UNITED STATES PATENT OFFICE.

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COLORING OR DYEING PHOTOGRAPHIC IMAGES

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To all whom it may concern:

Be it known that I, HOYT MILLER, a citizen of the United States, residing at New York, in the county and State of New York, have invented certain new and useful Improvements in Coloring or Dyeing Photographic Images, of which the following is a full, clear, and exact description.

This invention relates to the coloring or dyeing of photographic images on cinematographic film, lantern slides, transparencies, paper prints, etc., and for use in color photography. Briefly stated, its chief object is to convert the "black and white" image into a colored image and to change the silver present into a transparent form which will not materially interfere with the passage of light or materially degrade or alter the color of the dye, or other coloring matter used. To this and other ends the invention consists in the novel features hereinafter described.

In practising the invention in the preferred manner, the object mentioned above is attained by treating the silver image with iodin in a solution of an iodid (preferably potassium iodid). To the best of my knowledge and belief, the silver so treated is converted into silver iodid by the iodin and the silver iodid so produced then converted or "peptonized" by the potassium iodid into a "hydrosol" or "hydrogel" of silver iodid, or silver iodid in a colloidal form; the gelatin (or other vehicle) of the emulsion acting as a dialyzing medium to hold the particles of the hydrosol or colloidal iodid in the positions occupied by the corresponding silver particles that made up the original image. The substance into which the silver of the original image is converted is highly transparent, and possesses the property of absorbing and holding dyes; and since the particles composing the same occupy the positions of the silver particles of the original image, as stated above, they form an invisible (or at least a transparent) image exactly like the original. In short, the original opaque particles are replaced by transparent particles which are capable of absorbing and holding dyes, so that when the film is treated with the desired color or stain, as explained below, the original image is replaced by one consisting, at least in part, of the color used or some compound thereof with the substance of which the aforesaid transparent image was composed. Excess iodin or iodin stain in the film is got rid of, or "cleared," by a reducing agent, for example, sodium bisulfite; and after washing, the film or plate is treated with coloring matter of the desired tint, preferably an anilin dye, the dye used being preferably but not necessarily basic. The strength of the dye solution and the duration of the treatment are not material, as excess of dye can be washed out. The time for dyeing a good image with the dye known as malachite green in rather strong solution may be less than thirty seconds. If the image is to be viewed only by reflected light, like a paper print, the dyeing or coloring materials used may be opaque or capable of giving an opaque image but otherwise, if the image is to be viewed by transmitted light or is to be exhibited by projection.

After the above "bleaching" and while the film is wet (but before dyeing) there is ordinarily no trace of the image observable, though if the original image were very strong or dense an image in relief can sometimes be seen. If dried without dyeing, a faint image of a yellowish color usually appears, but there seems to be no material impairment of transparency. The faint image referred to probably consists of colloidal silver iodid, or possibly traces of ordinary (yellow) silver iodid.

In the dye treatment, basic dyes for the most part go chiefly into the image in proportion to the amount of silver in the original, leaving the high-lights colorless or nearly so. Usually a short wash suffices to clear the high-lights completely. Keeping the high-lights clear in the dye-bath is facilitated by hardening the film, as by means of formalin, before bleaching. It is also advantageous to have the dye-bath slightly acid, as by the addition of a little organic acid, for example acetic.

If the film is exposed to strong light, the image can be redeveloped by most of the developing agents, for example metol. If the hydrosol "image" is warmed while wet, or if immersed too long in a reducing solution, the hydrosol may lose transparency, indicating (probably) conversion into ordinary silver iodid.

I prefer that the image before bleaching be without trace of fog, full of detail, thin, and quite "soft", that is, devoid of harsh contrasts.

In practice, particularly in coloring films or plates for use in subtractive processes of color photography or cinematography, where it is desirable that the color-images be as little as possible degraded with residual black or other colored images, I proceed preferably as follows: The film bearing the image is first hardened in a ten per cent. solution of formalin or other suitable bath, then washed for a few minutes, and then bleached, by spraying or immersion, with a bath consisting of, say, iodin .1 (one-tenth) gram, potassium iodid 5 grams, and water to make 100 cc. This treatment is continued until the original image disappears and is replaced by a vague or faint image, having its high lights more or less stained with iodin, which usually takes from one to ten minutes. The film is then washed and treated with a one to two per cent. solution of sodium bisulfite or other reducing agent to remove the excess iodin or iodin stain, after which the film is washed to get rid of the reducing agent. The film should now be perfectly transparent with no image perceptible, except in slight relief if the original image were rather heavy. The film is then sprayed with or immersed in an aqueous dye bath, for example of malachite green or xylene red. The strength of the dye bath is immaterial. It may be very weak, or it may be a saturated solution. The time of treatment is also variable, depending, apparently, upon the strength of the dye bath, and the amount of silver in the original image, and may last from a few seconds to an hour. After thorough washing to suitably clear the high lights the film can be dried.

If the bleaching bath be acidified I prefer it to be approximately as follows: iodin 1 to 5 grams, potassium iodid 50 grams, acetic acid (three per cent. solution) 50 to 150 cc., water 1000 cc., depending on the rapidity of action desired.

If it is desired to color or "tone" monochromatic images on paper, plates, or cinematographic film, to represent night scenes, fire scenes, etc., or to secure a more pleasing or warmer tone than black and white, as for example, sepia, it is sometimes desirable to have a slightly stronger transparent residual image, in order to give the picture body or depth; in which case I may use a bleach of the following general type: potassium iodid 5 grams, acetic acid (three per cent. solution) 10 to 50 cc., potassium bichromate (one per cent. solution) 5 cc., water to make 100 cc. This bleaches the images rapidly and leaves the desired slight residual transparent yellow image.

Another excellent bleach, apparently producing its free iodin by the reaction of two or more of its ingredients, is composed of potassium iodid, acetic acid and potassium bichromate, say in about the proportion of 5 grams of the iodid, 5 cc. to 25 cc. of the acid (three per cent. solution), bichromate (one per cent. solution) 5 cc. to 25 cc., and water to make 100 cc.

Instead of a haloid salt the silver can be converted into a chromate, ferrocyanid or ferricyanid, as these salts in the form of a hydrosol or hydrogel are capable of acting as mordants for certain dyes or coloring matter. In lieu of iodin in the bleaching process chlorin or bromin (and theoretically fluorin) can be used, the potassium iodid being preferably replaced by the corresponding chlorid or bromid, or fluorid, as the case may be.

The acetic acid in the bleach can be replaced by hydriodic, nitric or formic acid, or by any other acid that does not have a harmful effect on the bleaching reaction or reactions. In the bleach last given, potassium permanganate or persulfate, or cerium permanganate or persulfate, or a similar substance, can be used with or instead of the potassium bichromate; the function of these reagents being (apparently) to release iodin from the potassium iodid. In short, I believe the bleach should contain a reagent adapted to convert the silver into a salt of silver (preferably a haloid salt) and one to convert the salt into a hydrosol, or adsorption compound, thereof.

The action of the first mentioned bleaching bath is accelerated or boosted by the addition of free iodin in alcohol, and the others by the addition of an oxidizing agent, as for example potassium bichromate. If by reason of the original image being overly dense or heavy the residual image is too strong for the purpose in hand the difficulty can, in general, be overcome by acidifying the bath or increasing the amount of acid therein. It has been observed that if the bleached film be dyed without being permitted to dry first, any residual image that the same may have had disappears or becomes less noticeable after dyeing and seems to have but little degrading effect on the color; whereas if the film with a considerable residual image

be dried first, the color of the image produced by dyeing is apt to be materially degraded.

The temperature of the various steps in the process is not important, except that at temperatures approximating 100° F. the transparent image (if wet) may become more or less opaque, probably by reversion of transparent hydrosol to opaque iodid, as stated above. This is in general disadvantageous if the image is to be viewed by transmitted light or exhibited by projection. For such purposes a temperature around 70° F. gives results that are eminently satisfactory.

Among the numerous dyes usable I may mention pyronin, acridin red B, xylene red, acridin orange, malachite green, thionin blue, methylene blue, auramin, methylene yellow, rhodamin, magenta, and methyl violet. In fact I have not found any basic anilin dye that is wholly unsatisfactory.

My belief that the silver is converted, at least in part, into a hydrosol, or a hydrogel finds confirmation in the work of Bancroft, Lottermoser, and Wall. See, for example, "*Journal of Physical Chemistry*" (Ithaca, N. Y.), vol. 14, and "*Journal f. Praktische Chemie*" (Leipzig), vol. 68, pp. 341–343, vol. 72, pp. 39–41, vol. 73, pp. 374–382.

It is to be understood that the invention is not limited to the precise materials and proportions given herein, but can be practised in other ways without departure from its spirit.

I claim:

1. The herein described method, comprising converting the silver of a photographic image into a transparent dye-absorptive substance, and treating the same with a dye of the desired color.

2. The herein described method, comprising converting the silver of a photographic image into a transparent adsorption compound of silver, and treating the same with a dye of the desired color.

3. The herein described method, comprising treating the silver of a photographic image with a halogen and a halogen salt, and treating the same with a dye of the desired color.

4. The herein described method, comprising treating the silver of a photographic image with a halogen and an iodid, and treating the same with a dye of the desired color.

5. The herein described method, comprising converting the silver of a photographic image into a hydrosol or hydrogel of a halogen compound of silver, and treating the same with a dye of the desired color.

6. The herein described method, comprising converting a photographic silver-image into an image composed of a hydrosol or hydrogel of silver iodid, and treating the same with a dye of the desired color.

7. The herein described method, comprising treating the silver of a photographic image with iodin in the presence of potassium iodid, and treating the same with a dye of the desired color.

8. The herein described method, comprising treating the silver of a photographic image with a bath containing an iodid, an acid, and an oxidizing agent, whereby iodin is set free until the image is suitably bleached, and treating the same with a dye of the desired color.

9. The herein described method, comprising treating the silver of a photographic image with iodin in the presence of a substance capable of converting silver iodid into a hydrosol or adsorption compound thereof, treating the image with a reducing agent, and treating the image with a dye of the desired color.

10. The herein described method, comprising bleaching a photographic image by treatment with iodin and an iodid, treating the bleached image with sodium bisulfite to clear the same of iodin, washing out the bisulfite, treating the image with a dye of the desired color, and then washing out the excess dye.

11. The herein described method, comprising bleaching the image with a solution containing potassium iodid, an acid, and potassium bichromate whereby iodin is set free; washing the bleached image; treating the washed image with sodium bisulfite to clear the same of iodin; washing the cleared image; treating the cleared and washed image with a dye of the desired color; and washing the dyed image to clear it of excess dye.

12. The herein described method, comprising hardening the emulsion which carries the silver composing the image by treatment with a suitable hardening agent; treating the image with a solution containing potassium iodid, acetic acid, and potassium bichromate, whereby iodin is set free and the image is bleached; washing the bleached image; treating the washed image with sodium bisulfite to clear the same; washing the cleared image; treating the cleared and washed image with a dye of the desired color; and washing the dyed image.

13. The herein described method of bleaching a photographic image, comprising treating the silver of the image with substances capable of converting the same into an adsorption compound of a silver salt.

14. The herein described method of bleaching a photographic image, compris-

ing converting the silver of the image into an adsorption compound or hydrosol of a silver salt.

15. The herein described method of bleaching a photographic image, which consists in treating the silver of the image with a halogen and a haloid salt.

16. A photograph having an image composed chiefly of a colored hydrosol or hydrogel of a salt of silver.

17. A photograph having an image composed chiefly of a colored hydrosol or hydrogel of a silver haloid.

18. A photograph having an image composed chiefly of a colored hydrosol or hydrogel of a silver iodid.

19. A photograph having an image composed chiefly of a hydrosol or hydrogel of a silver compound.

In testimony whereof I affix my signature in the presence of two subscribing witnesses.

HOYT MILLER.

Witnesses:
H. T. OLIVER,
E. G. MEYER.