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AN EXPERIMENTAL STUDY OF THE LIPPMANN COLOR PHOTOGRAPH

A DISSERTATION

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Photography in colors by means of standing light-waves was first accomplished by E. Becquerel about 1850, although he was unaware of the part they played in his results. Zenker[1] developed the theory that the polished silver surface, on which Becquerel's sensitive film was formed, reflecting the incident light, caused standing waves. In the loops of these waves the silver salt was reduced, forming parallel reflecting surfaces distant from each other one-half the wave-length of the incident light. Viewed by reflection, the developed film exhibited color as do thin films of oil on water, or, more exactly, the multiple interior surfaces of potassium chlorate crystals.[2]

Lippmann[3] in 1891 was the first to make practical application of this theory by developing the process of color-photography bearing his name. For the polished silver surface of Becquerel he substituted mercury, which could be flowed behind a transparent fine-grain sensitive film on glass during the exposure, and removed to permit development and the subsequent viewing.

The theory and practice of the process will be found discussed by Lippmann,[4] Wiener,[5] Neuhaus,[6] Valenta,[7] Lehmann,[8] and others.[9] Full use has been made in the following study of the results of their work, and details of theory and experimental methods not new with the writer will not be described at any length.

Good results have been obtained by the process as worked by these

[1] *Lehrbuch der Photochromie*, 1868.

[2] *Rayleigh, Phil. Mag.* (5), **26**, 256, 1888.

[3] *Comptes rendus*, **112**, 274, 1891.

[4] *Journal de Physique*, **3**, 97, 1894.

[5] *Annalen der Physik*, **69**, 488, 1899.

[6] *Die Farbenphotographie nach Lippmann's Verfahren*, 1898.

[7] *Die Photographie in natürlichen Farben*, 1894.

[8] *Beiträge zur Theorie und Praxis der directen Farbenphotographie*, 1, 1906.

[9] A historical account of the development of the process will be found in *Die Grundlagen der Farbenphotographie*, by B. Donath, 1906.

and other experimenters, but its difficulties have been found so great as to prevent its wide use. Some discrepancies with the theory have been found, and compromises with the best conditions as indicated by theory have been found necessary in practice.

The object of the present investigation has been to see how closely the conditions called for by theory could be approached, to find the cause of some of the difficulties met with in practice, and, if possible, to obviate these.

The separate problems will be stated as they are taken up, but may be briefly outlined here.

According to the theory as stated by Lippmann the most accurate reproduction of color should come from the use of a thick sensitive film, the film gaining in resolving power with the number of reflecting laminae. In practice very thin films have been used; reproductions of the spectrum show, on examination with the spectroscope, that the colors are very far from pure. The first investigation which follows was to determine whether films could not be prepared which would reproduce colors with a fidelity much greater than has hitherto been possible and whose thickness could be increased with corresponding increase in resolving power. The investigation has resulted in a method for producing films having these characteristics.

The production of pictures of natural objects has been a matter of uncertainty and difficulty; the production of whites has been a stumbling-block to many. The manipulation of the plates with the necessity for a mercury-holding plate-holder has been inconvenient. The causes of this uncertainty in results have been studied; the conditions governing the production of white fixed; and a substitute found for the hitherto indispensable mercury mirror.

In addition, an application of the process to three-color photography has been developed.

MANIPULATION OF PLATES IN GENERAL

The transparent fine-grain silver bromide plates were made, with only such changes as are noted, according to the published formulae of Lippmann, Neuhaus, and Valenta. Ordinary "chemically pure" silver nitrate and potassium bromide were used; the gelatine was either Eimer & Amend's "Gold Label," Nelson's "No. I," or a department store gelatine recommended as the best for puddings, etc., which was found very hard and free from grease. The emulsion was flowed on pieces of crystal plate glass cut three by three inches. A plate-holder not greatly different from that used by previous workers permitted the introduction of mercury behind the plate and in contact with the gelatine.

The scheme of exposure followed throughout was to expose a comparatively large surface (two by two inches) to the kind of light being investigated. This allowed of easy spectroscopic examination besides leaving room for stripping portions to be sectioned.

Development was mostly with pyrogallic acid and ammonia according to the formula of Valenta, with the one change that the pyrogallic acid was used in powder form, added by means of a spoon of proper capacity to the rest of the developer just before use with each plate. The resulting developer was always fresh and of uniform strength. The hydroquinone used in part of the work was made up according to Jewell's formula[1] with the omission of the potassium ferrocyanide.

After development and drying, the pictures were made ready for viewing by cementing a thin prism of small angle on the film to destroy the disturbing surface reflections, and the back of the glass was flowed with asphaltum varnish. The prism is usually cemented on by means of Canada balsam. As, however, the refractive index of the gelatine containing reduced silver is somewhat higher than that of the balsam, some medium of higher index is to be preferred. Gum styrax ($\mu = 1.58$) was found suitable, but the lower surface of the prism must be ground to avoid the reflection at glass-balsam surface. The latter procedure was uniformly adopted. The amount of light reflected from the laminae is at best small, so to obtain the purest colors all addition of white light is to be avoided. This white light may come from the prism-balsam, balsam-gelatine, gelatine-glass, or rear glass surfaces, and if all these reflections are not diminished as much as possible the dilution of colors is quite appreciable. The prism-balsam reflection is overcome by grinding the back of the prism with emery; the balsam-gelatine by correct choice of balsam; the gelatine-glass is unavoidable; the reflection from the back of the glass

[1] *Astrophysical Journal*, 11, 242, 1900.

can be destroyed completely by first grinding with emery and then flowing on asphaltum varnish, preferably mixed with machine oil to prevent its becoming brittle and flaking off. If the pictures are to be observed from the glass side, a second prism is cemented on in place of the black varnish.

When so mounted the pictures are ready for observation. It is of extreme importance that they be observed by parallel light and shielded from all side light. The best conditions are given by a small opening in a wall facing a brilliant white sky. If the observer stands with his back to the opening and holds the picture at arm's length reflecting the sky it appears at its best.

These precautions are most necessary in the case of pictures of natural objects, for reasons which will appear later. Spectra and similar subjects, where the reflecting laminae are numerous and deep in the film, are visible much more easily, but are of course best seen under the conditions given above.

WORK WITH MONOCHROMATIC LIGHT SOURCES

The first investigation was on the influence of two factors, fineness of grain, and film thickness, upon the correctness of color rendering. It is naturally to be expected that both factors will influence this. The smaller the silver particles the more minute the variations in the standing wave-system they will record. The thicker the film the more laminae and hence the greater purity of the reflected light.

There are comparatively few recorded experiments on variations in the size of the grain; the first published emulsion formulae have been closely followed by all experimenters. Cajal[1] recently observed that the size of the grain is influenced largely by the amount of agitation of the emulsion during preparation, and finds that the finer the grain the better the quality of the colors. He, however, was not working with pure spectrum colors. The present investigation of this point was prompted by the observation that when photographing monochromatic light sources for a special application of the process, the use of much less silver bromide gave more satisfactory results. This made it appear of interest to determine from this standpoint the best proportion of silver salt.

[1] *Zeitschrift für wissenschaftliche Photographie*, 5, 213–245, July 1907.

With regard to the best thickness of film, theory would call for the greatest thickness practicable to work. Yet the practice has been to work with extremely thin ones such as can be obtained by flowing the liquid gelatine on and off a warm glass plate. The section photographed by Neuhaus showed but seven or eight laminae. Wiener, by counting the laminae cutting the gelatine-glass surface in a spectrum photograph, found the number less than twenty, obviously too few to have much resolving power, and explaining the impure reflected light. There has indeed been reason to suppose that appreciably greater thickness would not help matters. The loss of light by absorption and reflection at each lamina is large, so that the effect of each lamina becomes rapidly less with increasing distance from the surface of the film, assuming them all equally well formed. Film sections indicate that the latter is not the case; the laminae are of rapidly decreasing strength. Lehmann has calculated, taking into account the effect of absorption, that the laminae should be more distinct, the greater the distance from the mirror. That they are not he ascribes to the reflected light losing the power of interfering after a short distance. These points were considered worth investigating more closely.

The size of the silver grain was varied entirely by the quantity of silver bromide in the emulsion. A set of emulsions was made up in which the content of silver nitrate varied between 0.03 and 0.18 gram per gram of gelatine, the quantity of potassium bromide constantly five-sixths of this. The resulting emulsion had from one-sixth to the same amount of silver bromide as used by Valenta and others. The emulsion was flowed on the level plates in measured quantities from a graduate, so that the thickness was under control. After flowing, the emulsion was pushed to the corners of the plate by means of a glass rod. The quantity used varied from one to ten cubic centimeters on a 3×3 inch plate. This gave films from about 0.007 to 0.07 mm, as sections afterward showed by the number of contained laminae.

Monochromatic green light was used for the greater part of the work. This was obtained from a Cooper Hewitt mercury vacuum lamp, an aperture of 1 sq cm illuminating the plate 25 cm distant. A cell of neodymium ammonium nitrate and potassium bichromate absorbed the yellow and blue radiations The plates were made sensitive to this color by erythrosine.

INFLUENCE OF SIZE OF GRAIN

A noticeable increase of purity in reflected light was found as the quantity of silver bromide was reduced. This increase is quite marked between 0.18 and 0.09 grams of silver nitrate per gram of gelatine, after that less so.

Besides the influence on the purity of the reproduced color the quantity of silver bromide affects the sensitiveness of the plates. A rather unlooked for result was that a smaller quantity of silver salt made the plates more sensitive, up to a certain point. This is readily explained; the light must pass through the film, and decreasing the silver content increases the transparency. If the amount of silver becomes too small the plates again become less sensitive. The fastest emulsion was found to be one containing half the silver salt used by previous workers. As this gave practically all the increase of purity resulting from decreased grain it was adopted as the standard emulsion for future work.

The formula and method of preparation were as follows:

A. Gelatine 1 gram	B. Gelatine 2 grams	C. $AgNO$ 0.3 gram
Water 25 cc	KBr 0.25 gram	Water 5 cc
	Water 50 cc	

A and B are heated till the gelatine melts, allowed to cool to 40 degrees, C added to A and then A to B slowly with stirring, the sensitizer added, and the whole filtered. After flowing and setting, the plates are washed for fifteen minutes and allowed to dry.

INFLUENCE OF THICKNESS OF FILM

The first work done on the influence of film thickness indicated that, viewed from the film side, there was no increase of purity with increase of thickness beyond one of about thirty half-wave-lengths, or about that given by flowing the emulsion on and off the cold glass plates. The single green line of mercury was rendered as an ill-defined green band in the spectrum, properly a continuous spectrum with strong maximum in the green. Fig. A, II, gives the mercury green line as rendered by the emulsion found best as above. The green light is considerably more monochromatic than that usually seen