Photographic Processes
Chemistry 103, Spring 2001

Daguerreotype

Dominant photographic process used in America, 1840-60

1. Photographic plate was made by plating Ag on Cu and then polishing surface
2. Ag-surface was made sensitive to light by exposing to iodine vapors to form AgI:

$$2\ Ag_{(s)} + I_2 \longrightarrow 2\ AgI_{(s)} \qquad (1)$$

Light reduces AgI to Ag:

$$AgI + h\nu \longrightarrow Ag_{(s)} + I \qquad (2)$$

3. Exposed daguerreotype was exposed to heated Hg to form an amalgam with silver in places exposed to light. Amalgam is the image.

$$Ag + Hg \longrightarrow Ag(Hg) \qquad (3)$$

4. Unexposed AgI was removed by washing with water and sodium thiosulphate solution:

$$AgI_{(s)} + 2\ S_2O_3^{2-} \longrightarrow [Ag(S_2O_3^{2-}]_2^{3-} + I^- \qquad (4)$$

5. After 1841, gold toning was done by immersing fixed plate in gold chloride solution to yield a protective coat of gold metal on the mercury amalgam surface.

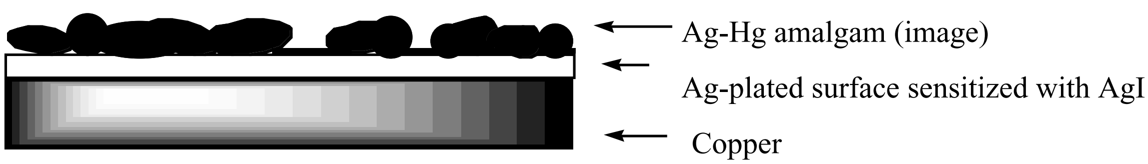

Figure 1. Daguerreotype

Ambrotype (developed by Frederick Scott Archer in 1851 and patented by Bostonian James Ambrose Cutting in 1854)

1. Colloidon emulsion containing KI was coated onto glass plate.
2. The plate was sensitized to light by dipping the plate in $AgNO_3$ to form AgI; the collodion had to be kept wet during entire process.
3. Exposure to light produced Ag as in equation (3) above.
4. The plate was developed to yield a stronger image.
5. The plate was fixed with potassium cyanide rather than thiosulfate:

$$AgI_{(s)} + 2\ CN^- \longrightarrow [Ag(CN)_2]^- + I^- \qquad (5)$$

6. After the plate had dried, the back of the glass was coated with black, often velvet, and placed under a brass mat with a clear glass cover. It was developed as an inexpensive alternative for portraiture to the daguerreotype.

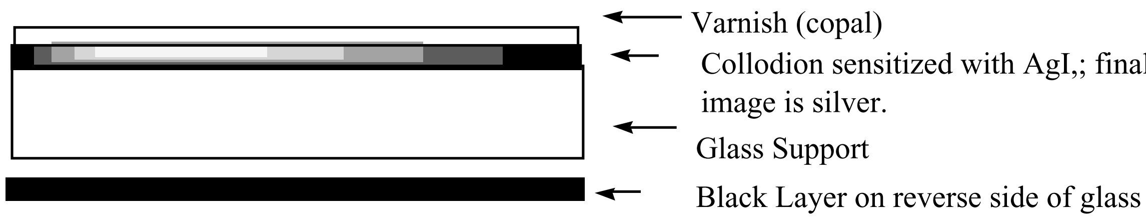

Figure 2. Ambrotype

Tintype or Ferrotype, patented by Hamilton Smith in the US in 1856, was particularly popular during the Civil War. These prints contain no tin, but use an iron plate, usually coated with a black varnish (of linseed oil, asphaltum, and lampblack) to yield a surface referred to as a "japanned surface." The plates were inexpensive and more robust than the ambrotype so that the final tintype could be sent through the mail or carried in a pocket.   The chemistry involved is identical to that of the ambrotype. The iron sheet was, however, much thinner than the glass of the ambrotype, contrary to what is shown in Figure 3.

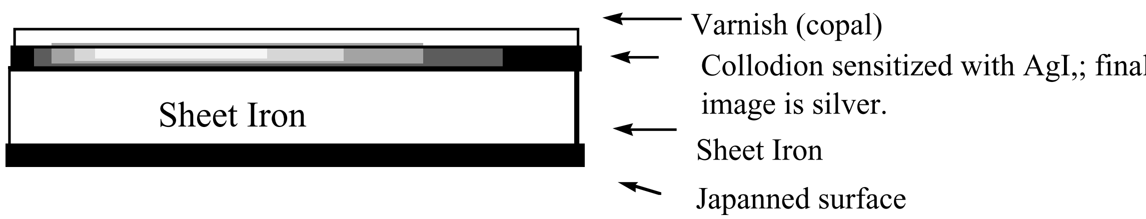

Figure 3. Tintype or ferrotype.

Calotype Negatives. The chemistry involved in producing the calotype is identical to that of the salted paper prints made in the Chemistry 103 lab: paper is sensitized by forming a silver halide on it by sequential dipping in a halide salt solutions and silver nitrate. William Henry Fox made these salted papers more light sensitive by additions of gallic acid. The papers were exposed to light to form an image, developed, and then fixed with sodium thiosulfate. In contrast to the salted paper print, the calotype was waxed to make the paper translucent. To make a print, the calotype negative was placed on top of more photo paper (sensitized with silver halide) and allowed to develop in sunlight.

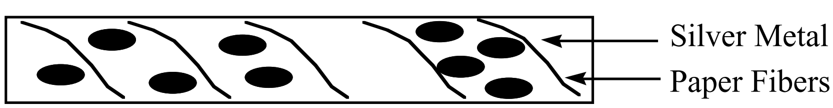

Figure 4. Salted paper (positive) or calotype (when waxed) negative.

Albumen Prints, first described by Blanquart Evrard at the French Academy of Sciences in 1850. Albumen papers were the dominant printed material by 1855 and the most common process from 1860-1885. Albumin paper uses a printing-out process (POP0, meaning that the image is formed by light alone, not developed chemically from the invisible latent image. Albumin papers were coated with egg white containing either ammonium chloride or sodium chloride. The papers were then sensitized by dipping them in silver nitrate. Prints were made by putting the negative in contact with the albumin paper and exposing to sunlight. Collodion negatives were generally used to print albumin papers. The chemical reactions involved in producing the images are identical to those used in salted paper prints. Albumen prints generally are warm browns, purplish-brown or black. They can often be identified from the crackle pattern developed as the albumen emulsion aged.

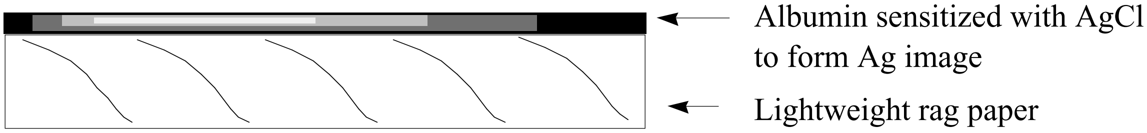

Figure 5. Albumin Print

Gelatin replaced collodion and albumen after about 1878 and served as the emulsion for negatives, film, and paper. Gelatin, sensitized with AgBr, could be coated onto glass to make negatives or onto paper to make photographic papers. Silver chloride papers were invented in the early 1880's and were generally available by 1890. The more sensitive AgBr-gelatine-coated papers were in wide use after 1886 when Kodak developed a process for machine coating paper. The chemistry involved both in capturing the image and in printing is that explored by Chemistry 103 students in making salted paper prints.

Platinum Prints are produced through iron-based chemistry. The actual process was patented in 1879, but did not become popular until the 1890's. The platinum process, and related systems, is based on the ability of ferrous [Fe (II) = Fe^{2+}] compounds to reduce salts of platinum, gold, copper, mercury, and silver. Papers are sensitized with a ferric oxalate or citrate and a reducible metal salt, exposed to light, and, finally, washed in water.

$$Fe^{3+} + h\nu \longrightarrow Fe^{2+} + e^- \quad (6)$$

$$Fe^{2+} + M^+ \longrightarrow Fe^{3+} + M_{(s)},\ M = \text{metal} \quad (7)$$

The image consists of finely divided metal. In the platinum process, potassium chloropatinite provides the source of this metal:

$$3\ Fe^{2+} + PtCl_4^- \longrightarrow 3\ Fe^{3+} + Pt_{(s)} + 4\ Cl^- \quad (8)$$

Platinum prints do not tarnish and have a broader scale of gray, although show less contrast, than silver ones.

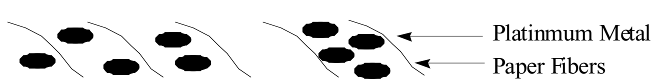

Figure 6. Platinum Print

Processes involving bichromates: Gum bichromate, carbon, Woodburytype, and collotype. Many polymers including gelatin, albumin, and gum arabic can be cross-linked (and, hence, permanently bond to their supports) when exposed to sunlight in the presence of the bichromate ion, $Cr_2O_7^{2-}$. Sunlight reduces this ion to Cr^{3+} which serves to cross-link the polymers.

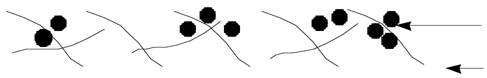

Figure 7. Gum dichromate print

In forming the gum dichromate print, sized paper is coated with a pigment in gum arabic (watercolor paint) and potassium dichromate. In the areas exposed to sunlight, the gum arabic polymerizes and become insoluble in water; pigment particles are trapped in the strands of cross-lined gum arabic. Both the gum arabic binder and dichromate are washed away in water from unexposed areas. The color of the print is determined by the color of the pigment used.

In the **carbon** process, gelatin was used as the media in which bichromate was incorporated with a variety of pigments. The final image was captured in gelatin which, when wet, could be transferred to different supports including canvas, paper, linen, silk, or metal. Carbon prints could be made in multiples from negatives. In the **photogravure**, the gelatin image was transferred to a copper plate; this image protected the plate from an etchant ($FeCl_3$). After the copper plate was etched in the areas unprotected by the carbon-gelatin resist; the plate was cleaned of gelatin and printed on an intaglio press like a traditional etching or engraving.

The **woodbury** process is based on the fact that bichromated- gelatin becomes hard and insoluble when exposed to light. A plate was covered with a thick layer of bichromate-sensitized gelatin, exposed to light, and then developed in warm water (to remove unreacted dichromate) to produce a positive relief image. After the image was dried, it was placed on a steel plate on a hydraulic press and covered with a lead plate. Applying pressure produced a lead mold containing the image. This mold was then used to make prints as follows: warm pigmented gelatins were poured into the lead mold and the paper to be printed was placed on top of this assembly. By application of pressure, the warm gelatin was transferred to the paper and, on cooling, the solid pigmented gelatin formed the image on paper, the **Woodburytype**.

Bichromated gelatin becomes water repellant as well as insoluble when exposed to light. This property was exploited to produce **collotypes**: Glass plates were coated with sensitized gelatin and exposed to light to form a hardened, water repellant image which could then inked with greasy lithographic ink and then be printed onto smooth paper.

M Merritt, February 2001