Pretty As A Picture

Part 1: Materials for Black-and-White Photography

The advent of photography and photographic materials profoundly affected not only scientific research but our view of history, law, and daily life. For science, photographic materials capture permanent images of experiments and phenomena. Photographic materials can integrate incoming light over time and record events too faint or too rapid to be seen by the human eye, or at wavelengths beyond the visible range.

This year, 1989, is the 150th anniversary of the rise of the daguerrotype process, the first widespread black-and-white photographic technique that created "pictures" of the world without requiring the skill and patience of a painter. This year is also the centennial of George Eastman's introduction of rolls of flexible photographic film plus the portable cameras to use them, which revolutionized photography and made it available to the general public. This month's Historical Note will look at the beginnings of photographic chemistry and early materials for capturing black-and-white images on metal or glass plates or on sensitized paper.

As early as 1565 some chemists had noticed the blackening of silver salts on exposure to light or heat. In 1725 German physician Johann Heinrich Schulze placed stenciled letters over a mixture of silver nitrate and chalk, showing that the darkening was caused by light alone. Schulze, however, merely wanted to investigate an unusual chemical phenomenon and did not attempt to develop it into a technique for producing images.

In 1777 Swedish chemist Karl Wilhelm Scheele exposed silver nitrate to a spectrum from the sun, and saw that blue and violet light produced a more pronounced effect than did red. Scheele also investigated the light-sensitive properties of other silver salts; he determined the chemical basis for the phenomenon in silver chloride, showing that light reduced the solution to metallic silver and free chlorine.

At the turn of the 19th century Thomas Wedgewood published the results of his experiments treating leather and paper with silver nitrate. Working with his partner Humphrey Davy (see the Historical Note in the January 1989 issue of the *MRS BULLETIN*), Wedgewood made silhouette images by placing leaves and other natural objects on top of the sensitized paper—but he had no way to stop the exposure or "fix" the image by dissolving away the unexposed silver salts, and the image turned completely dark in a short time.

The demand for inexpensive, quick, but realistic portraits caused 19th century artists and entrepreneurs to look for ways to solve the problem. Some artists created silhouettes, projecting a shadow of their subject onto a drawing surface and then filling in the outline. Lithography, the technique of drawing an image by hand onto a prepared stone surface, etching the stone with acid to allow the "undrawn" areas to absorb ink, and then printing the image onto paper, became popular around 1813.

> Bitumen of Judea [asphalt] hardened on exposure to light, and so proved ideal for capturing images that would also withstand the etching process for lithographic plates.

French inventor Joseph Nicéphore Niepce searched for a stone that would be perfect for lithography. Artistically untalented, Niepce had his son Isidore draw detailed images onto his test surfaces. Unfortunately, young Isidore was called away to military service, and Joseph Niepce had to find some other way to draw images on his lithographic stones. With the help of his brother Claude, Niepce investigated photographic techniques using silver chloride.

They tested the light sensitivities of iron, manganese, and other compounds, using stone, metal, and paper to support their chemical coatings, or emulsions. Finally, they used guaiacum resin and then asphalt, called bitumen of Judea, which had been known as an etching base since the days of Rembrandt (mid-1600s). Bitumen of Judea hardened on exposure to light, and so proved ideal for capturing images that would also withstand the etching process for metal lithographic plates.

Niepce coated a pewter plate with the asphalt solution, then exposed it through a crude camera to an outside image under bright sunlight. The brightly lit areas of the image hardened the asphalt, while the shadows remained soft and soluble. Removing the soft (or unexposed) asphalt with a solvent of lavender oil, Niepce was left with a metal plate on which all the light areas bore a raised coating of the hardened bitumen, while the rest was bare metal.

After etching the resulting pewter plate with acid, the plate could then be printed by the ordinary lithographic printing presses of the day. Niepce's first success is a blurry photograph of the barnyard taken from a window of his country estate in 1826. He called his technique "heliography" because of the need for bright sunlight.

A French scenic painter, Louis Jacques Mandé Daguerre, learned of Niepce's discovery and approached him about forming a partnership. Daguerre had himself experimented unsuccessfully with silver salts to record his scenes "by the spontaneous action of light." The two became partners in December 1829. Niepce died four years later, and Daguerre continued the research with Niepce's son Isidore, now returned from his military service. Daguerre eventually discarded the asphalt process because of the coarseness of detail and approached the problem in different ways.

In 1835 he found that a polished silver plate exposed to iodine fumes formed a light-sensitive layer of silver iodide. The plate exposed in a camera would produce a clear image if it was then fumed with mercury vapor. The remaining unexposed silver iodide was then removed by rinsing the plate in a strong solution of common salt and water. Daguerre himself claimed that "with this technique, without any knowledge of chemistry or physics, one will be able to make in a few minutes the most detailed views."

The "daguerrotype" process so impressed the French scientist Dominique Arago that Arago persuaded the French government to give Daguerre and his partner Isidore Niepce generous lifetime annual pensions of 6,000 and 4,000 francs, respectively, if only they would grant free use of their discovery.

Daguerrotyping proved to be a complete success. Other backyard inventors soon found various chemicals that im-

https://doi.org/10.1557/S0883769400062989 Published online by Cambridge University Press

proved the speed and resolution of the process, and local daguerrotype artists became commonplace.

The typical daguerrotype was made from a smooth copper plate, silvered and highly polished, which was then immersed in iodine fumes, and then exposed in a camera for several minutes. This proved adequate for landscape photography, but not for portraits—some early portrait subjects were made to sit absolutely motionless under blazing sunlight, their faces coated with white flour, for minutes on end!

A fresh daguerrotype could be developed over a cup of heated mercury, then rinsed in a solution of thiosulfate of soda and darkened with another rinse of gold chloride. The image itself was made of a milky white amalgam of the mercury and the nascent silver in the emulsion (showing the bright areas), with the dark areas showing only the plain silver of the plate. The original silver-coated copper plates were 6 1/2 by 8 1/2 inches.

Since the daguerrotype was formed by reflected light in the camera, the resulting picture was a "mirror image," which caused some problems. Each daguerrotype was also unique and could not be copied. Though it was the first commercially used photographic technique and immensely popular, daguerrotyping proved to have no real future in the development of photography.

Working independently of Daguerre and Niepce, William Henry Fox Talbot, an English archaeologist and philologist trained at Cambridge, had discovered many of the same principles before the first publication of the daguerrotype process. He worked mainly with paper, washing it in successive baths of salt water and silver nitrate solution, which left a deposit of silver chloride on the fibers of the paper. He then exposed the still-wet paper in a camera for several minutes until an image appeared.

Talbot also made an extremely important discovery—that a much shorter exposure (about 1/60th of that needed to make a visible image) would actually leave a "latent" image on the sensitized paper. The latent image could then be "developed" in a solution of gallic acid. Talbot fixed, washed, and dried the paper, which contained a negative image. By waxing or oiling the negative sheet, he could make the paper reasonably transparent, and if he then made a second exposure through the first paper onto another sensitized sheet, he produced a positive, though coarse and grainy, image. The graininess of the image was caused by the poor transparency of the paper and the coarse fibers on which the silver deposits rested.

Talbot's negative-to-positive approach is the basis of modern photography. He named his process the "calotype," from Greek for "beautiful picture." Talbot's friend, astronomer Sir John Herschel, named the discovery "photography."

Talbot's calotypes, while not as sharp as daguerrotypes, could be copied over and over again from the original negative paper. Later improvements to the calotype process included treating the sensitized paper first with one or more layers of albumen (egg white), which held the silver chloride deposits more on the surface of the paper rather than sinking deep into the fibers. Prints obtained from albumen-coated paper were yellowish, but could be darkened to a deep sepia tone by treating the paper with gold chloride. Albumen paper remained in common use until about 1900.

A fresh daguerrotype could be developed over a cup of heated mercury, then rinsed in a solution of thiosulfate of soda and darkened with another rinse of gold chloride.

English sculptor F. Scott Archer introduced the use of wet collodion (nitrocellulose, or dissolved gun cotton in a solution of alcohol or ether) as a coating for glass plates in 1851. The collodion solution contained potassium iodide or ammonium iodide and was allowed to stand until the collodion had set to a jelly-like consistency. In the dark, the coated plates were then immersed in silver nitrate immediately before use, forming a light-sensitive layer within the pores of the collodion emulsion.

The plates had to be coated, used immediately, and developed immediately. When the solvents evaporate entirely, collodion leaves a clear hard plastic-like film that is impervious to water—and therefore impervious to the chemicals needed to develop the image.

Collodion allowed exposure times short enough to make the photographic process useful for recording real life. Photographers using wet-collodion plates traveled the countryside carrying their own chemistry sets and tent-like portable darkrooms. The first news photographs of the American Civil War and the Crimean War were taken by such photographers. By the mid-1850s, the wet-collodion process had replaced both the daguerrotype and calotype. Because of the fine grain and high quality of negatives from wet collodion plates, this technique remained in use until the mid-20th century.

However, the need for preparing each plate before use and then developing immediately after exposure made the wet-collodion process inconvenient for most photography. Other improvements appeared in the 1860s and 1870s, first with a dry collodion process that had much of the excess silver salts washed out of the hardened emulsion before exposure.

In 1871 an English physician and amateur photographer, Robert L. Maddox, suggested using gelatin instead of collodion as an emulsion on glass plates. This proved successful, and within two years Richard Kennett marketed packets of prepared gelatin-based emulsions that photographers could dissolve in warm water and coat their own plates. By 1875 commercially prepared dry plates already coated with sensitive emulsion were available on the market. These ready-made plates could be stored for months and eventually years before a photographer needed to use them.

Between 1873 and 1885 the photographic journals were filled with accounts by amateur experimenters working on ways to improve the gelatin-based emulsions—the most important advance was the heating of the gelatin before coating plates, or "ripening," which further increased the sensitivity to light and therefore lowered the exposure times.

Next month's Historical Note will look at the development of flexible plastic films as supports for photographic emulsions, continuous roll films as used in the motion picture industry, and the discovery of pigmented and layered emulsions to produce color photographs.

KEVIN J. ANDERSON

About the Author: *In addition to contributing to the Historical Note section of the* MRS BULLETIN, *Kevin J. Anderson is also a prolific science fiction writer. He has published over 100 short stories, many of which have been nominated for major awards or selected as among the year's best. Two of his novels were recently published by Signet Books,* Resurrection, Inc. *(July 1988) and* Gamearth *(March 1989). Two more novels are forthcoming from Signet. He has recently been commissioned by Bantam Books to write three additional novels in collaboration with plasma physicist and novelist Doug Beason.* □

https://doi.org/10.1557/S0883769400062989 Published online by Cambridge University Press