Feb. 9, 1937. P. D. BREWSTER 2,070,222

PHOTOGRAPHY

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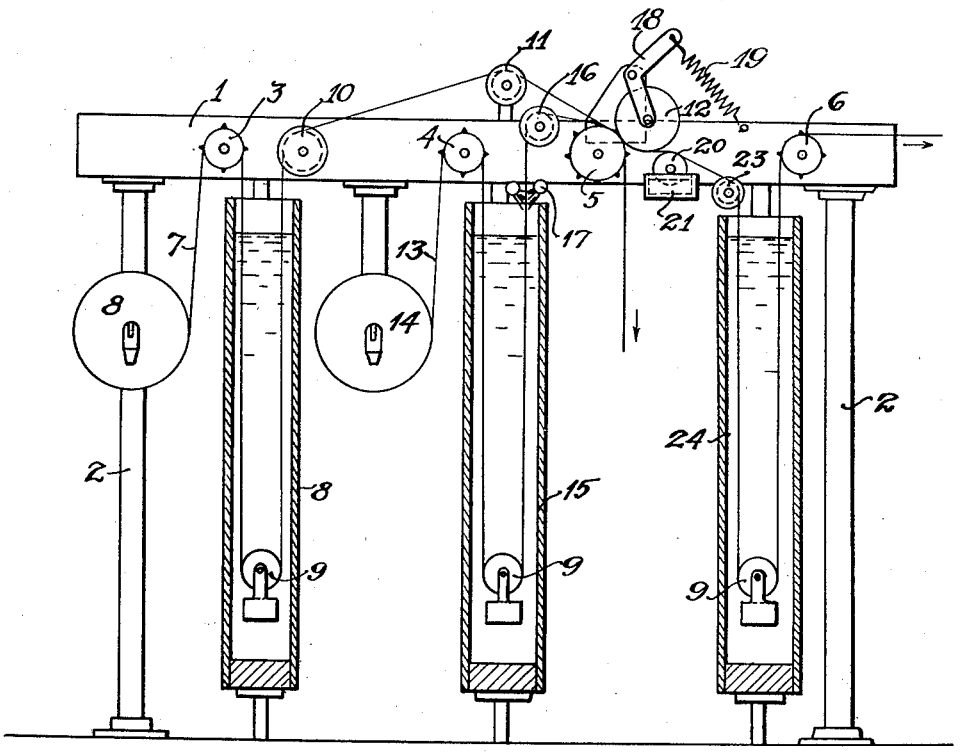

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PHOTOGRAPHY

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11 Claims. (Cl. 101—149)

This invention relates to subtractive color motion picture film, and more particularly to the production of two or more series of component color images on the same side of the film.

By at least one process of color cinematography now in use, a series of subtractive images of good definition, and in brilliant color can be produced in the gelatin coating on the film. The chief object of this invention is to add another series of images in a different color in suitable registry with and on the same side of the film with at least one other series of color images, produced by means easily applicable to long lengths of film with uniform results at low costs. Another object of the invention is the production of monochrome or black and white images on a plain gelatin coated film. To these and other ends the invention comprises the novel features hereinafter described.

The invention, in a simple form, comprises printing a matrix from a motion picture negative and processing it to produce relief images and impregnating the gelatin of the relief images with a salt. The matrix is pressed into contact with a gelatin coating on another film and some of the said salt is transferred and/or transfused into the said gelatin coating where it reacts with another substance already in the said gelatin coating, or to be applied later, to form a dye mordant. The gelatin is then treated with the proper dye to form an image series in black and white or monochrome.

In practice, I may impregnate the matrix with a 4% solution of silver nitrate, remove all excess liquid from the surface of the matrix and transfer the image in the form of this salt into the gelatin on a positive film and, as quickly as possible (to avoid image diffusion) treat the gelatin with a solution of potassium iodid, say 10%, to produce probably some form of silver iodid. After rinsing, the gelatin is treated with the proper colored dye, usually basic, such as Malachite Green, and washed to remove excess dye and dried. The sequence of these operations may be changed without departing from my invention, thus a precipitant (potassium iodid for example) can be transferred from the matrix to form the latent image which is rendered a dye mordant by being treated with a metallic salt (silver nitrate for example) and then dyed.

Good results are also obtained by coating a suitable support or base, usually celluloid with the following solution:—

Emulsion gelatin	g—	7
Silver nitrate	g—	1
Water to make	cc—	100

This solution may be coated at about 125° F. and at a speed of from 25 to 30 feet per minute, and dried. Methods for coating base with warm gelatin, immediately chilling and drying are well known, (see, for example, "Photographic Emulsions" by E. J. Wall). The matrix, carrying the images in the form of gelatin reliefs, is impregnated with a precipitant, such as potassium iodid, say in about a 10% solution, the excess liquid removed from the surface and the matrix pressed or rolled into contact with the gelatin coated film to transfer the precipitant to react with the silver nitrate to form a mordant image of silver iodid. The matrix or gelatin or both should be sufficiently moist to allow the transfer of the precipitant. The precipitant may be coated with the gelatin and the metallic salt transferred from the matrix or coating with plain gelatin and later impregnating with a salt or precipitant is permissible.

The gelatin coating on the positive may be impregnated first with a metallic salt (such as silver nitrate) or by the precipitant (such as potassium iodid) and the corresponding metallic salt or precipitant transferred from the matrix in the form of an image to react to form a relatively insoluble dye mordant. The gelatin on the positive may be saturated with dye and a latent image transferred to it from the matrix in the form of a metallic salt or precipitant and a mordant formed by treatment with the corresponding precipitant or metallic salt, which mordants the dye in situ with it.

An important feature of my invention is the transference of a series of images from a matrix in the form of diffusable ions into the gelatin coating of the positive film and the conversion of these ions by the action of other ions into a relatively insoluble dye mordant. It is not always essential that these ions be water soluble; for example, cuprous chlorid dissolved in hydrochloric acid transfers very well and after conversion to an iodid is an excellent mordant.

I am aware that a matrix has been impregnated with dye and the actual dye transferred into the gelatin on the color film, but this method requires the matrix to remain in actual contact with the color film for a considerable time, usually several minutes. By the present invention the transfer of the reagent from the matrix to the color film can be effected much more quickly, in some cases requiring but a fraction of a second, thus enabling the color film and the matrix to be brought together by a simple and inexpensive registry means at a rapid rate to produce a mordant that may be colored by a large number of dyes.

Dye-mordanting compounds of widely different composition can be formed within the gelatin by transferring one element or ion and causing it to react with another ion already in or later applied to the gelatin. A great vari-

ety of metallic salts act as mordants for certain dyes, as for example, salts of such metals as silver, copper, uranium, lead, tin, thorium, vanadium, cadmium, iron, nickel, cobalt and others. These metals usually mordant best when they are in the form of an iodid, thiocyanate, ferrocyanid, bromid or chlorid. The choice of a salt to be used for a particular purpose depends largely, of course, upon such factors as its mordanting power, its inherent color if any, its transparency, translucency, etc.

While these precipitants (iodid, ferrocyanid, etc.) are commonly used in the form of salts of ammonia or of the alkali metals, salts of other metals or earths may be used which are not incompatible with the salts of the heavier metals. Easily hydrolized acids, such as hydriotic or hydrobromic acids, may be used in place of their salts and are all referred to under the generic term reagents.

There are a number of well known means for producing a matrix. (See, for example, History of Three Color Photography, by E. J. Wall) such as printing from the negative through the celluloid onto the emulsion, developing in pyro very weak in sulfite (to harden the gelatin in situ with the image) fixing and washing in warm water to remove unhardened gelatin, leaving a relief image on the celluloid of hardened gelatin. The silver in the image may be removed by treating with potassium ferricyanid and hypo.

Black and white or monochrome pictures of good quality can be made by these methods without the use of silver emulsions and at a very low cost. Two or three color motion picture films may be made by transferring two or more series of latent component images from matrices (printed from proper color separation negatives) in suitable registry onto one or both sides of a film. All three color image series may be on one side of the film or two series of color images may be on one side and one series on the other of a double coated film. If two component color image series are to be produced by the above described method in the same gelatin coating I prefer to fix or lake the dye in the first image series before forming the second mordant. A method of laking is described later in this specification.

Color film having very good definition and color is being made commercially by "toning" the silver image into a suitably colored metallic salt or into a complex of salts of silver and other metals; or by "dye toning", which consists in converting the silver image into a dye mordant and treating with proper dye, all by means well known in the art. Prussian Blue (ferric ferrocyanid) is a well known example of "toning", while the dyed gel of silver iodid is an example of "dye toning."

Two color film can be made by these processes (toning or dye toning) in which one image series in color is on one side of a double coated film while the other image series in another color is on the other side of the film but in my opinion, it has been impossible to produce two image series in different colors and of satisfactory quality on one side of a film or in a single gelatin coating by "toning" or "dye toning" processes. It is very desirable, for production of three color film or two color single coated film, to be able to produce an additional image series in a different color in the same gelatin coating, or at least on the same side of the film. For example, two color film can be made by producing one image series, say red, on single coated film by "toning" or "dye toning" and producing by the methods described in this patent application, another color image series, say, green, on the same side of the film. Three color film can be made with a magenta (blue-red) image series on one side and a blue-green image series on the other side of a double coated film and the third image series in yellow produced on the same side as either the magenta or blue-green image series by the herein described means.

An important application of my invention is the production of an additional component color image series on the same side of the film, or in the same gelatin coating, bearing a component color image series produced by an entirely different process. In case the underlying mordants or dyes already in the film are affected by the chemicals or washes used for the production of the additional color images, I may prepare the film by "laking" the dyes to make them as insoluble as possible. Dyes, depending on their type or composition, may be fixed or laked by various means well known in the dyeing industry, such as treating with tannin, sodium acetate, aluminum sulphate, chromium sulphate, copper salts, such as the nitrate or sulphate, etc. I have found mixtures of several of these with tannin to be effective.

Recoating the film with gelatin, specially after the dyes have been laked, and forming the mordant in the recoated gelatin, makes the underlying images less liable to be affected by these chemicals.

In general, I prefer to use metallic salts for the production of the additional color image that are not too highly ionized as I find the more highly ionized salts have more tendency to attack the underlying mordants or dyes in the film. For example according to my experiments, cuprous chlorid (in hydrochloric acid) has much less effect on basic dyes mordanted on silver iodid than either silver nitrate or copper sulphate and by its use I can usually form the additional image in the same gelatin coating without laking the dyes or recoating. This greatly reduces the cost of processing and does not increase the thickness of the film, which are very important advantages.

If the film bearing the underlying color images is to be recoated, I prefer to use the same means for recoating with plain gelatin or gelatin containing metallic salts or precipitants that were described for production of monochrome images. Suitable means for securing registry between the underlying color images and the images transferred from the matrix are described later in the specification.

The preferred methods of producing two or three color film are similar except, that in making two color film a single coated film is used with a series of images of one component color in the gelatin, while in three color a double coated film is used and with a series of images of different component colors in the gelatin on opposite sides of the film. These images may be produced by any process provided that the mordant and dyes (if any are used) are not seriously affected by the chemicals used for the production of the additional color image series in the gelatin.

Three color film, by the preferred method, is made by printing from suitable separation negatives, in registry on the two sides of the double coated film, which is developed to pro-

duce a soft positive, full of detail. It is fixed, washed and treated with formaldehyde (about 4% by volume) and dried without washing, to produce silver images on the two sides.

These silver images are converted into dye mordants by the process described in my United States Patent Number 1,992,169 issued February 26, 1935, in which the film is then impregnated with a neutral or slightly alkalin solution of potassium iodid and potassium iodate in about an eight to one proportion, respectively, and forming together about a ten per cent solution. Excess liquid is removed and the film is subjected to a gas containing free acid ions (such as vapor from acetic acid) until the iodid and iodate react within the gelatin to produce sufficient free iodin to bleach or convert the silver image into probably a gel of silver iodid. Excess iodin is cleared by a reducing agent and the film rinsed and treated on the two sides with dyes of the proper color by well known means and washed to eliminate excess dye. The film with or without drying is ready for application of third color.

A suitable matrix or transfer film is printed through the celluloid from the separation negative, usually recorded by blue light, and processed to produce a series of images in the form of gelatin reliefs.

The preferred method consists in impregnating this matrix with the following solution:

Cuprous chlorid	g	25
Ammonium chlorid	g	100
Hydrochloric acid (conc)	cc	50
Potassium metabisulphite	g	10
Water to make	cc	1000

The cuprous chlorid, being insoluble in water, is dissolved by the hydrochloric acid, while the ammonium chlorid helps keep the copper in solution and the metabisulphite is present to decrease oxidization. Other solvents may be used for the copper chlorid or a water soluble copper salt such as the sulphate may be substituted. I prefer the cuprous chlorid as it seems to supply the necessary copper ions with least interference with the underlying mordants or dyes.

All excess liquid is removed or blown from the surface of the matrix which is rolled or pressed into contact with the color film so that the corresponding relief images on the matrix are superposed in proper registry with the images on the color film. Preferably, the color film is moistened before transfer. During this period of transfer, which may be less than a second, a portion of this copper salt passes or is transfused from the gelatin of the matrix into the color film, depending on the amount of gelatin relief in the matrix, to produce a latent image of good gradation in the metallic salt. As quickly as possible after the transfer, the color film is treated with a potassium iodid solution usually from 20% to 50% concentration, to convert the latent image into an insoluble mordant consisting of some form of copper iodid. The color film is then rinsed and treated with dye of proper color, such as auramin to produce a yellow. The film is washed, preferably with a weak acid, and dried to be ready for use. Copper thiocyanate (sulphocyanate), or copper ferrocyanid which are excellent mordants for basic dyes, may be produced by substituting a solution of ammonium thiocyanate or potassium ferrocyanid respectively (preferably 10%) for the potassium iodid.

In this preferred method for two or three color film production, the underlying images are mordanted on the gel of silver iodid which forms a strong bond with basic dyes, which tends to resist the solvent action of the metallic salts used for mordanting another color image in the same gelatin coating.

Any means can be used for pressing the matrix into contact with the two color film. Each individual image on the matrix may be registered with its corresponding image on the color film by being fed through a reciprocating transfer plate, equipped with registry pins that pass through the proper perforations in the matrix and the color film. By this method each image is printed separately. On account of the very short time usually required for the transfer of sufficient salts from the matrix into the color film, probably a tenth of a second or less, I prefer to roll them together between a sprocket, having registry teeth passing through the perforations in both films, and a rubber surfaced roller for forcing them in contact.

Such a mechanism is illustrated in the accompanying drawing, which is a side elevation, partially in section.

The mechanism consists of the gear box 1, supported on pipes 2, 2 from the floor. Suitable gearing, driven from a motor, operates the sprockets 3, 4, 5 and 6 at proper peripheral speed. The two color film 7, ready for the application of the third color, is mounted on the feed-off spool 8 and is fed, by means of sprocket 3 into the tube 8 where it is soaked in water. The film passes under the weighted roller 9 and guide rollers 10, 11 to the transfer sprocket 5. The matrix 13 is fed from the roll 14 by sprocket 4 and passed into tube 15 containing the metallic salt or precipitant to be transferred to the color film. In the preferred method this tube would contain cuprous chlorid dissolved in hydrochloric acid.

The matrix is drawn under the weighted roller 9 and over the guide roller 16 by the transfer sprocket 5. Before reaching this sprocket all the surplus moisture is preferably removed from the surface of the matrix by the air blasts 17, 17 on the two sides of the film. The matrix may be entirely dried at this point but I prefer that it should be moist without any drops or liquid on the surface which would be transferred and be converted into a dye mordant.

The transfer sprocket 5 preferably has teeth on one side that fit closely the sides of the perforations on both the color film and the matrix, thereby controlling the side registry of the images. The teeth on the other side of the sprocket are made narrower than the perforations, so they do not affect side registry at all, but serve to draw the film along, helped by the master teeth on the other side, against the pull of the weighted rollers, thereby registering the film horizontally. Teeth, on both sides of the sprocket, are made smaller than the perforations to avoid difficulty in rolling the films together.

The roller 12 is preferably made with a soft rubber periphery, recessed to allow the passage of the sprocket teeth, it serves to press the two films against the very smooth flat surface between the teeth on the sprocket. This roller may be conveniently mounted on the bellcrank lever 18 and be forced against the films by the spring 19. The pressure between the transfer sprocket and the roller causes the salts in the matrix to be transferred into the color film.

The film 7, after leaving the transfer sprocket,

passes over and rotates the roller **20**, which causes it to pick up liquid from the tray **21** and apply it to the side of the film which has received the salts from the matrix. In the preferred method this reagent is a 20% to 50% solution of potassium iodid. The color film is then drawn by sprocket **6** over roller **23** into the wash tube **24**, under the weighted roller **9** and is ready to be treated with dye of the proper color in tubes, or it may be treated with dye on one side only by mechanisms well known in this art.

If the color film was recoated with gelatin containing a metallic salt or precipitant, or coated with plain gelatin and impregnated with a metallic salt or reagent, the corresponding reagent or salt transferred from the matrix would react to form the dye mordant, and it is not necessary to treat the film with precipitant from tray **20**.

A separate patent application will be filed covering the mechanism above described.

Throughout the specification and claims "mordant" or "dye mordant" is understood to refer to a substance in or on the gelatin coating on the film that has the property of absorbing or fixing dyes in situ. "Latent image" is understood to refer to any image in or on the gelatin coating on the film consisting of a salt that may be invisible, but is or can be converted into a dye mordant, which also may be invisible, but when treated with the proper dyes, will appear as a colored image. "Metallic salt" is used to describe the salt, usually of a heavy metal, that provides the metallic ions for the mordant. "Precipitant" is understood to be a salt which provides other ions for the mordant, and is usually a halogen, thiocyanate or ferrocyanide, which reacts with the metallic salt to form the mordant. "A salt" when the term is used in connection with impregnating the gelatin or with the reaction of substances within the gelatin of the positive film, is understood to be a generic term covering either the "metallic salt" or "precipitant" as defined above. A "soluble salt" is understood to refer to a water soluble salt or a salt dissolved in any solvent which is not incompatible with the gelatin, salts or precipitants used for producing the additional mordant in the gelatin. By "insoluble mordant" is meant a mordant for dyes that is relatively insoluble and would not be seriously dissolved by treatment normally received by the film. "Component image" or "component color image" is understood to refer to any color image series, which may be combined with one or more component color image series to produce the picture in color. The two color component images are usually blue-green and orange-red, while in three color they are usually magenta (blue-red), blue-green and yellow. "A proper dye" is understood to mean a dye of the desired color that is capable of being fixed by the particular mordant used. "Gelatin", used for coating the film and in which these herein described reactions take place, is intended in a generic sense and refers to any substance that may be used photographically for this purpose, just as "celluloid" or any other material may be used for the supporting base.

I claim:

1. In a process for producing a series of dye images on a gelatin coated motion picture film, impregnating with a salt a series of gelatin matrix images, pressing the matrix against the gelatin coated film to transfer the series of images in the form of the salt into the gelatin, converting the said salt images into a dye mordant, and treating with proper dye.

2. In a process for producing a series of dye images fixed on a metallic mordant in gelatin coated motion picture film, impregnating a gelatin matrix bearing a series of images with a salt containing at least one ion of a dye mordant, pressing the matrix against the gelatin coated film to transfer the series of images in the form of the salt into the gelatin, converting the said salt images into dye mordants, and treating with proper dye.

3. In a process for producing two or more series of dye images in different colors, on the same side of a gelatin coated motion picture film already bearing one series of mordanted dye images comprising impregnating with a salt a series of gelatin matrix images, pressing the matrix against the gelatin coated film in proper image registry to transfer the series images in the form of a salt into the gelatin, converting the said salt images into a dye mordant, and treating with proper dye.

4. In a process for producing a series of dye images fixed on a metallic mordant in gelatin coated motion picture film comprising impregnating a gelatin matrix carrying a series of images with a salt containing at least one ion of the dye mordant, pressing the matrix against the gelatin coated film to transfer the images in the form of the salt into the gelatin, treating at any time during said process the said gelatin coating with another salt capable of reacting with the first named salt to form the dye mordant, and treating with proper dye.

5. In a process for producing a series of dye images fixed on a metallic mordant in gelatin coated motion picture film comprising impregnating a gelatin matrix bearing a series of images with a soluble metallic salt, pressing the matrix against the gelatin coated film to transfer the series of images in the form of the salt into the gelatin, treating the gelatin with a soluble precipitant to react with the metallic salt to form a dye mordant and treating with proper dye.

6. In a process for producing a series of dye images fixed on a metallic mordant in gelatin coated motion picture film comprising impregnating a gelatin matrix bearing a series of images with a soluble precipitant, pressing the matrix against the gelatin coated film to transfer the series of images in the form of a precipitant into the gelatin, treating the gelatin with a soluble metallic salt to react with the precipitant to form a dye mordant and treating with proper dye.

7. In a process for producing a series of dye images fixed on a metallic mordant in gelatin coated motion picture film comprising impregnating a gelatin matrix bearing a series of images with a soluble silver salt, pressing the matrix against the gelatin coated film to transfer the series of images in the form of the silver salt into the gelatin, treating the gelatin with a soluble precipitant to react with the silver salt to form a dye mordant and treating with proper dye.

8. In a process for producing a series of dye images fixed on a metallic mordant in gelatin coated motion picture film comprising impregnating a gelatin matrix bearing a series of images with a soluble copper salt, pressing the matrix against the gelatin coated film to trans-

fer the series of images in the form of the copper salt into the gelatin, treating the gelatin with a soluble precipitant to react with the copper salt to form a dye mordant and treating with proper dye.

9. In a process for producing a series of dye images fixed on a metallic mordant in gelatin coated motion picture film comprising impregnating a gelatin matrix bearing a series of images with a soluble metallic salt, pressing the matrix against the gelatin coated film to transfer the series of images in the form of the metallic salt into the gelatin, treating the gelatin with a soluble iodid to react with the metallic salt to form an iodid dye mordant and treating with proper dye.

10. In a process for producing a series of dye images fixed on a metallic mordant in gelatin coated motion picture film containing a metallic salt, impregnating a gelatin matrix bearing a series of images with a soluble precipitant, pressing the matrix against the gelatin coated film to transfer the precipitant into the gelatin to react with the metallic salt already there to form insoluble salt mordant images, and treating with proper dye.

11. In a process for producing a series of dye images fixed on a metallic mordant in gelatin coated motion picture film containing a precipitant, impregnating a gelatin matrix bearing a series of images with a soluble metallic salt, pressing the matrix against the gelatin coated film to transfer the metallic salt into the gelatin to react with the precipitant already there to form insoluble salt mordant images and treating with proper dye.

PERCY DOUGLAS BREWSTER.