UNITED STATES PATENT OFFICE.

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COLORED IMAGE AND PROCESS OF PRODUCING THE SAME.

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To all whom it may concern:

Be it known that I, JOHN I. CRABTREE, a resident of Rochester, in the county of Monroe and State of New York, have invented certain new and useful Improvements in Colored Images and Processes of Producing the Same, of which the following is a specification.

My invention relates to the production of colored images. More particularly it relates to the mordanting of dyes onto inorganic compounds which may be dispersed or distributed through a suitable transparent medium in the form of images. For example, I may add to or modify the image of a photographic picture so that a dye will be adsorbed thereon in correspondence with the original image, thus giving a colored image having approximately the same form and gradation as the original picture. The inorganic part of such colored picture may be further treated or removed. Flat or even tones may be similarly changed into colored tints suitable for light filters or general light-modifying purposes. A flat or even tone in the picture being but the image of an object having a flat or even tone, I shall use the word image generically to include flat tones as well as the more usual graded images.

The objects of my invention are to effect these results, carry out such a process, and obtain such a product by steps that will be under good control, that will be rapid, that will yield pictures having good gradation, that will not injure or impair the wearing qualities of the product, that will produce stable, clear and brilliant colors, and that will admit of ready duplication of effects. Other objects will hereinafter appear.

Since images made up of silver particles suspended in gelatin are most commonly met with in photographic practice, I will describe as an example of my invention, its application to a silver image. Generally stated, I treat or bleach the original or primary image in a suitable bath until there is present therein a silver and a copper salt, the latter being capable of acting as a mordant to dyes, especially basic dyes or amino derivatives. This resulting image may be considered as a secondary image. The bleached image is immersed in a suitable dye bath until sufficient dye is adsorbed or mordanted and the picture is thus colored. In certain cases I may dissolve away or fix out the silver salt wholly or partially, leaving an image of dye associated with the copper salt alone or with some of the silver salt. I may also convert the dye image into a lake.

To specifically illustrate my method I will describe the coloring of the silver images in motion-picture positive film. The film is immersed in any suitable or preferred fluid treating apparatus in a bleaching bath such as,—

Cupric sulfate	12 gr.
Potassium ferricyanid	12 gr.
Potassium citrate	75 gr.
Ammonium carbonate	6 gr.
Water to	1 liter.

This bleaching bath may be varied by substituting ingredients which will furnish equivalent ions. For example sodium salts may be used in place of the potassium salts.

After the film images have been bleached to the characteristic brown or copper tone, the film is rinsed free from the excess of the bleaching solution, and is then immersed in a bath of a suitable dye. The type of dye which may be employed is illustrated in the following list,—

Tannin heliotrope.
Rhodamin 6 G.
Thioflavin.
Methyl green.
Victoria green.
Methylene blue.

To best control the dyeing, the temperature of the bath may be around 70° F. and the strength of the bath may be about 0.1 or 0.2% to provide good speed without staining the highlights. Where desired, with

some dyes, such as methyl green, a little acid may be added (say 0.1% acetic acid) to accelerate the dyeing and to prevent the formation of a scum on the film. The speed of the action is also increased somewhat by a higher temperature. The end point of the dyeing action is recognized by the disappearance of the copper tone from the shadows of the image, although no serious results occur from a longer treatment.

After dyeing, the film is washed until the highlights are sufficiently free from dye. This may be for example twenty minutes to an hour at 50° F. The time of washing may be shortened by using dilute acetic acid solution, for example of 0.2% strength.

The images thus obtained contain the copper ferrocyanid mordant and are suitable for projection in that state. For certain purposes, such as polychrome photography, it is desirable to enhance the transparency of the colored image. This may be done by immersing the film in a fixing bath of sodium thiosulfate and then washing it. If the dyed image appears to be injured or diffused when the silver salt is wholly or partially dissolved away, the dye image can often be treated to form a lake, some reagents such as 0.25% tannic acid and 0.25% sodium acetate being added to the fixing bath.

The colored images may be obtained in a state of great transparency also by using a very fine grained primary or silver image, it being generally true that the finer the grains in the original image, the more brilliant and transparent will be the final results. Hence, it is possible to avoid using a fixing bath.

To give extra brilliancy to film that is to be projected, I may only partially bleach the black and white image in the first instance and subsequently fix out the same. The effect is to tone the lighter parts of the image and leave the shadows only partially colored.

The theory of what takes place in the example of my process given above, appears to be that the copper and ferricyanid ions react with the minute silver particles of the original image to form an image composed of both insoluble copper ferrocyanid and silver ferrocyanid, the sliver acting as a reducing agent with respect to the ferricyanid. The dye is adsorbed chiefly on the copper ferrocyanid, and the silver ferrocyanid is dissolved out by the thiosulfate bath. While this appears to be what takes place, a knowledge of the exact theory of the reactions is obviously not indispensable to carrying out my invention in practice. The colored film was found by comparative tests to be unimpaired in wearing qualities and, by attending to the manipulative details given hereinabove, effects could be duplicated with certainty. Since the mordanting salt was formed substantially in correspondence or proportion to the original image and since the dye was adsorbed substantially in proportion to the mordanting salt, the dyed image will have a gradation similar to that of the original image.

I claim:

1. The process of producing a colored image which comprises, forming an image containing copper ferrocyanid capable of acting as a mordant and treating said image containing copper ferrocyanid with a suitable dye until sufficient dye is mordanted by said copper ferrocyanid to produce a colored image.

2. The process of producing a colored image which comprises, forming an image containing a copper salt capable of acting as a mordant and treating said image containing said salt with a suitable dye until sufficient dye is mordanted by said copper salt to produce a colored image.

3. The process of converting a primary image into a colored image which comprises, forming in substantial proportion to the primary image a secondary image containing a copper salt capable of acting as a mordant and treating said secondary image containing the copper salt with a suitable dye until sufficient dye is mordanted by said copper salt to produce a colored image.

4. The process of producing a colored image from a metallic image which comprises, treating said metallic image in a bath containing copper ions and ferricyanid ions to form a secondary image containing a mordant, treating said secondary image with a suitable dye until sufficient dye is mordanted by said secondary image to produce a colored image.

5. The process of producing a colored image from a silver image which comprises, treating said silver image in a bath containing copper ions and ferricyanid ions to form a secondary image containing a mordant, treating said secondary image with a suitable basic dye until sufficient dye is mordanted by said secondary image to produce a colored image.

6. The process of producing a colored image from a silver image which comprises, treating said silver image in a bath containing copper ions and ferricyanid ions until a secondary image containing a mordant is formed, treating said secondary image with a dilute bath of a basic dye containing a dilute acid until sufficient dye is mordanted by said secondary image to produce a colored image.

7. The process of producing a colored image from a silver image which comprises, treating said silver image in a bath containing copper ions and ferricyanid ions to form a secondary image containing a mordant, rinsing, treating said secondary image with a suitable dye until sufficient dye is mor-

danted by said secondary image to produce a colored image, washing out soluble salts and unmordanted dye from said image, and treating said image with a bath containing a solvent for silver salts.

8. The process of producing a colored image from a primary silver image which comprises, treating said silver image in a bath containing copper ions and ferricyanid ions to form a secondary image containing a mordant but stopping the treatment before all the silver in the densest parts of the primary image is reached by said ions, rinsing to check further action by said ions, treating with a suitable dye until sufficient dye is mordanted by said secondary image, washing, and fixing the image.

9. The process of obtaining a very transparent colored image which comprises, treating a very fine grained metallic primary image with a bath containing copper ions and ferricyanid ions to form a secondary image containing a mordant, treating said secondary image with a suitable dye until sufficient dye is adsorbed by said secondary image to produce a very transparent colored image.

10. The process of producing a colored image from a silver image which comprises, treating said silver image in a bath containing copper ions and ferricyanid ions to form a secondary image containing a mordant, treating said secondary image with a suitable dye until sufficient dye is mordanted by said secondary image to produce a colored image, washing, and treating in a bath containing a solvent for silver salts and a substance which reacts with the dye to form a lake.

11. An article of manufacture comprising a transparent body containing a colored image which includes a copper salt associated with a dye.

12. An article of manufacture comprising a transparent colloid layer containing a colored image which includes copper ferrocyanid and a dye mordanted thereby.

13. An article of manufacture comprising a layer of gelatin on a transparent base, said layer containing a colored image including copper ferrocyanid, silver ferrocyanid, and an adsorbed dye.

14. A motion picture positive film comprising a flexible transparent base, a transparent gelatin layer thereon and a colored image in said gelatin including copper ferrocyanid and a dye mordanted thereby.

15. A colored photographic image consisting of a copper-toned and mordant-dyed image.

16. A colored photograph comprising a colloid layer containing a copper-toned red image and combined therewith a selectively mordant-dyed image.

17. The method of producing a color photographic image consisting in copper-toning a silver image and subjecting it to a bath of soluble dye capable of being selectively mordanted by the copper image.

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Witnesses:
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