Pretty as a Picture

Part 2: Photographic Film Materials and Color Photography

Last month's Historical Note discussed the birth of photographic processes and the various materials used in capturing black-and-white images. All these processes were messy and time-consuming, requiring photographers to carry chemical supplies to coat their own photographic plates before each exposure and then develop them immediately. By the 1880s, inventors were searching for a convenient method to supply pre-made plates that could be stored, used, and developed at the photographer's leisure.

A century ago this year, the American inventor George Eastman introduced rolls of flexible photographic film and portable cameras to use them, which revolutionized photography and made it available to the general public. This Historical Note will discuss the rise of flexible film supports for photographic emulsions and also look at the introduction of color films.

The availability of ready-made dry photographic plates was a vast improvement, but the weight and fragility of the glass plates caused many problems for photographers. Amateur inventors tried to find lighter and more flexible substitutes to support the photographic emulsion.

In 1884 American inventors George Eastman and W. H. Walker introduced rolls of sensitized paper coated with a gelatin emulsion. The rolls of paper were loaded into the roll holder mounted in the position of a camera's plate-holder.

Eastman had begun photography as a hobby while he was working for a bank, but in 1879 he developed a machine that could apply gelatin emulsion to glass plates, making possible the commercial manufacture of dry plates. He patented the machine several years later and formed the Eastman Dry Plate and Film Company. He introduced his rolled-paper film the same year.

At first, Eastman greased the paper to reduce the printing time necessary, but later he used a soluble gelatin coated with a gelatin emulsion on temporary paper; the entire coating could be stripped off the opaque paper and transferred to a glass plate after development.

However, this stripping process was

messy and complicated. Eastman attempted to make a flexible transparent film from cellulose nitrate (or collodion, which had been used to coat glass plates a decade or so before), but this resulted in films that were too thin for practical use. When it was discovered that wood alcohol could be a solvent for cellulose nitrate, much improved plastic films were possible. In 1888, J. Carbutt introduced photographic emulsions on sheets of plastic collodion cut from blocks. The following year Eastman marketed commercial film on rolls of transparent cellulose nitrate.

Although this type of film was patented independently in 1887 by the Rev. Hannibal Goodwin, Eastman used it in his first portable roll-film camera, the "Kodak No. 1." He realized that convenience and simplicity would be the key to making photography available to the mass public, rather than to just the few avid hobbyists willing to put up with the mess and the complications. When he introduced the Kodak camera, Eastman backed it with an aggressive advertising campaign—"You press the button, we do the rest" was their slogan.

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At the factory, the Kodak camera was loaded with a roll of photographic film, enough to make 100 circular exposures, each 2 ¹/₂ inches in diameter. Once a photographer exposed all the film, he returned the entire camera to one of the two Eastman factories (in Rochester, New York, or Harrow, Middlesex), where the film would be developed and printed. The photographer received his prints and his camera back, fully loaded once more. Thomas A. Edison was one of their first and best customers.

In 1891 a new Kodak camera appeared, this time with "celluloid" film (a trade name for cellulose nitrate in solid solution with a plasticizer and a flame-retardant) wound on a wooden core inside a lighttight box. The film was backed with black paper, and black cloth leaders were attached to each end. This allowed photographers to change film quickly and easily and return only the film pack for processing. In 1903, Eastman further improved the film support by coating the back with plain gelatin. This kept the developed negative from curling, making it easier to print, handle, and store.

The formation of photographic film in long celluloid rolls made possible the creation of the motion picture. In 1923 the first 16-mm film was made available, packaged in canisters that could be loaded into motion picture cameras without requiring a darkroom. In 1932 a similar film only 8 mm wide came into use.

However, celluloid film was very flammable (cellulose nitrate is, after all, another chemical form of guncotton), and this created hazards in its use and storage in large quantities. In 1909 Eastman first introduced "safety" film made of cellulose acetate instead of the cellulose nitrate for the plastic base. This slow-burning film replaced celluloid for motion pictures. In 1937 the Eastman Kodak company further improved the safety film by switching to cellulose acetate propionate; in 1948 they changed the plastic formula again to approach cellulose triacetate. In 1950 all Kodak film, for all uses, was made on the slow-burning plastic base, and other manufacturers followed suit.

In some special cases different polymers were used for plastic backing, especially when dimensional stability was particularly important, such as in mapping and graphic arts. Some of these other plastics were polyvinylchloride and its copolymers, polystyrene, polycarbonate, and some polyesters.

Color Film

Since the beginnings of photography, inventors searched for a way to take pictures that would capture the color, and not just the light and dark tones, of a subject. In 1810 German physicist Thomas Johann Seebeck found that wet silver chloride retained some faint colors of a spectrum to which it was exposed. However, the colors faded when the silver chloride dried. Others attempted unsuccessfully to make this technique practical.

In 1861 British physicist James Clerk Maxwell attempted color reproduction in a completely different way. He applied his new theories on color vision that all colors could be obtained by mixing red, green, or blue light in proper proportions. In a famous experiment, Maxwell made three wet-collodion photographs of a group of colored ribbons, each through a red, green, or blue filter. He made transparent black-and-white positives, which he then projected through the appropriate red, green, or blue filter. All three images were then superimposed on the screen, resulting in a reasonable reproduction of the ribbons' original colors. (This process turned out to be impractical at the time, though, as wet-collodion photography had very little sensitivity in the red and green portions of the spectrum.)

Charles Cros and Louis Ducos du Hauron made the first color photographs in 1869, using a film composed of three layers of colored gelatin (yellow, blue, and red). Each layer of gelatin served as a monochromatic transparency that combined to form a full-spectrum: image. Du Hauron also proposed that such photographs could be printed using a pigment process. After some improvements, their technique became the basis for color printing processes from the 1890s onward.

Some early attempts at color film used tiny blue, green, and red filter elements dispersed through the emulsion rather than three separate layers that had to be developed separately. The first successful use of this "screen process" was demonstrated by J. Joly and J. W. MacDonough in 1892, who placed their filter elements on a separate plate from the negative. Later, the "Lumiere Autochrome" photographic plate used a filter layer of dyed starch grains interspersed with carbon black.

In 1897 Ducos du Hauron patented the idea of making a color film with three superimposed emulsion layers (red, green, and blue), but it was not until 1912 that a viable method for this technique was discovered by the German chemist Rudolf Fischer. Fischer showed that "dyecoupling" developers could be used to make colored images from silver emulsions, and proposed that they be used in a multilayer film.

If each emulsion layer is complementary and inseparable from the others, different dyes of the appropriate colors could be coupled to each layer during developing. B. Homolka had discovered that when certain developers react with silver halide to form silver in the presence of a "coupling" compound, a dye image is also formed in proportion to the original silver image. The silver is then bleached out, leaving only the dye image.

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By proper selection of the coupling compound and the developer, Fischer showed that a great many colors could be obtained. The final dyes are of the indoaniline or azomethine types. For the three complementary colors used in this process (cyan, magenta, and yellow), phenols are usually used to couple with cyan dyes, nitriles or pyrazolones for magenta dyes, and esters, ketones, or amides for yellow dyes.

Fischer proposed a film using three superimposed layers, each containing the appropriate couplers that would affix the proper dyes during developing. He could not make his idea work, however, because the couplers and sensitizing dyes kept wandering from their own layers. Not until 1931 did nonwandering sensitizing dyes become available. Four years after the nonwandering dyes appeared, a film based on Fischer's dyecoupling principle became commercially available as "Kodachrome," developed by Leopold Mannes and Leopold Godowsky. The controlled-diffusion developing process was complicated, but resulted in good color quality. Kodachrome film was first released as 16-mm motion picture film, but then became available in 35-mm format for slides and later for 8-mm motion picture film and sheet film.

At about the same time the Agfa Company in Germany released Agfacolor Neu film, which was similar to Kodachrome but processed differently. Whereas the three layers in Kodachrome film contained silver emulsions and sensitizing dyes, Agfacolor had "color formers" in each layer as well. Agfacolor film was developed by a system of controlled-penetration developers that created the appropriate color in each layer in a processing single step. While Kodachrome processing was complicated and had to be done in a large facility with automatic machinery, amateur photographers could develop their own Agfacolor film.

Other systems appeared later, including the Kodacolor, Ektacolor, and Ektachrome processes, which also used nondiffusing dye-couplers. These couplers were not dispersed directly in the emulsions, but dissolved in an oily liquid sprayed on the emulsion in fine droplets. Kodacolor Aero Reversal film was the first film of this type, introduced in 1940 for aerial photography by the U.S. Army, and could be developed directly in the field.

Since then, many different photographic materials have been created to address specific needs in engineering, science, cartography, and graphic arts. New films are being developed to be sensitive in very narrow ranges of the spectrum, and to operate well beyond the visible range, as well as those requiring shorter exposure times and providing less graininess for extremely high-resolution images. Rarely has a single invention opened up so many different windows for progress.

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Coming in the July MRS BULLETIN... Focus on Fusion Materials Theodore Reuther, Guest Editor