

# AN EXPERIMENTAL STUDY OF THE LIPPMANN COLOR PHOTOGRAPH

BY HERBERT E. IVES

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<sup>1</sup> 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.<sup>2</sup>

Lippmann<sup>3</sup> 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,<sup>4</sup> Wiener,<sup>5</sup> Neuhaus,<sup>6</sup> Valenta,<sup>7</sup> Lehmann,<sup>8</sup> and others.<sup>9</sup> 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

<sup>1</sup> *Lehrbuch der Photochromie*, 1868.

<sup>2</sup> *Rayleigh, Phil. Mag.* (5), 26, 256, 1888.

<sup>3</sup> *Comptes rendus*, 112, 274, 1891.

<sup>4</sup> *Journal de Physique*, 3, 97, 1894.

<sup>5</sup> *Annalen der Physik*, 69, 488, 1899.

<sup>6</sup> *Die Farbenphotographie nach Lippmann's Verfahren*, 1898.

<sup>7</sup> *Die Photographie in natürlichen Farben*, 1894.

<sup>8</sup> *Beiträge zur Theorie und Praxis der directen Farbenphotographie*, 1, 1906.

<sup>9</sup> 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. 1," or a de-

partment 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<sup>1</sup> 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

<sup>1</sup> *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<sup>1</sup> 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.

<sup>1</sup> *Zeitschrift für wissenschaftliche Photographie*, 5, 213-245, July 1907.

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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

in Lippmann spectra. From the glass side the band was of a different character, showing more clearly defined edges, as given in Fig. A, III. This is explained by the stronger laminae being farther from the eye and by absorption being no more effective than the weaker ones. The reflecting surfaces are then comparable to the lines of a grating, each sending equal contributions to the total reflected light. Owing to the strongest laminae suffering so much absorption, the light from the glass side is much weaker than from the film side.

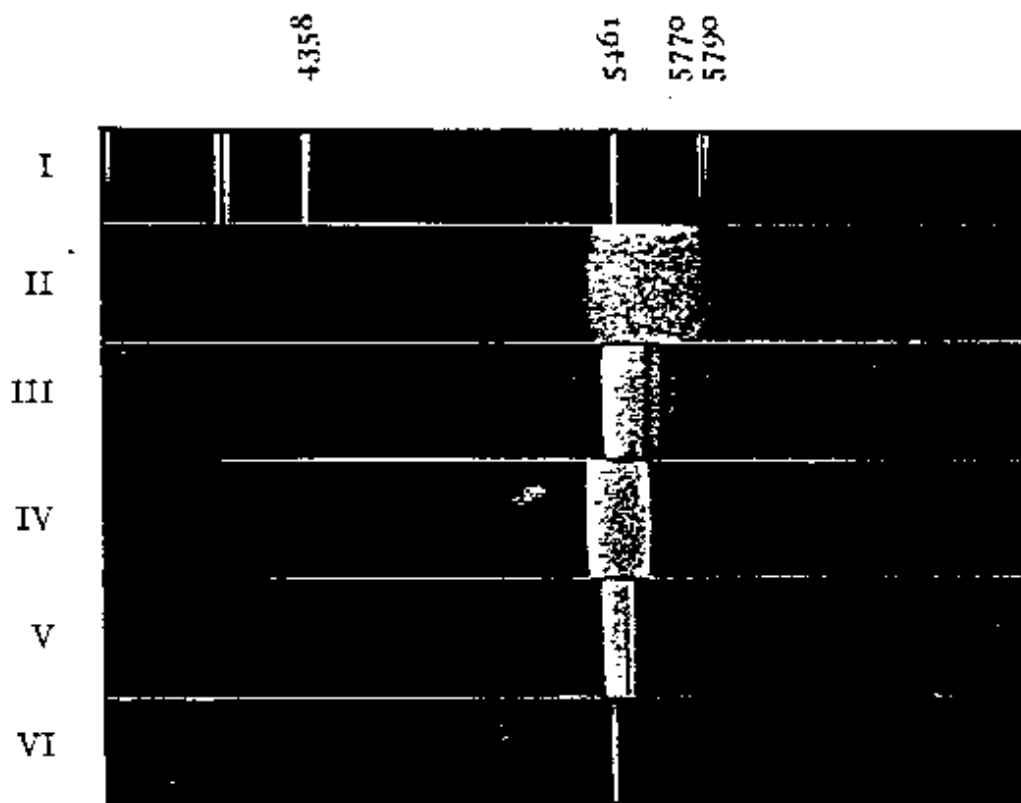


FIG. A

- I. Mercury vacuum arc.
- II.  $\lambda$  5461 as reproduced by fine-grain film, with pyrogallic acid development.
- III. Same from glass side.
- IV, V, VI. Hydroquinone-developed bleached films. 50, 150, 250 laminae.

Even from the glass side, however, increase of thickness beyond the above-given limit produced no corresponding increase of purity. Further light on this question was furnished by studying the effect of varying exposure and development.

#### EFFECT OF VARYING EXPOSURE

To study this, exposures were made through a graduated wedge of erythrosine solution, opaque to green light. Before noting the effect of varying exposure on the reflected colored light, the appearance of the film at angles other than the angle of specular reflection is worth



describing. By reflected light the film appears in the less exposed parts like an ordinary fine-grain negative, that is, there is a certain amount of diffuse reflection so that a positive image is seen. As the exposure proceeds the diffuse reflection becomes less and less until the film is quite grainless and black, except at the angle of specular reflection, behaving as a piece of unsilvered glass. By transmission the plate is greenish in the very slightly exposed parts, muddy brownish yellowish in the moderately exposed parts; where the film has been exposed until the diffuse light disappears by reflection it is clear, transparent yellow, like a piece of yellow glass. The appearance and behavior of the silver deposit is in all respects as though the particles of silver were first separate, scattering light, and on longer exposure fused together into a homogeneous mass. The appearances here described may be observed on almost any Lippmann photograph viewed at other than the angle to show color, the diffuse deposit forming a positive image which in the fully exposed high-lights appears reversed.

The colored light reflected from the laminae increases in intensity with increase of exposure until the diffusely reflected light disappears; after that for a long range of exposure no change in intensity occurs. This is probably because the individual laminae do not gain in reflecting power after the silver particles have fused together into a reflected surface. This fact makes it possible in photographing spectra with plates not evenly sensitized to secure uniform action throughout the spectrum merely by long exposure.

The greatest spectral purity of the reflected light occurs just before the "saturation" point is reached, dropping slightly for longer exposures and not changing perceptibly till many times the full exposure, when the color tends toward gray and white. From the glass side the purity increases with exposure to a maximum, and then remains constant except with very thin films, in which case the purity again decreases. The cause of this will appear shortly.

#### EFFECT OF VARYING LENGTH OF DEVELOPMENT

By lowering a plate slowly into the developer different amounts of development were obtained. The only effect of greatly increased development was to cause fog, decreasing somewhat the purity, if the picture was viewed from the film side. Viewed from the glass side

longer development had no effect whatever, except with thin films, when the purity decreased similarly to the effect noted with increasing exposure.

The practice was to develop the plates up to the point where fog began to appear, usually by time development. At temperatures near 20° C. from 45 seconds to a minute gave full development.

#### ACTION OF THE DEVELOPER ON THE FILM

Using thick films it was found, if development was sufficiently prolonged, that the laminae intersected the gelatine-glass surface, giving a watered-silk effect, the same phenomenon used by Wiener to estimate the thickness of the film. As in film sections heretofore made comparatively few laminae had been found, it has been assumed that but few are formed. The appearance just noted indicated that the laminae might be formed throughout the thickness of the film, provided development were continued long enough.

To study the action of the developer it was decided to section the films and observe them under the microscope. This has been done by Neuhaus, Lehmann, and Cajal. The latter swells the section in water to bring the structure, in its natural size too small to be satisfactorily resolved with the microscope, within reach of average powers. This method was pursued in the present investigation. After development a small oblong of film was cut out with a knife and then stripped from the glass by means of a narrow, straight-edged chisel. The strip of film was then laid on one-half of a split piece of pith. When dry the other half of the pith was laid over it, the whole placed in a microtome and sectioned. On laying the sections on a microscope slip, and wetting with a drop of water, the majority of the laminary structures were easily observable with a one-sixth inch objective. For much of the work where it was not important to have sections of exactly the same thickness, it was found convenient to dispense with the microtome, simply hold the pith in a pair of clothes pins and shave off sections with a razor guided by the forefinger, an operation easily performed after a little practice.

A section of a normally exposed and developed film is shown in Fig. 5 (Plate XIX). It will be observed that the laminae are strongest at the mirror-surface, decreasing in strength with distance from it.

Figs. 6 and 7 (sections of same thickness) show the results of short and long development. With short development the laminae are visible for only a short distance; with long development the laminae are present to a great depth, but a thick band of fog has progressed inward from the surface. The laminae corresponding to the surface ones in the short development are therefore in the long development at a greater depth. From the glass side their effect is precisely similar, unless the film is thin or development has been very long, in which case the fog band reaches to the glass and drowns out the clearly formed laminae. This makes clear the above-noted effects of long exposure and long development as seen from the glass side. A film exposed or developed progressively from edge to edge possesses a layer of well-formed clean laminae running diagonally down from the surface until the glass is reached.

It appears, therefore, that the standing waves are actually formed to a greater depth than has been supposed. To verify this several experiments were performed. A thick film was exposed as usual, then before development wetted and a piece stripped from the glass and so developed from both sides. A section showed the laminae to be formed equally well at both developed surfaces. This is shown in Fig. 8, where 150 distinct laminae may be counted. Another experiment consisted in flowing a plate with a thick solution of celluloid varnish, through which, after drying, the exposure was made as usual. On stripping the varnish coating from the gelatine, developing, and sectioning, laminae were found all through the film. They are, therefore, formed, with monochromatic light, under the conditions of this work, to a much greater depth than the thickest film used.

It follows from these observations that the small effective number of laminae (about 20 or 30 at the most) is due, not to few being formed, as has been assumed, but to the mode of action of the developer. This invited investigation of different modes of development and different developers, from which has resulted a substantial advance in the rendering of pure colors.

Experiments with different modes of development, using the same developer (pyrogallie acid), led to no results. Development with strong developer, with weak slow developer, and with a large proportion of bromide, showed no material difference in the character of

the deposit. Long development followed by application of weak Farmer's reducer was unsuccessful, as the reducing solution simply destroyed everything as it slowly worked through the film.

Attention was then turned to other developers with immediately gratifying results. Ferrous oxalate, glycin, and hydroquinone were tried. All of these developed with great uniformity throughout the depth of the film, without causing fog. Fig. 9 shows a section of film developed with hydroquinone, and should be compared with Fig. 6. Unfortunately, as it seemed at first, the deposit with these developers is black and opaque, making the reflected color dull in the extreme, and the absorption so great that only few of the laminae are effective. To obviate this difficulty the expedient was adopted of bleaching the film with mercuric chloride. This has been done previously by Neuhaus and results in a white, very transparent film. The reflecting power of the bleached deposit is not great, so that luminosity is lost with pyro-developed plates. With plates developed by the three above-mentioned developers this loss of reflecting power is more than compensated for by the greater number of effective laminae. So transparent is the deposit that the absorption is negligible and all the laminae act with practically equal strength. Consequently, instead of the reflected light being a somewhat diffuse band in the spectro-scope, it is a narrow bright line. Moreover, increased thickness with consequent greater number of laminae gives increased purity. Practically it was found possible to run the films up to about  $\frac{1}{10}$  mm (as determined by the number of laminae in sections) with continued increase of purity. A line source is reproduced by such a film as a brilliant line of about 20 Å. U. width. By transmission a narrow absorption line appears in the spectrum indistinguishable in a small spectro-scope from a Fraunhofer line. In Fig. A, IV, V, VI, are shown spectra of the mercury green line as reproduced by films containing approximately 50, 150, and 250 laminae. It will be observed that films of this character might serve for sources of comparatively monochromatic light.

The thickness to which the film may be carried is limited by the thickness of gelatine it is practicable to flow and dry satisfactorily. Greatly increased exposures due to the opacity and slow speed of the thick films made work with them difficult, but the conclusion may be

drawn from this work that the purity of reflected color is, with this procedure, directly dependent on film thickness. It is only a matter of emulsion making and flowing technique to secure films of as high resolving power as one desires.

### MIXED COLORS

#### GENERAL THEORY

Mixed colors, such as two or more spectral lines, or the broad ill-defined bands of the spectrum given by pigment colors, give standing waves which may be compared to the interference fringes they would give in a Michelson interferometer. That is, we have regions in the film where the different wave-lengths acting reinforce regions where they oppose each other. The visibility curves,<sup>1</sup> therefore, are applicable to the structure of the Lippmann film. Fig. 1 gives the resultant



FIG. 1.—Standing Wave System Due to Two Wave-Lengths.

of two wave-lengths, while the visibility curves figured show the manner in which we may expect the laminae to be distributed for various types of incident light. Photographs have been published by Lehmann showing that the resultant structure for two radiations agrees with the calculated. Fig. 12 shows a section of a film exposed to four radiations. The periodic variation in the clearness of the fringes corresponds to the variations of visibility of interferometer fringes.

Two points in connection with the reproduction of mixed colors were studied as of special interest. The first was the question of the degree of complexity of incident light the film is capable of recording. The second was the question of the luminosity values of mixed colors as compared with the component pure ones.

As to the amount of complexity in the incident light which may be reproduced, it is at once apparent that this is dependent on the effective thickness of film. A film developed with pyrogallic acid is, from the previous work, unsuitable where depth is called for, hence the

<sup>1</sup> A. A. Michelson, *Phil. Mag.* (5), 31, 338, 1891; 34, 280, 1892.

best results in the way of resolving power were obtained from hydroquinone-developed, bleached films.

Parallel series were carried out on films of the two types. These consisted in exposures to two, three, and four different wave-lengths, and to a broad spectrum band with sharply defined edges.

With pyrogallic-acid developed thick films, the greatest number of separate wave-lengths reproduced was three, and the result was merely a continuous spectrum with three maxima; four radiations produced ill-defined irregularities. The mercury yellow and green lines were well separated with such a film and probably somewhat closer lines would be. A sharp spectrum band of 600 Å. U. width in the green was rendered as a maximum in the green, but all trace of sharp limits was missing, the reproduction being identical with that of the transmission band of a naphthol green-dye solution. This is to be expected, as examination of Fig. 2 shows. The first part of the standing wave-system of the two types of color is identical, and in a thin film, or one whose effective portion is thin, will reproduce as such. The effect of development with pyrogallic acid is in short to reduce all colors to one general type.

With hydroquinone developer and bleaching, two, three, and four radiations were reproduced satisfactorily, except for loss in luminosity, the cause of which will be taken up presently. The spectrum band was reproduced with well-defined edges. From these tests it was concluded, as with monochromatic light, that the capacity of the film to reproduce any form of complex radiation is only limited by the gelatine thickness possible to be obtained practicably.

The second point studied, that of luminosity rendering, will be made clear by some considerations of the theories advanced as to the nature of the reflecting elements in the film. Lippmann developed the theory on the basis of minute reflecting particles distributed through the film. White, for instance, is due to a continuous irregular distribution of such particles. According to this view all the incident light produces reflecting deposit. Schütt<sup>1</sup> advanced the theory that the action of the light is merely to produce a periodic change in the refractive index. Wiener showed that the reflection in the case of bromide of silver plates was from metallic particles. It is possible,

<sup>1</sup> *Annalen der Physik*, 57, 533, 1896.

for instance, by exposing films of bichromated gelatine, to secure pictures in which the only change produced is in the refractive index.

The luminosities of all but monochromatic pictures will be rendered radically differently according to which mode of reflection takes place. For illustration take white. In the one case we have a large number of reflecting particles, in the other a single reflecting surface, practically the surface of the gelatine. A monochromatic source would give many such surfaces through the film with the structureless deposit and would be far more brilliantly rendered than a white visually as brilliant. Where two or three colors act together there are regions of the film in which, while the total amount of light action is say half the maximum amount, yet sharp changes of intensity are missing. If reflection is due to abrupt change of refractive index these portions would contribute little. A loss of luminosity of the combined with respect to the component colors would result. If this were marked, colors with two or more maxima, such as purple or a subjective yellow, would be weakly reproduced. Lehmann, working with superposed spectra, notes such a loss. The experiments which follow were made with the two kinds of development, and because of the large surfaces exposed, and the manner of exposing, critical examination was easy.

The first experiment was to mix two and three colors (red, yellow, green, and blue, in various combinations) under such conditions that their resultant intensity when acting together could be compared with their intensity separately. The apparatus used consisted of an opaque line screen, opaque spaces twice the width of the transparent. 100 lines to the inch, which was cut in two, and one half turned at right angles to the other. This was placed directly in front of the plate and by means of a screw could be moved any desired distance in the direction of the lines on one half. This motion caused one set of lines to uncover one-third of the surface at a time, the other to continually expose the same strips. In one half would therefore be obtained the three colors superposed, in the other half juxtaposed, in which case the mixing would be visual.

In carrying out this experiment the greatest care had to be taken to avoid the effects of overexposure. As we have seen, exposure beyond a certain point causes no increase of brilliancy. Hence if

each exposure was a full one we would have the entirely covered surface three times as brilliant (with three colors) as the partially covered, indicating a large luminosity loss in the superposed as compared with the juxtaposed. This was avoided by limiting the exposures so that the total exposure with all colors would not reach the saturation point.

The result of the tests was that with pyrogallic acid the loss of luminosity with two colors, as long as exposure was carefully kept below the saturation point, was hardly noticeable, the only effect being a slight tendency of the superposed colors to shift toward shorter wave-lengths. With three radiations a quite perceptible loss of luminosity was observable. In either case exposure beyond the saturation point caused loss of luminosity. With hydroquinone the luminosity loss was much more marked.

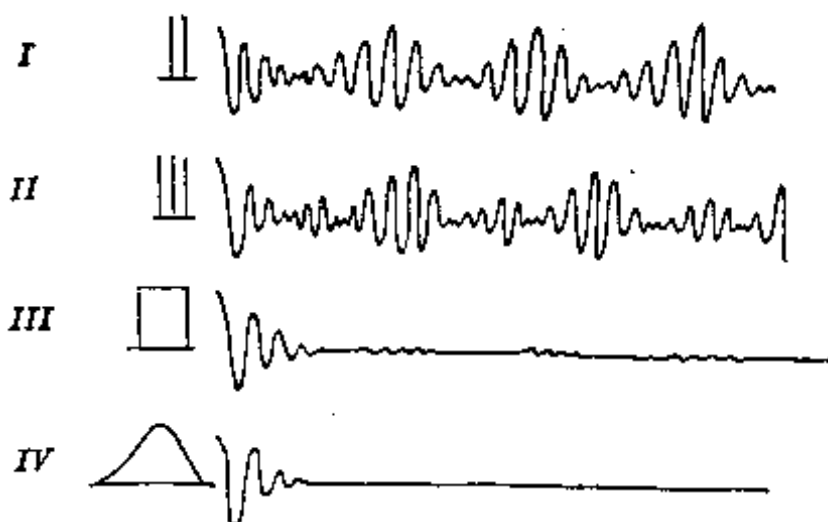
The most instructive test was to expose a plate to light of the green-mercury line and to a visual match in color and intensity consisting of a spectrum band of 600 Å. U. width. These gave equal densities in the negative. With hydroquinone development and bleaching the monochromatic side was many times the brilliancy of the other. With pyrogallic acid the two sides were nearly the same luminosity, the complex radiation only slightly less luminous.

Experiments on photographing natural objects whose colors are for the most part continuous spectra with diffuse maxima, besides showing the necessity for a reflecting deposit, emphasized the necessity of this being of high reflecting power. Very fine-grained emulsions proved unsuitable for the reproduction of such colors in their luminosity values, and satisfactory results were obtained only when the silver content of the film was made as large as would still give color. The reason is at once apparent when we observe that the colors under consideration give at most only a few laminae near the surface, as shown in Fig. 2 and in the photographed section, Fig. 13. It is necessary not only that the reflecting power of these be large but that the diffuse deposit behind contribute a share of light in proportion to the light acting to produce it. If the grain is too fine these experiments and work with white light indicate that the separate particles do not act as reflecting surfaces.

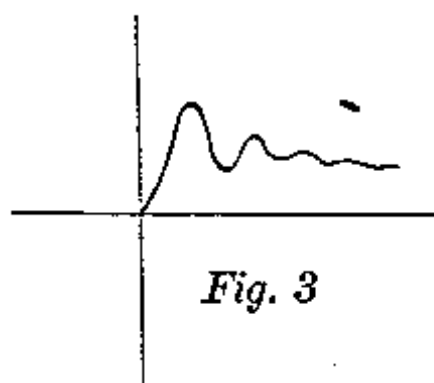
The outcome of the experiments is to indicate that with a fairly coarse grain, overexposure being carefully avoided, developed with



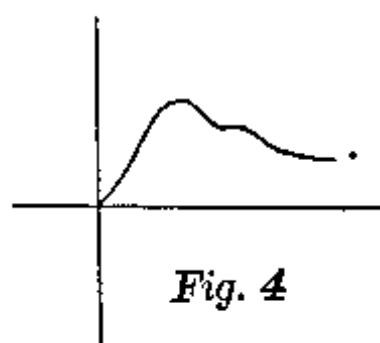
pyrogallic acid, there is probably a close approach to the condition of separate reflecting particles. With complex radiation, or with over-exposure, there cannot fail to be a certain amount of fusing together and consequent luminosity loss, and in the underexposed parts there is probably also a loss through the formation of deposit not starting



*Fig. 2*



*Fig. 3*



*Fig. 4*

FIG. 2.—Visibility curves for various sources:

- I. Two monochromatic sources.
- II. Three monochromatic sources.
- III. Spectrum band with sharp limits.
- IV. Type of spectrum of light from most natural objects.

FIG. 3.—Standing waves formed by white light from red to blue, as recorded in fine-grain emulsions.

FIG. 4.—Standing waves formed by white light from infra-red to ultra-violet, as recorded by coarse-grained emulsions.

till the light attains a certain intensity. With hydroquinone development and bleaching, the reflection is evidently more nearly of the type caused by changing refractive index.

This at once makes evident that for all photography where luminosity values must be preserved, a developer like pyrogallic acid giving a highly reflecting yet fairly transparent deposit is essential. On the

other hand, where complexity of spectral structure is to be reproduced, a deep-acting developer, which by proper treatment will give a transparent deposit, is desirable.

#### THE PRODUCTION OF WHITE

On Lippmann's theory, white is produced by reflection from particles of silver thickly and irregularly distributed through the film. Regularly spaced laminae would be entirely absent. Such a deposit would be formed in a perfectly isochromatic emulsion, provided the wave-lengths of the acting light varied between wide limits and the individual silver grains were of appreciable size. If, on the other hand, the acting light varied between rather narrow limits of wave-length, as from red to blue, the size of the silver grains being negligibly small in comparison to the shortest wave-length, a rapidly damped standing vibration of wave-length equal to the mean incident wave-length would result. In Fig. 3 is given the standing wave form due to light from red to blue, in Fig. 4 the form when the incident light is from infra-red to ultra-violet and the silver grain coarse.

Lippmann pictures have been made, exhibiting beautiful whites, yet general difficulty seems to have been experienced. This is partly due probably to the difficulty, with present known sensitizers, of securing isochromatism between wide limits. Several other theories have been proposed and other experimental methods tried to produce white. Lehmann concludes that the greenish appearance sometimes found in whites on short exposure is due to laminae formed in the manner described above. He corrects this by using a screen with three maxima of transmission: red, green, and blue. On short exposure whites will be reproduced as a mixture of these three colors. A serious objection to this method is that colors falling in the minima of transmission will be poorly reproduced.

Cajal from his work concludes that white is due to the formation of a mirror-like surface on the film and that this can be produced only by the use of amidol as an intensifier. The mirror-like appearance presented by the high-lights of Lippmann pictures readily lends itself to the idea that the surface is a silver mirror. That this is possible only when the picture is intensified with amidol is, however, a conclusion unsupported by other experimenters and contradicted by the

undoubted production of white by Neuhaus and others who did not use this intensifier.

The possible modes of production of white are therefore three: first, by a general diffuse deposit as an isochromatic emulsion; second, by forming laminae corresponding to red, green, and blue; third, by producing a mirror surface. The second method was not tried in the present investigation, as being obviously a compromise.

Attention was therefore turned to producing an isochromatic emulsion by combinations of color-screens and sensitizers. Numerous sensitizers were tried; of these much the best was isocol, in that it imparts a sensitiveness free of gaps or maxima. The sensitiveness given by it extends from deep red to blue and violet, gradually increasing toward the latter. Absorbing solutions of wool black, cobalt sulphocyanate, and iron sulphocyanate reduced the action in blue, green, and yellow to that in deep red and gave very satisfactory isochromatic action from red to ultra-violet.

Plates similar to those used in the study of monochromatic colors were prepared and exposed to white, at first with disappointing results. Not only was there practically no light reflected from the partially exposed parts, but the mirror-like high-lights were absolutely black. By intensification with amidol the plates could be made to reflect considerable light. This led to the question whether the intensifier did not merely increase the size of the grain, and whether this might not be done in the emulsion. That the grain was too fine to give whites by diffuse reflection was also indicated by the fact that a fogged plate appeared black and not white by reflection.

A series of emulsions were then made up containing increasing quantities of silver. These were exposed without the mercury mirror and the character of the deposit examined. It was at once apparent that while a very fine grain reflected diffusely very little light indeed, a coarser grain gave a strong white reflection which in the high lights became mirror-like. The brightest whites were given by an emulsion containing four times the silver content of that used for pure color work, or twice that used by Lippmann and others. This emulsion used with the mercury mirror gave perfect white. The theory that diffusely distributed reflecting particles formed in an isochromatic emulsion produce white is therefore supported.

As to the theory of Cajal that white is given only by a mirror-like surface, this was not supported by the results here obtained. The whites were quite perfect in the partially exposed parts. In fact it is the writer's opinion that the formation of the mirror appearance indicates rather the point where the white ceases to be good. A very slight exposure beyond this point, giving the clear yellow by transmission, results in the white becoming black. Everything is in agreement with the view before advanced that the mirror appearance is due to the merging-together of the separate particles with resulting loss in reflecting power. White will be given only so long as the particles are separate, being similar therefore to the white given by powdered glass or other substance transparent in the fused condition.

Since the range of sensitiveness of the emulsion is at best rather limited, and since the grain must be kept small enough to render all colors ordinarily met with, it would not be surprising if some tendency should exist to form laminae corresponding to the mean wave-length, i. e., green. No appearance of green on underexposure of whites was observed. Before mounting the prism the film had an orange tinge which turned to greenish on increasing the angle of incidence. The explanation of this is given by Fig. 4. Although complete laminae corresponding to green light are not formed the deposit of silver increases in density from the surface to the point where the first lamina would form. Rapid damping prevents the formation of more surfaces. There is therefore a slight gap between the surface and the heavy deposit, forming a single thin film. On mounting the prism the upper surface is virtually destroyed. The orange color is what we should expect from Wiener's explanation of the shift of all colors toward red as long as the surface reflection is active.

Sections supported these conclusions. Laminae were absent; in their place appeared a structureless deposit, increasing in strength toward the surface, reaching a maximum a short distance from it, the maximum corresponding to the distance in of the first laminae due to green light, as nearly as could be determined. This appearance is shown in Figure 11.

#### PHOTOGRAPHY OF NATURAL OBJECTS

To photograph natural objects conditions must be such as to give whites and colors of small spectral purity. This is secured by using

a fairly coarse-grained isochromatic emulsion developed with a developer giving a transparent highly reflecting deposit.

For experiments in this direction a number of different emulsions and modes of preparation were tried. Good results were obtained with very coarse-grained ones, but experience showed the proportions of silver bromide and gelatine in general use to be probably the most satisfactory. Little choice exists between the several modes of preparation published. The silver nitrate may be digested with part of the gelatine; dissolved in water and added, before mixing, to one part of the gelatine; dissolved in water and added to the gelatine containing the potassium bromide; or added in dry powdered form to the latter. The quantity of silver bromide is double that found best for monochromatic light-reproduction.

To secure isochromatism, isocol as a sensitizer, with the absorbing solutions above given, or, as the sensitiveness imparted by isocol is very fugitive, a more permanent combination of pinacyanol and pinaverdol, with a screen of wool black, was found to answer fairly well.

The only point in the manipulation not yet described is the choice of film thickness. The standing wave-structure being shallow, great thickness is no object. Speed, too, is gained by small depth. The thinnest film is obtained by flowing the warm emulsion on and off glass plates warmed to the same temperature. This gives a thickness of about  $\frac{1}{400}$  mm, on which most colors reproduce satisfactorily as far as the eye can tell. The resolving power is small of course, and some anomalous results are to be expected. Purple is about the only color of any complexity often met with, and the film should be thick enough to resolve its two maxima well. The most satisfactory thickness was obtained by flowing the emulsion on and off glass plates at room temperature, about  $\frac{1}{200}$  mm. Exposures with  $f/3.6$  on sunlit objects ranged from  $1\frac{1}{2}$  to 5 minutes according to sensitizers, etc.

With emulsions made up and used in this way good color rendering was obtained. The sum total of the results on photographing natural objects has been to vindicate the procedure indicated by theory and carried out by Lippmann. The deviations from that procedure by Lehmann and Cajal seem unnecessary to secure successful results.

The difficulties noted by all workers with the process as applied

PLATE XIX

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- 5. Section of film exposed to A 5461, developed with pyrogallic acid.
- 6. Film developed one minute with pyrogallic acid.
- 7. Film developed 15 minutes with pyrogallic acid.
- 8. Film stripped and developed from both sides.

- 9. Film developed with hydroquinone.
- 10. Bathed plate.
- 11. White (short exposure).
- 12. Four wave-lengths: A 6430, 5780, 5461, 5086.
- 13. Heterogeneous green light; naphthol-green color-screen.

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to photographing natural objects were found to be very real. They are in brief the great dependence of success on correct exposure and development. Very slight deviations will make the colors either weak or diluted with white. This is due to the laminae being few and close to the surface. With pure colors a certain amount of clogging up affects but a small part of all the laminae, in diluted colors practically all. A larger proportion (twice as much) of bromide in the developer than was used for pure colors was found materially to help the brilliancy of these colors. A larger percentage of failures is to be expected in any process of color photography than with black and white, since the eye is more sensitive to errors of treatment where color occurs. The sensitiveness of the Lippmann process to slight deviations from correct conditions is, however, much greater than the three-color method, and good results come only from repeated patient trials. When obtained they are extremely dependent on correct viewing conditions, to appear to any advantage. The colors being formed for the most part by two or three laminae backed up by a diffuse deposit, great care must be taken to exclude all light except that coming in the direction to be regularly reflected by the laminae. Light from other directions is not sent to the eye by the laminae but is by the diffuse deposit, causing a drowning-out of the colors with white light. By making the film excessively thin so that the laminae are formed, but not the deposit behind, the colors are more brilliant and less affected by conditions of illumination. Colors of any complexity, such as purple, however, suffer.

#### A SUBSTITUTE FOR THE MERCURY MIRROR

One of the obstacles to wide use of the Lippmann process is the necessity for a mercury mirror. Each plate-holder must be arranged as a tank into which before exposure mercury must be flowed. Several attempts have been made to obtain substitutes for the mercury. Krone<sup>1</sup> dispensed with it altogether, relying on the gelatine-air reflection, but the colors are then dull and unsatisfactory. Lehmann has flowed the emulsion on a collodion-coated polished metal plate. After exposure the composite film could be stripped and placed on a glass plate. Pure colors, spectra, etc., can be so reproduced, but those

<sup>1</sup> *Darstellung der natürlichen Farben durch Photographie*, 1894.

whose lamina system is close to the surface cannot, since that space is occupied by the collodion. Placing a silver mirror in close contact with the gelatine has the same objection.

The writer has recently discovered a substitute for the mercury mirror, of a form which permits the plates to be handled and used precisely as ordinary dry plates.

The procedure is as follows: A glass plate is heavily silvered and then flowed with a thick solution of celluloid in amyl-acetate. When this varnish is dry the plate is placed under water; this slowly works under the coating of celluloid, lifting it from the glass, and *bringing with it the silver*. This flexible silver mirror is immediately laid, silver surface down, on a wet Lippmann plate and allowed to dry there, a necessarily somewhat slow process. When dry, the gelatine film has the silver surface in optical contact with it. The plate may be then exposed at any time in an ordinary plate-holder. After exposure the celluloid film is stripped from the gelatine, taking with it most of the silver, the plate developed, and after thorough washing, the remains of the silver are removed with a tuft of wet cotton.

This substitute works perfectly for all types of colors, and except in the laboratory where a convenient dark room makes the use of the mercury mirror simple, facilitates the practical working of the process. Especially would it do so for the photographer who buys his plates ready made. In that case the only difference between ordinary and color photography would be the longer exposure in the latter case, and the necessary mounting of a prism on the picture, and of course the impossibility of copying.

A difficulty which has proved rather troublesome is that some of the best sensitizers are apt to lose their effect during the slow drying. Erythrosine acts perfectly; pinacyanol and pinaverdol are apt to fail. This can probably be overcome, either by different choice of sensitizers, by so treating these that slow drying does not harm, or perhaps by finding some more porous substance than celluloid which, acting the same in other respects, will permit quick drying. Collodion has been tried, but has not been found to strip off the gelatine well.

#### THREE-COLOR INTERFERENCE PICTURES

The capacity of the Lippmann film to reproduce pure spectrum colors easily and with certainty adapts it for an application to the



three-color process, published by the writer some time ago.<sup>1</sup> In the synthesis of the properly taken records of the three-color sensations spectrally pure red, green, and blue light are called for. The Lippmann film furnishes an unequalled means for securing these.

The method used was to place before the plate an opaque-line screen, having opaque spaces twice the width of the transparent. The three positive color records were projected one after the other with their appropriate colored lights, the line screen being moved each time the width of a clear space. The result was similar to the Joly picture, consisting of alternating lines of red, green, and blue.

In the first pictures so made the colored lights were obtained from sunlight by a monochromatic illuminator, but satisfactory purity and shortness of exposure were not secured. In experiments since carried out the line screen was removed from contact with the plate, as this necessitated a narrow source of light, and placed in contact with the three-color positive, an image of the screen and positive being formed by a Planar lens of fine defining power. For light-sources the cadmium red line ( $\lambda$  6439), the magnesium green ( $\lambda$  5170), and the lithium blue ( $\lambda$  4602) were found most available, obtained in the manner described in a following section.

The three-color interference pictures so made are of great brilliancy and beauty, especially if the hydroquinone development and bleaching are used, when the component colors are of practically ideal purity. Quite long exposures are necessary, amounting under the best conditions to a total of fifteen or twenty minutes. This time can probably be materially reduced. The pictures are, however, far more easy and certain besides being more brilliant than the regular Lippmann picture. They constitute an excellent means of carrying out the three-color principle, and have the interesting property of owing their color to the direct action of light and not to pigments or colored glasses as do the other three-color schemes. They can, besides, be duplicated indefinitely.

#### SENSITIZERS

During the progress of the work various color sensitizers were used, depending on the portion of the spectrum photographed. The list included erythrosine, cyanin, pinacyanol, pinaverdol, pinachrome,

<sup>1</sup> *Physical Review*, 24, 103, 1907.

isocol, homocol, and dicyanin. For bathing  $\frac{1}{100000}$  solutions in water were used, without ammonia; in the emulsion about one cc of a  $\frac{1}{1000}$  alcoholic solution to 100 cc of emulsion. Some observations of their behavior with these very slow emulsions are of interest.

In general it was found that bathed plates acted more cleanly and brilliantly, two sensitizers, isocol and homocol, acting very poorly in the emulsion. Ammonia was not used as it has a tendency to make the plates ripen, with consequent great increase in the grain. Bathed plates were, however, unsuitable for a large part of the work, since the sensitizing action extends only a short distance into the film, even with long bathing. Fig. 10 shows a section of a plate bathed fifteen minutes in a  $\frac{1}{100000}$  solution of homocol.

For green all of the sensitizers are good except cyanin, dicyanin, and pinacyanol. For the red, pinacyanol is far and away the best, the action of cyanin not extending far enough down, and that of dicyanin being too feeble. The great difficulty has been to sensitize for the light blue. On ordinary plates there is apt with many sensitizers to be a minimum in the blue green near  $\lambda$  5000. On these slow plates this gap is in the blue. This is owing to the natural sensitiveness of the plates only extending to the violet, while with fast plates it goes down to the blue. The descending curve of green sensitiveness imparted say by erythrosine meets the descending curve of the emulsions' own sensitiveness in the one case in the blue, in the other in the blue green. This was verified by greatly reducing the amount of sensitizer when the weak blue sensitiveness was stronger than the imparted sensitiveness in the blue green. This behavior of the plates makes sensitizer combinations, such as pinacyanol, homocol, and pinaverdol,<sup>1</sup> which fill the blue green in ordinary plates, inefficient here. A blue sensitizer, not needed for fast plates, is really required with the Lippmann plates. Isocol was the only sensitizer found which gave a sensitiveness free from gaps.<sup>2</sup>

As to the keeping qualities of the sensitized plates, it was found that the erythrosine-cyanin, or erythrosine-pinacyanol emulsion plates kept

<sup>1</sup> R. J. Wallace, *Astrophysical Journal*, 26, 299, 1907.

<sup>2</sup> The sensitizers used were of the following makes or sources: pinacyanol, pinaverdol, pinachrome, dicyanin, from Meister, Lucius, and Brüning; isocol, homocol, from the Bayer Co.; cyanin from Eimer & Amend, New York; erythrosine, from F. A. Reichardt, New York.

well, at least for a week or two. Bathed plates lost their sensitiveness quite rapidly; isocol-bathed plates in four or five hours, rendering them useful only for quickly carried out experiments. Pinaverdol in the emulsion in one case lost its action in four days. Pinacyanol and pinaverdol emulsions which dried slowly, as those prepared for use with the silver-celluloid mirror, sometimes showed complete loss of color-sensitiveness.

#### SOURCES OF MONOCHROMATIC LIGHT

In the study of monochromatic light reproduction and in making three-color interference pictures difficulty was experienced in finding suitable monochromatic sources. As the plates are very slow, and large surfaces were illuminated, sources capable of giving a large quantity of light for a long period were essential. Many ordinarily used sources were useless, either because of their small intrinsic brilliancy, or because of their too short life. The spark, the vacuum tube, the flame, arcs between easily melted metals, were among these. Another requisite was that the line used should not be so near other lines as to render its separation impossible by means of absorbing screens; resolution by means of a prism causing too much loss of light.

The following list of the most satisfactory sources found is given as of possible use in other lines of work where great intensity for a long period is required. It is by no means complete, since search was stopped when a satisfactory one for any color was found. Where obtainable the best sources are undoubtedly the Heraeus fused quartz lamps and the mercury vacuum arc. The open arcs here tested are as a rule more brilliant and are easily manipulated. Carbon was used uniformly as negative electrode:

*Red.* Lithium  $\lambda$  6708. Lithium sulphate in cored carbon.

Cadmium  $\lambda$  6439. Cadmium ordinarily burns with dense brown fumes which form a cake of brown oxide around the rapidly melting electrode. This may be avoided by melting the cadmium into a copper tube. The copper and cadmium lines appear together, but the red cadmium line is distant from the copper lines. A current of not more than four amperes is best.

*Orange.* Lithium  $\lambda$  6103. Lithium sulphate in cored carbon.

*Yellow.* Sodium  $\lambda$  5893. Sodium chloride in cored carbon.

*Green.* Thallium  $\lambda$  5360. Metallic thallium in cored carbon.

Magnesium  $\lambda$  5162. Magnesium powder in cored carbon.

5172

5167

Silver  $\lambda$  5460 and 5209. Silver, which in rods melts in a few seconds, burns steadily and brilliantly if a thick wire is placed in a cored carbon. Wire of 2 mm diameter in a carbon of 10 mm diameter gave excellent results.

Cadmium  $\lambda$  5085, obtained from an alloy of tin and cadmium in a cored carbon, one part by weight of cadmium to six of tin.

*Blue.* Lithium  $\lambda$  4602. Lithium sulphate in cored carbon.

Solutions of various aniline dyes separated most of these clearly. Copper chloride was found useful when either end of the spectrum was to be absorbed. With increasing concentration its absorption moves in, maintaining constantly a sharp boundary. Care must be taken that the temperature of the solution does not rise while in use as this causes widening of the absorption.

#### MISCELLANEOUS PHENOMENA

*Relative position of reproduced with reference to incident wave-lengths.*—Owing to the partial solubility of the gelatine and perhaps the washing-out of unaffected silver bromide the films show a general tendency to shrink in development and washing. This causes the colors to shift toward blue. This tendency is much more marked when the plates are fixed with "hypo." In most of the work fixing was dispensed with, Lehmann having found the pictures to keep perfectly without. This shift is much more marked with pure colors than with mixed, the interlaminary spaces being freer of deposit. This is well shown by photographing a continuous spectrum, using a rather wide slit, beside a line spectrum; the lines are reproduced as noticeably of shorter wave-length tint. If the slit is then closed up to extreme narrowness and exposure is made, the spectrum colors agree in tint with the monochromatic lines.

Bleaching with mercuric chloride, on the other hand, swells the film; the two processes of fixing and bleaching therefore tend to neutralize each other.

In working with very thick films a spurious "Doppler effect"

frequently occurs. The surface portions of the film wash away more than the deeper, so that a diffuse band of light appears on the blue side of the sharp line.

*Characteristic curve.*—In the photographic plate the density by transmission varies nearly directly with the time of exposure. This is because the deposit of silver is in logarithmic relation to the time of exposure, and the increase of opacity of an absorbing medium also follows such a law. When the deposit is viewed by reflection this relationship between exposure and intensity does not hold, the relation becomes logarithmic instead of linear. The exact relationship is complicated by absorption, which tends to hasten the "saturation point." A further complication arises in the Lippmann process with very short exposures, owing to the necessity for the reflecting particles to have a certain size and a certain closeness to each other to form a regularly reflecting surface. This was observed in a plate one-half of which was exposed behind a coarse opaque grating with lines covering  $\frac{2}{3}$  of the surface. The part behind the grating was exposed to nearly full exposure, the part not covered exposed until, when held at arm's length (where the lines were no longer visible), the two parts appeared of exactly the same density. By reflection the portion only partly covered by the full exposure was much more brilliant than the portion completely covered by the shorter exposure.

These several effects tend to shorten the scale of gradation of the plate, unfortunately, because the eye is more sensitive to this defect in colored than monochromatic pictures.

*Different rates of development for different colors.*—In developing three-color negatives where all three images are on one plate it has been observed that the three images develop at different rates although the exposures and the final densities are correctly proportioned. The Lippmann film exhibits the effect clearly. In making three-color interference pictures the colors were found to depend considerably on the time of development. With short development the green and blue predominated, with longer the red became stronger, the final picture showing, however, the relative exposures not too long for blue and green. Trouble from this effect was easily avoided by keeping the time of development constant and regulating the exposures for that development.

## SUMMARY OF RESULTS AND CONCLUSIONS

*Reproduction of monochromatic light.*—A smaller amount of silver bromide than usually employed gives purer reflected light from the Lippmann film.

Increase in thickness beyond about  $\frac{1}{200}$  mm causes no corresponding increase of purity so long as pyrogallic acid development is used.

The standing waves are formed throughout the thickness of the film; non-formation of laminae is due to surface action of the developer.

Other developers such as hydroquinone develop evenly through the film. By bleaching the deposit formed by their use films are obtained giving purer reflected colors than heretofore obtained and increasing in resolving power with thickness.

*Mixed colors.*—Films developed with pyrogallic acid have small capacity for rendering complex structure, but luminosity values are well preserved if the grain is not too fine or exposure too long.

With hydroquinone and bleaching, complex radiations are produced with a fidelity dependent only on the practically attainable thickness of film. This resolving power is at the cost of luminosity.

*White.*—White is produced by the action of white light on fairly coarse-grained rigidly isochromatic emulsions.

*Natural objects.*—The colors of natural objects are well reproduced by emulsions suitable for giving whites and mixed colors, i. e., of somewhat coarser grain than is best for pure colors.

Pictures of natural objects are more difficult to obtain than those of pure colors because of shallowness of the standing wave-structure.

*Substitute for the mercury mirror.*—A means has been found of affixing a silver reflecting surface in optical contact with the film, enabling the mercury mirror to be dispensed with.

*Three-color interference pictures.*—The Lippmann film, by reason of its capacity for reproducing pure colors, is well adapted to application to three-color photography.

In conclusion I wish to acknowledge my indebtedness to my father, Mr. Frederic E. Ives, whose life-long experience with photographic processes has always been freely placed at my service. I also wish to thank Professor J. S. Ames for the kindly interest he has shown in the progress of the work.

# AN EXPERIMENTAL STUDY OF THE LIPPMANN COLOR PHOTOGRAPH

BY HERBERT E. IVES

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<sup>1</sup> 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.<sup>2</sup>

Lippmann<sup>3</sup> 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,<sup>4</sup> Wiener,<sup>5</sup> Neuhaus,<sup>6</sup> Valenta,<sup>7</sup> Lehmann,<sup>8</sup> and others.<sup>9</sup> 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

<sup>1</sup> *Lehrbuch der Photochromie*, 1868.

<sup>2</sup> *Rayleigh, Phil. Mag.* (5), 26, 256, 1888.

<sup>3</sup> *Comptes rendus*, 112, 274, 1891.

<sup>4</sup> *Journal de Physique*, 3, 97, 1894.

<sup>5</sup> *Annalen der Physik*, 69, 488, 1899.

<sup>6</sup> *Die Farbenphotographie nach Lippmann's Verfahren*, 1898.

<sup>7</sup> *Die Photographie in natürlichen Farben*, 1894.

<sup>8</sup> *Beiträge zur Theorie und Praxis der directen Farbenphotographie*, 1, 1906.

<sup>9</sup> 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. 1," or a de-



partment 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<sup>1</sup> 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

<sup>1</sup> *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<sup>1</sup> 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.

<sup>1</sup> *Zeitschrift für wissenschaftliche Photographie*, 5, 213-245, July 1907.

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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

in Lippmann spectra. From the glass side the band was of a different character, showing more clearly defined edges, as given in Fig. A, III. This is explained by the stronger laminae being farther from the eye and by absorption being no more effective than the weaker ones. The reflecting surfaces are then comparable to the lines of a grating, each sending equal contributions to the total reflected light. Owing to the strongest laminae suffering so much absorption, the light from the glass side is much weaker than from the film side.

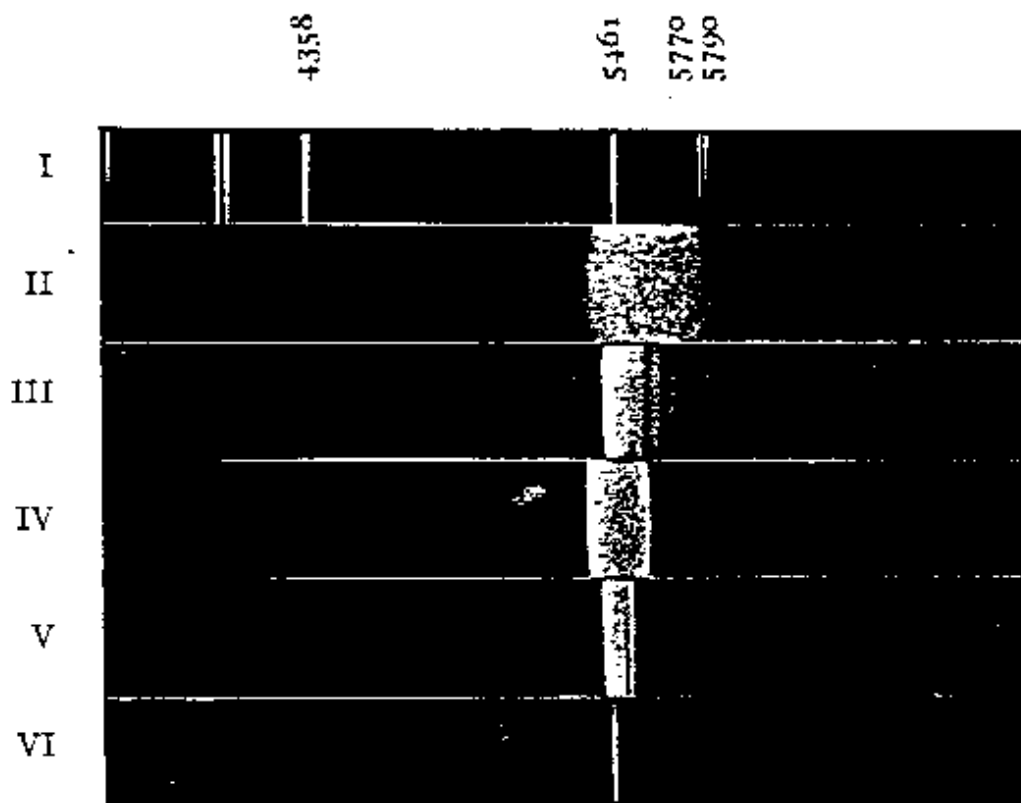


FIG. A

- I. Mercury vacuum arc.
- II.  $\lambda$  5461 as reproduced by fine-grain film, with pyrogallic acid development.
- III. Same from glass side.
- IV, V, VI. Hydroquinone-developed bleached films. 50, 150, 250 laminae.

Even from the glass side, however, increase of thickness beyond the above-given limit produced no corresponding increase of purity. Further light on this question was furnished by studying the effect of varying exposure and development.

#### EFFECT OF VARYING EXPOSURE

To study this, exposures were made through a graduated wedge of erythrosine solution, opaque to green light. Before noting the effect of varying exposure on the reflected colored light, the appearance of the film at angles other than the angle of specular reflection is worth

describing. By reflected light the film appears in the less exposed parts like an ordinary fine-grain negative, that is, there is a certain amount of diffuse reflection so that a positive image is seen. As the exposure proceeds the diffuse reflection becomes less and less until the film is quite grainless and black, except at the angle of specular reflection, behaving as a piece of unsilvered glass. By transmission the plate is greenish in the very slightly exposed parts, muddy brownish yellowish in the moderately exposed parts; where the film has been exposed until the diffuse light disappears by reflection it is clear, transparent yellow, like a piece of yellow glass. The appearance and behavior of the silver deposit is in all respects as though the particles of silver were first separate, scattering light, and on longer exposure fused together into a homogeneous mass. The appearances here described may be observed on almost any Lippmann photograph viewed at other than the angle to show color, the diffuse deposit forming a positive image which in the fully exposed high-lights appears reversed.

The colored light reflected from the laminae increases in intensity with increase of exposure until the diffusely reflected light disappears; after that for a long range of exposure no change in intensity occurs. This is probably because the individual laminae do not gain in reflecting power after the silver particles have fused together into a reflected surface. This fact makes it possible in photographing spectra with plates not evenly sensitized to secure uniform action throughout the spectrum merely by long exposure.

The greatest spectral purity of the reflected light occurs just before the "saturation" point is reached, dropping slightly for longer exposures and not changing perceptibly till many times the full exposure, when the color tends toward gray and white. From the glass side the purity increases with exposure to a maximum, and then remains constant except with very thin films, in which case the purity again decreases. The cause of this will appear shortly.

#### EFFECT OF VARYING LENGTH OF DEVELOPMENT

By lowering a plate slowly into the developer different amounts of development were obtained. The only effect of greatly increased development was to cause fog, decreasing somewhat the purity, if the picture was viewed from the film side. Viewed from the glass side

longer development had no effect whatever, except with thin films, when the purity decreased similarly to the effect noted with increasing exposure.

The practice was to develop the plates up to the point where fog began to appear, usually by time development. At temperatures near 20° C. from 45 seconds to a minute gave full development.

#### ACTION OF THE DEVELOPER ON THE FILM

Using thick films it was found, if development was sufficiently prolonged, that the laminae intersected the gelatine-glass surface, giving a watered-silk effect, the same phenomenon used by Wiener to estimate the thickness of the film. As in film sections heretofore made comparatively few laminae had been found, it has been assumed that but few are formed. The appearance just noted indicated that the laminae might be formed throughout the thickness of the film, provided development were continued long enough.

To study the action of the developer it was decided to section the films and observe them under the microscope. This has been done by Neuhaus, Lehmann, and Cajal. The latter swells the section in water to bring the structure, in its natural size too small to be satisfactorily resolved with the microscope, within reach of average powers. This method was pursued in the present investigation. After development a small oblong of film was cut out with a knife and then stripped from the glass by means of a narrow, straight-edged chisel. The strip of film was then laid on one-half of a split piece of pith. When dry the other half of the pith was laid over it, the whole placed in a microtome and sectioned. On laying the sections on a microscope slip, and wetting with a drop of water, the majority of the laminary structures were easily observable with a one-sixth inch objective. For much of the work where it was not important to have sections of exactly the same thickness, it was found convenient to dispense with the microtome, simply hold the pith in a pair of clothes pins and shave off sections with a razor guided by the forefinger, an operation easily performed after a little practice.

A section of a normally exposed and developed film is shown in Fig. 5 (Plate XIX). It will be observed that the laminae are strongest at the mirror-surface, decreasing in strength with distance from it.



Figs. 6 and 7 (sections of same thickness) show the results of short and long development. With short development the laminae are visible for only a short distance; with long development the laminae are present to a great depth, but a thick band of fog has progressed inward from the surface. The laminae corresponding to the surface ones in the short development are therefore in the long development at a greater depth. From the glass side their effect is precisely similar, unless the film is thin or development has been very long, in which case the fog band reaches to the glass and drowns out the clearly formed laminae. This makes clear the above-noted effects of long exposure and long development as seen from the glass side. A film exposed or developed progressively from edge to edge possesses a layer of well-formed clean laminae running diagonally down from the surface until the glass is reached.

It appears, therefore, that the standing waves are actually formed to a greater depth than has been supposed. To verify this several experiments were performed. A thick film was exposed as usual, then before development wetted and a piece stripped from the glass and so developed from both sides. A section showed the laminae to be formed equally well at both developed surfaces. This is shown in Fig. 8, where 150 distinct laminae may be counted. Another experiment consisted in flowing a plate with a thick solution of celluloid varnish, through which, after drying, the exposure was made as usual. On stripping the varnish coating from the gelatine, developing, and sectioning, laminae were found all through the film. They are, therefore, formed, with monochromatic light, under the conditions of this work, to a much greater depth than the thickest film used.

It follows from these observations that the small effective number of laminae (about 20 or 30 at the most) is due, not to few being formed, as has been assumed, but to the mode of action of the developer. This invited investigation of different modes of development and different developers, from which has resulted a substantial advance in the rendering of pure colors.

Experiments with different modes of development, using the same developer (pyrogallic acid), led to no results. Development with strong developer, with weak slow developer, and with a large proportion of bromide, showed no material difference in the character of

the deposit. Long development followed by application of weak Farmer's reducer was unsuccessful, as the reducing solution simply destroyed everything as it slowly worked through the film.

Attention was then turned to other developers with immediately gratifying results. Ferrous oxalate, glycin, and hydroquinone were tried. All of these developed with great uniformity throughout the depth of the film, without causing fog. Fig. 9 shows a section of film developed with hydroquinone, and should be compared with Fig. 6. Unfortunately, as it seemed at first, the deposit with these developers is black and opaque, making the reflected color dull in the extreme, and the absorption so great that only few of the laminae are effective. To obviate this difficulty the expedient was adopted of bleaching the film with mercuric chloride. This has been done previously by Neuhaus and results in a white, very transparent film. The reflecting power of the bleached deposit is not great, so that luminosity is lost with pyro-developed plates. With plates developed by the three above-mentioned developers this loss of reflecting power is more than compensated for by the greater number of effective laminae. So transparent is the deposit that the absorption is negligible and all the laminae act with practically equal strength. Consequently, instead of the reflected light being a somewhat diffuse band in the spectro-scope, it is a narrow bright line. Moreover, increased thickness with consequent greater number of laminae gives increased purity. Practically it was found possible to run the films up to about  $\frac{1}{10}$  mm (as determined by the number of laminae in sections) with continued increase of purity. A line source is reproduced by such a film as a brilliant line of about 20 Å. U. width. By transmission a narrow absorption line appears in the spectrum indistinguishable in a small spectro-scope from a Fraunhofer line. In Fig. A, IV, V, VI, are shown spectra of the mercury green line as reproduced by films containing approximately 50, 150, and 250 laminae. It will be observed that films of this character might serve for sources of comparatively monochromatic light.

The thickness to which the film may be carried is limited by the thickness of gelatine it is practicable to flow and dry satisfactorily. Greatly increased exposures due to the opacity and slow speed of the thick films made work with them difficult, but the conclusion may be

drawn from this work that the purity of reflected color is, with this procedure, directly dependent on film thickness. It is only a matter of emulsion making and flowing technique to secure films of as high resolving power as one desires.

### MIXED COLORS

#### GENERAL THEORY

Mixed colors, such as two or more spectral lines, or the broad ill-defined bands of the spectrum given by pigment colors, give standing waves which may be compared to the interference fringes they would give in a Michelson interferometer. That is, we have regions in the film where the different wave-lengths acting reinforce regions where they oppose each other. The visibility curves,<sup>1</sup> therefore, are applicable to the structure of the Lippmann film. Fig. 1 gives the resultant



FIG. 1.—Standing Wave System Due to Two Wave-Lengths.

of two wave-lengths, while the visibility curves figured show the manner in which we may expect the laminae to be distributed for various types of incident light. Photographs have been published by Lehmann showing that the resultant structure for two radiations agrees with the calculated. Fig. 12 shows a section of a film exposed to four radiations. The periodic variation in the clearness of the fringes corresponds to the variations of visibility of interferometer fringes.

Two points in connection with the reproduction of mixed colors were studied as of special interest. The first was the question of the degree of complexity of incident light the film is capable of recording. The second was the question of the luminosity values of mixed colors as compared with the component pure ones.

As to the amount of complexity in the incident light which may be reproduced, it is at once apparent that this is dependent on the effective thickness of film. A film developed with pyrogallie acid is, from the previous work, unsuitable where depth is called for, hence the

<sup>1</sup> A. A. Michelson, *Phil. Mag.* (5), 31, 338, 1891; 34, 280, 1892.

best results in the way of resolving power were obtained from hydroquinone-developed, bleached films.

Parallel series were carried out on films of the two types. These consisted in exposures to two, three, and four different wave-lengths, and to a broad spectrum band with sharply defined edges.

With pyrogallic-acid developed thick films, the greatest number of separate wave-lengths reproduced was three, and the result was merely a continuous spectrum with three maxima; four radiations produced ill-defined irregularities. The mercury yellow and green lines were well separated with such a film and probably somewhat closer lines would be. A sharp spectrum band of 600 Å. U. width in the green was rendered as a maximum in the green, but all trace of sharp limits was missing, the reproduction being identical with that of the transmission band of a naphthol green-dye solution. This is to be expected, as examination of Fig. 2 shows. The first part of the standing wave-system of the two types of color is identical, and in a thin film, or one whose effective portion is thin, will reproduce as such. The effect of development with pyrogallic acid is in short to reduce all colors to one general type.

With hydroquinone developer and bleaching, two, three, and four radiations were reproduced satisfactorily, except for loss in luminosity, the cause of which will be taken up presently. The spectrum band was reproduced with well-defined edges. From these tests it was concluded, as with monochromatic light, that the capacity of the film to reproduce any form of complex radiation is only limited by the gelatine thickness possible to be obtained practicably.

The second point studied, that of luminosity rendering, will be made clear by some considerations of the theories advanced as to the nature of the reflecting elements in the film. Lippmann developed the theory on the basis of minute reflecting particles distributed through the film. White, for instance, is due to a continuous irregular distribution of such particles. According to this view all the incident light produces reflecting deposit. Schütt<sup>1</sup> advanced the theory that the action of the light is merely to produce a periodic change in the refractive index. Wiener showed that the reflection in the case of bromide of silver plates was from metallic particles. It is possible,

<sup>1</sup> *Annalen der Physik*, 57, 533, 1896.

for instance, by exposing films of bichromated gelatine, to secure pictures in which the only change produced is in the refractive index.

The luminosities of all but monochromatic pictures will be rendered radically differently according to which mode of reflection takes place. For illustration take white. In the one case we have a large number of reflecting particles, in the other a single reflecting surface, practically the surface of the gelatine. A monochromatic source would give many such surfaces through the film with the structureless deposit and would be far more brilliantly rendered than a white visually as brilliant. Where two or three colors act together there are regions of the film in which, while the total amount of light action is say half the maximum amount, yet sharp changes of intensity are missing. If reflection is due to abrupt change of refractive index these portions would contribute little. A loss of luminosity of the combined with respect to the component colors would result. If this were marked, colors with two or more maxima, such as purple or a subjective yellow, would be weakly reproduced. Lehmann, working with superposed spectra, notes such a loss. The experiments which follow were made with the two kinds of development, and because of the large surfaces exposed, and the manner of exposing, critical examination was easy.

The first experiment was to mix two and three colors (red, yellow, green, and blue, in various combinations) under such conditions that their resultant intensity when acting together could be compared with their intensity separately. The apparatus used consisted of an opaque line screen, opaque spaces twice the width of the transparent. 100 lines to the inch, which was cut in two, and one half turned at right angles to the other. This was placed directly in front of the plate and by means of a screw could be moved any desired distance in the direction of the lines on one half. This motion caused one set of lines to uncover one-third of the surface at a time, the other to continually expose the same strips. In one half would therefore be obtained the three colors superposed, in the other half juxtaposed, in which case the mixing would be visual.

In carrying out this experiment the greatest care had to be taken to avoid the effects of overexposure. As we have seen, exposure beyond a certain point causes no increase of brilliancy. Hence if

each exposure was a full one we would have the entirely covered surface three times as brilliant (with three colors) as the partially covered, indicating a large luminosity loss in the superposed as compared with the juxtaposed. This was avoided by limiting the exposures so that the total exposure with all colors would not reach the saturation point.

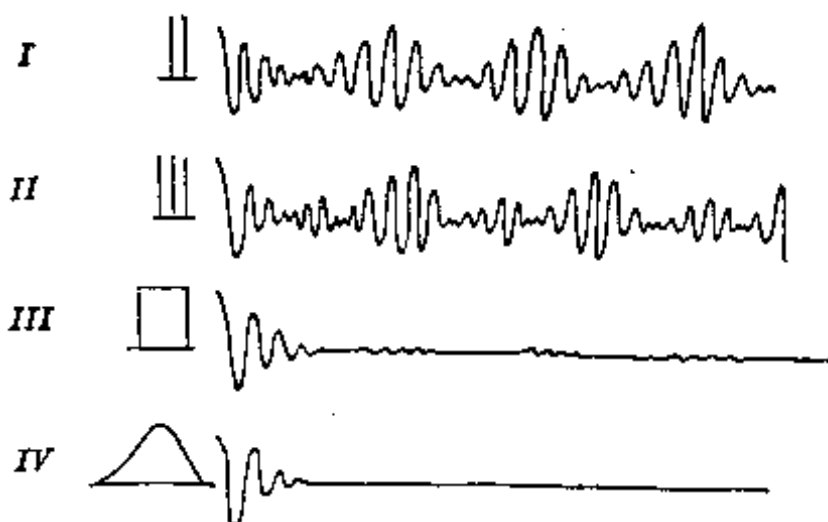
The result of the tests was that with pyrogallic acid the loss of luminosity with two colors, as long as exposure was carefully kept below the saturation point, was hardly noticeable, the only effect being a slight tendency of the superposed colors to shift toward shorter wave-lengths. With three radiations a quite perceptible loss of luminosity was observable. In either case exposure beyond the saturation point caused loss of luminosity. With hydroquinone the luminosity loss was much more marked.

The most instructive test was to expose a plate to light of the green-mercury line and to a visual match in color and intensity consisting of a spectrum band of 600 Å. U. width. These gave equal densities in the negative. With hydroquinone development and bleaching the monochromatic side was many times the brilliancy of the other. With pyrogallic acid the two sides were nearly the same luminosity, the complex radiation only slightly less luminous.

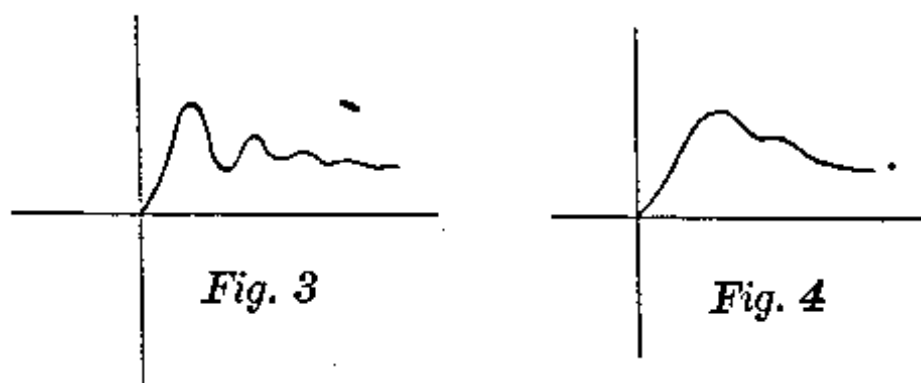
Experiments on photographing natural objects whose colors are for the most part continuous spectra with diffuse maxima, besides showing the necessity for a reflecting deposit, emphasized the necessity of this being of high reflecting power. Very fine-grained emulsions proved unsuitable for the reproduction of such colors in their luminosity values, and satisfactory results were obtained only when the silver content of the film was made as large as would still give color. The reason is at once apparent when we observe that the colors under consideration give at most only a few laminae near the surface, as shown in Fig. 2 and in the photographed section, Fig. 13. It is necessary not only that the reflecting power of these be large but that the diffuse deposit behind contribute a share of light in proportion to the light acting to produce it. If the grain is too fine these experiments and work with white light indicate that the separate particles do not act as reflecting surfaces.

The outcome of the experiments is to indicate that with a fairly coarse grain, overexposure being carefully avoided, developed with

pyrogallic acid, there is probably a close approach to the condition of separate reflecting particles. With complex radiation, or with over-exposure, there cannot fail to be a certain amount of fusing together and consequent luminosity loss, and in the underexposed parts there is probably also a loss through the formation of deposit not starting



*Fig. 2*



*Fig. 3*

*Fig. 4*

FIG. 2.—Visibility curves for various sources:

- I. Two monochromatic sources.
- II. Three monochromatic sources.
- III. Spectrum band with sharp limits.
- IV. Type of spectrum of light from most natural objects.

FIG. 3.—Standing waves formed by white light from red to blue, as recorded in fine-grain emulsions.

FIG. 4.—Standing waves formed by white light from infra-red to ultra-violet, as recorded by coarse-grained emulsions.

till the light attains a certain intensity. With hydroquinone development and bleaching, the reflection is evidently more nearly of the type caused by changing refractive index.

This at once makes evident that for all photography where luminosity values must be preserved, a developer like pyrogallic acid giving a highly reflecting yet fairly transparent deposit is essential. On the

other hand, where complexity of spectral structure is to be reproduced, a deep-acting developer, which by proper treatment will give a transparent deposit, is desirable.

#### THE PRODUCTION OF WHITE

On Lippmann's theory, white is produced by reflection from particles of silver thickly and irregularly distributed through the film. Regularly spaced laminae would be entirely absent. Such a deposit would be formed in a perfectly isochromatic emulsion, provided the wave-lengths of the acting light varied between wide limits and the individual silver grains were of appreciable size. If, on the other hand, the acting light varied between rather narrow limits of wave-length, as from red to blue, the size of the silver grains being negligibly small in comparison to the shortest wave-length, a rapidly damped standing vibration of wave-length equal to the mean incident wave-length would result. In Fig. 3 is given the standing wave form due to light from red to blue, in Fig. 4 the form when the incident light is from infra-red to ultra-violet and the silver grain coarse.

Lippmann pictures have been made, exhibiting beautiful whites, yet general difficulty seems to have been experienced. This is partly due probably to the difficulty, with present known sensitizers, of securing isochromatism between wide limits. Several other theories have been proposed and other experimental methods tried to produce white. Lehmann concludes that the greenish appearance sometimes found in whites on short exposure is due to laminae formed in the manner described above. He corrects this by using a screen with three maxima of transmission: red, green, and blue. On short exposure whites will be reproduced as a mixture of these three colors. A serious objection to this method is that colors falling in the minima of transmission will be poorly reproduced.

Cajal from his work concludes that white is due to the formation of a mirror-like surface on the film and that this can be produced only by the use of amidol as an intensifier. The mirror-like appearance presented by the high-lights of Lippmann pictures readily lends itself to the idea that the surface is a silver mirror. That this is possible only when the picture is intensified with amidol is, however, a conclusion unsupported by other experimenters and contradicted by the



undoubted production of white by Neuhaus and others who did not use this intensifier.

The possible modes of production of white are therefore three: first, by a general diffuse deposit as an isochromatic emulsion; second, by forming laminae corresponding to red, green, and blue; third, by producing a mirror surface. The second method was not tried in the present investigation, as being obviously a compromise.

Attention was therefore turned to producing an isochromatic emulsion by combinations of color-screens and sensitizers. Numerous sensitizers were tried; of these much the best was isocol, in that it imparts a sensitiveness free of gaps or maxima. The sensitiveness given by it extends from deep red to blue and violet, gradually increasing toward the latter. Absorbing solutions of wool black, cobalt sulphocyanate, and iron sulphocyanate reduced the action in blue, green, and yellow to that in deep red and gave very satisfactory isochromatic action from red to ultra-violet.

Plates similar to those used in the study of monochromatic colors were prepared and exposed to white, at first with disappointing results. Not only was there practically no light reflected from the partially exposed parts, but the mirror-like high-lights were absolutely black. By intensification with amidol the plates could be made to reflect considerable light. This led to the question whether the intensifier did not merely increase the size of the grain, and whether this might not be done in the emulsion. That the grain was too fine to give whites by diffuse reflection was also indicated by the fact that a fogged plate appeared black and not white by reflection.

A series of emulsions were then made up containing increasing quantities of silver. These were exposed without the mercury mirror and the character of the deposit examined. It was at once apparent that while a very fine grain reflected diffusely very little light indeed, a coarser grain gave a strong white reflection which in the high lights became mirror-like. The brightest whites were given by an emulsion containing four times the silver content of that used for pure color work, or twice that used by Lippmann and others. This emulsion used with the mercury mirror gave perfect white. The theory that diffusely distributed reflecting particles formed in an isochromatic emulsion produce white is therefore supported.

As to the theory of Cajal that white is given only by a mirror-like surface, this was not supported by the results here obtained. The whites were quite perfect in the partially exposed parts. In fact it is the writer's opinion that the formation of the mirror appearance indicates rather the point where the white ceases to be good. A very slight exposure beyond this point, giving the clear yellow by transmission, results in the white becoming black. Everything is in agreement with the view before advanced that the mirror appearance is due to the merging-together of the separate particles with resulting loss in reflecting power. White will be given only so long as the particles are separate, being similar therefore to the white given by powdered glass or other substance transparent in the fused condition.

Since the range of sensitiveness of the emulsion is at best rather limited, and since the grain must be kept small enough to render all colors ordinarily met with, it would not be surprising if some tendency should exist to form laminae corresponding to the mean wave-length, i. e., green. No appearance of green on underexposure of whites was observed. Before mounting the prism the film had an orange tinge which turned to greenish on increasing the angle of incidence. The explanation of this is given by Fig. 4. Although complete laminae corresponding to green light are not formed the deposit of silver increases in density from the surface to the point where the first lamina would form. Rapid damping prevents the formation of more surfaces. There is therefore a slight gap between the surface and the heavy deposit, forming a single thin film. On mounting the prism the upper surface is virtually destroyed. The orange color is what we should expect from Wiener's explanation of the shift of all colors toward red as long as the surface reflection is active.

Sections supported these conclusions. Laminae were absent; in their place appeared a structureless deposit, increasing in strength toward the surface, reaching a maximum a short distance from it, the maximum corresponding to the distance in of the first laminae due to green light, as nearly as could be determined. This appearance is shown in Figure 11.

#### PHOTOGRAPHY OF NATURAL OBJECTS

To photograph natural objects conditions must be such as to give whites and colors of small spectral purity. This is secured by using

a fairly coarse-grained isochromatic emulsion developed with a developer giving a transparent highly reflecting deposit.

For experiments in this direction a number of different emulsions and modes of preparation were tried. Good results were obtained with very coarse-grained ones, but experience showed the proportions of silver bromide and gelatine in general use to be probably the most satisfactory. Little choice exists between the several modes of preparation published. The silver nitrate may be digested with part of the gelatine; dissolved in water and added, before mixing, to one part of the gelatine; dissolved in water and added to the gelatine containing the potassium bromide; or added in dry powdered form to the latter. The quantity of silver bromide is double that found best for monochromatic light-reproduction.

To secure isochromatism, isocol as a sensitizer, with the absorbing solutions above given, or, as the sensitiveness imparted by isocol is very fugitive, a more permanent combination of pinacyanol and pinaverdol, with a screen of wool black, was found to answer fairly well.

The only point in the manipulation not yet described is the choice of film thickness. The standing wave-structure being shallow, great thickness is no object. Speed, too, is gained by small depth. The thinnest film is obtained by flowing the warm emulsion on and off glass plates warmed to the same temperature. This gives a thickness of about  $\frac{1}{400}$  mm, on which most colors reproduce satisfactorily as far as the eye can tell. The resolving power is small of course, and some anomalous results are to be expected. Purple is about the only color of any complexity often met with, and the film should be thick enough to resolve its two maxima well. The most satisfactory thickness was obtained by flowing the emulsion on and off glass plates at room temperature, about  $\frac{1}{200}$  mm. Exposures with  $f/3.6$  on sunlit objects ranged from  $1\frac{1}{2}$  to 5 minutes according to sensitizers, etc.

With emulsions made up and used in this way good color rendering was obtained. The sum total of the results on photographing natural objects has been to vindicate the procedure indicated by theory and carried out by Lippmann. The deviations from that procedure by Lehmann and Cajal seem unnecessary to secure successful results.

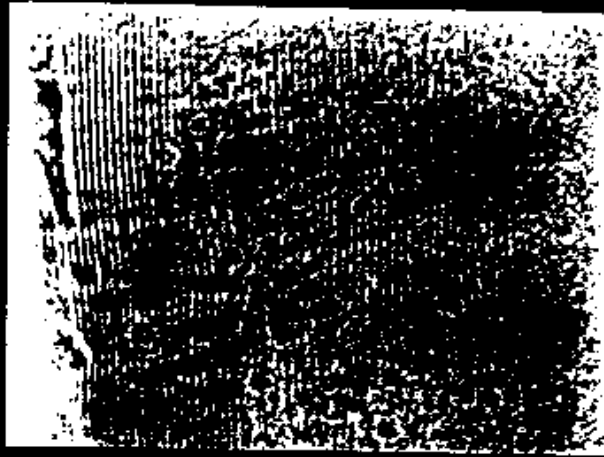
The difficulties noted by all workers with the process as applied

PLATE XIX

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- 5. Section of film exposed to A 5461, developed with pyrogallic acid.
- 6. Film developed one minute with pyrogallic acid.
- 7. Film developed 15 minutes with pyrogallic acid.
- 8. Film stripped and developed from both sides.

- 9. Film developed with hydroquinone.
- 10. Bathed plate.
- 11. White (short exposure).
- 12. Four wave-lengths: A 6430, 5780, 5461, 5086.
- 13. Heterogeneous green light; naphthol-green color-screen.

11

to photographing natural objects were found to be very real. They are in brief the great dependence of success on correct exposure and development. Very slight deviations will make the colors either weak or diluted with white. This is due to the laminae being few and close to the surface. With pure colors a certain amount of clogging up affects but a small part of all the laminae, in diluted colors practically all. A larger proportion (twice as much) of bromide in the developer than was used for pure colors was found materially to help the brilliancy of these colors. A larger percentage of failures is to be expected in any process of color photography than with black and white, since the eye is more sensitive to errors of treatment where color occurs. The sensitiveness of the Lippmann process to slight deviations from correct conditions is, however, much greater than the three-color method, and good results come only from repeated patient trials. When obtained they are extremely dependent on correct viewing conditions, to appear to any advantage. The colors being formed for the most part by two or three laminae backed up by a diffuse deposit, great care must be taken to exclude all light except that coming in the direction to be regularly reflected by the laminae. Light from other directions is not sent to the eye by the laminae but is by the diffuse deposit, causing a drowning-out of the colors with white light. By making the film excessively thin so that the laminae are formed, but not the deposit behind, the colors are more brilliant and less affected by conditions of illumination. Colors of any complexity, such as purple, however, suffer.

#### A SUBSTITUTE FOR THE MERCURY MIRROR

One of the obstacles to wide use of the Lippmann process is the necessity for a mercury mirror. Each plate-holder must be arranged as a tank into which before exposure mercury must be flowed. Several attempts have been made to obtain substitutes for the mercury. Krone<sup>1</sup> dispensed with it altogether, relying on the gelatine-air reflection, but the colors are then dull and unsatisfactory. Lehmann has flowed the emulsion on a collodion-coated polished metal plate. After exposure the composite film could be stripped and placed on a glass plate. Pure colors, spectra, etc., can be so reproduced, but those

<sup>1</sup> *Darstellung der natürlichen Farben durch Photographie*, 1894.

whose lamina system is close to the surface cannot, since that space is occupied by the collodion. Placing a silver mirror in close contact with the gelatine has the same objection.

The writer has recently discovered a substitute for the mercury mirror, of a form which permits the plates to be handled and used precisely as ordinary dry plates.

The procedure is as follows: A glass plate is heavily silvered and then flowed with a thick solution of celluloid in amyl-acetate. When this varnish is dry the plate is placed under water; this slowly works under the coating of celluloid, lifting it from the glass, and *bringing with it the silver*. This flexible silver mirror is immediately laid, silver surface down, on a wet Lippmann plate and allowed to dry there, a necessarily somewhat slow process. When dry, the gelatine film has the silver surface in optical contact with it. The plate may be then exposed at any time in an ordinary plate-holder. After exposure the celluloid film is stripped from the gelatine, taking with it most of the silver, the plate developed, and after thorough washing, the remains of the silver are removed with a tuft of wet cotton.

This substitute works perfectly for all types of colors, and except in the laboratory where a convenient dark room makes the use of the mercury mirror simple, facilitates the practical working of the process. Especially would it do so for the photographer who buys his plates ready made. In that case the only difference between ordinary and color photography would be the longer exposure in the latter case, and the necessary mounting of a prism on the picture, and of course the impossibility of copying.

A difficulty which has proved rather troublesome is that some of the best sensitizers are apt to lose their effect during the slow drying. Erythrosine acts perfectly; pinacyanol and pinaverdol are apt to fail. This can probably be overcome, either by different choice of sensitizers, by so treating these that slow drying does not harm, or perhaps by finding some more porous substance than celluloid which, acting the same in other respects, will permit quick drying. Collodion has been tried, but has not been found to strip off the gelatine well.

#### THREE-COLOR INTERFERENCE PICTURES

The capacity of the Lippmann film to reproduce pure spectrum colors easily and with certainty adapts it for an application to the

three-color process, published by the writer some time ago.<sup>1</sup> In the synthesis of the properly taken records of the three-color sensations spectrally pure red, green, and blue light are called for. The Lippmann film furnishes an unequalled means for securing these.

The method used was to place before the plate an opaque-line screen, having opaque spaces twice the width of the transparent. The three positive color records were projected one after the other with their appropriate colored lights, the line screen being moved each time the width of a clear space. The result was similar to the Joly picture, consisting of alternating lines of red, green, and blue.

In the first pictures so made the colored lights were obtained from sunlight by a monochromatic illuminator, but satisfactory purity and shortness of exposure were not secured. In experiments since carried out the line screen was removed from contact with the plate, as this necessitated a narrow source of light, and placed in contact with the three-color positive, an image of the screen and positive being formed by a Planar lens of fine defining power. For light-sources the cadmium red line ( $\lambda$  6439), the magnesium green ( $\lambda$  5170), and the lithium blue ( $\lambda$  4602) were found most available, obtained in the manner described in a following section.

The three-color interference pictures so made are of great brilliancy and beauty, especially if the hydroquinone development and bleaching are used, when the component colors are of practically ideal purity. Quite long exposures are necessary, amounting under the best conditions to a total of fifteen or twenty minutes. This time can probably be materially reduced. The pictures are, however, far more easy and certain besides being more brilliant than the regular Lippmann picture. They constitute an excellent means of carrying out the three-color principle, and have the interesting property of owing their color to the direct action of light and not to pigments or colored glasses as do the other three-color schemes. They can, besides, be duplicated indefinitely.

#### SENSITIZERS

During the progress of the work various color sensitizers were used, depending on the portion of the spectrum photographed. The list included erythrosine, cyanin, pinacyanol, pinaverdol, pinachrome,

<sup>1</sup> *Physical Review*, 24, 103, 1907.

isocol, homocol, and dicyanin. For bathing  $\frac{1}{100000}$  solutions in water were used, without ammonia; in the emulsion about one cc of a  $\frac{1}{1000}$  alcoholic solution to 100 cc of emulsion. Some observations of their behavior with these very slow emulsions are of interest.

In general it was found that bathed plates acted more cleanly and brilliantly, two sensitizers, isocol and homocol, acting very poorly in the emulsion. Ammonia was not used as it has a tendency to make the plates ripen, with consequent great increase in the grain. Bathed plates were, however, unsuitable for a large part of the work, since the sensitizing action extends only a short distance into the film, even with long bathing. Fig. 10 shows a section of a plate bathed fifteen minutes in a  $\frac{1}{100000}$  solution of homocol.

For green all of the sensitizers are good except cyanin, dicyanin, and pinacyanol. For the red, pinacyanol is far and away the best, the action of cyanin not extending far enough down, and that of dicyanin being too feeble. The great difficulty has been to sensitize for the light blue. On ordinary plates there is apt with many sensitizers to be a minimum in the blue green near  $\lambda$  5000. On these slow plates this gap is in the blue. This is owing to the natural sensitiveness of the plates only extending to the violet, while with fast plates it goes down to the blue. The descending curve of green sensitiveness imparted say by erythrosine meets the descending curve of the emulsions' own sensitiveness in the one case in the blue, in the other in the blue green. This was verified by greatly reducing the amount of sensitizer when the weak blue sensitiveness was stronger than the imparted sensitiveness in the blue green. This behavior of the plates makes sensitizer combinations, such as pinacyanol, homocol, and pinaverdol,<sup>1</sup> which fill the blue green in ordinary plates, inefficient here. A blue sensitizer, not needed for fast plates, is really required with the Lippmann plates. Isocol was the only sensitizer found which gave a sensitiveness free from gaps.<sup>2</sup>

As to the keeping qualities of the sensitized plates, it was found that the erythrosine-cyanin, or erythrosine-pinacyanol emulsion plates kept

<sup>1</sup> R. J. Wallace, *Astrophysical Journal*, 26, 299, 1907.

<sup>2</sup> The sensitizers used were of the following makes or sources: pinacyanol, pinaverdol, pinachrome, dicyanin, from Meister, Lucius, and Brüning; isocol, homocol, from the Bayer Co.; cyanin from Eimer & Amend, New York; erythrosine, from F. A. Reichardt, New York.



well, at least for a week or two. Bathed plates lost their sensitiveness quite rapidly; isocol-bathed plates in four or five hours, rendering them useful only for quickly carried out experiments. Pinaverdol in the emulsion in one case lost its action in four days. Pinacyanol and pinaverdol emulsions which dried slowly, as those prepared for use with the silver-celluloid mirror, sometimes showed complete loss of color-sensitiveness.

#### SOURCES OF MONOCHROMATIC LIGHT

In the study of monochromatic light reproduction and in making three-color interference pictures difficulty was experienced in finding suitable monochromatic sources. As the plates are very slow, and large surfaces were illuminated, sources capable of giving a large quantity of light for a long period were essential. Many ordinarily used sources were useless, either because of their small intrinsic brilliancy, or because of their too short life. The spark, the vacuum tube, the flame, arcs between easily melted metals, were among these. Another requisite was that the line used should not be so near other lines as to render its separation impossible by means of absorbing screens; resolution by means of a prism causing too much loss of light.

The following list of the most satisfactory sources found is given as of possible use in other lines of work where great intensity for a long period is required. It is by no means complete, since search was stopped when a satisfactory one for any color was found. Where obtainable the best sources are undoubtedly the Heraeus fused quartz lamps and the mercury vacuum arc. The open arcs here tested are as a rule more brilliant and are easily manipulated. Carbon was used uniformly as negative electrode:

*Red.* Lithium  $\lambda$  6708. Lithium sulphate in cored carbon.

Cadmium  $\lambda$  6439. Cadmium ordinarily burns with dense brown fumes which form a cake of brown oxide around the rapidly melting electrode. This may be avoided by melting the cadmium into a copper tube. The copper and cadmium lines appear together, but the red cadmium line is distant from the copper lines. A current of not more than four amperes is best.

*Orange.* Lithium  $\lambda$  6103. Lithium sulphate in cored carbon.

*Yellow.* Sodium  $\lambda$  5893. Sodium chloride in cored carbon.

*Green.* Thallium  $\lambda$  5360. Metallic thallium in cored carbon.

Magnesium  $\lambda$  5162. Magnesium powder in cored carbon.

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5167

Silver  $\lambda$  5460 and 5209. Silver, which in rods melts in a few seconds, burns steadily and brilliantly if a thick wire is placed in a cored carbon. Wire of 2 mm diameter in a carbon of 10 mm diameter gave excellent results.

Cadmium  $\lambda$  5085, obtained from an alloy of tin and cadmium in a cored carbon, one part by weight of cadmium to six of tin.

*Blue.* Lithium  $\lambda$  4602. Lithium sulphate in cored carbon.

Solutions of various aniline dyes separated most of these clearly. Copper chloride was found useful when either end of the spectrum was to be absorbed. With increasing concentration its absorption moves in, maintaining constantly a sharp boundary. Care must be taken that the temperature of the solution does not rise while in use as this causes widening of the absorption.

#### MISCELLANEOUS PHENOMENA

*Relative position of reproduced with reference to incident wave-lengths.*—Owing to the partial solubility of the gelatine and perhaps the washing-out of unaffected silver bromide the films show a general tendency to shrink in development and washing. This causes the colors to shift toward blue. This tendency is much more marked when the plates are fixed with "hypo." In most of the work fixing was dispensed with, Lehmann having found the pictures to keep perfectly without. This shift is much more marked with pure colors than with mixed, the interlaminary spaces being freer of deposit. This is well shown by photographing a continuous spectrum, using a rather wide slit, beside a line spectrum; the lines are reproduced as noticeably of shorter wave-length tint. If the slit is then closed up to extreme narrowness and exposure is made, the spectrum colors agree in tint with the monochromatic lines.

Bleaching with mercuric chloride, on the other hand, swells the film; the two processes of fixing and bleaching therefore tend to neutralize each other.

In working with very thick films a spurious "Doppler effect"

frequently occurs. The surface portions of the film wash away more than the deeper, so that a diffuse band of light appears on the blue side of the sharp line.

*Characteristic curve.*—In the photographic plate the density by transmission varies nearly directly with the time of exposure. This is because the deposit of silver is in logarithmic relation to the time of exposure, and the increase of opacity of an absorbing medium also follows such a law. When the deposit is viewed by reflection this relationship between exposure and intensity does not hold, the relation becomes logarithmic instead of linear. The exact relationship is complicated by absorption, which tends to hasten the "saturation point." A further complication arises in the Lippmann process with very short exposures, owing to the necessity for the reflecting particles to have a certain size and a certain closeness to each other to form a regularly reflecting surface. This was observed in a plate one-half of which was exposed behind a coarse opaque grating with lines covering  $\frac{2}{3}$  of the surface. The part behind the grating was exposed to nearly full exposure, the part not covered exposed until, when held at arm's length (where the lines were no longer visible), the two parts appeared of exactly the same density. By reflection the portion only partly covered by the full exposure was much more brilliant than the portion completely covered by the shorter exposure.

These several effects tend to shorten the scale of gradation of the plate, unfortunately, because the eye is more sensitive to this defect in colored than monochromatic pictures.

*Different rates of development for different colors.*—In developing three-color negatives where all three images are on one plate it has been observed that the three images develop at different rates although the exposures and the final densities are correctly proportioned. The Lippmann film exhibits the effect clearly. In making three-color interference pictures the colors were found to depend considerably on the time of development. With short development the green and blue predominated, with longer the red became stronger, the final picture showing, however, the relative exposures not too long for blue and green. Trouble from this effect was easily avoided by keeping the time of development constant and regulating the exposures for that development.

## SUMMARY OF RESULTS AND CONCLUSIONS

*Reproduction of monochromatic light.*—A smaller amount of silver bromide than usually employed gives purer reflected light from the Lippmann film.

Increase in thickness beyond about  $\frac{1}{200}$  mm causes no corresponding increase of purity so long as pyrogallic acid development is used.

The standing waves are formed throughout the thickness of the film; non-formation of laminae is due to surface action of the developer.

Other developers such as hydroquinone develop evenly through the film. By bleaching the deposit formed by their use films are obtained giving purer reflected colors than heretofore obtained and increasing in resolving power with thickness.

*Mixed colors.*—Films developed with pyrogallic acid have small capacity for rendering complex structure, but luminosity values are well preserved if the grain is not too fine or exposure too long.

With hydroquinone and bleaching, complex radiations are produced with a fidelity dependent only on the practically attainable thickness of film. This resolving power is at the cost of luminosity.

*White.*—White is produced by the action of white light on fairly coarse-grained rigidly isochromatic emulsions.

*Natural objects.*—The colors of natural objects are well reproduced by emulsions suitable for giving whites and mixed colors, i. e., of somewhat coarser grain than is best for pure colors.

Pictures of natural objects are more difficult to obtain than those of pure colors because of shallowness of the standing wave-structure.

*Substitute for the mercury mirror.*—A means has been found of affixing a silver reflecting surface in optical contact with the film, enabling the mercury mirror to be dispensed with.

*Three-color interference pictures.*—The Lippmann film, by reason of its capacity for reproducing pure colors, is well adapted to application to three-color photography.

In conclusion I wish to acknowledge my indebtedness to my father, Mr. Frederic E. Ives, whose life-long experience with photographic processes has always been freely placed at my service. I also wish to thank Professor J. S. Ames for the kindly interest he has shown in the progress of the work.

# AN EXPERIMENTAL STUDY OF THE LIPPMANN COLOR PHOTOGRAPH

BY HERBERT E. IVES

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<sup>1</sup> 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.<sup>2</sup>

Lippmann<sup>3</sup> 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,<sup>4</sup> Wiener,<sup>5</sup> Neuhaus,<sup>6</sup> Valenta,<sup>7</sup> Lehmann,<sup>8</sup> and others.<sup>9</sup> 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

<sup>1</sup> *Lehrbuch der Photochromie*, 1868.

<sup>2</sup> *Rayleigh, Phil. Mag.* (5), 26, 256, 1888.

<sup>3</sup> *Comptes rendus*, 112, 274, 1891.

<sup>4</sup> *Journal de Physique*, 3, 97, 1894.

<sup>5</sup> *Annalen der Physik*, 69, 488, 1899.

<sup>6</sup> *Die Farbenphotographie nach Lippmann's Verfahren*, 1898.

<sup>7</sup> *Die Photographie in natürlichen Farben*, 1894.

<sup>8</sup> *Beiträge zur Theorie und Praxis der directen Farbenphotographie*, 1, 1906.

<sup>9</sup> 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. 1," or a de-

partment 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<sup>1</sup> 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

<sup>1</sup> *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<sup>1</sup> 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.

<sup>1</sup> *Zeitschrift für wissenschaftliche Photographie*, 5, 213-245, July 1907.



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<sup>2</sup> *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

in Lippmann spectra. From the glass side the band was of a different character, showing more clearly defined edges, as given in Fig. A, III. This is explained by the stronger laminae being farther from the eye and by absorption being no more effective than the weaker ones. The reflecting surfaces are then comparable to the lines of a grating, each sending equal contributions to the total reflected light. Owing to the strongest laminae suffering so much absorption, the light from the glass side is much weaker than from the film side.

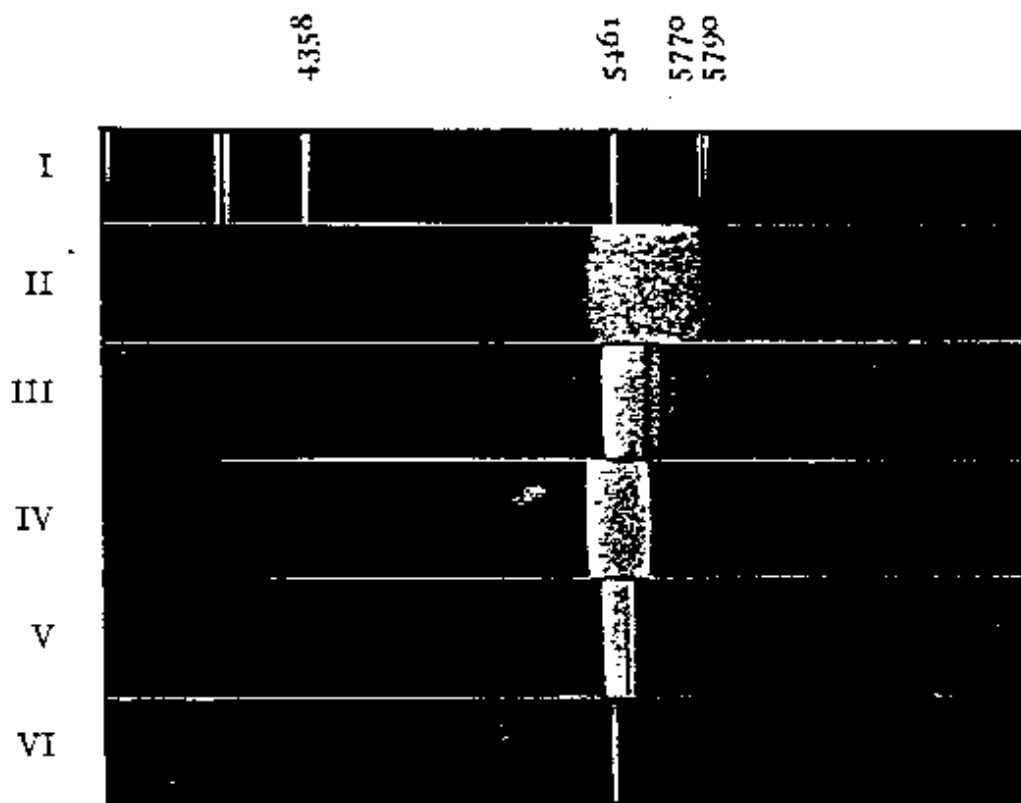


FIG. A

- I. Mercury vacuum arc.
- II.  $\lambda$  5461 as reproduced by fine-grain film, with pyrogallic acid development.
- III. Same from glass side.
- IV, V, VI. Hydroquinone-developed bleached films. 50, 150, 250 laminae.

Even from the glass side, however, increase of thickness beyond the above-given limit produced no corresponding increase of purity. Further light on this question was furnished by studying the effect of varying exposure and development.

#### EFFECT OF VARYING EXPOSURE

To study this, exposures were made through a graduated wedge of erythrosine solution, opaque to green light. Before noting the effect of varying exposure on the reflected colored light, the appearance of the film at angles other than the angle of specular reflection is worth

describing. By reflected light the film appears in the less exposed parts like an ordinary fine-grain negative, that is, there is a certain amount of diffuse reflection so that a positive image is seen. As the exposure proceeds the diffuse reflection becomes less and less until the film is quite grainless and black, except at the angle of specular reflection, behaving as a piece of unsilvered glass. By transmission the plate is greenish in the very slightly exposed parts, muddy brownish yellowish in the moderately exposed parts; where the film has been exposed until the diffuse light disappears by reflection it is clear, transparent yellow, like a piece of yellow glass. The appearance and behavior of the silver deposit is in all respects as though the particles of silver were first separate, scattering light, and on longer exposure fused together into a homogeneous mass. The appearances here described may be observed on almost any Lippmann photograph viewed at other than the angle to show color, the diffuse deposit forming a positive image which in the fully exposed high-lights appears reversed.

The colored light reflected from the laminae increases in intensity with increase of exposure until the diffusely reflected light disappears; after that for a long range of exposure no change in intensity occurs. This is probably because the individual laminae do not gain in reflecting power after the silver particles have fused together into a reflected surface. This fact makes it possible in photographing spectra with plates not evenly sensitized to secure uniform action throughout the spectrum merely by long exposure.

The greatest spectral purity of the reflected light occurs just before the "saturation" point is reached, dropping slightly for longer exposures and not changing perceptibly till many times the full exposure, when the color tends toward gray and white. From the glass side the purity increases with exposure to a maximum, and then remains constant except with very thin films, in which case the purity again decreases. The cause of this will appear shortly.

#### EFFECT OF VARYING LENGTH OF DEVELOPMENT

By lowering a plate slowly into the developer different amounts of development were obtained. The only effect of greatly increased development was to cause fog, decreasing somewhat the purity, if the picture was viewed from the film side. Viewed from the glass side

longer development had no effect whatever, except with thin films, when the purity decreased similarly to the effect noted with increasing exposure.

The practice was to develop the plates up to the point where fog began to appear, usually by time development. At temperatures near 20° C. from 45 seconds to a minute gave full development.

#### ACTION OF THE DEVELOPER ON THE FILM

Using thick films it was found, if development was sufficiently prolonged, that the laminae intersected the gelatine-glass surface, giving a watered-silk effect, the same phenomenon used by Wiener to estimate the thickness of the film. As in film sections heretofore made comparatively few laminae had been found, it has been assumed that but few are formed. The appearance just noted indicated that the laminae might be formed throughout the thickness of the film, provided development were continued long enough.

To study the action of the developer it was decided to section the films and observe them under the microscope. This has been done by Neuhaus, Lehmann, and Cajal. The latter swells the section in water to bring the structure, in its natural size too small to be satisfactorily resolved with the microscope, within reach of average powers. This method was pursued in the present investigation. After development a small oblong of film was cut out with a knife and then stripped from the glass by means of a narrow, straight-edged chisel. The strip of film was then laid on one-half of a split piece of pith. When dry the other half of the pith was laid over it, the whole placed in a microtome and sectioned. On laying the sections on a microscope slip, and wetting with a drop of water, the majority of the laminary structures were easily observable with a one-sixth inch objective. For much of the work where it was not important to have sections of exactly the same thickness, it was found convenient to dispense with the microtome, simply hold the pith in a pair of clothes pins and shave off sections with a razor guided by the forefinger, an operation easily performed after a little practice.

A section of a normally exposed and developed film is shown in Fig. 5 (Plate XIX). It will be observed that the laminae are strongest at the mirror-surface, decreasing in strength with distance from it.

Figs. 6 and 7 (sections of same thickness) show the results of short and long development. With short development the laminae are visible for only a short distance; with long development the laminae are present to a great depth, but a thick band of fog has progressed inward from the surface. The laminae corresponding to the surface ones in the short development are therefore in the long development at a greater depth. From the glass side their effect is precisely similar, unless the film is thin or development has been very long, in which case the fog band reaches to the glass and drowns out the clearly formed laminae. This makes clear the above-noted effects of long exposure and long development as seen from the glass side. A film exposed or developed progressively from edge to edge possesses a layer of well-formed clean laminae running diagonally down from the surface until the glass is reached.

It appears, therefore, that the standing waves are actually formed to a greater depth than has been supposed. To verify this several experiments were performed. A thick film was exposed as usual, then before development wetted and a piece stripped from the glass and so developed from both sides. A section showed the laminae to be formed equally well at both developed surfaces. This is shown in Fig. 8, where 150 distinct laminae may be counted. Another experiment consisted in flowing a plate with a thick solution of celluloid varnish, through which, after drying, the exposure was made as usual. On stripping the varnish coating from the gelatine, developing, and sectioning, laminae were found all through the film. They are, therefore, formed, with monochromatic light, under the conditions of this work, to a much greater depth than the thickest film used.

It follows from these observations that the small effective number of laminae (about 20 or 30 at the most) is due, not to few being formed, as has been assumed, but to the mode of action of the developer. This invited investigation of different modes of development and different developers, from which has resulted a substantial advance in the rendering of pure colors.

Experiments with different modes of development, using the same developer (pyrogallie acid), led to no results. Development with strong developer, with weak slow developer, and with a large proportion of bromide, showed no material difference in the character of

the deposit. Long development followed by application of weak Farmer's reducer was unsuccessful, as the reducing solution simply destroyed everything as it slowly worked through the film.

Attention was then turned to other developers with immediately gratifying results. Ferrous oxalate, glycin, and hydroquinone were tried. All of these developed with great uniformity throughout the depth of the film, without causing fog. Fig. 9 shows a section of film developed with hydroquinone, and should be compared with Fig. 6. Unfortunately, as it seemed at first, the deposit with these developers is black and opaque, making the reflected color dull in the extreme, and the absorption so great that only few of the laminae are effective. To obviate this difficulty the expedient was adopted of bleaching the film with mercuric chloride. This has been done previously by Neuhaus and results in a white, very transparent film. The reflecting power of the bleached deposit is not great, so that luminosity is lost with pyro-developed plates. With plates developed by the three above-mentioned developers this loss of reflecting power is more than compensated for by the greater number of effective laminae. So transparent is the deposit that the absorption is negligible and all the laminae act with practically equal strength. Consequently, instead of the reflected light being a somewhat diffuse band in the spectro-scope, it is a narrow bright line. Moreover, increased thickness with consequent greater number of laminae gives increased purity. Practically it was found possible to run the films up to about  $\frac{1}{10}$  mm (as determined by the number of laminae in sections) with continued increase of purity. A line source is reproduced by such a film as a brilliant line of about 20 Å. U. width. By transmission a narrow absorption line appears in the spectrum indistinguishable in a small spectro-scope from a Fraunhofer line. In Fig. A, IV, V, VI, are shown spectra of the mercury green line as reproduced by films containing approximately 50, 150, and 250 laminae. It will be observed that films of this character might serve for sources of comparatively monochromatic light.

The thickness to which the film may be carried is limited by the thickness of gelatine it is practicable to flow and dry satisfactorily. Greatly increased exposures due to the opacity and slow speed of the thick films made work with them difficult, but the conclusion may be



drawn from this work that the purity of reflected color is, with this procedure, directly dependent on film thickness. It is only a matter of emulsion making and flowing technique to secure films of as high resolving power as one desires.

### MIXED COLORS

#### GENERAL THEORY

Mixed colors, such as two or more spectral lines, or the broad ill-defined bands of the spectrum given by pigment colors, give standing waves which may be compared to the interference fringes they would give in a Michelson interferometer. That is, we have regions in the film where the different wave-lengths acting reinforce regions where they oppose each other. The visibility curves,<sup>1</sup> therefore, are applicable to the structure of the Lippmann film. Fig. 1 gives the resultant



FIG. 1.—Standing Wave System Due to Two Wave-Lengths.

of two wave-lengths, while the visibility curves figured show the manner in which we may expect the laminae to be distributed for various types of incident light. Photographs have been published by Lehmann showing that the resultant structure for two radiations agrees with the calculated. Fig. 12 shows a section of a film exposed to four radiations. The periodic variation in the clearness of the fringes corresponds to the variations of visibility of interferometer fringes.

Two points in connection with the reproduction of mixed colors were studied as of special interest. The first was the question of the degree of complexity of incident light the film is capable of recording. The second was the question of the luminosity values of mixed colors as compared with the component pure ones.

As to the amount of complexity in the incident light which may be reproduced, it is at once apparent that this is dependent on the effective thickness of film. A film developed with pyrogallic acid is, from the previous work, unsuitable where depth is called for, hence the

<sup>1</sup> A. A. Michelson, *Phil. Mag.* (5), 31, 338, 1891; 34, 280, 1892.

best results in the way of resolving power were obtained from hydroquinone-developed, bleached films.

Parallel series were carried out on films of the two types. These consisted in exposures to two, three, and four different wave-lengths, and to a broad spectrum band with sharply defined edges.

With pyrogallic-acid developed thick films, the greatest number of separate wave-lengths reproduced was three, and the result was merely a continuous spectrum with three maxima; four radiations produced ill-defined irregularities. The mercury yellow and green lines were well separated with such a film and probably somewhat closer lines would be. A sharp spectrum band of 600 Å. U. width in the green was rendered as a maximum in the green, but all trace of sharp limits was missing, the reproduction being identical with that of the transmission band of a naphthol green-dye solution. This is to be expected, as examination of Fig. 2 shows. The first part of the standing wave-system of the two types of color is identical, and in a thin film, or one whose effective portion is thin, will reproduce as such. The effect of development with pyrogallic acid is in short to reduce all colors to one general type.

With hydroquinone developer and bleaching, two, three, and four radiations were reproduced satisfactorily, except for loss in luminosity, the cause of which will be taken up presently. The spectrum band was reproduced with well-defined edges. From these tests it was concluded, as with monochromatic light, that the capacity of the film to reproduce any form of complex radiation is only limited by the gelatine thickness possible to be obtained practicably.

The second point studied, that of luminosity rendering, will be made clear by some considerations of the theories advanced as to the nature of the reflecting elements in the film. Lippmann developed the theory on the basis of minute reflecting particles distributed through the film. White, for instance, is due to a continuous irregular distribution of such particles. According to this view all the incident light produces reflecting deposit. Schütt<sup>1</sup> advanced the theory that the action of the light is merely to produce a periodic change in the refractive index. Wiener showed that the reflection in the case of bromide of silver plates was from metallic particles. It is possible,

<sup>1</sup> *Annalen der Physik*, 57, 533, 1896.

for instance, by exposing films of bichromated gelatine, to secure pictures in which the only change produced is in the refractive index.

The luminosities of all but monochromatic pictures will be rendered radically differently according to which mode of reflection takes place. For illustration take white. In the one case we have a large number of reflecting particles, in the other a single reflecting surface, practically the surface of the gelatine. A monochromatic source would give many such surfaces through the film with the structureless deposit and would be far more brilliantly rendered than a white visually as brilliant. Where two or three colors act together there are regions of the film in which, while the total amount of light action is say half the maximum amount, yet sharp changes of intensity are missing. If reflection is due to abrupt change of refractive index these portions would contribute little. A loss of luminosity of the combined with respect to the component colors would result. If this were marked, colors with two or more maxima, such as purple or a subjective yellow, would be weakly reproduced. Lehmann, working with superposed spectra, notes such a loss. The experiments which follow were made with the two kinds of development, and because of the large surfaces exposed, and the manner of exposing, critical examination was easy.

The first experiment was to mix two and three colors (red, yellow, green, and blue, in various combinations) under such conditions that their resultant intensity when acting together could be compared with their intensity separately. The apparatus used consisted of an opaque line screen, opaque spaces twice the width of the transparent. 100 lines to the inch, which was cut in two, and one half turned at right angles to the other. This was placed directly in front of the plate and by means of a screw could be moved any desired distance in the direction of the lines on one half. This motion caused one set of lines to uncover one-third of the surface at a time, the other to continually expose the same strips. In one half would therefore be obtained the three colors superposed, in the other half juxtaposed, in which case the mixing would be visual.

In carrying out this experiment the greatest care had to be taken to avoid the effects of overexposure. As we have seen, exposure beyond a certain point causes no increase of brilliancy. Hence if

each exposure was a full one we would have the entirely covered surface three times as brilliant (with three colors) as the partially covered, indicating a large luminosity loss in the superposed as compared with the juxtaposed. This was avoided by limiting the exposures so that the total exposure with all colors would not reach the saturation point.

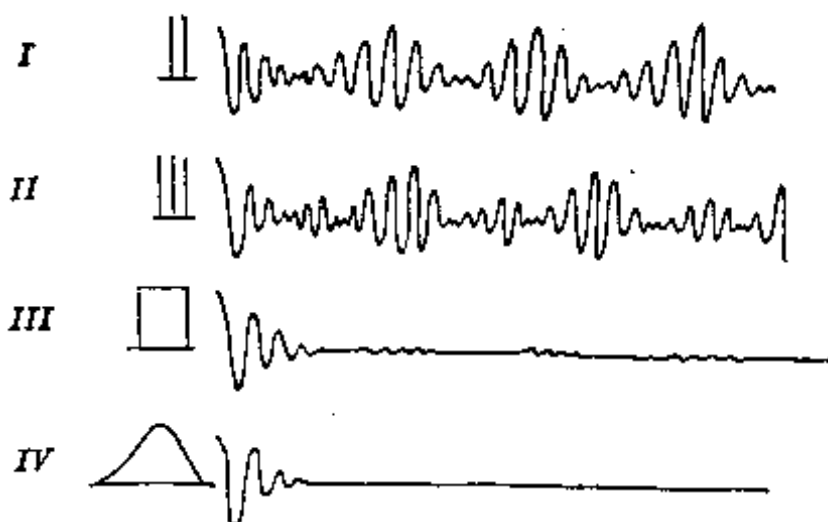
The result of the tests was that with pyrogallic acid the loss of luminosity with two colors, as long as exposure was carefully kept below the saturation point, was hardly noticeable, the only effect being a slight tendency of the superposed colors to shift toward shorter wave-lengths. With three radiations a quite perceptible loss of luminosity was observable. In either case exposure beyond the saturation point caused loss of luminosity. With hydroquinone the luminosity loss was much more marked.

The most instructive test was to expose a plate to light of the green-mercury line and to a visual match in color and intensity consisting of a spectrum band of 600 Å. U. width. These gave equal densities in the negative. With hydroquinone development and bleaching the monochromatic side was many times the brilliancy of the other. With pyrogallic acid the two sides were nearly the same luminosity, the complex radiation only slightly less luminous.

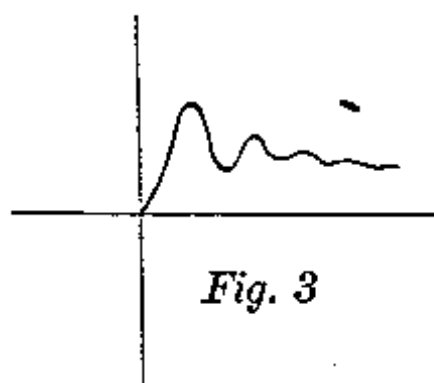
Experiments on photographing natural objects whose colors are for the most part continuous spectra with diffuse maxima, besides showing the necessity for a reflecting deposit, emphasized the necessity of this being of high reflecting power. Very fine-grained emulsions proved unsuitable for the reproduction of such colors in their luminosity values, and satisfactory results were obtained only when the silver content of the film was made as large as would still give color. The reason is at once apparent when we observe that the colors under consideration give at most only a few laminae near the surface, as shown in Fig. 2 and in the photographed section, Fig. 13. It is necessary not only that the reflecting power of these be large but that the diffuse deposit behind contribute a share of light in proportion to the light acting to produce it. If the grain is too fine these experiments and work with white light indicate that the separate particles do not act as reflecting surfaces.

The outcome of the experiments is to indicate that with a fairly coarse grain, overexposure being carefully avoided, developed with

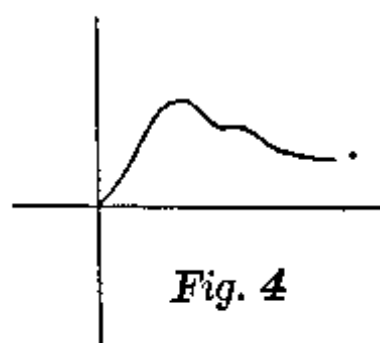
pyrogallic acid, there is probably a close approach to the condition of separate reflecting particles. With complex radiation, or with over-exposure, there cannot fail to be a certain amount of fusing together and consequent luminosity loss, and in the underexposed parts there is probably also a loss through the formation of deposit not starting



*Fig. 2*



*Fig. 3*



*Fig. 4*

FIG. 2.—Visibility curves for various sources:

- I. Two monochromatic sources.
- II. Three monochromatic sources.
- III. Spectrum band with sharp limits.
- IV. Type of spectrum of light from most natural objects.

FIG. 3.—Standing waves formed by white light from red to blue, as recorded in fine-grain emulsions.

FIG. 4.—Standing waves formed by white light from infra-red to ultra-violet, as recorded by coarse-grained emulsions.

till the light attains a certain intensity. With hydroquinone development and bleaching, the reflection is evidently more nearly of the type caused by changing refractive index.

This at once makes evident that for all photography where luminosity values must be preserved, a developer like pyrogallic acid giving a highly reflecting yet fairly transparent deposit is essential. On the

other hand, where complexity of spectral structure is to be reproduced, a deep-acting developer, which by proper treatment will give a transparent deposit, is desirable.

#### THE PRODUCTION OF WHITE

On Lippmann's theory, white is produced by reflection from particles of silver thickly and irregularly distributed through the film. Regularly spaced laminae would be entirely absent. Such a deposit would be formed in a perfectly isochromatic emulsion, provided the wave-lengths of the acting light varied between wide limits and the individual silver grains were of appreciable size. If, on the other hand, the acting light varied between rather narrow limits of wave-length, as from red to blue, the size of the silver grains being negligibly small in comparison to the shortest wave-length, a rapidly damped standing vibration of wave-length equal to the mean incident wave-length would result. In Fig. 3 is given the standing wave form due to light from red to blue, in Fig. 4 the form when the incident light is from infra-red to ultra-violet and the silver grain coarse.

Lippmann pictures have been made, exhibiting beautiful whites, yet general difficulty seems to have been experienced. This is partly due probably to the difficulty, with present known sensitizers, of securing isochromatism between wide limits. Several other theories have been proposed and other experimental methods tried to produce white. Lehmann concludes that the greenish appearance sometimes found in whites on short exposure is due to laminae formed in the manner described above. He corrects this by using a screen with three maxima of transmission: red, green, and blue. On short exposure whites will be reproduced as a mixture of these three colors. A serious objection to this method is that colors falling in the minima of transmission will be poorly reproduced.

Cajal from his work concludes that white is due to the formation of a mirror-like surface on the film and that this can be produced only by the use of amidol as an intensifier. The mirror-like appearance presented by the high-lights of Lippmann pictures readily lends itself to the idea that the surface is a silver mirror. That this is possible only when the picture is intensified with amidol is, however, a conclusion unsupported by other experimenters and contradicted by the

undoubted production of white by Neuhaus and others who did not use this intensifier.

The possible modes of production of white are therefore three: first, by a general diffuse deposit as an isochromatic emulsion; second, by forming laminae corresponding to red, green, and blue; third, by producing a mirror surface. The second method was not tried in the present investigation, as being obviously a compromise.

Attention was therefore turned to producing an isochromatic emulsion by combinations of color-screens and sensitizers. Numerous sensitizers were tried; of these much the best was isocol, in that it imparts a sensitiveness free of gaps or maxima. The sensitiveness given by it extends from deep red to blue and violet, gradually increasing toward the latter. Absorbing solutions of wool black, cobalt sulphocyanate, and iron sulphocyanate reduced the action in blue, green, and yellow to that in deep red and gave very satisfactory isochromatic action from red to ultra-violet.

Plates similar to those used in the study of monochromatic colors were prepared and exposed to white, at first with disappointing results. Not only was there practically no light reflected from the partially exposed parts, but the mirror-like high-lights were absolutely black. By intensification with amidol the plates could be made to reflect considerable light. This led to the question whether the intensifier did not merely increase the size of the grain, and whether this might not be done in the emulsion. That the grain was too fine to give whites by diffuse reflection was also indicated by the fact that a fogged plate appeared black and not white by reflection.

A series of emulsions were then made up containing increasing quantities of silver. These were exposed without the mercury mirror and the character of the deposit examined. It was at once apparent that while a very fine grain reflected diffusely very little light indeed, a coarser grain gave a strong white reflection which in the high lights became mirror-like. The brightest whites were given by an emulsion containing four times the silver content of that used for pure color work, or twice that used by Lippmann and others. This emulsion used with the mercury mirror gave perfect white. The theory that diffusely distributed reflecting particles formed in an isochromatic emulsion produce white is therefore supported.

As to the theory of Cajal that white is given only by a mirror-like surface, this was not supported by the results here obtained. The whites were quite perfect in the partially exposed parts. In fact it is the writer's opinion that the formation of the mirror appearance indicates rather the point where the white ceases to be good. A very slight exposure beyond this point, giving the clear yellow by transmission, results in the white becoming black. Everything is in agreement with the view before advanced that the mirror appearance is due to the merging-together of the separate particles with resulting loss in reflecting power. White will be given only so long as the particles are separate, being similar therefore to the white given by powdered glass or other substance transparent in the fused condition.

Since the range of sensitiveness of the emulsion is at best rather limited, and since the grain must be kept small enough to render all colors ordinarily met with, it would not be surprising if some tendency should exist to form laminae corresponding to the mean wave-length, i. e., green. No appearance of green on underexposure of whites was observed. Before mounting the prism the film had an orange tinge which turned to greenish on increasing the angle of incidence. The explanation of this is given by Fig. 4. Although complete laminae corresponding to green light are not formed the deposit of silver increases in density from the surface to the point where the first lamina would form. Rapid damping prevents the formation of more surfaces. There is therefore a slight gap between the surface and the heavy deposit, forming a single thin film. On mounting the prism the upper surface is virtually destroyed. The orange color is what we should expect from Wiener's explanation of the shift of all colors toward red as long as the surface reflection is active.

Sections supported these conclusions. Laminae were absent; in their place appeared a structureless deposit, increasing in strength toward the surface, reaching a maximum a short distance from it, the maximum corresponding to the distance in of the first laminae due to green light, as nearly as could be determined. This appearance is shown in Figure 11.

#### PHOTOGRAPHY OF NATURAL OBJECTS

To photograph natural objects conditions must be such as to give whites and colors of small spectral purity. This is secured by using



a fairly coarse-grained isochromatic emulsion developed with a developer giving a transparent highly reflecting deposit.

For experiments in this direction a number of different emulsions and modes of preparation were tried. Good results were obtained with very coarse-grained ones, but experience showed the proportions of silver bromide and gelatine in general use to be probably the most satisfactory. Little choice exists between the several modes of preparation published. The silver nitrate may be digested with part of the gelatine; dissolved in water and added, before mixing, to one part of the gelatine; dissolved in water and added to the gelatine containing the potassium bromide; or added in dry powdered form to the latter. The quantity of silver bromide is double that found best for monochromatic light-reproduction.

To secure isochromatism, isocol as a sensitizer, with the absorbing solutions above given, or, as the sensitiveness imparted by isocol is very fugitive, a more permanent combination of pinacyanol and pinaverdol, with a screen of wool black, was found to answer fairly well.

The only point in the manipulation not yet described is the choice of film thickness. The standing wave-structure being shallow, great thickness is no object. Speed, too, is gained by small depth. The thinnest film is obtained by flowing the warm emulsion on and off glass plates warmed to the same temperature. This gives a thickness of about  $\frac{1}{400}$  mm, on which most colors reproduce satisfactorily as far as the eye can tell. The resolving power is small of course, and some anomalous results are to be expected. Purple is about the only color of any complexity often met with, and the film should be thick enough to resolve its two maxima well. The most satisfactory thickness was obtained by flowing the emulsion on and off glass plates at room temperature, about  $\frac{1}{200}$  mm. Exposures with  $f/3.6$  on sunlit objects ranged from  $1\frac{1}{2}$  to 5 minutes according to sensitizers, etc.

With emulsions made up and used in this way good color rendering was obtained. The sum total of the results on photographing natural objects has been to vindicate the procedure indicated by theory and carried out by Lippmann. The deviations from that procedure by Lehmann and Cajal seem unnecessary to secure successful results.

The difficulties noted by all workers with the process as applied

PLATE XIX

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- 5. Section of film exposed to A 5461, developed with pyrogallic acid.
- 6. Film developed one minute with pyrogallic acid.
- 7. Film developed 15 minutes with pyrogallic acid.
- 8. Film stripped and developed from both sides.

- 9. Film developed with hydroquinone.
- 10. Bathed plate.
- 11. White (short exposure).
- 12. Four wave-lengths: A 6430, 5780, 5461, 5086.
- 13. Heterogeneous green light; naphthol-green color-screen.

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to photographing natural objects were found to be very real. They are in brief the great dependence of success on correct exposure and development. Very slight deviations will make the colors either weak or diluted with white. This is due to the laminae being few and close to the surface. With pure colors a certain amount of clogging up affects but a small part of all the laminae, in diluted colors practically all. A larger proportion (twice as much) of bromide in the developer than was used for pure colors was found materially to help the brilliancy of these colors. A larger percentage of failures is to be expected in any process of color photography than with black and white, since the eye is more sensitive to errors of treatment where color occurs. The sensitiveness of the Lippmann process to slight deviations from correct conditions is, however, much greater than the three-color method, and good results come only from repeated patient trials. When obtained they are extremely dependent on correct viewing conditions, to appear to any advantage. The colors being formed for the most part by two or three laminae backed up by a diffuse deposit, great care must be taken to exclude all light except that coming in the direction to be regularly reflected by the laminae. Light from other directions is not sent to the eye by the laminae but is by the diffuse deposit, causing a drowning-out of the colors with white light. By making the film excessively thin so that the laminae are formed, but not the deposit behind, the colors are more brilliant and less affected by conditions of illumination. Colors of any complexity, such as purple, however, suffer.

#### A SUBSTITUTE FOR THE MERCURY MIRROR

One of the obstacles to wide use of the Lippmann process is the necessity for a mercury mirror. Each plate-holder must be arranged as a tank into which before exposure mercury must be flowed. Several attempts have been made to obtain substitutes for the mercury. Krone<sup>1</sup> dispensed with it altogether, relying on the gelatine-air reflection, but the colors are then dull and unsatisfactory. Lehmann has flowed the emulsion on a collodion-coated polished metal plate. After exposure the composite film could be stripped and placed on a glass plate. Pure colors, spectra, etc., can be so reproduced, but those

<sup>1</sup> *Darstellung der natürlichen Farben durch Photographie*, 1894.

whose lamina system is close to the surface cannot, since that space is occupied by the collodion. Placing a silver mirror in close contact with the gelatine has the same objection.

The writer has recently discovered a substitute for the mercury mirror, of a form which permits the plates to be handled and used precisely as ordinary dry plates.

The procedure is as follows: A glass plate is heavily silvered and then flowed with a thick solution of celluloid in amyl-acetate. When this varnish is dry the plate is placed under water; this slowly works under the coating of celluloid, lifting it from the glass, and *bringing with it the silver*. This flexible silver mirror is immediately laid, silver surface down, on a wet Lippmann plate and allowed to dry there, a necessarily somewhat slow process. When dry, the gelatine film has the silver surface in optical contact with it. The plate may be then exposed at any time in an ordinary plate-holder. After exposure the celluloid film is stripped from the gelatine, taking with it most of the silver, the plate developed, and after thorough washing, the remains of the silver are removed with a tuft of wet cotton.

This substitute works perfectly for all types of colors, and except in the laboratory where a convenient dark room makes the use of the mercury mirror simple, facilitates the practical working of the process. Especially would it do so for the photographer who buys his plates ready made. In that case the only difference between ordinary and color photography would be the longer exposure in the latter case, and the necessary mounting of a prism on the picture, and of course the impossibility of copying.

A difficulty which has proved rather troublesome is that some of the best sensitizers are apt to lose their effect during the slow drying. Erythrosine acts perfectly; pinacyanol and pinaverdol are apt to fail. This can probably be overcome, either by different choice of sensitizers, by so treating these that slow drying does not harm, or perhaps by finding some more porous substance than celluloid which, acting the same in other respects, will permit quick drying. Collodion has been tried, but has not been found to strip off the gelatine well.

#### THREE-COLOR INTERFERENCE PICTURES

The capacity of the Lippmann film to reproduce pure spectrum colors easily and with certainty adapts it for an application to the

three-color process, published by the writer some time ago.<sup>1</sup> In the synthesis of the properly taken records of the three-color sensations spectrally pure red, green, and blue light are called for. The Lippmann film furnishes an unequalled means for securing these.

The method used was to place before the plate an opaque-line screen, having opaque spaces twice the width of the transparent. The three positive color records were projected one after the other with their appropriate colored lights, the line screen being moved each time the width of a clear space. The result was similar to the Joly picture, consisting of alternating lines of red, green, and blue.

In the first pictures so made the colored lights were obtained from sunlight by a monochromatic illuminator, but satisfactory purity and shortness of exposure were not secured. In experiments since carried out the line screen was removed from contact with the plate, as this necessitated a narrow source of light, and placed in contact with the three-color positive, an image of the screen and positive being formed by a Planar lens of fine defining power. For light-sources the cadmium red line ( $\lambda$  6439), the magnesium green ( $\lambda$  5170), and the lithium blue ( $\lambda$  4602) were found most available, obtained in the manner described in a following section.

The three-color interference pictures so made are of great brilliancy and beauty, especially if the hydroquinone development and bleaching are used, when the component colors are of practically ideal purity. Quite long exposures are necessary, amounting under the best conditions to a total of fifteen or twenty minutes. This time can probably be materially reduced. The pictures are, however, far more easy and certain besides being more brilliant than the regular Lippmann picture. They constitute an excellent means of carrying out the three-color principle, and have the interesting property of owing their color to the direct action of light and not to pigments or colored glasses as do the other three-color schemes. They can, besides, be duplicated indefinitely.

#### SENSITIZERS

During the progress of the work various color sensitizers were used, depending on the portion of the spectrum photographed. The list included erythrosine, cyanin, pinacyanol, pinaverdol, pinachrome,

<sup>1</sup> *Physical Review*, 24, 103, 1907.

isocol, homocol, and dicyanin. For bathing  $\frac{1}{100000}$  solutions in water were used, without ammonia; in the emulsion about one cc of a  $\frac{1}{1000}$  alcoholic solution to 100 cc of emulsion. Some observations of their behavior with these very slow emulsions are of interest.

In general it was found that bathed plates acted more cleanly and brilliantly, two sensitizers, isocol and homocol, acting very poorly in the emulsion. Ammonia was not used as it has a tendency to make the plates ripen, with consequent great increase in the grain. Bathed plates were, however, unsuitable for a large part of the work, since the sensitizing action extends only a short distance into the film, even with long bathing. Fig. 10 shows a section of a plate bathed fifteen minutes in a  $\frac{1}{100000}$  solution of homocol.

For green all of the sensitizers are good except cyanin, dicyanin, and pinacyanol. For the red, pinacyanol is far and away the best, the action of cyanin not extending far enough down, and that of dicyanin being too feeble. The great difficulty has been to sensitize for the light blue. On ordinary plates there is apt with many sensitizers to be a minimum in the blue green near  $\lambda$  5000. On these slow plates this gap is in the blue. This is owing to the natural sensitiveness of the plates only extending to the violet, while with fast plates it goes down to the blue. The descending curve of green sensitiveness imparted say by erythrosine meets the descending curve of the emulsions' own sensitiveness in the one case in the blue, in the other in the blue green. This was verified by greatly reducing the amount of sensitizer when the weak blue sensitiveness was stronger than the imparted sensitiveness in the blue green. This behavior of the plates makes sensitizer combinations, such as pinacyanol, homocol, and pinaverdol,<sup>1</sup> which fill the blue green in ordinary plates, inefficient here. A blue sensitizer, not needed for fast plates, is really required with the Lippmann plates. Isocol was the only sensitizer found which gave a sensitiveness free from gaps.<sup>2</sup>

As to the keeping qualities of the sensitized plates, it was found that the erythrosine-cyanin, or erythrosine-pinacyanol emulsion plates kept

<sup>1</sup> R. J. Wallace, *Astrophysical Journal*, 26, 299, 1907.

<sup>2</sup> The sensitizers used were of the following makes or sources: pinacyanol, pinaverdol, pinachrome, dicyanin, from Meister, Lucius, and Brüning; isocol, homocol, from the Bayer Co.; cyanin from Eimer & Amend, New York; erythrosine, from F. A. Reichardt, New York.

well, at least for a week or two. Bathed plates lost their sensitiveness quite rapidly; isocol-bathed plates in four or five hours, rendering them useful only for quickly carried out experiments. Pinaverdol in the emulsion in one case lost its action in four days. Pinacyanol and pinaverdol emulsions which dried slowly, as those prepared for use with the silver-celluloid mirror, sometimes showed complete loss of color-sensitiveness.

#### SOURCES OF MONOCHROMATIC LIGHT

In the study of monochromatic light reproduction and in making three-color interference pictures difficulty was experienced in finding suitable monochromatic sources. As the plates are very slow, and large surfaces were illuminated, sources capable of giving a large quantity of light for a long period were essential. Many ordinarily used sources were useless, either because of their small intrinsic brilliancy, or because of their too short life. The spark, the vacuum tube, the flame, arcs between easily melted metals, were among these. Another requisite was that the line used should not be so near other lines as to render its separation impossible by means of absorbing screens; resolution by means of a prism causing too much loss of light.

The following list of the most satisfactory sources found is given as of possible use in other lines of work where great intensity for a long period is required. It is by no means complete, since search was stopped when a satisfactory one for any color was found. Where obtainable the best sources are undoubtedly the Heraeus fused quartz lamps and the mercury vacuum arc. The open arcs here tested are as a rule more brilliant and are easily manipulated. Carbon was used uniformly as negative electrode:

*Red.* Lithium  $\lambda$  6708. Lithium sulphate in cored carbon.

Cadmium  $\lambda$  6439. Cadmium ordinarily burns with dense brown fumes which form a cake of brown oxide around the rapidly melting electrode. This may be avoided by melting the cadmium into a copper tube. The copper and cadmium lines appear together, but the red cadmium line is distant from the copper lines. A current of not more than four amperes is best.

*Orange.* Lithium  $\lambda$  6103. Lithium sulphate in cored carbon.

*Yellow.* Sodium  $\lambda$  5893. Sodium chloride in cored carbon.

*Green.* Thallium  $\lambda$  5360. Metallic thallium in cored carbon.

Magnesium  $\lambda$  5162. Magnesium powder in cored carbon.

5172

5167

Silver  $\lambda$  5460 and 5209. Silver, which in rods melts in a few seconds, burns steadily and brilliantly if a thick wire is placed in a cored carbon. Wire of 2 mm diameter in a carbon of 10 mm diameter gave excellent results.

Cadmium  $\lambda$  5085, obtained from an alloy of tin and cadmium in a cored carbon, one part by weight of cadmium to six of tin.

*Blue.* Lithium  $\lambda$  4602. Lithium sulphate in cored carbon.

Solutions of various aniline dyes separated most of these clearly. Copper chloride was found useful when either end of the spectrum was to be absorbed. With increasing concentration its absorption moves in, maintaining constantly a sharp boundary. Care must be taken that the temperature of the solution does not rise while in use as this causes widening of the absorption.

#### MISCELLANEOUS PHENOMENA

*Relative position of reproduced with reference to incident wave-lengths.*—Owing to the partial solubility of the gelatine and perhaps the washing-out of unaffected silver bromide the films show a general tendency to shrink in development and washing. This causes the colors to shift toward blue. This tendency is much more marked when the plates are fixed with "hypo." In most of the work fixing was dispensed with, Lehmann having found the pictures to keep perfectly without. This shift is much more marked with pure colors than with mixed, the interlaminary spaces being freer of deposit. This is well shown by photographing a continuous spectrum, using a rather wide slit, beside a line spectrum; the lines are reproduced as noticeably of shorter wave-length tint. If the slit is then closed up to extreme narrowness and exposure is made, the spectrum colors agree in tint with the monochromatic lines.

Bleaching with mercuric chloride, on the other hand, swells the film; the two processes of fixing and bleaching therefore tend to neutralize each other.

In working with very thick films a spurious "Doppler effect"



frequently occurs. The surface portions of the film wash away more than the deeper, so that a diffuse band of light appears on the blue side of the sharp line.

*Characteristic curve.*—In the photographic plate the density by transmission varies nearly directly with the time of exposure. This is because the deposit of silver is in logarithmic relation to the time of exposure, and the increase of opacity of an absorbing medium also follows such a law. When the deposit is viewed by reflection this relationship between exposure and intensity does not hold, the relation becomes logarithmic instead of linear. The exact relationship is complicated by absorption, which tends to hasten the "saturation point." A further complication arises in the Lippmann process with very short exposures, owing to the necessity for the reflecting particles to have a certain size and a certain closeness to each other to form a regularly reflecting surface. This was observed in a plate one-half of which was exposed behind a coarse opaque grating with lines covering  $\frac{2}{3}$  of the surface. The part behind the grating was exposed to nearly full exposure, the part not covered exposed until, when held at arm's length (where the lines were no longer visible), the two parts appeared of exactly the same density. By reflection the portion only partly covered by the full exposure was much more brilliant than the portion completely covered by the shorter exposure.

These several effects tend to shorten the scale of gradation of the plate, unfortunately, because the eye is more sensitive to this defect in colored than monochromatic pictures.

*Different rates of development for different colors.*—In developing three-color negatives where all three images are on one plate it has been observed that the three images develop at different rates although the exposures and the final densities are correctly proportioned. The Lippmann film exhibits the effect clearly. In making three-color interference pictures the colors were found to depend considerably on the time of development. With short development the green and blue predominated, with longer the red became stronger, the final picture showing, however, the relative exposures not too long for blue and green. Trouble from this effect was easily avoided by keeping the time of development constant and regulating the exposures for that development.

## SUMMARY OF RESULTS AND CONCLUSIONS

*Reproduction of monochromatic light.*—A smaller amount of silver bromide than usually employed gives purer reflected light from the Lippmann film.

Increase in thickness beyond about  $\frac{1}{200}$  mm causes no corresponding increase of purity so long as pyrogallic acid development is used.

The standing waves are formed throughout the thickness of the film; non-formation of laminae is due to surface action of the developer.

Other developers such as hydroquinone develop evenly through the film. By bleaching the deposit formed by their use films are obtained giving purer reflected colors than heretofore obtained and increasing in resolving power with thickness.

*Mixed colors.*—Films developed with pyrogallic acid have small capacity for rendering complex structure, but luminosity values are well preserved if the grain is not too fine or exposure too long.

With hydroquinone and bleaching, complex radiations are produced with a fidelity dependent only on the practically attainable thickness of film. This resolving power is at the cost of luminosity.

*White.*—White is produced by the action of white light on fairly coarse-grained rigidly isochromatic emulsions.

*Natural objects.*—The colors of natural objects are well reproduced by emulsions suitable for giving whites and mixed colors, i. e., of somewhat coarser grain than is best for pure colors.

Pictures of natural objects are more difficult to obtain than those of pure colors because of shallowness of the standing wave-structure.

*Substitute for the mercury mirror.*—A means has been found of affixing a silver reflecting surface in optical contact with the film, enabling the mercury mirror to be dispensed with.

*Three-color interference pictures.*—The Lippmann film, by reason of its capacity for reproducing pure colors, is well adapted to application to three-color photography.

In conclusion I wish to acknowledge my indebtedness to my father, Mr. Frederic E. Ives, whose life-long experience with photographic processes has always been freely placed at my service. I also wish to thank Professor J. S. Ames for the kindly interest he has shown in the progress of the work.