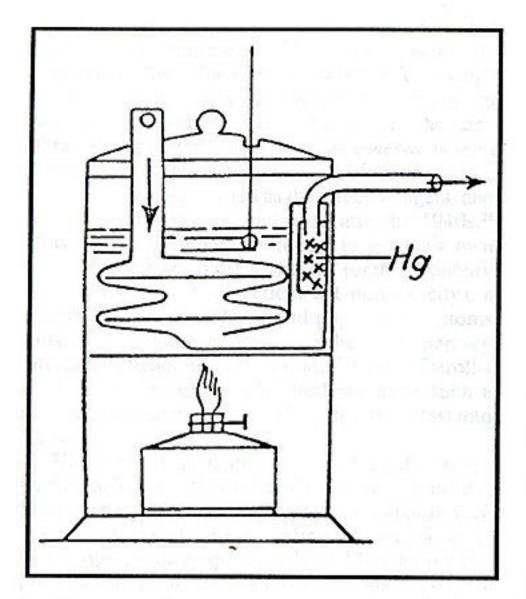


Fig. 2. A twentieth-century mercury vaporizer for Dr. Engelbreth's Inhalation Apparatus for the treatment of syphilis, in use at least as late as 1928. The patient breathed a mixture of warm mercury vapor and steam. The standard dose was 20 minutes at 100 degrees C., but it is not known if the air was saturated with mercury in this apparatus. (From Goldwater, Mercury; A History of Quicksilver, p. 162.)

"antiseptics" that do not contain enough mercury to be toxic to humans in casual application has long been in question. 16 Because of folklore and tradition, these products persist, in spite of labels warning that "frequent or prolonged use or application to large areas may cause serious mercury poisoning." 17

Industrial and Technical Uses

According to Goldwater, "there is general agreement among historians that the name 'mercury' was given to quicksilver by alchemists" in about the 6th century AD., who held mercury, sulfur, and salt as the three principals. ¹⁸ The tenet of alchemy known to most is the goal of transmuting base metals into gold. Goldwater comments that "historians of science in the mid-twentieth century frequently use the word 'paradigm' in describing a system of beliefs, and have pointed out how that old paradigms do not easily give way to new. The transition from alchemy

to chemistry illustrates this thesis very well with mercury responsible for much of the difficulty and at the same time serving as a link between the old and the new." In a remarkable "paradigm shift" (to use a buzz-word of the 1990s), ironic to alchemy, gold can be transmuted into mercury: a stable mercury isotope, 198Hg, can be produced by bombarding gold with neutrons.

Mercury even took a toll among men at the bridge between alchemy and science: "It is alleged that Sir Isaac Newton went mad for a period of one year while engaged heavily in alchemy. Recent analyses of samples of his hair showed high concentrations of mercury." Mercury has also figured in the equally obscure search for perpetual motion, as well as the more pedestrian quest for accurate time keeping. ²¹ Between these extremes, it is not surprising to find that mercury was also the breakthrough component in the world's first practical photographic process.

It is fitting that the popular story of Daguerre's discovery of mercury's fundamental role in his experiments to fix an image from the camera obscura is so apocryphal, and yet so enduring. The idea of an overlooked "few drops of spilt mercury" in a chemical cabinet into which his exposed (and supposed ruined) plates were placed is fully in keeping-with the metal's mysterious and alchemical reputation.22 The Gernsheims give evidence that, in fact, Daguerre was far more methodical in his application of mercury in the experiments that led to the daguerreotype, but nonetheless, they provide the apocryphal chemical cabinet story first in their description of the invention of photography.23 What is surprising, according to Barger and White, is that "this method of image formation is not intuitively obvious, and the fact the Daguerre devised this process is even more remarkable, in light of its true technological details."24

The same casual, inadvertent presence of mercury figures in remarkably similar stories that have worked their way into scientific folklore. Goldwater cites two such stories: one, originating in 1895, concerned the search for efficient production of phthalic anhydride, necessary for the manufacture of synthetic indigo dye; and one from modern biochemistry that resulted in the production of a purified form of the enzyme enolase. As with the story of Daguerre's cabinet, in both these cases the desired result of the experiments was achieved, but discovery of the key role of mercury was accidental, in the form of mercury thermometers broken in the apparatus during the experiments.²⁵

It has been suggested that serendipity connected the mercury treatment of syphilitics with the discovery of the value of mercury in the "carroting" of fur for felt. Early felting practice involved processing the animal hides with urine, and the urine of men being mercurialized for lues venerea worked so much better than any other Mercuric nitrate in the urine was identified as the effective agent, and it was widely adopted and used into the 1940s.26 Thus, it was common for felters to get their own scourge called the "hatters' shakes" (or the "Danbury shakes" after the Connecticut hat making city), a complex set of neurologic and physical symptoms caused by chronic exposure to the very mercury nitrate so efficacious in their trade.27 Lewis Carroll's Mad Hatter is supposedly modeled after such a sufferer, though the direct linkage has been cast into doubt.28

The physical and chemical properties of mercury particularly lend themselves to scientific utility. Mercury has played a significant role in the discovery of twenty-two elements, including oxygen, nitrogen, magnesium, aluminum, and helium. Mercury figured prominently in the work of Priestley and Lavoisier (who first identified mercury as an element) that led to the discovery of oxygen and the discreditation of the phlogiston theory. Mercury also contributed to Boyle's law, Avogadro's hypothesis, the discovery of dialysis, studies in Brownian movement, and validation for Einstein's formula for the diffusion of colloidal particles. Gabriel Lippmann "began in 1875 an intensive study of relationships between electrical potential and surface tension in mercury/water interfaces" which portended his discovery of the mercury-dependent interference color photographic process that bears his name.29

Mercury's ability to amalgamate with gold and silver has also figured prominently in its history. Metallic mercury has long been used in the extraction of finely divided gold and silver from the ores, but relative to the earth's composition, mercury is only slightly more common than the gold it helps uncover. Mercury is the sixteenth rarest element on earth, while gold ranks sixth. By comparison, the 78 least common elements comprise only 0.6 percent of the lithosphere.30 Mercury accounts for 2 x 10-6 percent, and gold 2 x 10-7 percent, yet the utilitarian nature of mercury has demeaned its rarity.31 If mercury were priced at \$40 per ounce in correct reference to gold's current \$400 per ounce, a standard 76 pound flask of mercury would cost \$48,600 instead of the current \$185 to \$190.

The modern uses of mercury include electrical apparatus (mercury vapor lamps, fluorescent tubes; batteries, switches, and relays), agricultural chemicals (insecticides, fungicides, herbicides, and bactericides), detonators (mercuric fulminate), dental amalgam, control instruments such as thermometers, and the electrolytic preparation of chlorine and sodium hydroxide for industry.

The Physical Characteristics and Occurrence of Mercury

Mercury, atomic number 80 in the periodic table, is a "silver-white, heavy, mobile, liquid metal; slightly volatile at ordinary temp..." and 13.5 times denser than water. It freezes at -38.9° C. (-38.0° F.) and in that state may be cut with a knife. Mercury boils at 356.7° C. (674.1° F.), a temperature probably hotter than nineteenth-century daguerreian spirit-lamp-heated mercury pots were capable of reaching. Reports of sputtering or boiling mercury, then, were probably mis-diagnoses of small amounts of water or other volatile materials trapped within the mercury in the bath that exploded when heated above their boiling points.

Pure mercury does not readily tarnish in air at ordinary temperatures, but slowly forms mercuric oxide when heated to near its boiling point. Mercury alloys with most metals except iron, which makes iron a good choice for mercury baths. Mercury amalgamates with several metals, including copper, which therefore should be used cautiously, or avoided, in the construction of equipment to contain mercury in the daguerreotype process. The same reasoning would hold for copper alloys such as brass, bronze, or brazing rod.

Metallic mercury readily combines with sulfur at ordinary temperatures to form mercuric sulfide, or cinnabar.33 Sulfur is sometimes recommended as an aid to detecting and suppressing mercury spills, since yellow sulfur turns red or brown as cinnabar is formed, and cinnabar binds mercury in a non-volatile form. Mercury is notably soluble in water for a metal, but in such relatively small amounts that mercury is often stored under a layer of water to prevent vaporization.34 This technique would not be recommended for daguerreotypists, because of the risk of trapping small amounts of water with the mercury during transfer to the mercury bath. When heated in the bath, trapped water might cause dangerous mercuryspattering steam explosions if the temperature were raised above 100° C. (212° F.)

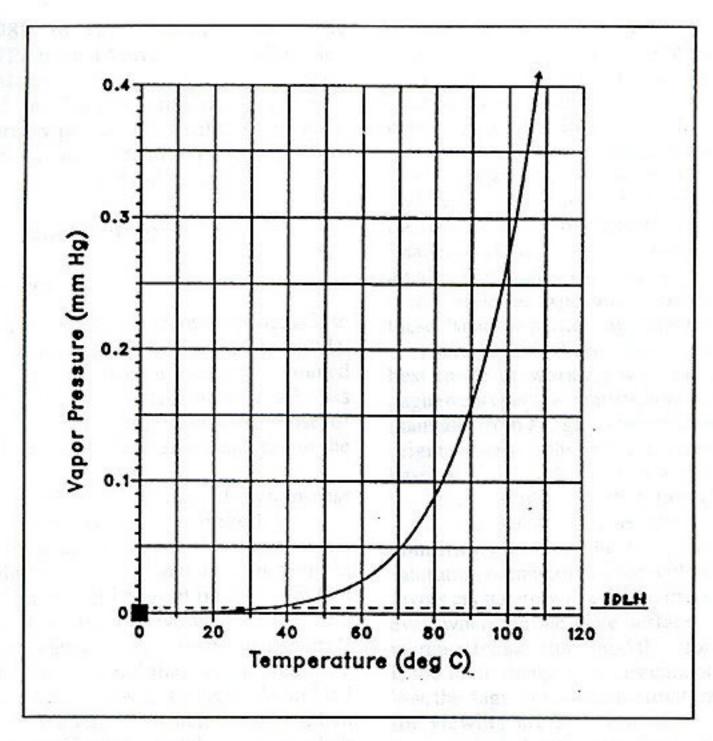


Fig. 3. Vapor pressure curve for mercury, plotted from data in Lange's Handbook of Chemistry.

Although mercury is only "slightly volatile" at ordinary temperatures, but its volatility increases dramatically as it is heated (fig. 3). Heating mercury from 20° C. (68° F.) to 90° C. (194° F.), a temperature routinely used by daguerreotypists, increases its vapor pressure by about 200 times. To put things into perspective, an open container of mercury allowed to evaporate at 20° C.(68° F) in a closed room until the air can't hold more (equilibrium vapor pressure) will result in air that contains more than 100 times the current permissible exposure levels (PEL) of mercury in a workplace. 33 However, during development within the enclosed mercury pot at 90° C. (194° F.), the daguerreotype plate is subjected to a small amount of air that contains approximately 20,000 times more mercury by volume than is considered permissible for people to breathe.

Despite its rarity in the earth's crust, averaging 0.5 parts per million (ppm), 36 mercury is apparently

ubiquitous. According to Goldwater, mercury "has been found wherever it has been sought in the lithosphere, hydrosphere, biosphere, and atmosphere of the Earth." Interestingly, 0.5 ppm is also about the average trace level of mercury in the human body. 38

Mercury cycles through nature, and man contributes to the turnover, but by far the largest contributor to mobile mercury in the environment is nature itself. The U. S. Public Health Service states that "the major source of atmospheric mercury has been reported to be global degassing of mineral mercury from the lithosphere and hydrosphere at a rate of 25,000-150,000 metric tons/year. Anthropogenic (man-made) releases of mercury to the atmosphere have been estimated to be 2,000 - 3,000 metric tons/year, (1984 data) mostly from the mining and smelting of mercury ores, industrial processes involving the use of mercury, and combustion of fossil fuels, primarily coal." 39

As of 1989 in the United States, the Environmental Protection Agency National Emission Standard for Mercury permits atmospheric release of between 2.3 and 3.2 kilograms (roughly 5 to 7 pounds) of mercury per day per facility involved in activities such as waste treatment, mercury ore processing, or chlor-alkali production.⁴⁰

Mercury in Daguerreotypy

Role in Image Formation

Mercury's role in the daguerreotype process is to render the latent image on an exposed plate visible. Just how it does that has been repeatedly examined with no model serving to solve the riddle in all of its aspects. Modern investigations include those of Barger and White and Brodie and Thackray in the 1980s.

Brodie and Thackray wrote that "the sharp-ness with which edges were reproduced in . . . daguerreotypes led us to suspect that electrostatic processes might be involved" much as they are in xerography. Their model is based on "the fact that some fraction of all finely divided particles and droplets is usually electrically charged," in mercury's case, positively charged, and that "those areas of a daguerreotype plate exposed to light do indeed become negatively charged" which would explain mercury's apparent affinity for just the exposed silver halide. This they experimentally demonstrated by creating simple latent images with sunlight and a stencil on iodized daguerreotype plates, which were rendered visible using positively charged copier toner. Their work with copier toner did not extend to daguerreotype plates given a continuous-tone exposure.41

In the most complete work to date, Barger and White model mercury "as a vapor-phase mineralizer collecting both latent image (photolytic) silver and the random photolytic silver and causing the metastable photolytic silver to recrystallize into stable silver image particles. Mercury plays the role of a solvent for crystal growth; it is not a chemical reactant in this process." This is only the briefest of sketches of a complex and elegant system of image formation described by Barger and White in The Daguerreotype; Nineteenth-Century Technology and Modern Science.

Contrary to previous notions that postulated a constant composition of mercury and silver in image particles, Barger and White show that composition

of image particles varies, not only in relation to exposure, but also during the process of image particle growth in the mercury bath. Image particles change from mercury-rich to silver-rich during mercurizing, and in areas of highlight exposure, become densely packed tiny particles of pure silver. In shadow areas of the image, the particles remain widely spaced, mercury-rich and clumpy "because they occur in areas of the plate that do not have latent image silver available for initiating the mineralizing amalgamation process that occurs in image areas receiving more exposure." Barger and White call these "shadow particle agglomerates."

There has also been ample speculation over the best mode of working with the mercury among daguerreotypists, scientists, and authors of practical manuals, from Arago's interpretation of Daguerre's original process through the present day.46 On the basis of their model, Barger and White summarize that the "conditions that favor optimal image formation include . . . carefully controlled mercury conditions so that the temperature and supersaturation of mercury vapor within the mercury bath favors crystal growth at latent image sites rather than everywhere on the plate surface" and "if the mercury temperature (and therefore, concentration) is too high, image particles cannot form; if it is too low, the daguerreian microstructures most favorable for viewing are not created."47 "The amount of control needed in this process is rigorous. As stated over and over again in daguerreian manuals, the daguerreotypist must be persistent while getting the process to work and then must be diligent in managing the process. Thus, the control of the process requires an intangible element—a degree of skill."48 Within that context, however, there is considerable latitude, and opinions and practical methodology vary widely.

Regarding the quantity of mercury required for the process, Daguerre recommended "au moins un kilo," though he went on to say that probably the kilogram (2.2 pounds) would be needed to fill the container in the mercury bath illustrated in his pamphlet sufficient to cover the ball of the thermometer. In translation to the American process, the quantity of mercury was reduced to where only 2 to 4 ounces were commonly recommended, and in American equipment, the bulb of the thermometer was often not inside the mercury bath at all, let alone covered by the mercury. In what many consider to be the definitive manual of the daguerreian era, the 1858 edition of The American

The Daguerreian

Hand Book of the Daguerreotype, author S. D. Humphrey stated he was "of the opinion that one ounce will answer as well as a larger quantity" and goes on to recount an episode where a traveling daguerreotypist produced "some 10 or 12 very superior impressions . . . fine, clear and well developed."51 Only then did the daguerreotypist discover "to his surprise, when he took up the bottle he carried the mercury in, he found it still filled, and none in the bath, except only such particles as had adhered to the sides "52 In what may be the impractical minimum amount of mercury necessary to effect image formation in daguerreotypes, two daguerreotypists in the 1970s and 80s experimented with richly amalgamated copper plates as sources of mercury vapor, but with only limited success.53

Opinions vary over operating temperature as well. Daguerre described a ramped heating scenario in which the mercury is heated only after the plate is put over the bath, and the heat applied until the thermometer "indicates a heat of 60 degrees centigrade, when the lamp must be removed[;] if the thermometer has risen rapidly it will continue to ascend without the aid of a lamp, but it must not be allowed to exceed 75 degrees . . . [and] must be left until the thermometer has descended to 45 degrees; it is then to be withdrawn and the operation is over."54 In this scenario, development was equipmentspecific, regulated by rate of temperature change, and highly impractical for making more than one daguerreotype at a time. As daguerreotypy became an industry, mercury baths were heated to constant temperatures during business hours to accommodate a steady stream of plates coming from the sitting rooms. The control of development became timetemperature dependent, as it is in photography today, and Humphrey noted that "by this means you have a uniformity of action, that cannot otherwise be obtained."55

The accuracy of temperature measurement has always been an issue. N. P. Lerebours was downright cavalier: "At first it will be good to consult a thermometer; but once the operator has learnt to appreciate the proper degree of heat, by applying his fingers to the bottom of the cup containing the mercury, it will be better for him to dispense with it." Nineteenth-century American equipment (as noted) often made use of a thermometer almost as an afterthought, and Humphrey cautioned that "those [thermometers] furnished by the manufacturers are not always correct, and it requires some experience to find the proper degree on the scale." 57

Many operators favored "high temperature and short exposure" over the mercury, claiming improved image quality. High temperature usually meant 80° to 90° C. (176° to 194° F.), and short exposure meant between 2 and 3 minutes. This author has noted recommended practical mercury temperatures that range from 49° to 150° C. (120° to 302°F.).

The length of time the plate is exposed to the mercury vapor can vary, but is generally dependent upon the temperature of the mercury. Generally, the cooler the mercury, the longer the time required to produce a fully formed image. Barger and White describe the scenario of image particle formation over time, and note that at 80° C. (176° F.) image particle morphology is not mature until after 1 minute.60 Humphrey describes the progress of an exposed plate over time in the mercury but gives a confused report when he says "the time more usually required in developing the image over the mercurial vapors, is about two minutes, and the temperature is raised to a point necessary to produce the desired effect in that time. This point varies as indicated by different scales, but for the ordinary scales is not far from 90° cen."61 He then goes on to describe the look of the plate at two minutes at 90° C. (194° F.) as "shallow or watery." After 21/2 minutes, however, he says the image is "clear and pearly; shadows, clear and positive, of a purple tint; drapery, jet black, with the dark shades slightly frosted with mercury."62 (Samuel Humphrey dedicated the 5th edition of his American Hand Book of the Daguerreotype to Jeremiah Gurney, and may as well have had the Gurney portrait illustrated in figures 4 and 5 in front of him when he wrote this description.) After 23/4 to 3 minutes the magic is lost, and Humphrey describes the image as "hard and chalky . . . misty with excess of mercury."63

In the modern age, mercurizing times continue to vary widely. There has been considerable improvisation in mercury bath design, for both better process performance and reduced mercury release, and clearly this has had an effect on the control of the process. Irving Pobboravsky, a modern master of the process, used to mercurize his plates for 75 to 90 seconds at 90° C. in his old bath, but when he replaced it with a more compact bath, he found he needed to increase the mercurizing time to 6 minutes at the same temperature. The discovery of that necessity was not without significant frustration. This author, working with an inverted-pyramid mercury pot closely resembling nineteenth-century examples, converted it from an alcohol lamp heat

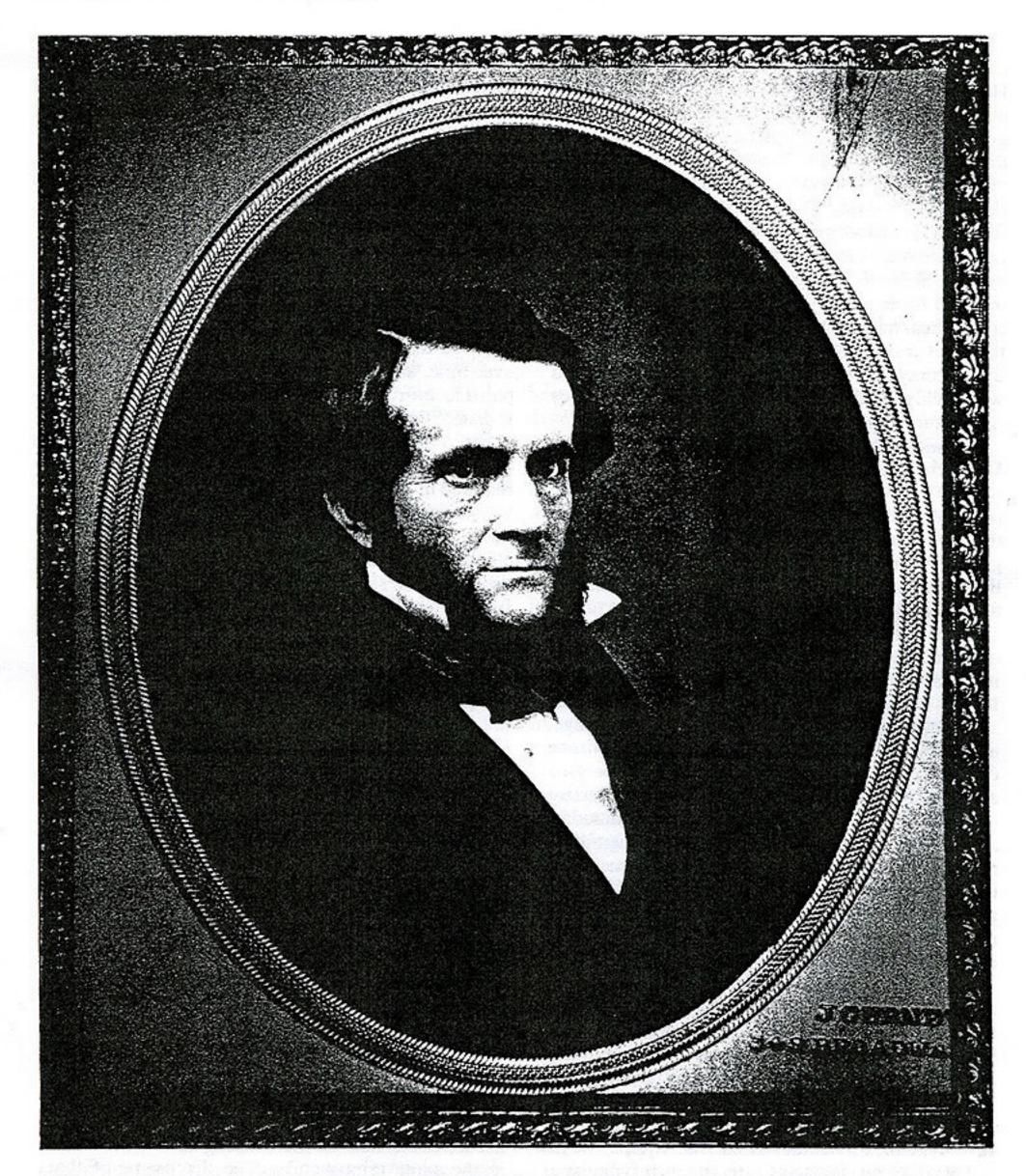


Fig. 4. Unidentified man, by Jeremiah Gurney, ca. 1852-57. Sixth-plate daguerreotype. (Collection of the author.)

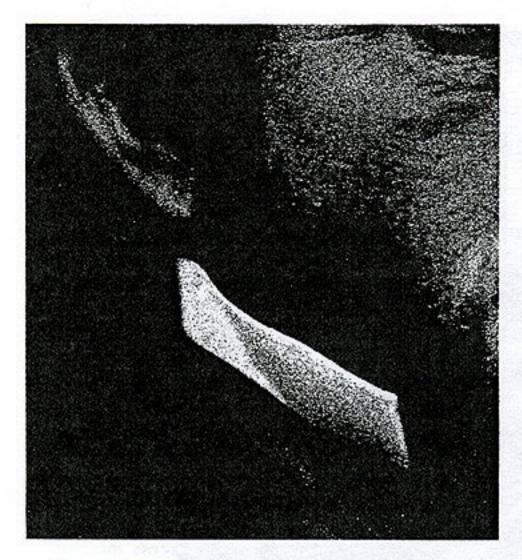


Fig. 5. Detail of the daguerreotype in fig. 4, photographed under point-source illumination to highlight the daguerreotype image particles and illustrate the "mercury frosting" described in Humphrey's American Hand Book of the Daguerreotype. Figures 4 and 5 were printed from different 35mm negatives at the same degree of enlargement. (Photographs by the author.)

source to electronically controlled heating tape. Even though the 80° C. (176° F.) development temperature was not changed in the conversion, a change in development time from 2¾ minutes to 4 minutes was required to restore optimum image quality with the new electronic temperature control. Attempts to raise the temperature while keeping the 2¾ minute time constant were met with plates as Humphrey described, "misty with excess of mercury," or that Barger and White would describe as clogged with non-image shadow particle agglomerates. In the final analysis, Pobboravsky notes that "it is valuable to consult the manuals, but ultimately you must consult your process" to find the answers that result in good daguerreotypes. 65

Controlling Mercury in the Daguerreian Laboratory

When the severity of occupational exposure to mercury (or anything else) is such that it regularly produces classical manifestations of intoxication, diagnosis becomes obvious and presents no difficulties. In modern industrial hygiene the objective is to eliminate all adverse effects, not only severe ones. This creates real problems, first, in recognizing even the slightest degree of poisoning; second, in establishing acceptable limits of exposure; and third, in applying control measures that will eliminate unacceptable exposures.—
Goldwater⁶⁶

Historical

The toxicity of mercury was well-known by the time people started making daguerreotypes in 1839. But medicinal uses of mercury were also very popular when people started experimenting with daguerreotypes, which may have tempered their sense of caution. And, as happens today, people probably heard about daguerreotypy and started working in ignorance of the hazards of the constituents, particularly of mercury vapor, which is undetectable by human senses.

Even well known daguerreotypists suffered from the ill-effects of mercury. Antoine Claudet precautioned mercury and recommended the use of a fume hood of his own design.67 Jeremiah Gurney apparently was nearly killed by mercury, and his plight was published as a "A Warning To All" in Humphrey's Journal, which noted "he has suffered the most accute [sic] pain, and been unable to move his limbs; his legs and arms have been swollen to nearly double the ordinary size, and his situation has been of the most perilous nature."68 Charles Meade described the state of the common mercury room in a letter to Snelling's The Photographic Art-Journal, saying that, "still we swallow much more than does us good, as any Operator will testify We all know that a ring or the guard chain [for a watch] of the Operator becomes coated with mercury by working in the same room containing the [mercury] bath." The editor responded that, "We shall give in our next an engraving of a new apparatus, with a description, manufactured by Mr. E. Anthony, intended to obviate the difficulty spoken of in this communication, which we hesitate not to say will be adopted by every daguerrean who values his health."69 The promised engraving failed to appear, but figure 6 illustrates such a bath as it appeared in Snelling's 1854 A Dictionary of the Photographic Art.70 Evidence suggests that this bath was not widely adopted.

In 1852, S. D. Humphrey published what was a most condemning assessment of occupational safety

in the daguerreian industry of the mid-nineteenth century when he "tested the purity of the atmosphere in his own workroom by hanging a piece of gold foil 'four feet above, and two from the perpendicular, at the side of the [mercury] bath; and in two days the leaf began to turn slightly white, and at the expiration of the fifth day it was so alloyed as to cause the amalgam to drop." In recounting the history of qualitative assessment of mercury in a workplace, Goldwater says "methods for demonstrating the presence of mercury vapor were not described until the middle of the 19th century. A textbook published in 1875 states that 'the best test for the detection of this vapor is suspension of a slip of pure gold-leaf in the apartment. If mercury be present, this will become slowly whitened by amalgamation." It is therefore apparent to this author that the daguerreian industry was at the vanguard of knowledge about practical mercury assessment in the workplace. Indeed Humphrey's experiment may push back by twenty-three years the first-known reference of the gold-leaf test, since no reference to the daguerreotype was made by any of the non-photographic sources canvassed in the course of this research.

Modern

There is a great need for you to investigate the nature of the chemicals you are using Do not rush into making daguerreotypes and do not be lazy about being disciplined in your operations. You may be endangering others as well as yourself by not paying strict attention to safety.—"Report of the Convocation of Latter Day Daguerreians," 1976.73

Unfortunately, daguerreotypists occasionally still poison themselves in the modern age and would-be daguerreotypists may continue to poison themselves, for instance, by following casual instructions that have been published for making mercury-process daguerreotypes in which "no attempt is made to go into the minute, time consuming details" and in which precaution against breathing mercury vapor is addressed entirely in the phrases "make sure there is adequate ventilation" which appears a total of twice in the document.⁷⁴

When dealing with mercury, MINUTE AND TIME-CONSUMING DETAILS ARE THE ORDER OF THE DAY and should become a fundamental matter of knowledge and common sense and care. Working with mercury without proper ventilation, or in any other uncontrolled situation,

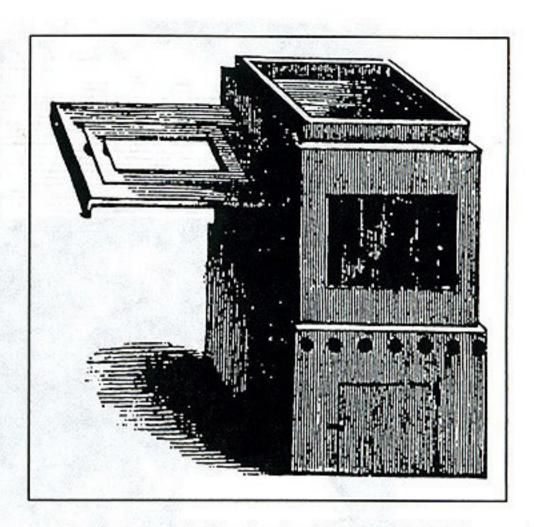


Fig. 6. Anthony's Condensing Mercury Bath. The bath was designed to condense excess mercury vapor and return it to the reservoir, rather than release it to workroom air. (From Snelling, A Dictionary of the Photographic Art, p. 131.)

must be considered as nonsensical as leaving the unlit gas on in the kitchen stove.

Control Equipment: Normal Operation

By design, the mercury bath concentrates mercury vapor to levels which make the process work, but the volume of the bath is small and experience shows that mercury loss through vaporization in the bath is also small. Proper venting of the mercury vapor to outdoor air, however, is required to reduce its concentration to safe levels. Improper venting of the mercury will allow it to accumulate within the work room, and thus will pose a very serious threat to health.

Therefore, a fully enclosed fume hood must be used for removing mercury vapor from the work area. Whether the fume hood is home made or commercially built, it must be tested thoroughly. Material cost and the time taken to design, fabricate, test, and trouble-shoot a home-built hood does add up.

Commercially built fume hoods are designed to withstand the gamut of chemicals found in a chemistry lab rather than just mercury and will have features to accommodate the widest range of uses.

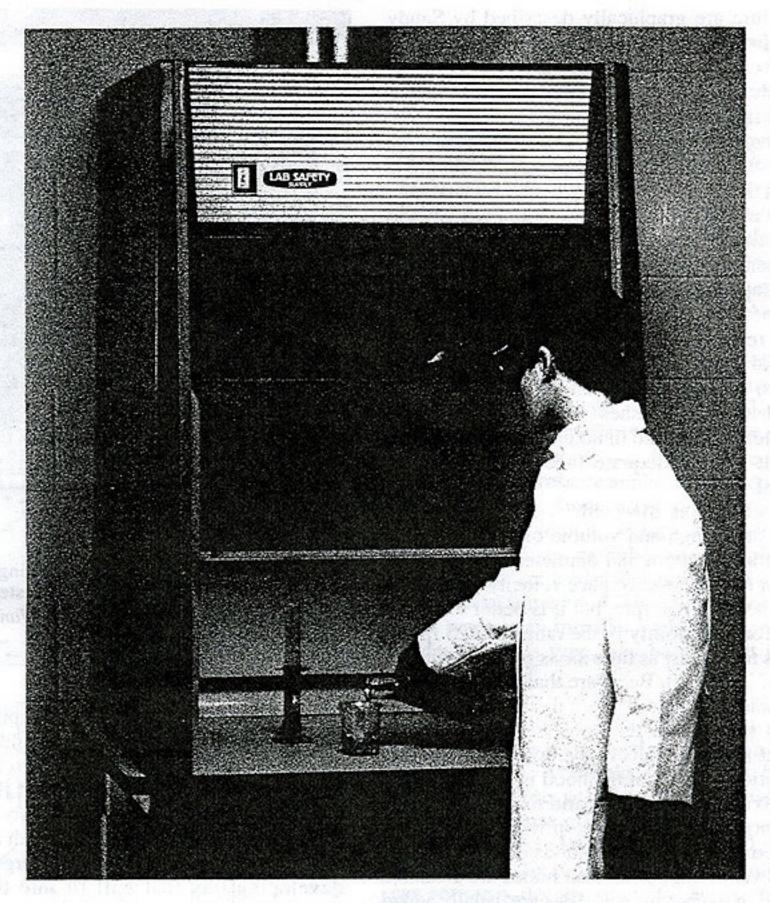


Fig. 7. A commercially made laboratory fume hood. (Photo courtesy of Lab Safety Supply, Inc., Janesville, WI.)

Although these features come at a costly price tag, a commercially built fume hood must be recommended as the first option for a safe daguerreian lab (fig. 7). The following are some important considerations for any fume hood:

•Air exhaust. ALL hoods used for daguerreotypy, filtered or not, MUST exhaust 100 percent of the contaminated air out-of-doors and suitably clear of obstacles that might impede the rapid dispersal of the mercury vapor to non-toxic levels in the atmosphere. Fixed exhaust pipes must be directed above the roof line of the building to avoid the

possibility of wind currents around the building inhibiting dispersal. Portable hood exhaust outlets, of course, must be positioned significantly downwind of the hood and operator. Air capture within the hood, and air dispersal outside of the hood, can be tested with non-explosive "smoke bombs" available from sources listed in Appendix B.

Danger: Hoods that filter and release air back into the work environment ARE NOT to be used with mercury vapor, since the vapor is odorless and colorless at toxic concentrations and thus provides no warning of a filter failure. The consequences of such a failure are graphically described by Sandy Barrie in the Daguerreian Annual, 1992.76

•Face velocity. Face velocity is the speed of air entering the opening of the fume hood, usually measured in feet per minute (fpm). In the CRC Handbook of Laboratory Safety, Furr states that "the minimum face velocity must be great enough to ensure that the direction of air movement at any point in the area of the open face of the hood will always be into the hood."77 Small velometers or anemometers (fig. 8) may be purchased at reasonable cost from suppliers such as Laboratory Safety Supply to measure face velocity (see Appendix B: Suppliers). They are recommended for either home built or commercial hoods, and may be mounted in the hood opening to continuously monitor efficiency. For hoods with adjustable sashes (see Access below), the anemometer can be used to note the maximum sash opening at which adequate face velocity can be maintained.

Face velocity is affected by several factors, including the design and volume of the hood, area of the opening, pattern and diameter of duct work, and blower motor capacity. Face velocity of the hood should be at least 100 fpm, but it is better to design the hood for a capability in the range of 125 fpm. 78 The aim is to exhaust as little air as possible without any risk of backdraft. Be aware that the body of the operator standing at the front of the hood may affect airflow at the face of the hood, so checking face velocity at several points in the opening while in a work position in front of the hood is advisable.

•Construction materials and design. The hood must be large enough to work in without impeding airflow. Commercially built hoods come in several sizes, and very simple, compact hoods are available from some manufacturers. Baffles are usually added to commercially made hoods to distribute airflow evenly within the hood and should be considered for home-built designs. (See diagrams, fig. 9)

A wide variety of construction materials can be considered for home-built hoods, but the final finish on the inside of the hood should be smooth and "seamless" for reduced air drag and ease of cleaning. PVC (polyvinyl chloride) plastic is readily available in smooth-surfaced sheets that are easily welded with PVC cement. Other materials can be painted with a smoothing, chemically resistant paint such as epoxy.

The floor of the hood is of particular concern, since it plays a key role in the easy containment of any spilled mercury. It should be as smooth as possible, with joints at walls and corners filled-in to

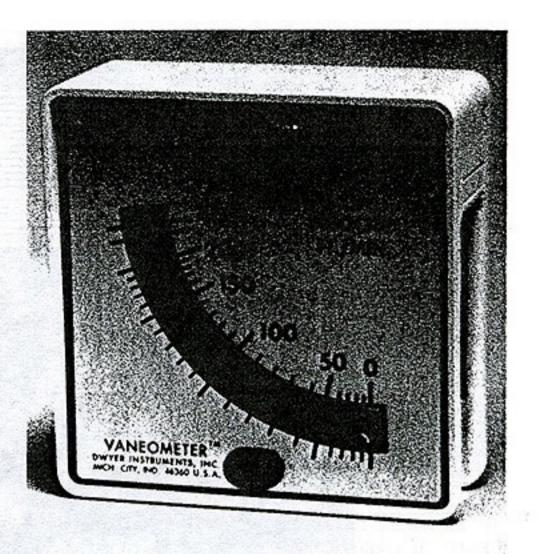


Fig. 8. A small velometer for measuring air velocity in fume hoods and ventilation systems. (Photo courtesy of Lab Safety Supply, Inc., Janesville, WI.)

produce a smooth fairing, free of pits or crevices that could hold mercury. There should be a lip at the front edge so that spilled mercury cannot roll out through the sash opening. A hood floor of a light color will make it easier to spot any tiny drops of spilled mercury for clean-up. If such a floor cannot be built for the hood, use the largest darkroom developing tray that will fit into the hood as a containment.

•Access. Most hoods have a sash, or front window, that can be raised or lowered to accommodate loading and using the hood. To maintain face velocity, or for reasons of economy, many home-built hoods are designed with portholes, or a similarly small opening in a fixed front panel, rather than a movable "sash." This requires the addition of a door through which equipment can be loaded into the hood. Adjustable sashes must be used carefully, since as the sash is opened, the critical face velocity of air entering the hood drops, which increases the possibility of contaminated air escaping into the work area. A hood should be designed to be closed air-tight when not in use, thus increasing the safety margin for workroom air.

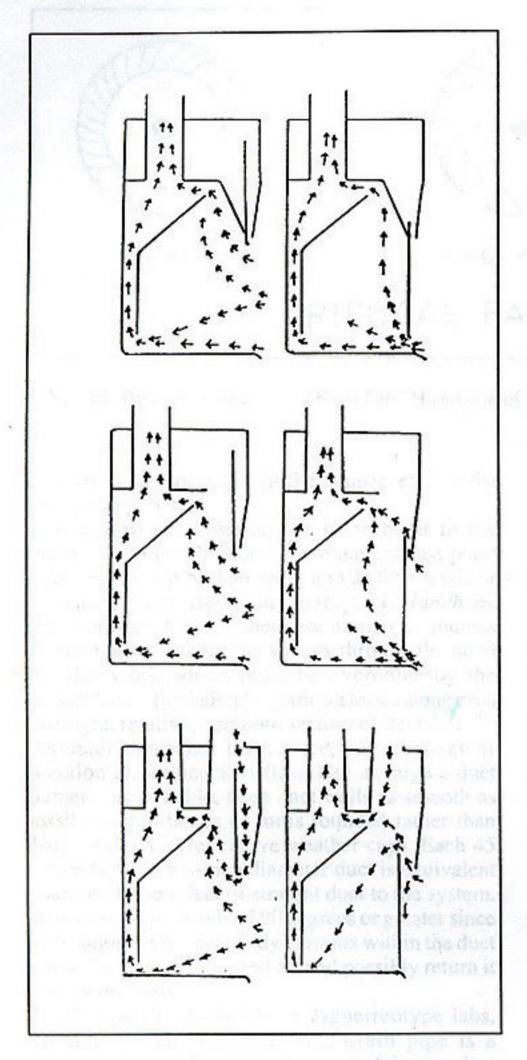


Fig. 9. Types of laboratory fume hoods. In these illustrations, the sash is open on the left drawing and closed on the right. Arrows indicate air flow. From top to bottom: conventional fume hood, with vertical sash and baffle; bypass fume hood, with air space at the sash to keep face velocity constant when the sash is closed; and auxiliary-air fume hood, that draws outdoor air to reduce the amount of laboratory air exhausted. (From CRC Handbook of Laboratory Safety, p. 146-47.)

·Fans and motors. The exhaust fan that removes contaminated air from the work area operates at negative pressure on the intake side and positive pressure on the output side. The exhaust fan should be positioned outside the confined work area, so that the hood and all duct work within the work area is at negative pressure. Therefore, any leaks in the hood or duct work in the room area will pull clean air IN to the hood or duct work, rather than push contaminated air out into the work area. Explosion-proof fan motors are available but are very expensive and not necessary

for the daguerreotype process.

"Centrifugal" fans are most common in fume hood applications and come in three basic types (fig. 10.) Of the three, the "squirrel cage" or forward-curved impeller will most commonly be found at surplus stores, etc., but they are primarily suited for low-pressure applications and so should be tested in the fume hood system to confirm adequate face velocity before mercury is used. Paddle-wheel, or radial-blade impellers, are probably more powerful than is required for a small daguerreian fume hood. The most efficient of the three types is an impeller with backward-curved blades, but this type may be difficult to locate inexpensively.80

Fan capacity is often expressed in volume, or cubic feet of air per minute (cfm), and fume hood face velocity is expressed as speed in feet per minute (fpm). A simple conversion from fan capacity to face velocity is nearly worthless, however, because of the added effects of drag in the duct work (see Duct work below). Drag occurs naturally any time air moves past a surface and can seriously decrease fan efficiency, so be very conservative with estimates when choosing a fan. Confirm adequate face velocity with an anemometer after installation of the fan.

Mercury vapor does not attack iron in steel fan blades, but iodine and bromine will.81 If the hood will also be used for charging sensitizing boxes or mixing accelerators such as bromide of lime, coating the metal fan components with epoxy paint or PVC (and then inspecting them frequently) is a low-cost alternative to chemically resistant all-PVC fans.

Since a fan failure with hot mercury in the hood would be unacceptable, in-line fans such as "muffin" fans for electronic equipment ventilation (that have sometimes been used in home-made fume hoods for daguerreotypy) are not recommended because of the corrosive action of

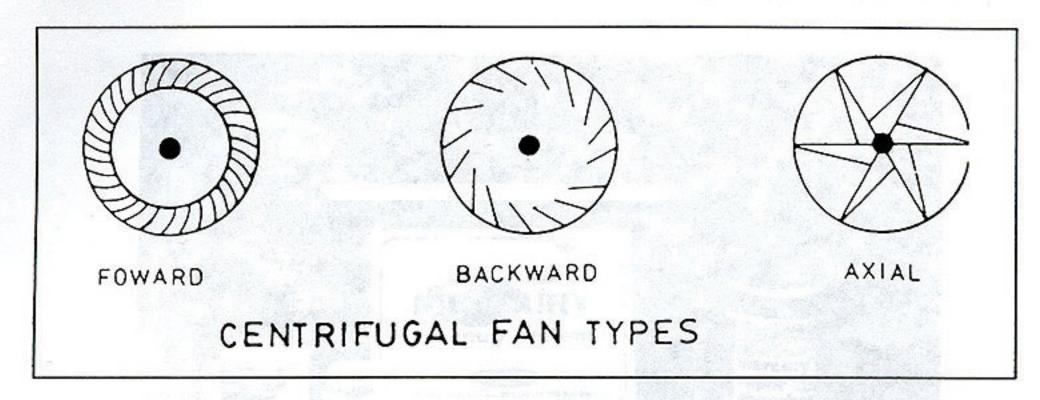


Fig. 10. Types of blower fans. (From CRC Handbook of Laboratory Safety, p. 161.)

mercury (and halogens) on the copper, etc., in the motor components.

 Duct work. Position the fume hood in the workroom to get the hood air to the exhaust point with a minimum of duct work and as few bends or turns as possible. According to the CRC Handbook of Laboratory Safety, "there are numerous sources of frictional losses for the airflow through the hood and ductwork which must be overcome by the exhaust fan . . . [including] significant losses along even a straight, relatively smooth section of duct "82 Diameter, material, turbulence, and changes of direction all influence airflow. Use as large a duct diameter as possible, keep duct walls as smooth as possible, keep bends or turns rounded rather than sharp, and avoid restrictive weather caps. Each 45 degree bend in a 6-inch diameter duct is equivalent to adding 6 more feet of straight duct to the system. Do not use sharp bends of 90 degrees or greater since acute angles can create eddy currents within the duct that will trap contaminated air and possibly return it to the work area.

For small fume hoods in daguerreotype labs, circular 4-inch diameter PVC drain pipe is a common, chemically resistant, easy-to-fabricate duct material. Six-inch is vastly more efficient but less easy to obtain. A fan motor must be found that can overcome the high resistance of the small duct diameter and still deliver adequate face velocity. For portable hoods, 4-inch diameter dryer hose is often used for duct, but the pleated walls reduce fan efficiency considerably over even short lengths.

 Air supply. When properly operating, a fume hood will become a major component of lab ventilation. Adequate air must be admitted to the workroom space that contains the fume hood so that the draw of the hood is unimpeded.83 The fume hood design can affect how much room air is vented outof-doors. This is a significant factor if the hood is run in a room that is heated or cooled, since the conditioned air is what is pumped out, forcing heating or cooling equipment to work more, which increases energy costs. "Auxiliary air" or "add-air" hoods (fig. 9, bottom) reduce this effect by drawing some portion of the ventilating air from outside the controlled environment. Because precise airflow is required within these hoods to keep them effective, consider only commercially built and installed addair hoods.84

More information on fume hoods should be sought in reference works such as the CRC Handbook of Laboratory Safety (see Appendix A).

Control Equipment: Spills

In spite of the best precautions, every daguerreotypist should be prepared for a mercury spill. If the spill is contained by the floor of the fume hood, recovery should present minimal hazard. Should the spill occur outside the hood, the ability to quickly bring the spill under control becomes of utmost importance. No spill is insignificant, since even the drop of mercury from a broken thermometer can cause serious poisoning if allowed to vaporize in an enclosed room. Each daguerreotypist should



Fig. 11. A mercury spill control kit. Several kits are available from a number of manufacturers. Components of the kits vary depending on where or how they will be used. This kit, for small spills in a lab, contains mercury indicator, absorbent powder for liquid mercury, absorbent powder for vapor, absorbent-impregnated sponge-jars that can be sealed after use, a small scoop, eye protection, and gloves. (Photo courtesy of Lab Safety Supply, Inc., Janesville, WI.)

make every effort to eliminate any possibility of a spill occurring outside the fume hood. Following are some guidelines in the event of a spill:

Forewarned is forearmed. Consult reference books on handling chemicals, such as the CRC Handbook of Laboratory Safety, or the Chemical Technicians' Ready Reference Handbook for more detailed information than is contained here (see Appendix A). It is also prudent to consult regulations and research courses of action that might involve Federal, state, or local authorities, such as 911 service. Regarding mercury, Levi Hill invoked King Philip—"Remember thou art mortal." In the 1990s, this author would add "and thou mayest also be liable."

Spills outside of the hood will require the immediate availability of a face-mask respirator with an appropriate metallic mercury absorbing filter so that clean up can be conducted safely (see Appendix B). Since mercury vapor is odorless and colorless, choose only those face-mask filters that have a saturation indicator. Face masks are only effective if a complete seal can be achieved; they are not effective when worn over a beard. Do not use "nuisance masks" such as those made by the 3-M Company that are designed to absorb small amounts of mercury vapor but have no saturation indicator. Product literature states that they are not to be used in atmospheres above 0.5 milligrams per cubic meter (mg/m3), and almost any uncontrolled mercury spill in an enclosed, unventilated area will rapidly exceed this value. Do not even consider these masks as emergency gear.

Ventilation is critical in the case of an uncontrolled spill. Do whatever it takes to freely circulate clean air through the work area and exhaust it outdoors. Do so until the spill is entirely controlled. Fans should be positioned to pull air out of the affected area rather than blowing it in, to limit forced-air spreading of the mercury within the work area.

Danger: DO NOT, under any circumstances, use a household vacuum cleaner to capture spilled metallic mercury! The mercury will be aggressively volatized in the vacuum hose and bag and then blasted back out into the work area as dangerous aerosol and vapor, making a bad situation vastly worse. In the process, the vacuum cleaner will also be completely contaminated with mercury. Mercury-approved electric vacuums are made but are very expensive, and intended for industrial applications. 86

Commercially assembled kits are available that contain eye protection, gloves, small vacuum handpumps to capture and recycle mercury, compounds and sponges that amalgamate spilled mercury droplets, and powders that detect missed mercury or absorb vapor from the immediate vicinity of irretrievable losses, along with plain directions for dealing with spills (fig. 11). One of these kits, or an equivalent, should be ready for use in the daguerreian lab, since even a controlled, in-hood accident will require clean up. Prices range from about \$60 to \$275. Various components of these kits which might prove particularly useful to the daguerreotypist for controlling small spills, such as Hg Absorbor MercJarsTM, are available separately from suppliers.

Generic substitutes for components of mercury spill kits come at reduced cost but lack application-testing by the manufacturers. As mentioned above, sulfur powder is known to react with mercury and mercury vapor at room temperature and bind it into mineral cinnabar, and some metal filings such as zinc will amalgamate with mercury, but for peace-of-mind in demanding situations, reliance on a tested spill-control product is advisable.⁸⁷ Research generic possibilities thoroughly before application.

Note: Consult local regulations for disposal of any non-recyclable mercury recovered from spills.

Mercury Vapor Detection

Quantitative detection assesses the amount of mercury in a work place, either actually present in a volume of air or assessed over a span of time, usually expressed as Time Weighted Average. Quantitative detection of mercury vapor in a work place is an exacting and expensive proposition, involving either sophisticated meters or "sniffers" that require frequent calibration, air sampling that is sent to a laboratory for testing, or dosimeter patches that are worn on clothing for a specified period of time and then analyzed for mercury accumulated in that time. Quantitative assessment is necessary for compliance with OSHA guidelines for mercury in industrial situations where a certain mercury exposure is expected or is unavoidable, such as mining or work in mercury cell rooms of chlor-alkali plants. In daguerreotypy, exposure to mercury that would result in body accumulation is considered avoidable, since all work with mercury should be done in the fume hood.

Qualtitative detection of mercury usually involves a simple pass-fail test. In the daguerreian lab, where mercury should be controlled in the fume hood at all times, and any free mercury in the work area is considered unacceptable, a reliable qualitative mercury detector can warn of a hazardous condition. A qualitative tool called the Williams DetecterTM changed color when mercury at 0.5 mg/m³ or greater was present in air. Unfortunately, the very valuable Williams DetecterTM was recently discontinued by the manufacturer without substitution, and a similar product has yet to be found. Spill control products that change color upon exposure to mercury, such as Mercury Indicator from Lab Safety Supply, are inexpensive qualitative tools that help gauge if a clean-up has been successful (see Appendix B).

Mercury Storage

Mercury has about the same viscosity as water but is 13.5 times heavier. Therefore, any activity that involves pouring or moving open mercury has great potential for loss in the form of splashed, fine droplets, that by virtue of their weight, can travel great distances before coming to rest. Careful lab technique is critical.

Nineteenth-century daguerreotypists routinely poured mercury back and forth from ceramic (fig. 12) or glass storage containers into simple inverted-pyramid mercury baths, especially when traveling. Mercury was often stored right in the bath in the daguerreian studio, and manuals advised that it "may be left uncovered during the day but should be kept covered during the night to keep out the dust." Access to the mercury in the bath was considered necessary, since manuals noted that mercury "frequently is adulterated with lead, tin, and bismuth,



Fig. 12. Small ceramic mercury jars, with a 35mm film magazine for scale. These jars came in several sizes, and were commonly used in the ninteenth and early twentieth centuries. (Collection of the author.)

which it dissolves; the amalgums [sic] of these metals oxidizes readily and produces a film upon its surface."90 Routine filtering through chamois and paper was recommended to clear the oxide scum.91

Mercury available today is mostly of very high purity, which lessens the need for filtration, so some modern daguerreotypists have built mercury baths designed both to mercurize plates and hold the mercury when not in use. The safety demands on such a bath are great, since plates have to be admitted to the bath through some opening that must also be able to be sealed to prevent loss of vapor at other times. For this system to be secure, great care must be taken in design, selection of materials, and fabrication.

Mercury can be stored in glass, ceramic, and some plastic containers. Some disadvantages of these are obvious: glass and ceramic are breakable and ceramic is not transparent (which can inhibit careful pouring). Plastic offers excellent resistance to breakage, but mercury can permeate many plastics over time. (Suppliers of laboratory plastic and glass ware often include chemical resistance charts in their catalogs, which should be consulted.)

Given the risk and difficulty associated with cleaning up even a small uncontrolled mercury spill in a confined space, storage that combines the advantages of more than one material, while not very convenient, can offer the best security. This author stores mercury in a stoppered glass flask inside an airtight steel military "ammo box" that is only opened in the fume hood. Attitudes have indeed changed since the 1840s and 50s.

Mercury in the Human Body

Mercury exists in three basic forms, all of which can affect the human body. Two of these forms are encountered rarely, if at all, in the daguerreotype process, but knowledge of their basic characteristics is useful:

 Organic mercury compounds, formed on hydrocarbon complexes with mercury usually at the 2+ oxidation state, such as methylmercuric chloride (CH, HgCl). These compounds vary widely in toxicity, with the "short-chain," or alkyl mercurials like methyl mercury, being the most toxic.92 Ingestion of methyl mercury from seafood harvested near a Japanese chemical plant resulted in the infamous "Minamata disease" in the mid-1950s93 Organic mercurials are the source of recurrent cautions about mercury-levels in lake fish, swordfish, and tuna.94 The daguerreotypist would never encounter these chemicals in the practice of the process.

 Inorganic mercury compounds, with mercury at the 1+ or 2+ oxidation state, such as mercurous chloride (Hg,Cl,) or mercuric chloride (HgCl,), respectively. They can be very toxic, but the route of toxic exposure is usually by ingestion or absorption through the skin.95 Mercury does combine readily with the halogens, which are integral to daguerreotypy, to form toxic mercury halides (such as mercuric chloride). The chemistry of the daguerreotype process, however, requires that mercury not be allowed to contaminate the iodine and bromine at any time, and vise versa, or the process will fail utterly. Modern daguerreotypists using metallic mercury will have no reason to encounter inorganic mercurials in the normal course of the process, and though they are mentioned in the historical daguerreian literature, they have never played a direct role in the process.96 Controlling a mercury spill with sulfur creates a stable inorganic mercurial, HgS, or cinnabar.

The third basic form of mercury is fundamental to the daguerreotype process:

•Metallic or elemental mercury, at the 0 oxidation state. Metallic mercury commonly takes the forms of liquid, finely divided mist (aerosol), or vapor. Mercury aerosol and vapor are often unnoticed since they are odorless and colorless in air. 97 Daguerreotypists routinely work with liquid mercury to produce the vapor by heating, but normal handling in the course of the process should not produce the aerosol form.

In vapor or aerosol form, metallic mercury can be extremely toxic when breathed, and both acute and chronic poisoning can result. Because mercury vapor is odorless and colorless, and because it must be used at elevated temperature and in enclosed spaces in the daguerreotype process, daguerreotypists must pay critical attention when handling mercury. In this paper, further discussion of mercury and the human body will concern metallic (elemental) mercury in either liquid or vapor form.

The most common avenues for metallic mercury to enter the body are via the mouth, skin, and lungs.

Swallowed liquid mercury passes through the body largely without incident, with only about 0.01 percent of the dose being absorbed by the intestines. 98 Oral exposure to liquid mercury could only occur in the strangest of scenarios in a daguerreotype laboratory.

Absorption of metallic mercury though unbroken skin is only slight, which is probably why little boys and girls survive their celebrations of curiosity over the treasure released by broken thermometers. Fine droplets of mercury will find their way to corrugations and separations in skin, such as near cuticles, etc., where it can be absorbed over time, so any skin contact with mercury should be followed by vigorous soap-and-water rinsing. Impervious gloves, such as those made of latex or nitrile, are recommended when handling mercury.

Clearly, the most dangerous way for the body to receive metallic mercury is by inhaling the vapor. The body will retain more than 75 percent of the mercury available in each lung-full of air. 101 If the dose is massive enough, acute damage to the lungs will result, and death is possible. Most cases of mercury intoxication do not fatally damage the lungs, and so subsequent complications are caused by the body's attempt to process and eliminate the mercury that the lungs have absorbed.

Metallic mercury absorbed by the lung is quickly passed through the alveolar membranes (the linings in the air-sacs of the lung) into the circulatory system, and is thus distributed to all the organs of the body

within minutes of the exposure. Once in the body, mercury is highly diffusible in the blood as long as it stays elemental, i.e., in the 0 oxidation state. In this state, it evades many of the body's most important filtering mechanisms, including the bloodbrain and placental barriers. 102 As it is circulated in the body, elemental mercury is rapidly oxidized to the mercuric ion, Hg++, by body processes. Following the oxidation of mercury in the body, most of it is taken up, or bound, by proteins and other body components that contain complexes of sulfur and hydrogen called sulfhydryl, or SH, groups. Retention of the mercury by the tissues of the body following exposure to vapor "reaches peak levels within 24 hours except in the brain where peak levels are achieved within 2-3 days."103 Where the oxidation and binding occurs in the body is of critical importance to the body's ability to rid itself of the metal.104

The blood-brain and placental barriers exist to protect the brain and developing fetuses from toxic agents, but these barriers can work both ways. If mercury at the oxidized Hg++ state is provided to the body, as it would be through ingestion of an inorganic mercury compound such as mercuric chloride, it is bound up by body protein and blocked by the protective barriers to the brain and fetus, and toxic effect to the brain and fetus is mitigated. But owing to its lack of charge, elemental mercury remains dissolved in the blood. In this state it can readily pass these barriers, where a portion of it is inevitably oxidized to the Hg++ state "behind the curtain" in protected tissues. After oxidation, the mercury is quickly bound to available SH groups within protein in the brain and fetus, which prevents it from being diffused back out to the body through the same protective barriers. It becomes resident, and substantially cumulative, within these "protected" tissues. 105 In cases of chronic exposure to mercury vapor, the accumulation of mercury in the brain has been shown to cause decided neurologic effects and necrosis (cell decay) in brain tissue. 106

When mercury leaves the body, it does so primarily via urine and feces, and also via sweat, breath, and saliva. Most of the body burden of mercury will find its way to the kidney or liver for disposition. The kidney becomes the ultimate target for the body's accumulation of mercury, with "concentrations in the kidney orders of magnitude higher than in other tissues." 107

Quantities of metallic mercury can be passed with the urine shortly after an acute exposure, 1008 but as more of the available mercury is oxidized by body processes, the kidneys are progressively attacked by the corrosive quality of the mercuric (Hg**) ion. Gradually, the acute effects of mercury vapor poisoning give way to the more systemic effects of inorganic mercury. Damage to the kidneys can result, particularly if the exposure is chronic or if acute exposure is left untreated. According to the U. S. Department of Labor, "after a brief mercury exposure in humans, urinary excretion accounts for 13% of the total body burden. After long-term exposure, urinary excretion increases to 58%." 109

Bile from the liver, sweat, and saliva are also routes of elimination, but they are less easily quantified than urine. The liver processes most of the mercury not trapped in the kidney and passes it as Hg++ to the feces via bile, where unfortunately some quantity of it is reabsorbed by the intestines.110 Mercury has been proven to be expelled in sweat and saliva by some miners' ability to amalgamate a copper coin by rubbing it on their skin or holding it in their mouths. III Since most saliva is involuntarily swallowed, the mercury it contains is probably sent back through the body to leave via the feces. Mercury miners are routinely placed in "hot-boxes" to try to sweat accumulated mercury out of the body. (One such room at the Almaden mines is called "the beach").112

Elimination of mercury from the body takes place in phases over time. The lung is cleared of mercury first, by either absorption or exhalation. Mercury is cleared from the blood in an initially rapid phase where body burden is decreased by about 55%, followed by a longer phase (halftime of 30 days) where most of the remainder of the dose is eliminated. "There may be a very long terminal eliminator phase accounting for the remaining 15 percent of the dose, because mercury appears to accumulate or persist as seen in the brain."

The kidney is the limiting factor in the elimination of the metal from the body, since "overall elimination of inorganic mercury [Hg**, converted by body processes] from the body occurs at the same rate that inorganic mercury is eliminated from the kidney, where most of the body burden is localized."

Therefore, any compromise of kidney efficiency can slow the rate at which mercury is eliminated from the body, and thus exacerbate damage, particularly to that organ.

Symptoms of Mercury Poisoning

With proper precaution in handling, the risk of toxic exposure to mercury while making daguerreotypes should be small. There might be times, however, when mercury exposure might be suspected. The following is intended to acquaint the daguerreotypist with the most notable symptoms of mercury poisoning. It is highly recommended that further reading be done into the subject of the pharmacology and toxicology of mercury; the bibliography of this paper provides a reasonable starting point. Because of the relative rarity of mercury poisoning today, each daguerreotypist should have a working knowledge of the subject for purposes of monitoring his or her own well-being, and to be able to accurately describe symptoms or situations to medical professionals, should the need arise.

There is no symptom that is a "telltale heart" where mercury is concerned. Almost all of the symptoms exhibited from either acute or chronic exposure to mercury vapor have other, more common sources, and so the potential for mis-diagnosis is high. 115 For instance, following is a list of symptoms associated with mercury poisoning: headache, dry mouth, chest pain, shaking hands, blurred vision, insomnia, diarrhea, fatigue, irritability, forgetfulness, depression, hostility, and difficulty concentrating. This list, however, was culled from a list called "Identify Common Signs and Symptoms of Negative Stress" published in a health newsletter to employees of a large corporation. 116 More than one-third of the symptoms of stress listed in this source are also symptoms of mercury poisoning.

The toxic effect of mercury vapor depends on the dose received, the nature of exposure, and, to a large extent, the individual receiving the dose. Acute exposure to high levels of mercury vapor result in a different set of characteristic symptoms than do low-level, chronic exposures. Between the two extremes, the symptoms might exhibit characteristics of each scenario, but not necessarily in proportion to the exposure. Studies demonstrate that people show widely varying sensitivities to acute and/or chronic mercury exposure. 117

Acute Exposure to Mercury

The U.S. National Institute for Occupational Safety and Health (NIOSH) has established 28 milligrams of mercury vapor per cubic meter (28 mg/ m³) of air as an atmosphere "Immediately Dangerous to Life or Health" (IDLH). Mercury in air at equilibrium at 20° C. (68° F.) is at 14 mg/m³, already one-half of NIOSH's IDLH level. The NIOSH IDLH level is met at about 30° C. (86° F.), and if the mercury is heated to 90° C. (194° F.) and allowed to saturate air in an unventilated room, the air would contain nearly 500 times more mercury than NIOSH IDLH level (see fig. 3).

Acute exposure to mercury vapor "may produce symptoms within several hours; these include weakness, chills, metallic taste, nausea, vomiting, diarrhea, dyspnea [difficult or labored breathing], cough, and a feeling of tightness in the chest" and can lead to relatively rapid death. 119 High concentrations of mercury deposited in the alveolar tissues of the lung can result in dyspnea, pneumonitis (inflammation of lung tissues, with consolidation of the lung), pulmonary edema (the presence of abnormally large amounts of fluid in and between the lung tissues), and ultimately, failure of the lung to process air. Exposures to these very high levels of mercury are accidental, and thus the actual concentration is usually estimated. Given the same massive dose, some sufferers survive, others do not. 120 Gosselin notes that "if the exposure is not fatal, recovery from the acute illness usually occurs over several days to weeks with only mild exertional dyspnea and a dry cough persisting for longer periods."121

As noted before, mercury is rapidly cleared from the lungs into the bloodstream, where it is circulated throughout the body. The aftereffects of a single dose may be minimal (see above paragraph) or may enter a more prolonged phase of additional symptoms as the absorbed mercury is processed by the body. 122 There may be a "silent period" of several days between even a single dose of mercury vapor and the onset of additional symptoms. 123 These symptoms may include profuse sweating, severe salivation, swollen salivary glands, stomatitis (inflammation of mucus membranes in the mouth), gingivitis (inflammation of the gums), loosening of teeth, and ulceration of lips and cheeks.124 Repetition of the exposure increases the likelihood of additional symptoms considerably, and will lead to chronic poisoning.125

Chronic Mercury Poisoning

Exposure to mercury vapor at levels below those necessary to produce acute symptoms in the respiratory system may go unnoticed for a considerable period of time unless qualitative vapor detection methods are used in the lab. With chronic mercury exposure, the "major target organs are the central nervous system and the kidney." 126

The following passages will reflect the common combination of physiological and neurological symptoms associated with chronic exposure. Several passages are provided to illustrate the differing descriptions and weights given to symptoms associated with chronic exposure.

U. S. Department of Health:

"At low levels, the onset of symptoms resulting from chronic exposure is insidious; fine tremors of the hands, eyelids, lips and tongue are often the presenting complaint. Coarse jerky movements and incoordination may interfere with the fine movements considered necessary for writing and eating. Psychic disturbances such as insomnia, irritability, and indecision occur; headache, excessive fatigue, anorexia, digestive disturbances, and weight loss are common; stomatitis with excessive salivation is sometimes severe; muscle weakness has been reported." 127

Gilman:

Chronic exposure to mercury vapor produces a more insidious form of toxicity that is dominated by neurological effects tremor becomes quite noticeable and psychological changes consist of depression, irritability, excessive shyness, insomnia, emotional instability, forgetfulness, confusion, and vasomotor disturbances (such as excessive perspiration and uncontrolled blushing, which together are referred to as erethism). Common features of intoxication from mercury vapor are severe salivation and gingivitis. The triad of increased excitability, tremors, and gingivitis has been recognized historically as the major manifestation of exposure to mercury vapor when mercury nitrate was used in the fur, felt, and hat industries. Renal dysfunction has also been reported to result from long-term industrial exposure to mercury vapor. 128

Casarett and Doull:

In mercury vapor exposure the tremor progresses in severity with duration of exposure. Initially it involves only the hands but later may spread to other parts of the body. Tremors are triggered by voluntary use of the affected muscles (intentional tremor). Neuropsychiatric signs also occur at relatively low levels of exposure, notably excessive shyness, insomnia, and emotional instability with depressive moods and irritability most frequently reported. This neuropsychiatric complex is known as 'erethism.' 129

Gosselin:

Erethism consists of subtle or dramatic changes in behavior and personality: depression, despondency, fearfulness, restlessness, irritability, irascibility, timidity, indecision, and easy embarrassment In advanced cases, memory loss, hallucinations, and mental deterioration may occur. 130

Some effects of chronic mercury poisoning are reversible upon cessation of exposure, including erethism and tremors. ¹³¹ Rothstein suggests "the removal of exposed personnel from further mercury exposure results in a slow [months to years] disappearance of symptoms, provided the toxicity was not too severe or long standing. Thus the disease is reversible in early stages. The slow recovery suggests a slow mobilization of mercury from the sensitive tissues."¹³²

The long-term effect to the brain, however, would indicate that recovery is only partial. Tucker writes:

There are two immensely important factors which make damage to the brain extremely serious. First the neural cells of which it is composed cannot replicate and therefore, once seriously damaged or killed, cannot be replaced. Second the interconnections are not self-repairing, and again, once damaged, go out of action forever the co-ordination of movements or, indeed, any activity, are not the outcome of the activity of single neural cells. All are the outcome of processes which involve thousands and probably millions of interconnected cells. Such systems have what electronic engineers are prone to call a high level of redundancy. That means that many pathways are not strictly necessary for the function to be carried out efficiently, but simply duplicate or triplicate other pathways in case some kind of blockage or breakdown occurs. . . . by the time clinical symptoms of nervous disorder appear, such as lack of co-ordination, then enormous damage has already been done.133

Autopsy has shown that "in the brain of workers exposed to mercury vapor, very high concentrations remained after the cessation of exposure." "In severe cases, spongeous degeneration of brain cortex can occur as a late sequela to past exposure." Or, put in non-medical terms, "first it damages the organ [brain] without appreciable loss of cells, then erodes whole pockets of tissue." 136

Detection of Mercury in the Human Body

Assessment of mercury in the body is problematic. Acute exposure to mercury vapor is characterized by a predominance of metallic mercury found in red cells of the blood. 137 Within a few hours

of exposure, enough of the metallic mercury has been metabolized to mercuric (Hg**) ion to exist in a ratio in red blood cells and blood plasma that is difficult to distinguish from chronic exposure. The kidneys process mercury to the urine, but the rate may be affected by an individual's capacity to retain mercury rather than pass it through to the kidneys.

The two common methods used to assess mercury in the human system are analysis of mercury in the blood and analysis of mercury in the urine. Neither test can be completely correlated with symptomatology when the amount of mercury detected is small. Goldfrank points out that the "severity of symptoms varies widely, even among individuals with similar urinary levels; i.e., correlation between mercury levels and symptoms is poor." ¹⁴⁰ Instead, symptoms that suggest mercury poisoning will usually direct a person to seek testing and depending on the nature of the mercury exposure, it is possible that a symptomatologic diagnosis could be accurate without corroboration by blood or urine mercury levels.

Because of the high presence of mercuryattracting sulfhydryl groups in the protein of hair, the analysis of mercury in hair "has become a vogue procedure. The procedure does have merit in analyzing long-term exposure to heavy metals It is of no benefit in acute heavy metal exposures . . . "141 Therefore, it is at best a history of mercury exposure over the period of hair growth.

Mercury in Urine

Goldfrank suggests that "the type of exposure determines what tests will be most accurate in indicating the extent of poisoning. Since the mercuric ion [Hg⁺⁺] is excreted in the kidney, poisoning from elemental . . . mercury can be best assessed by measuring the 24-hour urinary excretion of mercury. This test is most useful in diagnosing an acute exposure or in assessing the success of treatment . . . Less than 10 μg/l [micrograms per liter] is within normal limits If a 24-hour collection, either before or after therapy, is greater than 100 µg/l significant exposure has occurred . . . "142 Generally, for tests run prior to therapy, "as urine mercury increases above 200 µg/l, increased incidence of tremors, poor eye-hand coordination, and poor performance on memory and verbal intelligence tests and reduced nerve function are noted."143

A 1985 study found that for mercury metabolized to Hg⁺⁺ in the body, levels of Hg⁺⁺ in the urine correlated better with actual mercury vapor exposure than did levels of Hg** in the blood. The study also found that for elemental mercury not yet metabolized, urinary concentrations correlated well with blood concentrations "and thus are likely to serve as a better indicator for evaluating recent exposure." 144 Dr. Thomas Clarkson of the University of Rochester adds that since the body does not pass methyl mercury in urine, the urine test is preferred for suspected mercury vapor exposure, since it will not be affected by levels of methyl mercury that might be in the body from other sources, such as seafood. 145

Mercury in Blood

Gilman notes that the "measurement of the concentration of mercury in blood should be performed as soon as possible after poisoning with any form of the metal," and further states "the upper limit of a normal concentration of mercury in blood is generally considered to be 3 to 4 µg/dl [micrograms per deciliter]. A concentration of mercury in blood in excess of 4 µg/dl should be considered abnormal in adults." Gilman does not differentiate whether the mercury detected would be elemental, Hg**, methyl mercury, or a combined total.

Treatment of Mercury Poisoning

The following refers to mercury vapor inhalation. It is in no way intended to direct the course of treatment. As with material presented in previous sections, the intent is to briefly review some common treatment methods and allow the daguerreotypist to understand the need for prompt treatment should the need arise.

First aid: Withdrawal from the source of mercury exposure is imperative. Seek medical attention immediately, since removal of mercury from the body by chelation (see below) is most effective when started promptly. If the exposure has been acute and severe, supplementary oxygen, bronchiodilation, and "positive end-expiratory pressure (PEEP)" may assist ventilation of the lungs and may reduce mercury levels in alveolar tissues prior to absorption.¹⁴⁷

Subsequent treatment: Subsequent treatment to first aid could range from monitoring the excretion of mercury from the system by natural processes to aggressive administration of compounds to bind and remove mercury. The condition of the individual victim and the nature of the exposure will affect the treatment chosen by the physician.

The common chemical therapy for mercury poisoning is "chelation," or the binding of mercury to receptive compounds that facilitate excretion. Several chelators have been used for mercury poisoning, and there may be recent additions not mentioned here. Chelators for mercury operate on mercury's affinity for sulfhydryl groups, and when promptly and properly applied, successfully compete with sulfhydryl-rich body proteins to capture and remove available mercury before it is absorbed, particularly by the brain. Prompt application aids in the effectiveness of chelation therapy. 148

The chelator BAL (British Anti-Lewisite) was developed during World War II as an antidote for arsenic-based Lewisite gas poisoning. The chemical name is 1,2- dimercaptopropanol, or dimercaprol. ("Mercapto" is a synonym for the sulfhydryl group, so named because of its affinity for capturing mercury.)149 BAL was introduced into the pharmacopoeia in 1945-46 after the end of the war and has been widely used to treat heavy metal poisoning. 150 When applied for mercury poisoning, it is "maximally effective when given early in the course of an acute episode."151 Because BAL is unstable in water, administration is by injection into muscle tissue in a solution of peanut oil. 152 The BALmercury chelate is excreted into both the intestine (via bile) and the urine. 153 BAL is not very effective in the treatment of chronic mercury exposure but is a chelator of choice for high-level exposures or symptomatic patients.154

The penicillamine chelators are more effective in the treatment of chronic mercury exposure than BAL and are used for acute exposures as well. Common varieties are D-penicillamine, D,L-penicillamine, and N-acetyl-D,L-penicillamine (also called NAP). NAP appears to have fewer toxic side effects than D,L-penicillamine. The penicillamines can be administered by mouth, and the release of penicillamine-mercury chelate is only to the urine. Thus, according to Gilman, penicillamine should be used with extreme caution when renal [kidney] function is impaired. The penicillamines should not be given to patients with a penicillin allergy.

Other chelators that have been used in treatment of mercury poisoning include calcium ethylenediamine tetraacetic acid (Ca-EDTA), which has been shown to bind poorly to mercury, and the BAL derivatives 2,3-dimercaptosuccinic acid (DMSA) and 2,3-dimercaptopropane-1-sulfonate (DMPS). DMSA and DMPS have recently shown

promise as effective, water-soluble, orally administered chelators with few side effects. 158

Conclusion

Making daguerreotypes is a detailed and technically demanding craft. Like many such crafts, daguerreotypy requires the use of chemicals and processes that, if applied incorrectly, can be hazardous. Knowledge and awareness stand as the difference between safe working methods and success with the process or hazard and failure.

As regards the education and technology necessary to do the process safely, mercury-process daguerreotypy has enjoyed a revolution since the "daguerreian era." Responsible modern daguerreotypists appreciate the nature of the chemicals that make the process work and have embraced fume hoods and release-limiting mercury bath designs. Without a doubt, safe working method is an overarching interest among practitioners of the daguerreotype process today and the prime motivation for the publication of this paper.

As thorough as this author has attempted to be, this paper is still only another step toward the complete understanding of mercury and the daguerreotype process. Opportunities abound for continued important research and contribution, both for historical understanding and for the goal of safe, prudent, and continuing practice of the art in the modern age. Levi Hill's admonition to daguerreotypists that to "remember, thou art mortal" is still true of all people. But in contrast to J. Woodall's assessment that opened this paper, in this day in age, mercury need not lie.

Notes:

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³For example, as noted by William Welling, Photography in America; The Formative Years, 1839– 1900 (NY: Thomas Y. Crowell Co., 1978), p. 94.

⁴Richard Rudisill, Mirror Image; The Influence of the Daguerreotype on American Society (Albuquerque, NM: University of New Mexico Press, 1971), pp. 197–198. Rudisill is quoting from a chart found in Robert Taft, Photography and the American Scene (NY: Macmillan, 1938), p. 61. The chart is based on the U.S. Decennial Census Reports for 1840 to 1930.

Jacques P. J. Maurissen, "History of Mercury and Mercurialism," New York State Journal of Medicine (Dec. 1981):1902.

'Goldwater, p. 72.

⁷John J. Putman, "Quicksilver and Slow Death," National Geographic Magazine 142 (Oct. 1972): 510.

*Goldwater, pp. 49-50.

Putman, p. 510.

10Goldwater, pp. 41, 239, 252, 226.

"Maurissen, p. 1905.

¹²U.S. Public Health Service, Agency for Toxic Substances and Disease Registry, *Toxicological Profile* for Mercury (Washington, D.C.: Government Printing Office, 1989), p. 70. Hereinafter cited as USPHS.

¹³Goldwater, pp. 246, 194, 166-67.

¹⁴Louis R. Goldfrank, et al., Goldfrank's Toxicologic Emergencies, 4th ed. (Norwalk, CT: Appleton & Lange, 1990), p. 644.

15Goldwater, p. 258.

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²⁵Goldwater, p. 28.

²⁶Ibid., p. 275.

²⁷Putman, p. 511.

²⁸Goldwater, p. 274.

²⁹Ibid., pp. 101-105, 124.

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³¹Frank Press and Raymond Siever, Earth (San Francisco, CA: W. H. Freeman and Company, 1974), p. 860.

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33Ibid.

³⁴A. F. Trotman-Dickenson, et al., eds., Comprehensive Inorganic Chemistry (Oxford, England: Pergammon Press, 1973), p. 280.

³⁵A. Keith Furr, ed., CRC Handbook of Laboratory Safety, 3rd ed. (Boca Raton, FL: CRC Press, 1989), p. 290.

³⁶Windholz, p. 842.

³⁷Goldwater, p. 2.

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³⁹USPHS, pp. 105–06.

40Ibid, p. 124.

41I. Brodie and M. Thackray, "Photocharging thin films of silver iodide and its relevance to the Daguerre photographic process," Nature 312 (20 Dec. 1984):744-46.

⁴²Barger and White, p. 156.

⁴³Ibid., pp. 144, 156–57.

⁴⁴Ibid., p. 157. ⁴⁵Ibid., p. 119.

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detail is known of their work in this area.

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⁵⁷Humphrey, American Hand Book, p. 36.

⁵⁸S. D. Humphrey and M. Finley, A System of Photography (New York: S. D. Humphrey, 1849); reprinted in Robert A. Sobieszek, comp., The Daguerreotype Process: Three Treatises, 1840–1849 (NY:

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⁸⁹A. Bisbee, The History and Practice of Daguerreotyping (Dayton, OH: L. F. Claflin & Co., 1853; reprint ed. NY: Arno Press, Inc., 1973), p. 47.

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