

UNITED STATES PATENT OFFICE.

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BLEACHED AND COLORED IMAGE AND PROCESS OF MAKING THE SAME.

1,411,968.

Specification of Letters Patent.

Patented Apr. 4, 1922.

No Drawing.

Application filed April 25, 1918. Serial No. 230,676.

To all whom it may concern:

Be it known that I, WILLIAM V. D. KELLEY, citizen of the United States, and resident of Brooklyn, in the county of Kings and State of New York, have invented certain new and useful Improvements in Bleached and Colored Images and Processes of Making the Same, of which the following is a specification.

10 This invention relates to treating photographic images, and has for its object to enable the coloring of photographic images to be more accurately and easily accomplished than in processes heretofore proposed.

15 The invention is of especial use in the production of long strips of colored images for motion picture projection, such as disclosed in my Patent 1,259,411, issued March 20 12, 1918, but the invention is also applicable to plates, films, gum, and paper prints of various kinds, whether transparent or opaque.

25 The principal chemical processes for coloring images with which I am familiar obtain the color either by means of a metallic salt of the desired color, such as Prussian blue, known as toning, as in British Patent to Cox 15,648 dated June 30, 1914; or by 30 transforming the opaque silver of the image to a more or less transparent silver halid salt which will take up dye, as in Patent to Traube 1,093,503, April 14, 1914, or Miller 1,214,940, Feb. 6, 1917; or by treating the 35 gelatine with potassium bichromate so that it will absorb dye where not hardened by light. Some single colors are satisfactorily obtained by toning, but not all, especially the reds which are desired to be combined with 40 blue or blue green for natural color motion picture projection. In previous processes employing dyes mordanted by silver, the range of choice has been restricted to basic dyes because of the peculiar characteristics 45 of silver halid as mordanting agents. Also, basic dyes are dichroic, that is they alter in color at different densities, and furthermore there are no known unmixed basic colors entirely suitable for complementary two or 50 four color cycle projecting transparencies such as described in my aforesaid patent. It is characteristic of images bleached by the process of this invention that they do

not redevelop when treated with reducing agents, such as developers. Each of the 55 foregoing processes has presented one or more difficulties, such as in proper balancing of color, degradation of color, as in washing to clear the whites, since one color of the mixture will often wash out faster than 60 the other, thus changing the color entirely, prolonged time of treatment and delicacy of handling required, or lack of sharpness in color definition, all of which should be overcome in order that pictures in natural 65 colors may be commercially produced with any black and white motion picture projector.

This invention provides a process wherein acid and azo colors such as ponceaus, fast 70 reds, blues and greens, acid fuchsine, and yellows, now used in the wool dyeing industry, can be employed for dyeing photographic images, with the advantages of providing the necessary choice of pure, non- 75 dichroic colors, and complete transparency, fastness, brilliancy and sharpness of colored image in long lengths of commercial film.

80 The process starts with a black and white color value positive, which has been developed, and surplus silver halids removed by fixing in the usual manner. The coating is then hardened by immersion in a 10% formalin bath, and washed to remove excess of formalin. This sets the gelatine coating 85 and renders it dye repellant or tends to prevent it from retaining the dyes. The image containing metallic silver is next treated with a bath which precipitates or 90 deposits a transparent insoluble metallic mordant in situ with the silver, and in exact proportion thereto. This bath also changes the silver to a form, such as an oxide or halid, which can be dissolved out without 95 affecting the transparent metallic mordant. The action of this bath is, I believe, to deposit a transparent salt of copper or of chromium, or salts of both, or a transparent double salt of copper and chromium, in and proportionate to the silver, since the image 100 now has a brown color, possibly due to silver oxid, which color entirely disappears by treatment in the subsequent fixing bath, leaving no silver or silver compound in the residual transparent image. At the same 105 time, the transparent copper or chromium

compound is not affected either as to its transparency, or its character as a mordant.

The conversion bath preferably comprises potassium bichromate, 4.75 g.; potassium bromide, 9.5 g.; copper sulphate, 14 g.; hydrochloric acid, 10 cc.; water 1000 cc. Nitric or acetic acid can be used instead of hydrochloric acid. This is a hot bath, of from 100° F. to 110° F., and only requires a few minutes. The image, strip, plate or print, is then treated in a fixing bath to dissolve out the silver oxide, halid, or other silver compound. This may be done after as well as before the dyeing, without affecting the coloring. The fixing bath is an acid bath composed of sodium thiosulphate and sodium metabisulphite. After washing for five minutes, the image is ready for dyeing, being now transparent and containing agents capable of fixing the dyes. At this stage, owing to the action of the conversion bath, the gelatin in situ with the original silver has probably been additionally hardened, so that the gelatin as a whole is least absorbent to dye, and the transparent silver free mordanting image most absorbent to dye. This makes it easy to obtain brilliant whites and sharp contrasts in the final colored image.

The dye bath may vary in strength and temperature, but is preferably of about one-half per cent strength at a temperature of from 110° to 130° F. About two minutes' immersion will be sufficient. The previous treatments of hardening and conversion have so affected the coating that even a steaming hot dye bath will not injure the film, nor affect the mordanting and dye absorptive qualities of the transparent copper, or other silver free compounds composing the image. Washing in hot water at about 120° F. for about three minutes will clear the dye from the whites without degrading or weakening the dyed image, which has the original sharpness, is as transparent as a pure dye image, and has the requisite brilliancy of coloring.

An important feature of this invention is in its applicability to dyeing of photographic images, which increases the strength, brilliancy and fastness of the color, and gives perfectly clear whites. I believe I am the first to dye positive transparent silverless images with acid or azo dyes.

I have found that acid and azo dyes, and particularly those used in wool dyeing, such as ponceaus, fast reds, blues and greens, fuchsine, and yellows, when mordanted and treated in accordance with this invention, furnish the necessary range of pure transparent colors, and preserve their color characteristics at all densities. It is important in making motion picture projecting transparencies to use colors having these prop-

erties, as they answer all commercial requirements.

An alternative method which gives good results is to employ a 1/2% solution of sulphurous acid for brightening the color. This can be put in the dye bath, or used as a dip after the whites have been cleared of dye by washing. The dye bath can be at a temperature of 70° F., and its working will sometimes be improved by the addition of 20 cc. of acetic acid for each gram of dye. These colors may be in coatings on opposite sides of the support as in my patent aforesaid, the images in all cases preferably being registered by pins in the printing apparatus with reference to a predetermined perforation or perforations as a standard, as described in said patent. Also, both colors may be produced by this process, or three or more colors, so combined as to render complete color on each image area, or additively on successive image areas in projection as described in said patent. Reference is also made to said patent for directions as to handling double coated film in printing, and for protecting one color while applying the other, as all such details are fully illustrated therein and need not be repeated herein.

In this specification, where I say "transparent", I mean that the deposit is of such character as to transmit light without substantial loss, although it does not necessarily have the same degree of transparency as the natural pellicle or film. The transparent image of this invention before dyeing, can usually be faintly seen in transmitted light, and more clearly in reflected light.

While I prefer and specifically claim herein a process involving the production of a transparent silverless metallic compound capable of mordanting acid dyes, together with the resulting undyed and hot dyed images, I do not restrict myself to any particular temperature or metal, nor solely to acid or azo dyes, except as required by the appended claims. Where the claims specify acid dyes, I intend to cover azo dyes as well without expressly so stating in the alternative form. The invention in its broad aspects is applicable to other uses than photography, and is not to be restricted to any particular use except as stated.

What is claimed is:

1. Process of treating a light exposed developed silver image in a colloid carrier, which consists in bleaching said image with a bath which will produce an image capable of mordanting a dye and which will convert the silver into a salt non-redevelopable by a developer.

2. Process of treating a light exposed developed silver image in a colloid carrier, which consists in bleaching said image with

a bath which will convert the silver into a salt non-redevelopable by a developer and which will produce an image capable of mordanting an acid dye.

5 3. Process which consists in treating a photographic silver image in a colloid carrier to deposit therein and in proportion to the density thereof a substance capable of mordanting a dye and to render the silver salt non-redevelopable by a developer, and in then dyeing the image to produce a colored image.

15 4. The process which consists in treating a photographic silver image in a colloid carrier to deposit therein and in proportion to the density thereof a transparent substance capable of mordanting a dye and to render the silver salt non-redevelopable by a developer, and in then dyeing the image to produce a colored image.

20 5. The process which consists in treating a photographic silver image in a colloid carrier to deposit therein and in proportion to the density thereof a transparent substance capable of mordanting an acid dye and to form a silver salt non-redevelopable by a developer, and in then dyeing the image to produce an acid dye image.

30 6. The process which consists in treating a photographic image containing silver in a colloid carrier to form in situ with the silver a substance capable of mordanting a dye and to form a silver salt non-redevelopable by a developer, and in dyeing the mordanting substance.

35 7. The process which consists in treating a photographic silver image in a colloid carrier to deposit in situ with a silver salt a substance capable of mordanting an acid dye, and in dyeing the mordanting substance with an acid dye.

40 8. The process which consists in treating a photographic silver image in a colloid carrier to produce a silver salt non-redevelopable by a developer and to simultaneously deposit in situ with the silver salt a transparent substance capable of mordanting a dye, and in dyeing the deposited substance.

45 9. The process which consists in treating a photographic silver image in a colloid carrier to produce a silver salt non-redevelopable by a developer and to simultaneously deposit in situ with the silver salt a transparent substance capable of mordanting an acid dye, and in dyeing the deposited substance with an acid dye.

50 10. The process which consists in converting a photographic silver image in a colloid carrier into a soluble silver compound by treating such image to deposit in situ with said silver compound, a transparent substance comprising a copper salt capable of mordanting an acid dye, and in dyeing the copper salt with an acid dye.

55 11. The process which consists in harden-

ing a photographic coating containing a developed silver image, in bleaching the image so as to be non-redevelopable in a developer and capable of fixing a dye, and in dyeing the image.

70 12. The process which consists in hardening a photographic coating containing a developed silver image, in bleaching the image so as to be non-redevelopable in a developer and capable of fixing an acid dye, and in dyeing the image with an acid dye.

75 13. The process which consists in hardening a photographic coating containing a silver image, in treating the silver to form a transparent deposit capable of mordanting a dye and a silver salt non-redevelopable by a developer, in dyeing the transparent deposit, and in clearing the whites.

80 14. The process which consists in hardening a photographic coating containing a silver image, in treating the silver to form a transparent deposit capable of mordanting an acid dye and a silver salt non-redevelopable by a developer, in dyeing the transparent deposit with an acid dye, and in clearing the whites.

85 15. The process of treating a light exposed developed silver image which consists in hardening the emulsion containing said image, and in bleaching said image with a bath which will produce an image capable of mordanting a dye and which will convert the silver into a salt non-redevelopable by a developer.

90 16. The process of treating a light exposed developed silver image which consists in bleaching said image with a bath containing copper and chromium salts, which will form an image capable of mordanting a dye and which will react with the silver to form a silver salt non-redevelopable by a developer.

95 17. The process of treating a light exposed developed silver image which consists in hardening the emulsion containing said image and in bleaching said image with a bath containing copper and chromium salts, which will form an image capable of mordanting a dye and which will react with the silver to form a silver salt non-redevelopable by a developer.

100 18. The process of treating a light exposed developed silver image which consists in hardening the emulsion containing said image and in bleaching said image with a bath containing copper and chromium salts, which will form an image capable of mordanting an acid dye and which will react with the silver to form a silver salt non-redevelopable by a developer.

105 19. The process which consists in converting a photographic silver image in a colloid carrier into a silver compound non-redevelopable by a developer and in depositing in situ therewith a transparent com- 120 125 130

- pound of a metal capable of mordanting a dye, and in dyeing the carrier in a dye capable of being fixed by said deposited compound.
- 5 20. The process which consists in converting a photographic silver image in a colloid carrier into a silver compound soluble in a fixing bath and non-redevelopable by a developer and in depositing in situ
10 therewith a transparent compound of a metal capable of mordanting a dye, in dyeing the carrier in a dye capable of being fixed by said deposited compound, in clearing the whites, and in brightening the dyed
15 image.
21. The process which consists in dyeing a mordanting transparent image on a colloid carrier in a hot dye bath, and washing the image in hot water.
- 20 22. The process which consists in treating a photographic silver image in a colloid carrier to form both a transparent compound comprising copper and chromium salts capable of fixing a dye and a silver
25 compound non-redevelopable in a developer, and in dyeing such transparent compound.
23. The process which consists in treating a photographic silver image in a colloid
30 carrier to form both a transparent compound comprising copper and chromium salts capable of fixing an acid dye and a silver compound non-redevelopable in a developer, and in dyeing such transparent
35 compound with an acid dye.
24. A transparent photographic image in gelatin composed of a silver salt non-redevelopable in a developer and a salt of another metal capable of fixing a dye.
- 40 25. A transparent photographic image in gelatin composed of a silver salt non-redevelopable in a developer and a salt of another metal capable of fixing an acid dye.
26. A transparent photographic image in gelatin composed of a silver salt non-redevelopable in a developer and a salt of copper capable of fixing a dye.
- 45 27. A transparent photographic image in gelatin composed of a silver salt non-redevelopable in a developer and salts of copper and chromium capable of fixing a dye. 50
28. A color image in gelatin composed of a silver salt non-redevelopable in a developer, a salt of another metal, and a dye fixed to the latter.
29. A color image in gelatin composed of a transparent salt of a metal impregnated with an acid dye. 55
30. A color image in gelatin composed of a transparent copper salt impregnated with an acid dye. 60
31. A color image in gelatin composed of transparent copper-chromium salts impregnated with an acid dye.
32. A colloid carrier having therein an image comprising a light insensitive non-redevelopable silver salt and a salt of another metal capable of fixing a dye. 65
33. A photographic image in gelatin comprising a copper-chromium salt capable of fixing a dye. 70
34. A photographic image in gelatin comprising a copper-chromium salt capable of fixing an acid dye.
35. A color image in gelatin comprising a copper-chromium salt impregnated with a dye. 75
36. A color image in gelatin comprising a copper-chromium salt impregnated with an acid dye.
37. A color image in hardened gelatin composed of a transparent salt of a metal impregnated with an acid dye. 80
38. A color image in hardened gelatin comprising a copper-chromium salt impregnated with a dye. 85
39. A color image in hardened gelatin comprising a copper-chromium salt impregnated with an acid dye.
40. A photographic image in hardened gelatin comprising a copper-chromium salt capable of fixing an acid dye. 90
- Signed at New York city, in the county of New York and State of New York, this 24th day of April, A. D. 1918.

WILLIAM V. D. KELLEY.