Natural Color Photography in Colloidal Silver[1]

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NATURAL COLOR PHOTOGRAPHS can now be made on ordinary photographic plates or films designed for the production of negatives or positives in black and white. The colors are provided by finely divided silver or colloidal silver produced by development.[2] The process involved is the result of the discovery that any black-and-white photographic image in gelatin can be converted by simple chemical procedures, including development, into a variety of colors of colloidal silver, depending on the various densities present in the material treated.

Seebeck's discovery (1810), that the solar spectrum allowed to fall on a freshly prepared moist layer of silver chloride registered on the latter in colors closely corresponding to the colors of the spectrum itself, contained the promise of future direct color photography in reduced silver. After the discovery of the daguerrotype, much effort was expended in the attempt to realize a practical solution of the problem of color photography by this method. According to the testimony of contemporaries, some of the results were very beautiful; and Eder, in his *History of Photography,* mentions that he has in his possession such a photograph made by Niepce de St. Victor which had preserved its beauty for more than sixty years. Photographs made by this method, however, required a long exposure, could not be fixed, and had to be guarded with great care against exposure to strong light.

The production of color by development has for the most part been confined to the development of various colors on slow, fine-grained plates, such as the Ilford Alpha Lantern plates, and various slow plates of other sorts. These plates, when given a normal exposure, developed a pleasing brown image; but, with longer exposures and restrained development, they produced various colors, culminating, with very long exposures, in red. One color, and one color only, was developed by any given exposure, whatever the range of densities of the negative from which the prints were made.

The only reference to the production of more than one color by development that I have been able to find in the literature is contained in a communication by A. Hoffmann, of Mehlen, published in *Photographische Industrie* and reproduced as a translation in the monthly supplement on color photography of the *British Journal of Photography* for August 1, 1924.[3]

This important communication failed to create any

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[1] The experiments recorded in this paper were carried out in the photographic laboratories of the Department of Anatomy of The University of Chicago. The writer wishes to express to the members of this department his appreciation of courtesies so graciously extended over many years.

[2] This is the substance of the results disclosed in U. S. Patent No. 2,473,131, granted to this writer on June 14, 1949.

[3] Hoffmann wrote:

When, by accident, the development of a number of landscape negatives had been carried far beyond the usual point, I made the observation that two of the plates showed strong natural colors in their central portions. When I came to trace the cause of this phenomenon, I made sure first of all as to the type of plate upon which this curious result had been obtained. It proved that the plates had come from a rather old packet of Guilleminot slow (silver chloride) lantern plates. In their development, a partially exhausted pyro developer, rich in bromide, was used. The plates were made with an unripened fine grain emulsion and had been washed in distilled water and packed in boxes for subsequent use. On account of the fact that the film side is not easily identified by the red light of the dark room lamp, my assistant had examined the plates for a few moments by the light of the lamp, so as to place them the correct way around in the dark slides. Consequently, the plates had had a certain small preliminary exposure.

Further experiments gave no results, and further experiments are therefore necessary. In these experiments the camera had been set up on one bank of a fairly large pond, and it was the reflection of the landscape in the surface of the water that had been rendered in its natural color. Since the light coming from the surface of the water was probably polarized, this explains why the color rendering faded from the axis out.

enthusiasm in photographic circles, and one may assume that the experiment was tried by many others without success.

It is to be noted, however, that in these experiments of Hoffmann we find the same factor that appears again and again in the history of photochromy: namely, the favorable influence on color production of a previous exposure to diffuse light. Is it any wonder that Chapman Jones, summing up the results and prospects of this type of color photography, said in his book, *Photography of Today,* published in 1913: "There seems to be but the feeblest shadow of a foundation for the hope that such a method of color photography will ever be realized. . . . The success may be compared to the will-o'-the-wisp that lures the traveler onwards without helping him home." That this pessimistic forecast was not justified will be made apparent in the following pages.

PRELIMINARY EXPERIMENTS

Some years ago, I was engaged in investigation of the histology of the mammalian kidney and at the same time in experiments on high-resolution photomicrography, using for the latter purpose the Ilford Alpha Lantern plates sensitized to the longer light waves by being bathed in erythrosin and pinacyanol.

In the kidney investigation, I used an acid solution of silver citrate, with which I perfused the kidney from the aorta. After perfusion, the kidney was fixed in formalin, sections were cut, and the silver developed after exposure to light by a metol-quinol developer. In these preparations I found the lining cells of the blood vessels delineated in black silver as expected; but, in addition, there was a puzzling deposit of black granules along the surface of the tubules, doubtless caused by the precipitation of silver chloride at this point. Two possibilities were thus presented: that this was the real locus of the chlorides, or that the chlorides had moved to a new location because of differences in mobility between chloride and silver ions. The latter possibility could be tested experimentally.

Accordingly, I prepared a number of gelatin-coated plates by fixing lantern plates in sodium thiosulphate and washing them thoroughly. Some of the plates I immersed first in a solution of ammonium chloride and, after a brief rinsing, in a solution of silver nitrate. The chloride of silver was precipitated for the most part in the solution outside of the gelatin. When the experiment was reversed, however, and the plates were immersed first in the solution of silver nitrate and then in a solution of ammonium chloride, the silver chloride was deposited almost exclusively in the gelatin and the solution was almost free of deposited silver chloride. By this means I prepared photographic plates of incredibly fine grain for high-resolution photography.

At the time these experiments were proceeding, the methods used for the screen plates of making positives by reversal were also being widely used in cinematography. The processors insisted that positives made by reversal were of much finer grain than the negative from which they were made. It occurred to me that the results would be still further improved if a new, practically grainless silver chloride were substituted for the residual halide of the usual reversal process. Accordingly, I prepared a rather thin negative of an outdoor scene, fixed it in thiosulphate solution, and thoroughly washed it. This plate was then impregnated with chloride of silver by the method indicated and the negative image removed by the usual bichromate sulphuric acid bleach. The new silver chloride was then developed in the usual way with a solution containing amidol and sodium sulphite. The result was most astonishing. Instead of the fine-grained positive that was expected, the plate flashed up in a number of colors, forming a combination negative-positive; for the negative that had been bleached redeveloped rapidly, adding a new group of colors to those resulting from development of the new halide.

This experiment was repeated many times with the same result. In addition, it was found that it made little difference whether the bleaching was done before or after rehaliding, or if it were omitted altogether. Indeed, every part of the process except the bathing in silver nitrate solution and development could be omitted, with little difference in the result.

In cases where the negative was bleached before rehaliding, an interesting phenomenon occurred. The silver chloride was taken up by the gelatin in inverse proportion to the densities of the silver removed. In other words, the gelatin adjacent to the silver particles was hardened or tanned during development proportionally to the amount of reduction product, and was less able to take up silver chloride than the other parts of the plate.

In these experiments the development was so rapid that it was difficult to observe the progress. Since silver chloride is freely soluble in solutions of sodium sulphite, the new silver halide was quickly removed. The development thus resolved itself into two stages. At first, chemical development proceeded for a brief period, followed by a period of physical development. In cases where the negative image had not been bleached, certain very interesting phenomena occurred. For example, a portion of the negative image, gray in color, would assume for a short time a fine blue color and then fade to a gray lighter than in the beginning. This indicated that there was not only a fill-in of the portions of the negative not occupied by the negative image, but also a modification of the negative image itself. This change is undoubtedly of the nature of a Sabattier reversal, though the conditions are somewhat different from those usually present.[4] In this case the residual halide was removed by fixing in thiosulphate, and the plate was thoroughly washed and rehalided. This phenomenon doubtless requires further investigation, but in the meantime is of much importance, regardless of the explanation, in the production of the colors requiring a blue component.

These results, however fantastic they may appear at first sight, may be quickly verified by anyone having at his disposal a freshly developed gelatin plate which has been fixed in thiosulphate and thoroughly washed, and solutions of silver nitrate, ammonium chloride, and amidol sulphite developer.

It is obvious from the foregoing that any black-and-white photographic image, positive or negative, in a gelatin medium can be quickly transformed into a picture in many colors. The goal of photography in natural colors, however, has not been reached, although often negatives so reversed show an astonishing resemblance to the natural colors. An inspection of the results reveals that the colors obtained are strictly dependent on the densities of the negative treated. For example, zero density develops red, and the intermediate densities a series of colors trailing through the spectrum to blue and finally black. The problem is to produce such a distribution of densities that the colors will be correct and in the right places.

Obviously, this cannot be accomplished by a negative process. The problem of black intrudes as always, and black can only be achieved by a positive process. This constitutes the first limitation that must be met. Furthermore, since red must be black in the negative in order to print minus in the positive, a negative taken on a panchromatic plate is indicated. In order not to have the blue values too pronounced, this negative must be taken through a red filter.

The second limitation of the process at this point was the fact that the chemical development proceeded rapidly to completion, and desirable phases of color were very quickly passed. This difficulty was met by shifting to slow physical development.

The third obstacle to full natural color development was due to the fact that the screening provided by the silver already present and the differential rehaliding were not sufficient to produce the required colors. This difficulty was solved by exposing the rehalided plate through a negative made on an orthochromatic plate through a yellow filter, or on a panchromatic plate through a blue-green filter.

Much research is still necessary fully to solve the problem, but sufficient success has been obtained to justify the hope that the solution will eventually be attained.

NATURAL COLOR PHOTOGRAPHS

For photographs in natural colors two negatives are necessary—one representing the values of the red end of the spectrum and the other those of the blue end. These negatives may be prepared in the case of stationary subjects by successive exposures through appropriate filters. Where movement is present, however, either a beam-splitter camera may be employed, or the negatives may be taken on a two-film pack such as Defender Dupac, designed for the two-color process.

The choice of filters is not an easy one, since not only must the color temperature of the light be considered but also the special properties of the emulsion employed. Much research is still necessary in this field to obtain the best results. Excellent results have been obtained under studio conditions with photoflood illumination, using an orthochromatic plate and a K1 filter for the blue-green negative, and a panchromatic plate and a Wratten 28 filter for the orange-red negative. Good results have also been obtained by using panchromatic plates for both negatives, with Wratten filters Nos. 28 and 40A, respectively.

In the descriptions which follow, the negatives are referred to as the blue-green negative and the orange-red negative, respectively. A lightly printed positive is made from the orange-red negative on positive stock, or preferably on a stock of longer scale and slightly larger grains, such as Eastman 33 or commercial film. This black-and-white positive is fixed in a nonhardening bath, such as

Sodium thiosulphate	300 g
Potassium metabisulphite	25 g
Distilled water	1,000 ml

for at least double the time necessary for the plate to look cleared. It is then washed in four changes of distilled water, 5 minutes for each change, and then for 1–2 hours in running water.

It is then resensitized. This resensitizing operation may be carried out as follows: First, the plate is immersed in a 1.7 percent solution of silver nitrate. I find it advantageous to confer a slight acidity on the solution by the addition of 0.36 g of citric acid per liter. The immersion in this solution lasts preferably for about 2 minutes, after which the film or plate is

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[4] The Sabattier reversal is produced by exposing the residual halide image of an unfixed negative to light and redeveloping. The result is a positive image.

rinsed for about 20 seconds and then immersed in a 10 percent solution of ammonium chloride for about 4 minutes. The plate is then thoroughly washed and dried.

The resulting plate is a black-and-white positive with a very fine-grained deposit of silver halide around, behind, and possibly even within the particles of silver in the plate. The plate may be handled readily in bright-yellow light. It is then matched in perfect register with the blue-green negative. While so held, the plate is exposed through this blue-green negative. This exposure is close to a crash exposure. (It is my practice to test the transmission of the blue-green negative with a photoelectric exposure meter, using a photoflood light and moving the negative back until the transmission registers 10 foot-candles. The blue-green negative is then matched in register with the orange-red positive plate and given an exposure, at the predetermined distance, of 30–35 seconds.)

During this exposure, the sensitive silver halide is screened not only by the blue-green negative, but also by the reduced silver in the positive already present. Thus, those portions of the image that were clear in the negative will be black in the positive, and the amount of new silver halide will be relatively small. On the other hand, the dark portions of the negative will be light in the positive, and so take up a large amount of silver chloride.

The result, it will be noted, accentuates greatly the differentiation between the red and blue values of the picture. That is, the red portions are light, they have a maximum of new silver chloride, and they also are exposed through the lightest portions of the blue-green negative. On the other hand, blue portions are dark in the positive, they have a minimum of resensitized material, and they are exposed through the darkest portions of the blue-green negative.

The plate is then developed in a suitable developer, such as

Glycine (*p*-hydroxyphenylglycine)	1 g
Sodium sulphite	10 g
Distilled water	100 ml.

At time of using, add 2 ml of 1.7 percent silver nitrate. This is a slow physical developer that takes some time to develop, but in due course the image on the plate will gradually change to an image in full natural colors. This development may also be accomplished by highly restrained chemical developers. The glycine developer quickly removes all silver chloride from the plate. When this is done, the room lights should be turned on so that the development may be judged by vision. At this stage the glycine developer can be replaced by a stronger physical developer, such as Odell's formula, and development time thus reduced to a few minutes.[5] The finished color picture must be fixed 5 minutes in thiosulphate solution, washed thoroughly, and dried.

During development, those portions of the final picture that are to be red pass through a series of transformations ranging from canary yellow through orange, gradually merging into red. The yellow portions begin to show a hint of yellow color about the time the red portions are orange and then become fully yellow at about the time that the reds reach their proper color, although the yellow lags slightly behind the red. The greens do not begin to show color until the reds are verging on red, at which time the greens begin to show traces of yellow and then become green. The blues are, of course, dark in the positive from the orange-red negative, and they change to blue late in the development.

If this process is carried out faithfully and with proper exercise of judgment gained from experience, the results are truly amazing. A print is obtained in full color and of high transparency.

It should be emphasized at this point that this is not just another two-color process in the ordinary sense. The purpose of the filters is to so balance the densities of the two negatives that, by interaction of the silver deposit in the first print from the one negative with the new silver resulting from exposure through the other, the appropriate colors may be produced. For example, in one experiment a colored print of a young girl wearing a blue dress was photographed through red and green tricolor filters, and the delicate blue of the dress was reproduced perfectly notwithstanding the fact that neither filter transmitted any blue light.

Moreover, any negative or positive can be transformed into a many-colored product simply by rehaliding, exposing to light, and redeveloping as described. For example, an x-ray photograph can be transformed into a colored product with a variety of colors representing the various densities. Two photomicrographs taken with different wavelengths of monochromatic light can be combined in a colored picture representing in different colors the specific areas of transmission.

To produce photographs in natural colors, it is necessary not so much to register the color values as to produce a pair of negatives with the densities so balanced as to be capable of producing a print in natural colors; to produce from one of these nega-

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[5] To make up Odell's formula, proceed as follows: Dissolve 50 g of anhydrous sodium sulphite in 250 ml of distilled water; dissolve 8 g of silver nitrate in 200 ml of distilled water; add the silver nitrate to the sodium sulphite slowly, with continuous stirring, the white precipitate formed being redissolved in the excess of sodium sulphite. When the solution is clear, add 80 g of anhydrous sodium thiosulphate. The above is a stock solution. The working developer is made by diluting 15 ml of this stock solution with 85 ml of distilled water and adding .25 g of amidol.

tives a print of proper density; to rehalide this print as described; to expose it behind the second negative; and to develop it to the proper grade of color. Study of the properties of the negative materials and of the color temperature of the illuminant is required, as is a selection of suitable filters.

There are certain aspects of the process that a beginner should keep in mind:

1. It is good practice to wash all plates or films to be processed in distilled water, in order to prevent double salts of sodium and silver thiosulphate from being carried over to react with lime salts in tap water.

2. The final development should be closely watched until the desired colors are obtained and then promptly stopped by immersion in strong hypo solution. The plate should then be thoroughly washed and dried. If the development is carried too far, the colors may change materially on drying and the reds may even become blue. Such a result is probably due to underexposure and overdevelopment. If, however, the whites display a light-yellow fog, overexposure is indicated.

3. White fog throughout the gelatin may be due to insufficient washing in distilled water.

To the amateur or professional worker this process presents obvious advantages:

a) The negative materials are available at all places where photographic supplies are sold. They are the ordinary supplies of commerce.

b) The detail is much clearer, since the outlines of objects are not diffused, as in the dye-toning and dye-coupling processes, by extension of the reaction.

c) Any number of color positives desired can be prepared from a single pair of negatives.

d) The pictures are permanent.

e) All silver may be removed from colored pictures made by this process by treatment with ferricyanide and thiosulphate until only clear gelatin is left. The picture may then be redeveloped physically in full color.

A question of deep interest is: How are these colors produced? It is easy to understand the source of yellow, orange, and red. But how can we account for the production of blues, greens, browns, and other colors that require a blue component, and also for all the variants of red, which appear in the finished product? In my patent application I left this question undecided, but I have done much experimentation since, and I have come to the conclusion that the finished picture is reached not merely by the addition of highly dispersed silver to the positive print already present but also by progressive change in this positive itself.

There are many grounds for this conclusion. Herschel reported that in repeating the Seebeck experiment he found that the red portion of the spectrum reduced a deposit of silver already present owing to exposure to diffuse daylight. This Herschel effect forecast the well-known Sabattier effect. In my own experience in reversing a negative by the process of rehaliding, exposing, and chemical development, I have frequently seen a patch of gray in the negative pass through a brilliant blue phase in development. Also, a positive or negative completely removed by ferricyanide and weak thiosulphate may be redeveloped physically, in which case the image passes through yellow, orange, red, and blue to black. Obviously, a reduction to the proper degree would reproduce blue. This interpretation would also explain why, in my process, green develops without passing through a blue phase. In this instance, the reduction of the old silver and the development of the new yellow silver proceed hand in hand.

Obviously, if the foregoing is true, the character of the silver deposit in the primary positive is of much importance, since a spongy type of black grain would be much more likely to display the Sabattier effect than the more solid gray type of grain. This is a field in which much more investigation is indicated. The qualities of the gelatin matrix and the degree to which it is tanned by the first exposure and development are also important.

The nature of the silver colors produced is still obscure, although there are many adherents to the theory of Chapman Jones that the color transmitted is determined by the size of the silver particles. With the wide range of colors which it is now possible to produce by the method here disclosed, an interesting field of research is opened up.

Another interesting question also presents itself. Can a film be prepared which would combine in a single medium the properties required to produce a black-and-white positive after exposure behind the orange-red negative and, following adequate washing and drying, give a colored result after a second exposure of the blue-green negative? I have given much attention to this, and my answer is unequivocally yes. I have produced excellent colored prints on certain chlorobromide plates and on gaslight papers with good coincident rendering of gray scale and color patches. The medium was first exposed behind the orange-red negative. After development, the process was quick-stopped with dilute acetic acid and the print thoroughly washed and dried. It was then given an exposure of suitable length, after accurate matching behind the blue-green negative, and developed.