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METHOD OF PRODUCING PHOTOGRAPHIC PICTURES IN COLORS

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This invention relates to a method of producing photographic pictures in colors.

The present invention avoids the disadvantages of all former known methods it being possible according to the invention to obtain in direct fashion from diffusely colored positive or negative silver-deposit images, respectively positive or negative color images. There is a wide range of selection as regards the dyes employed, as it is possible to use dyes of different classes. It is possible to convert a silver image into a color picture in a shortness of time heretofore unknown.

The method of producing reversed dyestuff images according to the present invention is characterized in that photographic images, diffusely colored with non-leuco base forming dyestuffs and consisting of a metal deposit image, have the dyestuff permanently decolorized, bleached or destroyed at the points of the metal deposit by means of a fluid agent which itself is incapable, during the normal time of treatment, of destroying the dye by oxidation or reduction but de-colorizes, bleaches or destroys the dye by the formation of reducing reaction products or reducing complex compounds of the metal. These reducing agents are formed and act while the finely distributed metal is attacked by the treating agent.

These reagents will be referred to as "non-destructive means" in the claims, or "non-destructive compounds", as the same do not attack the dyestuff at the points free of metal deposit for such periods of treatment as are concerned in actual practice.

An example of such a non-destructive bath, is given below:

	Grammes
Thiourea	10
Citric acid	5
Water	200

In the case of these baths there occurs a destruction of the dyes simultaneously with an oxidation of the metallic image at the points where silver is present, i. e. the metallic silver is converted into a silver compound, which may be dssolved.

Reagents which are "destructive" within the meaning of the present invention are, for example, the following substances which act detrimentally on the dyestuffs or on the photographic layer: powerful oxidizing and etching agents such as potassium permanganate, bromic acid and hydrogen peroxide; powerful reducing agents such as sodium hydrosulphite and stannous chloride ($SnCl_2$); powerful concentrated acids such as concentrated sulphuric acid and concentrated solutions of potassium or sodium hydroxide. This is not intended to be a complete list of "destructive" reagents, but serves to indicate the types of reagents which are not used in the present invention.

It has been found that a large number of compounds act in a manner to reverse a silver deposit image, i. e. to destroy the dye in a diffusely colored silver image at the points of the silver deposit, there being formed at first silver salts and reducing agents, which act locally in destructive fashion on the dye, or the metallic silver image passing into solution with formation of a complex compound, this also acting in color-destructive manner. Practically all sulphur compounds which possess the above-mentioned properties are suitable for this purpose, organic or inorganic, also nitrous organic compounds of the urea group for example allylthiourea, diphenyl thiourea, or similar compounds, or isomers of sulphuric ureas, cyanides, thio-cyanates, etc., for example sodium sulphide, calcium polysulphide, cystein salts, guanidine, amino guanidines, thiodiglycolic acid, thio-semicarbazide, semi-carbazide, etc. It is shown that these substances are effective in neutral, alkaline or acid solution. The effectiveness of these compounds, however, greatly varies, and is in part of a very slow kind, so that the same are not all equally suitable for practical purposes. According to the invention, however, the effect may be greatly accelerated if reducing substances are added with or without acid, which substances alone do not destroy the dye or are only effective in very slow fashion, or also by adding a plurality of little effective agents. Reducing substances of this nature are phenols, amino phenols and their substitutional products, aldehyde, sugar, etc., or possibly also acids. The addition of these substances also acts in accelerating fashion in the case of the means referred to above.

To the above baths it is also possible to add a hardening means, such as alum.

Obviously it is also possible under certain circumstances to replace the metallic silver-deposit image by a deposit of equal effect of another metal, for example mercury.

The majority of the substantive and acid azo-dyes, and some basic dyes, vat dyes, alizarine dyes, etc., may be used for this purpose. By way of example there may be mentioned Heliotrope BB (321), Chlor-Amine light red 7BL (Sandoz,

Basel, Switzerland), Diamine rose G (119), BBF (Casella), Diamine pure blue FF (424), Naphtamine light blue 4B (Kalle & Co., Biebrich), etc. All of these dyestuffs can be permanently destroyed by reducing means and they lose their dyestuff character by this reduction process Their chemical constitution excludes the formation, by reduction, of a leuco-base. Therefore the colorless parts of the image, produced by the present invention, remain in this condition for a substantially unlimited period of time. Silver images colored throughout the layer are treated in a color-destructive bath set forth below. The colors are here identified by numbers where known from the Schultz-Farbstoff-tabellen, edit. 5, 1920.

As example of color-destructive baths there may be mentioned the following:

COMPOUNDS OF THE UREA (THIO-UREA AND IMIDO-UREA) GROUPS

1. *Thiocarbamide.*—A halogen silver layer is colored with azo-dyestuffs, for example, Helitrope BB, Chloramine light red 7, Diamine fast pink G, BBF (Casella), Diamine pure blue FF, Naphthamine light blue 4B, this emulsion being poured in the known fashion on to a suitable backing. After developing and fixing, merely the silver image is visible. The image is then treated with a solution of 5 grammes of thiocarbamide, 2½ grammes of citric acid and 100 grammes of water. In this bath the silver is dissolved out simultaneously with the destruction of the dyestuff, and should any traces of silver deposit still remain in the picture, these are removed in a reducer.

2. *Semi-carbazide.*—A layer colored with Diamine fast pink G is treated with a solution comprising

	Grammes
Water	100
Semi-carbazide	5
Sulphuric acid	1

Following this treatment, during which the dyestuff is destroyed at the points of the metallic image, the remnant silver is finally expelled in a photographic reducing agent of any known kind, such, for example, as a Farmer reducer.

3. *Thio semi-carbazide.*—A layer colored with Diamine fast pink G is treated with a solution comprising

	Grammes
Water	100
Thio semi-carbazide	5
Sulphuric acid	1

The following treatment is then as in the preceding examples.

4. *Guanidine.*—A layer colored with Heliotrope BB treated therewith.

5. *Amido-Guanidine.*—A layer colored with Diamine fast pink G treated therewith. The following treatment is then as above.

INDIFFERENT INORGANIC SULPHUR COMPOUNDS

1. *Sodium sulphide.*—A layer colored with Diamine pure blue FF is treated with a solution comprising

	Grammes
Water	100
Sodium sulphide	5

and an addition of monomethyl paramido phenol sulphate. The following treatment is then as above.

INDIFFERENT ORGANIC SULPHUR COMPOUNDS

1. *Thiodiglycolic acid.*—A layer colored with Diamine fast pink G is treated with a solution comprising

	Grammes
Water	100
Thiodiglycolic acid and grape sugar	5

This example is also one of the uses of indifferent acids.

Naturally a short washing is required in water after the toning process. The baths may also be employed immediately following the development.

The rate of the color destruction depends in the case of numerous dyes on the amount of free acids which may be present.

This method of simple conversion of the silver image into a color image may be employed with particular advantage in the case of color photography and kinematography. Variously colored part-layers selectively sensitive to different spectral regions are poured one on top of the other, or differently colored and sensitized emulsions mixed together by a re-emulsifying process (as described by Schinzel in the "Chemiker Zeitung" 1908, page 665 Köthen, Anhalt, Germany) are simultaneously exposed and developed. The images, consisting of intimately connected part-images, are converted into the corresponding negative or positive multi-color image in one of the baths referred to in the above examples. Suitable dyes are, for example, Diamine pure blue FF (424) Mordant yellow GG (177), Diamine rose BBF (Casella).

This method also provides the possibility of simple, cheap and rapid reversal of negatives and kinematograph films. In addition, this reversing process also permits of the use of kinematograph films prior to the reversal as negatives.

In the case of substantive and acid dyes it is usually unnecessary to fix these in the gelatine. It is desirable, however, if a plurality of different colored layers are disposed one above the other to fix these in the known manner by mordant formation or deposition. The sharpness of kinematograph films thus toned is also improved. For many purposes it is desirable to employ dyes which bleach out with different speeds, for example if the layers in the case of multi-color photography are poured one upon the other and the destructive bath is more effective on the surface than in the depth of the part-layers a more slowly bleaching dye will therefore be employed. For the production of double tones very effective colors may also be obtained if dyes of varying bleaching rapidity are employed, for example azo Fuchsine B. (71) and Diamine pure blue FF (424). The first of these dyes bleaches very rapidly in a bath as described in Example 1 under compounds of the urea groups, so that a blue color only remains in the deeper shadows. The effectiveness of these baths may be enhanced by the addition of catalytically acting salts, for example Va, U, Mo, Fe, etc.

This method may also be used with advantage in the hand-coloring or stencil-coloring of kinematograph films, advertisement diapositives, photographs, etc. Thus, for example, in the case of a landscape illustration the sky may be dyed an intensive blue and the ground an intensive green. The dyes are then positively de-colored at the points of the silver image and converted into a reversed image. The concentration may be determined right at the commencement, and

in the application of the colors there is no requirement to adhere to outlines.

According to the invention, a negative or a positive may be used. The de-colorization takes place in proportion to the quantity of silver at the silver points. The unexposed parts accordingly remained colored. The image will be the lightest at the points of the greatest deposit. This image is referred to as a "reversed image." If copying is performed from a negative, the image obtained is also a negative. To obtain a positive, the image copied must also be a positive.

An additional form of embodiment resides in the fact that the colors may be impressed, sprayed on or otherwise applied side by side or partly overlapping in the manner of a screen in mixture possibly with sensitizers and filter dyes readily capable of being washed out, for example filter yellow. This application of the colors may be performed prior to or after the exposure. After developing and fixing the pictures are treated in one of the above-mentioned color-destructive baths, and accordingly a positive or negative multi-color picture is obtained selectively in one bath.

The method according to the invention is naturally also adapted for the light toning of pictures, and in this case the silver image remains, i. e., the dye is more readily destroyed than the silver image. In addition thereto any remnant of the metallic silver image may upon the toning or reversing operation be removed in a known weakening agent. This may be necessary, for example, in the case of multi-color photographs in which the dyes more readily tend to bleach than the silver image.

Advantage is also obtained in applying the method according to the invention to films which are sensitized on both sides, in which for example on the one side the sensitized layer contains a red dye and on the opposite side a blue-green dye. Naturally, it is not necessary for the dye to be present in the emulsion, and the same may be applied later in a coloring process. The conversion of the silver image into the color image is performed according to the above examples. The layers may also contain corresponding sensitizing dyes, for example in the red layer a red sensitizer and in the green layer a green sensitizer. According to the invention there are employed for coloring purposes, or incorporated in the emulsion respectively, acid or substantive dyes, and more particularly azo-dyes, for example Diamine pure blue FF (424) and Chlor-Amine orange G (11). Copying is performed with ordinary white light on both sides of the film. The color of the layers themselves prevents the white copying light from penetrating from the one side to the other.

What I claim as new and desire to secure by Letters Patent is:

1. A method of producing photographic dyestuff images in a photographic material, diffusely colored with a non-leuco base forming dyestuff which is permanently destroyable by reducing means and contains a finely divided metal deposit image, which consists in treating the said image with a fluid agent which is non-destructive with respect to the dyestuff, but reacts with the said metal deposit to oxidize it and substantially simultaneously to form a reducing substance which destroys said permanently destroyable dyestuff at the point of said metallic deposit.

2. A method of producing photographic dyestuff images in a photographic material, diffusely colored with a non-leuco base forming dyestuff which is permanently destroyable by reducing means and contains a finely divided metal deposit image, which consists in treating the said image with a fluid agent which is non-destructive with respect to the dye stuff, but reacts with the said metal deposit to oxidize it and substantially simultaneously to form a reducing complex-compound which destroys said permanently destroyable dyestuff at the point of said metallic deposit.

3. A method of producing photographic dyestuff images in a photographic material, diffusely colored with a non-leuco base forming dyestuff which is permanently destroyable by reducing means and contains a finely divided silver deposit image, which consists in treating the said image with a fluid agent which is non-destructive with respect to the dyestuff, but reacts with the said silver deposit to oxidize it and substantially simultaneously to form a reducing substance which destroys said permanently destroyable dyestuff at the point of said silver deposit.

4. A method of producing photographic dyestuff images in a photographic material, diffusely colored with a non-leuco base forming dyestuff which is permanently destroyable by reducing means and contains a finely divided silver deposit image, which consists in treating the said image with a fluid agent which is non-destructive with respect to the dyestuff, but reacts with the said metal deposit to oxidize it and substantially simultaneously to form a reducing complex-compound which destroys said permanently destroyable dyestuff at the point of said silver deposit.

5. A method of producing photographic dyestuff images in a photographic material, diffusely colored with a non-leuco base forming dyestuff which is permanently destroyable by reducing means and contains a finely divided metal deposit image, which consists in treating the said image with a fluid agent comprising an acid which is non-destructive with respect to the dyestuff, but reacts with the said metal deposit to oxidize it and substantially simultaneously to form a reducing substance which destroys said permanently destroyable dyestuff at the point of said metallic deposit.

6. A method of producing photographic dyestuff images in a photographic material, diffusely colored with a non-leuco base forming dyestuff which is permanently destroyable by reducing means and contains a finely divided silver deposit image, which consists in treating the said image with a fluid agent comprising weakly reducing compounds in addition to an acid which is non-destructive with respect to the dyestuff but reacts with the said silver deposit to oxidize it and substantially simultaneously to form a reducing substance which destroys said permanently destroyable dyestuff at the point of said silver deposit.

7. A method of producing photographic dyestuff images in a photographic material, diffusely colored with a non-leuco base forming dyestuff which is permanently destroyable by reducing means and contains a finely divided metal deposit image, which consists in treating said image with a fluid agent comprising a salt solution which is non-destructive with respect to the dyestuff but reacts with the said metal deposit to oxidize it and substantially simultaneously to form a reducing substance which destroys said permanently destroyable dyestuff at the point of said metallic deposit.

8. A method of producing photographic dye-

stuff images in a photographic material, diffusely colored with a non-leuco base forming dyestuff which is permanently destroyable by reducing means and contains a finely divided metal deposit image, which consists in treating said image with a fluid agent comprising a sulfur containing inorganic salt solution which is non-destructive with respect to the dyestuff, but reacts with the said metal deposit to oxidize it and substantially simultaneously to form a reducing substance which destroys said permanently destroyable dyestuff at the point of said metallic deposit.

9. A method of producing photographic dyestuff images in a photographic material, diffusely colored with a non-leuco base forming dyestuff which is permanently destroyable by reducing means and contains a finely divided silver deposit image, which consists in treating the said image with a fluid agent comprising weakly reducing compounds in addition to a salt solution which is non-destructive with respect to the dyestuff, but reacts with the said silver deposit to oxidize it and substantially simultaneously to form a reducing substance which destroys said permanently destroyable dye-stuff at the point of said silver deposit.

10. A method of producing photographic dyestuff images in a photographic material, diffusely colored with a non-leuco base forming dyestuff which is permanently destroyable by reducing means and contains a finely divided metal deposit image, which consists in treating the said image with a fluid agent comprising an organic compound which is non-destructive with respect to the dyestuff, but reacts with the said metal deposit to oxidize it and substantially simultaneously to form a reducing substance which destroys said permanently destroyable dyestuff at the point of said metallic deposit.

11. A method of producing photographic dyestuff images in a photographic material, diffusely colored with a non-leuco base forming dyestuff which is permanently destroyable by reducing means and contains a finely divided silver deposit image, which consists in treating the said image with a fluid agent comprising an organic compound which is non-destructive with respect to the dyestuff, but reacts with the said silver deposit to oxidize it and substantially simultaneously to form a reducing substance which destroys said permanently destroyable dyestuff at the point of said silver deposit.

12. A method of producing photographic dyestuff images in a photographic material, diffusely colored with a non-leuco base forming dyestuff which is permanently destroyable by reducing means and contains a finely divided silver deposit image, which consists in treating the said image with a fluid agent comprising weakly reducing compounds in addition to an organic compound which is non-destructive with respect to the dyestuff, but reacts with the said silver deposit to oxidize it and substantially simultaneously to form a reducing substance which destroys said permanently destroyable dyestuff at the point of said silver deposit.

13. A method of producing photographic dyestuff images in a photographic material, diffusely colored with a non-leuco base forming dyestuff which is permanently destroyable by reducing means and contains a finely divided silver deposit image, which consists in treating the said image with a fluid agent comprising a nitrogeneous organic compound which is non-destructive with respect to the dyestuff, but reacts with the said silver deposit to oxidize it and substantially simultaneously to form a reducing substance which destroys said permanently destroyable dyestuff at the point of said silver deposit.

14. A method of producing photographic dyestuff images in a photographic material, diffusely colored with a non-leuco base forming dyestuff which is permanently destroyable by reducing means and contains a finely divided silver deposit image, which consists in treating the said image with a fluid agent comprising a nitrogeneous organic sulphur compound which is non-destructive with respect to the dyestuff, but reacts with the said silver deposit to oxidize it and substantially simultaneously to form a reducing substance which destroys said permanently destroyable dyestuff at the point of said silver deposit.

15. A method of producing photographic dyestuff images in a photographic material, diffusely colored with a non-leuco base forming dyestuff which is permanently destroyable by reducing means and contains a finely divided silver deposit image, which consists in treating the said image with a fluid agent comprising a substance selected from a group consisting of urea, thiourea, guanidine, amino-guanidine, semi-carbazide, thio-semi-carbazide, thio-diglycolic acid, cyanide and thiocyanate.

16. A method of producing photographic dyestuff images in a photographic material, diffusely colored with a non-leuco base forming dyestuff which is permanently destroyable by reducing means and contains a finely divided silver deposit image, which consists in treating the said image with a fluid agent comprising an acid in addition to a substance selected from a group consisting of urea, thiourea, guanidine, amino-guanidine, semi-carbazide, thio-semi-carbazide, thio-diglycolic acid, cyanide and thiocyanate.

17. A method of producing photographic dyestuff images in a photographic material, diffusely colored with a non-leuco base forming dyestuff which is permanently destroyable by reducing means and contains a finely divided silver deposit image, which consists in treating the said image with a fluid agent comprising a weekly reducing agent in addition to a substance selected from a group consisting of urea, thiourea, guanidine, amino-guanidine, semi-carbazide, thio-semi-carbazide, thio-diglycolic acid, cyanide and thiocyanate.

18. A method of producing photographic dyestuff images in a photographic material, diffusely colored with a non-leuco base forming azo dyestuff which is permanently destroyable by reducing means and contains a finely divided metal deposit image, which consists in treating the said image with a fluid agent which is non-destructive with respect to the dyestuff, but reacts with the said metal deposit to oxidize it and substantially simultaneously to form a reducing substance which destroys said permanently destroyable dyestuff at the point of said metallic deposit.

19. A method of producing photographic dyestuff images in a photographic material, diffusely colored with a non-leuco base forming acid azo dyestuff which is permanently destroyable by reducing means and contains a finely divided metal deposit image, which consists in treating the said image with a fluid agent which is non-destructive with respect to the dyestuff, but reacts with the said metal deposit to oxidize it and substantially simultaneously to form a reducing substance

which destroys said permanently destroyable dyestuff at the point of said metallic deposit.

20. A method of producing photographic dyestuff images in a photographic material, diffusely colored with a non-leuco base forming substantive acid azo dyestuff which is permanently destroyable by reducing means and contains a finely divided metal deposit image, which consists in treating the said image with a fluid agent which is non-destructive with respect to the dyestuff; but reacts with the said metal deposit to oxidize it and substantially simultaneously to form a reducing substance which destroys said permanently destroyable dyestuff at the point of said metallic deposit.

21. A method of producing photographic dyestuff images in a photographic material, which consists in diffusely incorporating a permanently reducible non-leuco base forming azo dyestuff in a light-sensitive photographic silver salt emulsion, applying the colored light-sensitive emulsion to a support, producing in the emulsion a silver deposit image in the usual manner and then treating said image with a fluid agent comprising a substance selected from a group consisting of urea, thiourea, guanidine, amino-guanidine, semi-carbazide, thio-semi-carbazide, thio-diglycolic acid, cyanide and thio-cyanate.

22. A method of producing photographic dyestuff images in a photographic material, which consists in diffusely incorporating a permanently reducible non-leuco base forming acid azo dyestuff in a light-sensitive photographic silver salt emulsion, applying the colored light-sensitive emulsion to a support, producing in the emulsion a silver deposit image in the usual manner and then treating the said image with a fluid agent comprising a substance selected from a group consisting of urea, thiourea, guanidine, amino-guanidine, semi-carbazide, thio-semi-carbazide, thio-diglycolic acid, cyanide and thio-cyanate.

23. A method of producing photographic dyestuff images in a photographic material, which consists in diffusely incorporating permanently reducible non-leuco base forming substantive acid azo dyestuffs in a light-sensitive photographic silver salt emulsion, applying the colored light-sensitive emulsion to a support, producing a silver deposit image in the usual manner in the emulsion and then treating the said image with a fluid agent comprising a substance selected from a group consisting of urea, thiourea, guanidine, amino-guanidine, semi-carbazide, thio-semi-carbazide, thio-diglycolic acid, cyanide and thio-cyanate.

24. A method of producing photographic dyestuff images in a photographic material, which consists in diffusely incorporating a permanently reducible non-leuco base forming acid azo dyestuff in a light-sensitive photographic silver salt emulsion, applying the colored light-sensitive emulsion to a support, producing a silver deposit image in the usual manner in the emulsion and then treating the said image with a fluid agent containing weakly reducing compounds in addition to a substance selected from a group consisting of urea, thiourea, guanidine, amino-guanidine, semi-carbazide, thio-semi-carbazide, thio-diglycolic acid, cyanide and thio-cyanate.

25. A method of producing photographic dyestuff images in a photographic material, which consists in diffusely incorporating a permanently reducible non-leuco base forming acid azo dyestuff in a light-sensitive photographic silver salt emulsion, applying the colored light-sensitive emulsion to a support, producing a silver deposit image in the usual manner in the emulsion and then treating said image with a fluid agent containing an acid and a weakly reducing compound in addition to a substance selected from a group consisting of urea, thiourea, guanidine, amino-guanidine, semi-carbazide, thio-semi-carbazide, thio-diglycolic acid, cyanide and thio-cyanate.

26. A method of producing photographic dyestuff images in a photographic material, which consists in incorporating permanently reducible non-leuco base forming azo dyestuffs in a plurality of light-sensitive photographic silver salt emulsions, applying these emulsions in a screen-like manner to a support, producing silver deposit images in each of the particles of said emulsion and then treating the said images with a fluid agent which is non-destructive with respect to the dyestuff, but reacts with said silver deposit to oxidize it and substantially simultaneously to form a reducing substance which destroys said permanently reducible dyestuffs at the point of said silver deposit.

27. A method of producing photographic dyestuff images in a photographic material, which consists in incorporating permanently reducible non-leuco base forming azo dyestuffs of different bleaching rapidity into different photographic silver halide emulsions, applying the emulsion containing the dyestuff of the highest bleaching rapidity to a support and applying the emulsion containing the dyestuff of the lowest bleaching rapidity over said first emulsion on the same support, producing silver deposit images in each of said layers of emulsion and then treating said silver deposit images with a fluid agent which is non-destructive with respect to the dyestuffs, but reacts with the silver deposit to oxidize it and substantially simultaneously to form a reducing substance which destroys said permanently reducible dye-stuffs at the point of said silver deposit.

28. A method of producing photographic dyestuff images in a photographic material, which consists in incorporating permanently reducible deposits of non-leuco base forming acid azo dyestuffs of different bleaching rapidity into different photographic silver halide emulsions, applying the emulsion containing the dyestuff of the highest bleaching rapidity to a support and applying the emulsion containing the dyestuff of the lowest bleaching rapidity over said first emulsion on the same support, producing silver deposit images in each of said layers of emulsion and then treating said silver deposit images with a fluid agent which is non-destructive with respect to the dyestuffs, but reacts with the silver deposit to oxidize it and substantially simultaneously to form a reducing substance which destroys said permanently reducible dyestuffs at the point of said silver deposit.

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