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A. HAMBURGER

COLOR PHOTOGRAPHY AND THE LIKE

Filed March 5, 1923

Fig. 2.

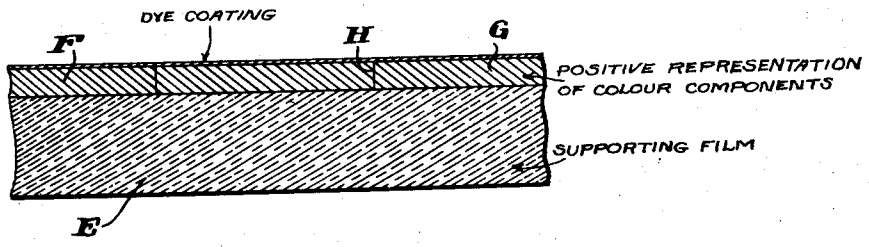
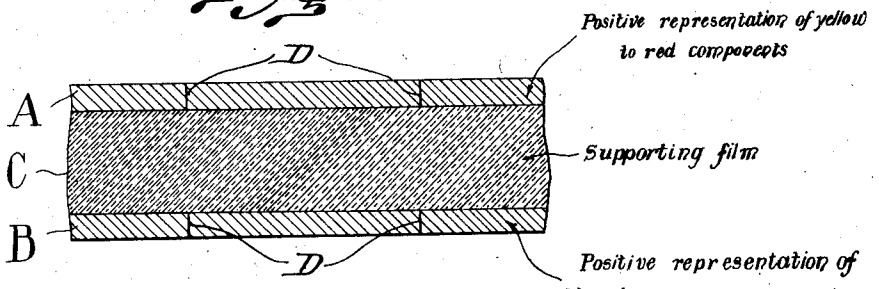


Fig. 1.



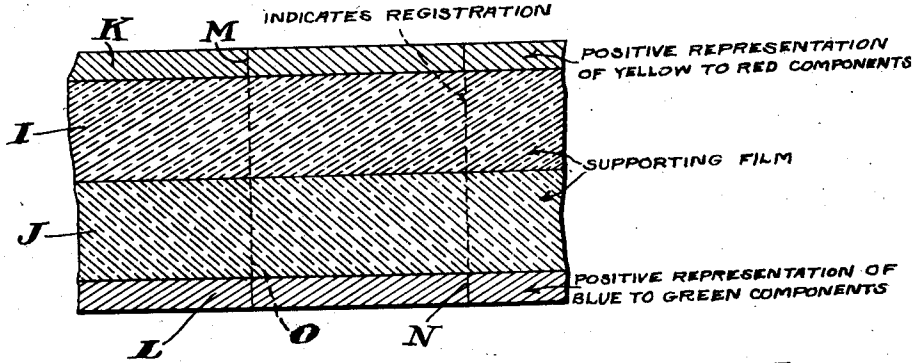


Fig. 3.

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UNITED STATES PATENT OFFICE.

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COLOR PHOTOGRAPHY AND THE LIKE.

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This invention relates to the production by photographic methods of pictures in color by dye toning, whether for direct observation or projection.

The invention is applicable in connection with color cinematography and for the production of color transparencies, color prints on a paper or other nontransparent base. It will herein be described mainly in connection with the production of color cinematograph films for projection in the usual projector. At present the processes for producing cinematograph films in colors are very complex or the results are not entirely pleasing. As a means towards reducing the complexity of the problem two color processes of cinematography have been provided in recent years but in these the color rendering is by no means akin to the colors of the originals from which the pictures have been made.

It has also been proposed to reduce silver positives and to dye them subsequently by certain basic dyes capable of being mordanted into the reduced silver, blended effects being sought by using first, say, a red basic dye and subsequently by a second dyeing by means, say of a yellow basic dye.

The result is a variation of shade down from red through red-orange to a pale shade called yellow but in reality still containing some red and should be more accurately described as yellow-orange. This effect is obtained by the absorption of these dyes due to varying degrees of dilution. In fact it is impracticable to obtain uniform results with a process of this character, presumably owing to the mordanting of the silver by such methods not giving a dyed image sufficiently stable to ensure safety in the washing which is necessary to free the non-silver portions of the image from the dyes without discharging the dye from the silver image.

It has also been proposed to modify the color of toned silver images by submitting a copper toned silver positive to a dye bath composed of suitable colors capable of being mordanted by the copper image, for example, a bath containing fuschin and auramin.

Similar objections arise in respect to this process as in the other mordanting process referred to above or any further process involving the dyeing of a previously reduced or mordanted silver image.

The object of the present invention is to provide an improved process which may be carried into effect in a very simple manner and give pictures pleasing in character with a wide range of colors and readily producible on an industrial basis free of the disadvantages referred to above.

To that end I have made a large number of experiments and have found that by the selection of suitable dyestuffs I can produce pictures in color having the advantages referred to above.

The invention in brief consists in applying to an emulsion containing a silver positive image a combination of dyes of different colors so chosen that on subsequent treatment of the film they will be retained in the film in accordance with the gradations of light and shade and yield colors due to the dye components substantially individually and to a certain extent in addition owing to the blending of the colors of the components.

In the accompanying briefed diagrammatic drawings:

Figure 1 illustrates one form of the present invention in which a supporting film is coated on two sides;

Figure 2 illustrates a modification in which a film in coated on one side only and indicates suitable dyestuffs applied thereto;

Figure 3 shows two supporting films, each coated with emulsion applied thereto, the two supports being superposed and registered.

In carrying this invention into effect in one form by way of example applied as an illustration to the production of cinematograph film for projection in colors, I prepare two negatives approximately representing the component complementary color values so that these component color values are represented in the image which is to be dyed by a density which will vary with the color value of each component color in the object photographed.

According to one method I employ two films (*a*) and (*b*), one, the (*a*) film, sensitized principally to green and blue-violet colors by erythrosine, and the other or (*b*) film sensitized principally to red, orange and yellow by bathing in a solution of pinacyanol (understood to be 1:1′-diethyl-carbocyanine iodide). The (*a*) film may be exposed without a light filter and the (*b*) film exposed through a tricolor red or red orange filter. The negatives after developing, fixing, washing and drying in the usual manner are printed onto films to form positives. I prefer to print them onto opposite sides of a film coated on both sides with light-sensitive emulsion.

In Figure 1 a middle supporting film C is shown coated on one side by a layer A which is intended to indicate the positive silver image representation of the yellow and red components and on the other side with a layer B, being the positive silver image representation of the blue and green components. Short lines D through the layer A are inserted to indicate division of the portion of film shown into a series of images. Next I apply a mixture of two or more dyes to each of the emulsions forming the two images one on each side of the film.

To the side of the film corresponding to the (*a*) negative I apply, for example, a mixture of rhodamine B and auramine in equal parts of 3% solutions, such solutions having been well mixed together. To the other side of the film, namely, that corresponding to the (*b*) negative I apply, for example, a mixture of malachite green containing a small amount, say 5%, of xylene red and brilliant green of similar strength to the former. These mixtures are conveniently applied in any suitable coating machine and the film is then allowed to stand for a few moments so that they set to a certain extent. It is then immersed in a bleaching liquor formed for example of a mixture of equal parts of 1% solutions of pure chromic acid and pure potassium ferricyanide to which 1/10th part of a 2% solution of thiocarbamide may be added. It remains in this bath for a few minutes until the silver has been thoroughly bleached and on removal therefrom is washed until the high lights and non-silver parts of the film are sufficiently clear. It will then be found that in the case of the series of pictures which have received the mixture of red and yellow dyes the result in color is a pleasing gradation from red to yellow in the color of the dyed image corresponding with the density of the original silver image so that the darker portions of the picture approach a dark red, while the lighter portions are approximately yellow, the dyes being discharged from the non-silver portion of each image leaving clear unstained whites. A similar action occurs on the other side of the film, the process resulting in emphasis of blue in the darker parts and a greenish coloration in the lighter parts.

As a whole therefore the double-coated film gives approximately the effect of a four-color process, or more accurately, a five-color process when proceeding on the lines given above because the bleached silver image of itself acts to give a ground work or greyish key varying in intensity according to the lights and shades of the object photographed.

The above dyes work well but other suitable dyes may be employed and it is a simple matter to test any particular dye mixtures because when applied to a film and treated as described above if on washing the lighter portions are colored substantially to the color of one dye and the shadows substantially to the color of the other with gradations between, they are suitable but it does not necessarily follow that the result will be so pleasing as with the dyes I have mentioned.

This gives a convenient method therefore of ascertaining whether any other dyes that it is desired to use are suitable for the process or not.

As regards the amount of dye applied to coat the surface the quantity of say the yellow dye should be such that it will on subsequent bleaching of the silver represent approximately the amount of pure yellow required to saturate the silver in the image which represents the yellow value of the negative from which it was printed.

Similarly the dye on the other side which represents the green and blue components of the picture is adjusted in strength to the green and blue values of the negative from which it was printed.

When the lightest portion of the silver image on either side becomes, on bleaching, saturated with a suitable yellow or light green dye such dye seems to act as a resist to further saturation of either image in proportion to the color value or density of the silver image representing it and such silver images being only partially saturated as regards the silver representing the other color components will absorb dye from successively applied layers or strata of two or more suitable dyes in the proportions required to represent practically all the color components of the object photographed, when two or more groups of dyed positives are thus combined.

It appears that as a result of this process a new series of dye compounds is formed comprising complexes of the dye with silver and chromium. The result is altogether distinct from that obtained when submitting a silver positive to the same bleaching or reducing solution and subsequently submitting this bleached silver positive to a dyeing process with the same basic dyes. In the latter case the result is unstable. This renders the result on the washing which is necessary to clear the non-silver portion of the image, both uneven and uncertain and according to the present invention the treatment yields an image which resists washing and has not the above defects. Apparently according to the process of this invention, referring for example to the yellow and red mixture of dyes, the silver or the reduction compound formed in the nascent state in the reducing bath has a greater affinity for the yellow dye than for the red dye so that there is a definite selection of the one color, namely the yellow, first from the mixture of the two colors, namely the yellow and red, as distinct from any effect due to dilution of a mixture. If therefore

there be present in the mixed dyes only sufficient yellow to saturate the portions of the image corresponding to the yellow sensation, it appears that this yellow dye is fully taken up or substantially so before the red begins to act with the result that the yellow is substantially the yellow of the dye and not that yellow mixed with red which would form a light shade of orange. In the deep red parts of the image the small amount of yellow employed is not sufficient to materially affect the color.

According to a modified process therefore instead of applying mixtures of the dyes to each side I first apply one dye, say, of each pair of dyes, and then apply the remaining dyes. Thus, the double coated film may be dyed as to the appropriate side first yellow and then re-dyed with a suitable red dye, the other side of the film first being dyed, say, green and then re-dyed with a suitable blue dye.

The second dye coatings should be sufficiently concentrated to yield on subsequent bleaching fully dyed silver images which thus become saturated with color, bleaching not being effected until all dyeing has been completed; the strength of both dye solutions and the strength of the bleach should be adjusted so that the bleaching and dyeing of the image take place practically simultaneously.

If it is desired to use only two colors instead of four for the purpose of obtaining in an easier and cheap manner color representations of limited range or for use, for example, in connection with the title parts of a cinematograph film this may be effected by employing a positive film coated on one side only and applying the two suitable colors thereto.

Such a modification is illustrated in Figure 2 in which a central supporting film E is coated on one side with a positive representation of two colors, this being indicated by the reference F, a mixture of suitable dyes being indicated at G so that the representation illustrates the film prior to its introduction into the bleaching solution. The part F is shown divided into a series of images by reference lines H.

In place of employing a film coated on both sides separate sensitized bases may be used which are superposed and sufficiently accurately registered. Figure 3 shows a modification of this kind, the two supporting films being indicated by the reference letters I and J, respectively, the emulsions on them being the positive representations of, in one case, yellow to red components and, in the other case, green to blue components, being indicated by the reference letters K and L, respectively. Subdivision into a series of images is shown by the short lines M and N and registration by the dotted lines O Instead of using special color sensitized films for the preparation of the negatives commercial panchromatic emulsions may be employed with the appropriate color filter. Also any other suitable color sensitizers than those mentioned above may be used.

In place of the bleaching bath described any other suitable bleaching solution may be used.

It is preferred to employ a bleaching solution in which the dyes are insoluble as I have found that with such dyes and a suitable bleaching agent the reduced silver images appear to have a catalytic action on the dyes and form stable dye salts with the reduced silver images, and at the same time all dye not absorbed by the actual silver image becomes washed out of the non-silver portions of the image when soaked in water, thus leaving the whites clear.

The names of the dyes given above are their usual commercial names. As far as possible the correct chemical names are given below, these mostly being taken from a manual of dyeing by Knecht, Rawson & Loewenthal, published in 1922 by Charles Griffin & Co., London, and "Colour Index", published by Society of Dyers and Colourists, Bradford, England:—

General name.	Scientific name.
Auramine	Amino-tetra-methyl-diamino-diphenylmethane chloride.
Brilliant green	Ethyl homologue of malachite green.
Malachite green	Oxalate or zinc double chloride of diamido-triphenyl-methane.
Pinacyanol	Is usually understood to be diethyl-carbocyanine iodide.
Rhodamine B	Basic hydrochloride of tetra-ethyl-meta-amido-phenol phthalein.
Xylene red	Sodium salt of tetra-ethyl-diamino-sulphophenyl-xanethyl sulphonate.

These are the chemical names of the various dyes as far as applicant can ascertain them, but it is recommended that dyes be obtained by the trade names and even then before using they should be tested to see that they give the results stated above because it is found that dyes made by different makers and supplied under the same name are liable to vary.

Where in this specification and claims I use the word "reduction" or "reducing agent" I mean photographic reduction or photographic reducing agent, respectively.

Having now described my invention, what I claim as new and desire to secure by Letters Patent is:—

1. A transparent base having on one side a single film continuous tone positive image corresponding substantially to yellow and red sensations and on the other a single film continuous tone positive image corresponding substantially to green and blue-green sensations of the same object.

2. A translucent film having on one side a

series of single layer continuous tone positive images suitable for projection, each corresponding substantially to yellow and red sensations and on the other side a series of single layer continuous tone positive images suitable for projection corresponding substantially to green and blue-green sensations.

3. A process for producing photographs in colors which consists in coating a positive silver image with a mixture of basic dyes and submitting the coated emulsion to a chromium reducing solution.

4. A process for producing photographs in colors which consists in coating an emulsion containing a positive image in silver with a mixture of basic dyes and submitting the coated emulsion to a solution containing chromic acid and potassium ferricyanide.

5. A process for the production of a colored image which consists in applying an organic dyestuff to an emulsion containing a photographic silver image and submitting the resultant product to the action of a photographic reducing agent.

6. A process for the production of a colored image which consists in applying an organic dyestuff to an emulsion containing a photographic silver image and submitting the resultant product to the action of a photographic reducing agent formed of potassium ferri-cyanide and chromic acid.

7. A process as claimed in claim 5 in which the photographic reducing agent contains chromium in acid form.

8. A process as claimed in claim 5 in which the photographic reducing agent contains chromic acid.

9. A method of producing color effects which includes the step of applying to a positive silver image a combination of dyes of different colors separable during a process of reduction to form translucent dye silver pigments suitable for projection.

10. A method for producing color effects which consists in applying to a positive silver image a combination of dyes of different colors which will separate during a process of reduction to a dye silver pigment state in proportion to density.

11. A positive silver image coated with a combination of dyes of different colors separable during a process of reduction to form translucent dye silver pigments suitable for projection.

12. An emulsion containing a developed and fixed silver image to which has been applied a combination of dyes of different colors which will separate to a dye silver pigment state during a process of reduction and form translucent dye silver pigments suitable for projection.

13. A support, an emulsion on said support and stable dye salts of silver in said emulsion.

14. A colored photographic image substantially insoluble in water and comprising a complex of silver, chromium and an organic dyestuff varying in intensity substantially in accordance with gradations of light and shade.

15. A cinematograph film including a series of colored photographic images substantially insoluble in water each comprising a complex of silver, chromium and an organic dyestuff varying in intensity substantially in accordance with gradations of light and shade.

16. A method of producing color effects which includes the step of applying to two emulsions on a single support, each emulsion containing a positive silver image, a combination of two separable dyes of different colors to one emulsion and a different combination of two separable dyes of different colors to the other emulsion.

17. A method of producing color effects which includes the step of applying to two emulsions on a single support, each emulsion containing a positive silver image, a combination of a mixture of red and yellow dyes to one emulsion and a mixture of green and blue dyes to the other emulsion.

18. A method of producing color effects which includes the step of applying to two emulsions on a single support, each emulsion containing a positive silver image, a combination of a mixture of auramine and rhodamine to one emulsion and a mixture of brilliant green and malachite green containing a small proportion of xylene red to the other emulsion.

19. A process for producing photographs in colors which consists in coating a photographic silver image with a mixture of dyes and subsequently submitting this dye coated silver image to the action of a reducing agent in which the dyes are substantially insoluble.

20. A photographic silver image coated uniformly with a paste containing a mixture of dyestuffs.

21. A photographic silver image coated uniformly with a mixture of dyestuffs which are insoluble in a solution containing chromic acid and potassium ferricyanide.

22. A process for producing photographs in colors which consists in coating a photographic silver image with a mixture of dyes, one of which is brilliant green and submitting this dye coated silver image to the action of a reducing agent in which the dyes are substantially insoluble.

23. A process for producing photographs in colors which consists in coating a photographic silver image with a mixture of dyes of which one is auramine and subsequently submitting this dye coated silver image to the action of a reducing agent in which the dyes are substantially insoluble.

24. The process which consists in submitting a dye coated emulsion containing a silver image to the action of a reducing agent in

which the dye coating is substantially insoluble.

25. A process for the production of a colored image which consists in applying an organic dyestuff to an emulsion containing a photographic silver image and submitting the resultant product to the action of a photographic reducing agent in which the organic dyestuff aforesaid is substantially insoluble.

26. A photographic representation in colors comprising a support, an emulsion on one side thereof, a photographic image containing a salt of silver in said emulsion and also containing at least two distinct colors substantially insoluble in water which vary substantially in accordance with the depth of the image for any particular color and are resistant to the action of a solution of potassium meta bisulphite.

27. A colored photographic image substantially insoluble in water and substantially resistant to the action of potassium meta bisulphite and comprising a complex of silver chromium and an organic dyestuff varying in intensity substantially in accordance with gradations of light and shade.

28. A colored photographic image comprising a complex including silver and an organic dyestuff substantially insoluble in water and substantially resistant to the action of a solution of potassium meta bisulphite and varying in intensity substantially in accordance with gradations of light and shade.

29. A colored photographic image comprising a complex containing silver and a basic organic dyestuff varying in intensity substantially in accordance with gradations of light and shade and substantially resistant to the action of water and a solution of potassium meta bisulphite.

30. A support, an emulsion on said support and stable derivatives of silver and of an organic dyestuff substantially insoluble in water and substantially resistant to the action of an aqueous solution of potassium meta bisulphite in said emulsion.

31. A support, an emulsion on said support and stable salts of silver and of an organic dyestuff substantially insoluble in water and substantially resistant to the action of an aqueous solution of potassium meta bisulphite, said salts comprising a complex of silver and of a dyestuff as aforesaid varying in intensity substantially in accordance with gradations of light and shade.

In testimony whereof I have signed my name to this specification.

ARON HAMBURGER.