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PROCESS FOR THE PRODUCTION OF COLOR PHOTOGRAPHIC IMAGES

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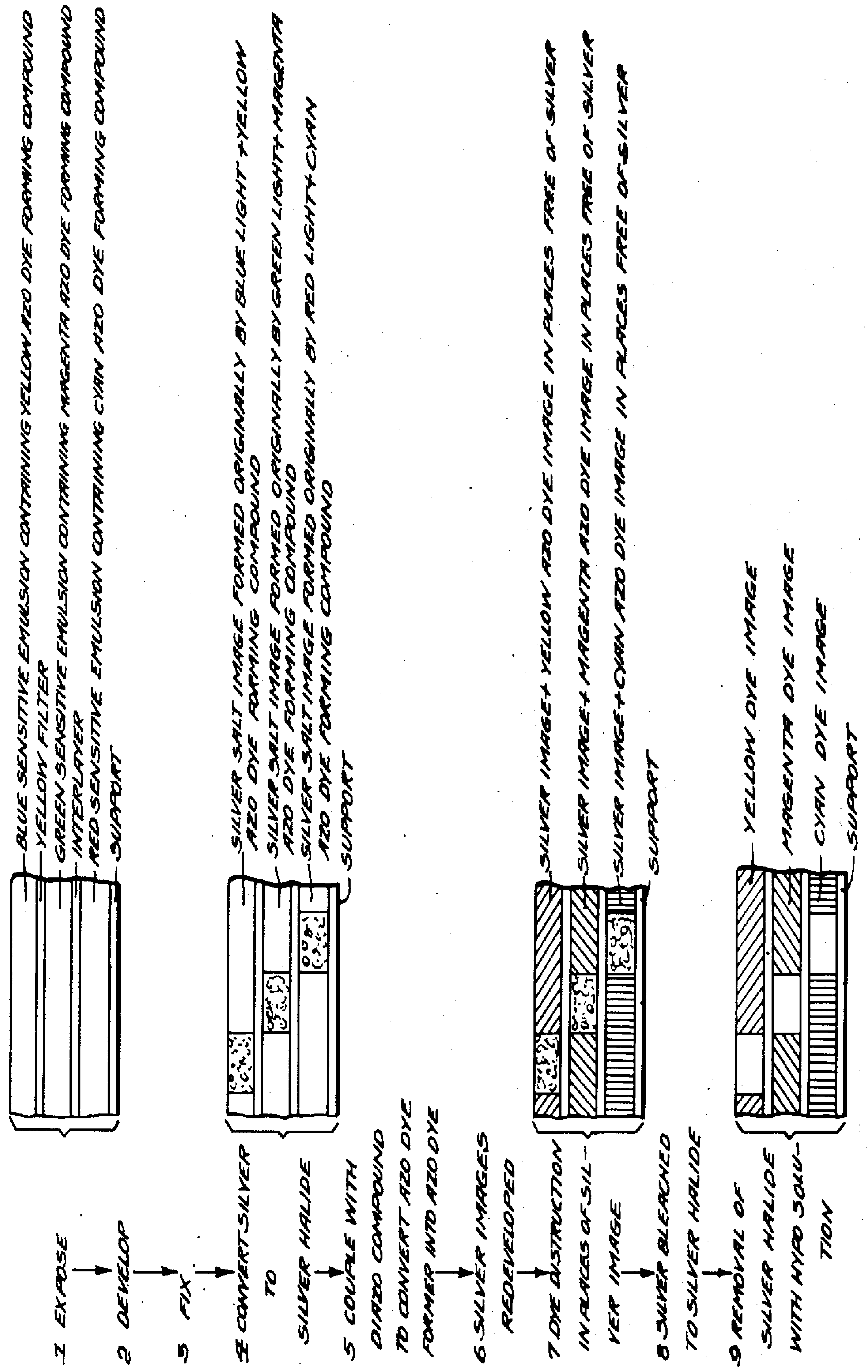

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PROCESS FOR THE PRODUCTION OF COLOR PHOTOGRAPHIC IMAGES

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This invention relates to the production of dye images from photographic silver images by a process which comprises the synthesis of an azo dye in the exposed photographic emulsion layer.

In the United States Letters Patent 2,071,688 dated February 23, 1937 is described and claimed a method of producing color photographic images in which the photographic layer is subjected to two treatments, the first treatment consisting of the conversion of a dye-forming substance into a dye, and the second treatment consisting of the local dye destruction at the required points. Thus, for example, a diazo compound is transformed into an azo dye by coupling with a phenol; or a phenol or other azo coupler is transformed into an azo dye by treatment with a diazo compound, the azo dyes thus formed then being destroyed locally. In the same patent is described and claimed an alternative process in which the first treatment consists of the local destruction of the dye-forming substance; the second treatment then consists of the conversion of the remaining dye-forming substance into the dye. Further alternative processes are described in the U. S. Patents 2,166,049; 2,271,176; 2,333,126; 2,361,541; 2,368,463 and in the co-pending patent applications S. N. 518,256 filed January 14, 1944, now Patent No. 2,514,233, and S. N. 541,282 filed June 20, 1944, now abandoned.

It is known that diazo compounds are easily reduced by metallic silver, particularly in the presence of acids. This behaviour of diazo compounds can successfully serve to produce dye images directly from coupling components in one step. This process has the advantage of simplicity, but it is sometimes difficult to control. A much better control is obtained when the diazo compound is decomposed at a pH which is low enough to avoid coupling at this stage, the coupling being performed in a successive step at a higher pH as described in Letters Patent 2,271,176.

The process, described hereafter, in spite of requiring some additional processing steps has the advantage of being controlled with particular ease and of giving more reproducible results as regards density and gradation of the dye images.

The object of the present invention is the process which consists of a first treatment whereby a dye-forming substance is converted into a diffusely dispersed dye and in a second treatment whereby the dye is destroyed locally at the required points. More particularly, it is the object of this invention to provide a novel process whereby the contact of free diazo compounds with metallic silver is avoided, the metallic silver images being converted, prior to the diazo treatment, into such other images which are inert towards diazo compounds, said other images being capable of reacting directly or indirectly with the azo dyes formed in the coupling.

Whereas diazo compounds are decomposed by metallic silver in the presence of acids, they are stable in the presence of silver salts. It is therefore possible to produce a dye image in the following way: A photographic material comprising at least one silver halide emulsion layer and an azo coupling component diffusely distributed therein is exposed to light, developed and fixed. Thereupon the metallic silver image is converted into a silver salt image and the azo coupling component is coupled with a diazo compound whereby a homogeneous dyeing is produced. The silver salt image is reconverted into a metallic silver image, and the dye is destroyed locally where metallic silver is present. After removing the silver, a dye image is obtained.

The accompanying drawing shows a flow diagram of a modification of the process according to the invention.

The difference in the results between previously known procedures and the process of the present invention is clearly shown by the comparative steps described in Example 1 below.

Example 1

(*a*) A light sensitive silver halide emulsion layer is treated in a bath containing 1% N-toluenesulfo-H-acid, thereupon in a solution containing 1% diphenylguanidine acetate, washed and dried. The layer is exposed, developed and fixed in the usual manner. Instead of impregnating the layer with the diphenylguanidine salt of toluenesulfo-H-acid before the exposure, the impregnation may also be effected with the exposed and developed layer containing the silver image.

(*b*) The layer, treated as above, is immersed in a strongly acid diazo solution, e. g., in a solution containing 0.5% diazotized sulfanilic acid and 1% hydrochloric acid. Thereupon the layer is immersed in a sodium acetate or sodium carbonate solution. The silver is oxidized in an acid copper chloride bath and removed in a hypo bath. A reversed magenta dye image is obtained.

(*c*) The layer, treated as described in Section *a*, is immersed in an acid copper chloride bath and washed. Thereupon it is treated in an acid diazo solution and in a buffering solution as described in Section *b*, and finally the silver is removed in a hypo bath. A uniformly magenta dyed layer is obtained which shows no trace of an image.

(*d*) The layer, treated as described in Section *a*, is immersed in an acid copper chloride bath and washed. Thereupon it is treated in an acid diazo solution and in a buffering solution as described in Section *b*. The silver salt image is reduced in a developer to metallic silver and the azo dye is then destroyed locally in a bleaching bath containing 2% hydrochloric acid and 0.002% 2,3-diaminophenazine. After the oxidation of the residual silver in an acid copper chloride bath and after its removal in a hypo bath, a reversed magenta dye image is obtained.

A comparison of the images obtained in the processes *b* and *d* shows that the image (*d*) has much better definition than the image (*b*). The image (*a*) being a step wedge which shows 12 steps, the image (*d*) shows 10 to 11 steps, whereas the image (*b*) shows only 8 steps. Furthermore the image (*d*) has much clearer whites at the places of complete bleaching than has the image (*b*).

As the decomposition of diazo compounds by metallic silver is speeded up by strong acids, the inactivation of the silver image is of particular importance whenever the photographic material must be treated with diazo compounds in the presence of strong acids. This is the case when diazo compounds, such as 1,4-phenylene-tetrazonium borofluoride or 2-bromo-4-nitrobenzene-diazonium sulfate, stable only in acid solution, are being used. Other compounds such as antidiazotates, nitrosoarylamides or diazoamino compounds sometimes need strong acids for their conversion into diazonium salts. Still other diazo compounds are best coupled in acid solutions. In all these cases, a homogeneous dyeing of the photographic material is more readily obtained with a process which includes the previous inactivation of the silver image.

This inactivation of the silver image is effected after the development. The removal of the undeveloped silver halide is not necessary at this stage, as it is possible to convert the metallic silver into a compound which is different from the original silver halide; e. g., a layer comprising silver chloride and a silver image is treated in a copper bromide bath. Silver chloride and bromide are attacked with different ease by reducing agents and they have different solubilities in silver salt solvents. It is therefore possible to convert one of said salts into metallic silver while the other of said salts is removed after the azo coupling has taken place.

The preferred inactivated image consisting of silver chloride or silver bromide as the metallic silver image is easily converted into such silver salt image, and this silver salt image can easily be converted into a metallic image which is able to react with the azo dye, with no loss in image details through this chain of reactions.

However, this invention is not limited to the conversion into said salts. The metallic silver images may be converted into silver thiocyanate, into a mixture of silver chloride and mercurous chloride, into complex salts such as ferrocyanides and other compounds which are well known in the arts of reduction, intensification and toning of silver images. Many of these compounds are inert with regard to diazo compounds and afterwards can serve for the local destruction of the azo dyes.

The method, consisting of the inactivation of the metallic silver image is suitable for obtaining diffusely dyed layers by diazo coupling, no matter how the diazonium salt is brought into contact with the photographic layers. For example, the diazo compound may be dissolved in a photographic bath which is acid or alkaline or it may be produced within the photographic layer from a diazo forming substance evenly distributed therein.

Example 2

The following layers are coated in successive order on a transparent film base:

1. A red sensitive silver halide emulsion, having incorporated therein the dye 4-nitraniline-2-sulfonic acid→N-benzoyl-1,5-aminonaphthol in its weakly colored (acidic) form.
2. A silver halide emulsion, which is sensitized for green light and which contains the coupling component N-N′-(naphthalene-1,5-disulfo)-8-amino-1-naphthol-3,6-disulfonic acid and the diazo-forming component 2,2′-disulfodiphenyl-4,4′-bis-diazopiperidide, both components precipitated with the base described in Example 2 of U. S. Patent 2,317,184, namely, anhydrobiguanidobenzylalcohol acetate.
3. An interlayer containing colloidal silver.
4. A blue sensitive silver halide emulsion containing 1,1′-[2,2′-disulfodiphenylene-(4,4′)]-bis-[pyrazolone-(5)-carboxylic acid-(3)] and the same diazo-forming component and precipitating agent as in layer (2) above.

The diazo-forming component 2,2′-disulfodiphenyl-4,4′-bis-diazopiperidide is prepared by tetrazotizing benzidine-2,2′-disulfonic acid and pouring the tetrazotized solution into an aqueous piperidine solution. The barium salt of the piperidide is isolated as an oil which is washed with water. It becomes solid by washing with ethanol.

The multilayer material, produced in the indicated manner, is exposed to light, developed and fixed. Thereupon, the superimposed silver images are rehalogenized in a potassium ferricyanide potassium bromide bath. The piperidide is split in a diluted hydrochloric acid bath and the tetrazonium salt, freed in this last bath, is coupled with the azo components by immersing the material in a sodium acetate bath. The silver salt image is reduced in an alkaline developer, and all three of the azo dyes are destroyed in the places where silver is present, e. g., according to Reissue Patent 22,308. The residual silver is oxidized in an acid copper chloride bath and removed in a hypo bath. Finally the film is treated in an alkaline bath to turn the dye in the bottom layer into its cyan form, and dried.

The splitting of the piperidide and the coupling of the components to form the azo dye can be performed in a single step, i. e., the hydrochloric acid bath and the sodium acetate bath of the above directions are omitted and replaced by a diluted acetic acid or an acetic acid-sodium acetate bath. If the pH of this bath is high enough to ease the coupling, the splitting takes place only slowly. If, on the other hand, the pH is low enough to allow the splitting in a short time the coupling becomes sluggish. A method permitting the splitting and coupling in one step consists of the exposure of the weakly acidic buffered material to a higher temperature, e. g., by hanging the buffered material in an air current of 50° C. Furthermore, it was found that the splitting of the piperidide can be accelerated by compounds other than acids, e. g., the piperidide splits easily, even at a higher pH in the presence of formaldehyde. It is possible, therefore, to effect in a short time and at low temperature the splitting and the coupling in one bath containing sodium acetate, acetic acid and formaldehyde.

The 4,4′-tetrazodiphenyl-2,2′-disulfonic acid, liberated from the piperidide in acid solution, diffuses sufficiently to permit a variation from the above procedure: the piperidide may be omitted from the green sensitive emulsion layer (2) and from the blue sensitive emulsion layer (4) and incorporated instead in the interlayer (3).

Example 3

A red sensitive emulsion containing the azo coupling component naphthalene-1,5-di-(sulfonaphthionyl-1′,5′-aminonaphthol) is coated on a transparent base. On top of this emulsion layer is coated a clear gelatin interlayer and then a high speed green sensitive emulsion containing the n-amyl ether of m-(N,N-diethylamino)-phenol. Thereupon follows a gelatin layer containing a yellow filter dye, and finally the top layer consisting of a blue sensitive emulsion containing N,N′-decamethylene-bis-(2,4-dioxo-1,2,3,4-tetrahydroquinoline).

The material is exposed, developed, fixed, rehalogenized in an acid copper chloride bath and treated for 7 minutes in a bath containing 1% acetic acid and 0.1% 4-nitro-1-diazonaphthalene-6-sulfonic acid. Thereupon it is developed again and treated in a dye destruction bath as in the foregoing example. After the silver is removed in known manner the material is immersed for a short time in an aqueous solution containing 0.4% ethanolamine and 3% "polyethylene glycol 300" (Carbide & Carbon Corp.). After drying, a photograph in natural colors is obtained.

Further applications of this invention are obvious for anyone skilled in the art. For example, a multilayer material comprising three superimposed silver images may be partially rehalogenized before the coupling. The parts containing metallic silver will produce more contrasty dye images than the parts containing the rehalogenized image. The material may be locally rehalogenized by controlled diffusion of a rehalogenizing or of a redeveloping solution or by local application of the reagents; e. g., the dye formation in the sound track of a film is avoided by the presence of metallic silver only in the sound track, whereas the other parts of the film are rehalogenized.

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

I claim:

1. In a process of producing a photographic dye image which includes exposing and developing a silver halide emulsion layer to produce a metallic silver image in said layer, the steps which comprise converting the metallic silver image in the developed emulsion layer into a silver salt image which is different from any remaining silver halide still contained in the layer and which is inert to diazo compounds in acid baths, then treating the emulsion layer containing such silver salt image with a diazo compound under an acid condition, coupling within said layer said diazo compound with an azo coupling component in the presence of said silver salt image to dye said layer and developing a metallic silver image in said layer from a silver salt therein and destroying said azo dye in said layer in proportion to the metallic silver image in said layer.

2. In a process of producing a photographic dye image which includes exposing and developing a silver halide emulsion layer to produce a metallic silver image in said layer, the steps which comprise converting the metallic silver image in the developed emulsion layer into a silver halide image which is different from any remaining silver halide still contained in the layer, then treating the emulsion layer containing such silver halide image with a diazo compound under an acid condition, coupling within said layer said diazo compound with an azo coupling component in the presence of said silver halide image to dye the layer, developing a metallic silver image in said layer from a silver halide therein and destroying said azo dye in said layer in proportion to the metallic silver image within the layer to form a photographic dye image.

3. In a process of producing a photographic dye image the steps which comprise exposing a silver halide emulsion layer, developing said layer to produce a metallic silver image in the presence of an undeveloped image of said silver halide, converting the metallic silver image in said layer into an image of a silver halide other than the first mentioned silver halide, then treating the emulsion layer containing said silver halide images with a diazo compound under an acid condition, coupling within said layer said diazo compound with an azo coupling component in the presence of said silver halide images to dye the layer diffusely, developing a metallic silver image in said layer from one of said silver halide images and destroying said azo dye in said layer in proportion to the metallic silver image within the layer to form a photographic dye image.

4. In a process of producing a photographic dye image the steps which comprise exposing a silver halide emulsion layer, developing said layer to produce a metallic silver image, fixing out any remaining undeveloped silver halide, converting the metallic silver image in said layer into a silver halide image, then treating the emulsion layer containing said silver halide image with a diazo compound under acid conditions, coupling within said layer said diazo compound with an azo coupling component in the presence of said silver halide image to dye said layer diffusely, developing a metallic silver image from said silver halide image and destroying said azo dye in said layer in proportion to the metallic silver image within the layer to form a photographic dye image.

5. In a process of producing a photographic dye image which includes exposing and developing a silver halide emulsion layer containing an azo coupling component to produce a metallic silver image in said layer, the steps which comprise converting the metallic silver image in the developed emulsion layer into a silver salt image which is different from any remaining silver halide still contained in the layer and which is inert to diazo compounds in acid baths, then treating said layer containing said silver salt image with a solution of a diazo compound under acid conditions, coupling the diazo compound with the azo coupling component within the layer in the presence of said silver salt image to dye such layer diffusely, developing a metallic silver image in said layer from a silver salt therein and de-

stroying said azo dye in said layer in proportion to the metallic silver image in said layer.

6. In a process of producing a photographic dye image which includes exposing and developing a silver halide emulsion layer to produce a metallic silver image in said layer, the steps which comprise converting the metallic silver image in the developed emulsion layer into a silver salt image which is different from any remaining silver halide still contained in the layer and which is inert to diazo compounds in acid baths, then forming a diazo compound within said layer containing said silver salt image under an acid condition, coupling within said layer said diazo compound with an azo coupling component in the presence of said silver salt image to dye said layer and developing a metallic silver image in said layer from a silver salt therein and destroying

said azo dye in said layer in proportion to the metallic silver image in said layer.

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