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3,567,448

## IMAGE-FORMING PROCESS UTILIZING A COLORED COMPLEX OF TITANIUM DIOXIDE

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9 Claims

### ABSTRACT OF THE DISCLOSURE

Utilizing the silver-dye-bleach process, photographic dye images are prepared on imagewise exposed photographic elements having, as the light-sensitive component, a colored complex of titanium dioxide and an unsaturated organic ligand compound including at least one nitrogen-containing linkage. A silver metal image is first physically developed on the exposed areas of such an element, after which a bleaching step reduces the colored complex to a colorless form in those areas having a silver image, thereby preparing positive, colored photographic dye images.

This invention relates to photography and more particularly to the production of positive, colored dye images utilizing the silver-dye-bleach process.

The selective destruction of bleachable dyes to obtain positive dye images is well known in the photographic art. Such operations are typically designated dye-bleach processes which operate to reduce a colored dye to a colorless form in the presence of photographically developed silver.

The reductive dye bleaching is accomplished by one of two known processes, namely as a stoichiometric reaction in an acid solution, wherein the photographic silver functions as the reducing agent, or as a silver catalyzed reaction wherein the reducing agent is a highly alkaline substance such as sodium stannite (alkaline stannous chloride).

A typical multicolor silver-dye-bleach element is composed essentially of a support coated with silver halide layers differentially sensitized to blue, green and red radiation and having in association therewith, respectively, bleachable yellow, magenta and cyan colored dyes. After an imagewise exposure, these elements can be developed in a black-and-white silver halide developer solution to form low contrast silver images in the exposed layers. Subsequent to such development, the element is subjected to one or more acidic bleaching solutions comprising, as an active component, an agent commonly referred to as a bleach catalyst. This bleach catalyst oxidizes the metallic silver formed during development and in so doing is itself reduced. The reduced catalyst then acts at the points where silver was present to reduce the colored, bleachable dye in each layer to a colorless product, while the catalyst is simultaneously oxidized to its original state. Residual silver salt is then removed by fixing and washing. A positive, colored dye image is thereby produced which is photographically the inverse of the initial silver image.

In presently employed dye-bleach elements, silver halide is the conventional photosensitive species. Also, in multicolor elements spectral sensitizing dyes separate from and additional to the bleachable dyes are required to sensitize the photosensitive silver halide to record red, green and yellow light, since the bleachable dyes used to form the final colored dye image, although of a similar hue and having an adsorption spectra comparable to that of conventional sensitizers, have not functioned adequately as sensitizing dyes. It would be desirable to provide photosensitive species for dye-bleaching systems additional to silver halide. Also, the spectral sensitizing dyes now re-

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quired in known dye-bleach elements could be advantageously replaced with bleachable dyes having an adsorption to the photosensitive species such that they operate as well to spectrally sensitize the photosensitive component to a selected spectral image.

Accordingly, it is an object of this invention to provide, for dye-bleach processing, new photographic elements having a photosensitive species other than silver halide.

It is another object of the present invention to provide, for dye-bleach processing, novel photographic elements wherein the bleachable dye is also the spectral sensitizing dye.

Yet an additional object of the instant invention is to provide a new photographic process for producing positive, colored dye images by dye-bleach means.

These and other objects of the present invention will become apparent from a consideration of the following specification and appended claims.

The objects of this invention are accomplished with a dye-bleaching process for producing positive, colored photographic dye images on an imagewise exposed photographic element including a support having coated thereon at least one light-sensitive layer comprising a colored complex of titanium dioxide and an unsaturated organic ligand compound having at least one nitrogen-containing linkage and a polydentate-chelating group comprising electron-donating atoms which are separated from each other on said organic ligand compound by 2 to 3 intervening atoms, which process includes:

- (a) physically developing a silver metal image on the imagewise exposed areas of said photographic element, and
- (b) treating said photographic element with a photographic dye-bleaching solution for a period of time sufficient to render said colored complex colorless in the exposed areas having a metallic silver image,

whereupon a positive, colored photographic image remains on said element.

Transition metals such as titanium form metal chelates. Titanium typically has a valence number of four, but possesses the capability of receiving two additional bonds from compounds bearing a chelating group or moiety, a functional grouping containing at least two atoms having unshared electrons and also intervening atoms that join the atoms having unshared electrons. Compounds which possess one or more chelating groups and are amenable to the formation of such chelate complexes are conventionally designated ligands or ligand compounds. Chelating groups having two atoms with unshared electrons are termed bidentate, with three such atoms the designation is tridentate etc., and the like for other polydentate chelating groups. The ligand compounds are designated in like fashion as bidentate, tridentate or other polydentate ligands.

The active component of a bidentate chelating group is a pair of electron-donating atoms that are conventionally those atoms, such as oxygen and nitrogen, which after being chemically bonded to another atom or atoms in a compound such as the ligands described herein, possess the capability of donating remaining unshared electrons to coordinate covalent bonds and thereby forming chelate rings with, for example, a titanium atom or ion. The electron donating atoms can be part of the nucleus or backbone of a ligand compound such as the nitrogen atom of a quinoline nucleus, or they can be attached thereto as substituents. When they are substituents, each can be either the entire substituent as a keto group oxygen atom, or directly attached to the nucleus as part of a larger grouping like the oxygen atom of a hydroxyl radical or the nitrogen atom of an amino group or an azo linkage.

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Alternatively, the electron-donating atoms can be attached to the nucleus or backbone via an intervening atom, as in the case of an oxygen atom joined to a ligand nucleus through the carbon atom of a carbonyl group.

These electron-donating atoms are, for optimum chelate ring stability, typically separated from each other on the ligand compound by either two or three intervening atoms. All of the interposed ligand atoms, including such atoms as the carbon atom of a carbonyl or carboxyl radical also containing an electron-donating oxygen atom, are deemed intervening atoms since they affect the size and therefore the stability of the ultimate chelate ring.

As noted herein, the subject invention is concerned with the spectral sensitization of titanium dioxide to visible light radiation by complexing it with various unsaturated ligand compounds bearing chelating moieties to form visible-light-sensitive, colored complexes. The mechanism whereby the colored complexes of this invention are formed is not completely understood, but it is speculated that titanium atoms at the outer surface of an octahedral titanium dioxide crystalline structure lack the coordinate saturation which is present for such atoms within the crystal, and the occurrence of coordinate unsaturation at the outer surface operates to render the titanium dioxide receptive to forming a new, complex photosensitive species with suitable ligands via the coordinate covalent bonding of chelate ring formation. More specifically, it is theorized that the coordinate unsaturated titanium atom of surface titanium dioxide molecules produces 5 or 6 membered, polydentate chelate ring complexes with ligand compounds bearing at least one bidentate chelating moiety such as those described herein.

It is to be emphasized that the instant invention comprehends the formation of a new photosensitive species. Titanium dioxide, sensitive to blue-ultraviolet radiation, is complexed with such polydentate ligand compounds as are described herein to provide a colored photosensitive species which exhibits sensitivity to visible light radiation. It is unnecessary that a ligand exhibit color prior to complexing. In particular, certain colorless or slightly colored ligand compounds such as catechols, tannic acid and other polyhydroxylic gallate esters produce strongly colored titanium dioxide complexes of a hue different from that of the ligand.

Additionally, where initially colored ligands are complexed with titanium dioxide at a site in or near the chromophore, a pronounced shift in color and absorption spectra is obtained in the complex from that which was characteristic of the uncomplexed ligand; this effect decreases as the ligand's complexing site becomes more removed from the conjugated chain or nucleus which conventionally defines a chromophore.

Generally, ligands useful in the present invention are limited only by their potential to form a colored complex with titanium dioxide. The formation of such a complex renders titanium dioxide visible-light-sensitive to a degree which, at the spectra of maximum absorption, is substantially equivalent to the ultraviolet photoresponse of unsensitized titanium dioxide. In the formation of a stable complex between a transition metal ion or atom and a bidentate ligand, the cyclic nucleus containing both the metal component and the electron-donating and intervening atoms of the ligand's chelating group is for advantageous stability of five- or six-membered ring. Hence, a suitable ligand structure, as noted hereinabove, includes compounds wherein only two or three interposed atoms can separate the electron-donating atoms of the chelating groups noted herein.

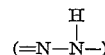
More particularly, in the formation of the subject titanium dioxide complexes, advantageous bidentate and other polydentate ligands contain such electron-donating atoms as an oxygen atom and a nitrogen atom in a variety of structural relationships such as those mentioned hereinabove. Particularly suitable ligands are aromatic vicinal polyols including aryl vicinal polyols, 8-hydroxyquinolines,

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aromatic compounds having a hydroxyl radical substituted ortho to a basic nitrogen atom and aromatic compounds having a hydroxyl radical substituted ortho to a carbonyl radical. The remaining portion of the ligand can be a typical chromophore or another conjugated or other potential chromophoric configuration which becomes colored in the ultimate visible light absorbing complex.

In the practice of the present invention, it is advantageous that the chromophoric portion of the ligand compound have included therein at least one nitrogen containing linkage that is susceptible of reduction when treated with a reducing agent (such as those included in dye-bleaching solutions) in the presence of a silver image according to conventional dye-bleach procedures.

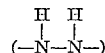
Exemplary of nitrogen-containing linkages are such configurations as a diazo radical ( $\text{--N=N--}$ ), a hydrazone-type linkage



a bivalent amino linkage



and a hydrazo linkage



Other nitrogen-containing linkages are likewise advantageous as long as they are reducible when contacted with dye-bleaching solutions as described herein.

Complex-promoting ligands such as the types mentioned herein, form visible-light-sensitive, colored complexes with both microcrystalline, vacuum-deposited titanium dioxide and particulate titanium dioxide such as colloidal titanium dioxide having, for example, rutile or anatase crystalline structure. When the titanium dioxide and a ligand compound having a polydentate chelating moiety as described herein are complexed, generally by conventional means such as admixing with stirring or dipping, the two reagents are typically present with a molar excess of ligand compound since it is desirable to ensure that all of the surface titanium dioxide which is amenable to complexing is so reacted. The presence of excess ligand compound does not detrimentally affect spectral sensitization, and amounts up to complete monolayer coverage can be advantageously complexed with surface titanium dioxide without experiencing desensitization.

The production of a composite, light-sensitive photographic element is accomplished either by coating the visible-light-sensitive, colored titanium dioxide complex on a support material or, subsequent to coating, by treating the titanium dioxide with a ligand compound to form the desired colored complex in situ on the support. Support materials upon which to coat the photosensitive titanium dioxide are subject to wide variation and are limited only by the use to which the completed photograph will be applied. Additionally, where vacuum deposited titanium dioxide is utilized, the support material must necessarily be resistant to degradation by those temperatures incurred during the actual vacuum deposition. Glass is suitably employed as are metals such as aluminum, copper, zinc and tin. Conventional photographic film bases, such as cellulose acetate, cellulose nitrate, cellulose acetate butyrate, poly(ethylene terephthalate), poly-styrene and paper including polyethylene-coated paper and poly-propylene-coated paper are all susceptible of advantageous use.

Where vacuum-deposited titanium dioxide is used, the coating operation is accomplished by well-known vacuum deposition techniques, such as those described for vacuum depositing silver halide as in U.S. Pat. No. 1,970,496. Typically, the support material is placed within a sealable enclosure along with metallic titanium which can be used as the source of titanium dioxide by

introducing oxygen into the vacuum system. Alternatively, titanium dioxide can be used in lieu of titanium metal. The enclosure is sealed, the pressure reduced and the temperature elevated, which combination of conditions produces the sublimation of titanium dioxide microcrystals upon such support material.

Coating thickness can be typically varied between about .02 micron and about .5 micron, with thicknesses of between about .05 micron and about .4 micron preferred. At substantially less than .02 micron, there is insufficient titanium dioxide present to afford adequate photographic sensitivity, and when coatings are prepared at thicknesses significantly in excess of about .6 micron, photographic response declines.

Subsequent to vacuum-deposition, the titanium dioxide is rendered visible-light-sensitive by forming the subject colored complexes. Complexing is typically obtained by contacting the layer of vacuum-deposited titanium dioxide with an organic solvent or aqueous solution of one or more of the subject ligands. Alternatively, mixtures of solvents can be used. The method of contacting can be immersion, spraying, dipping, swabbing or any other means whereby the ligand compound contacts the titanium dioxide for a period of time sufficient to promote the colored complexes of the present invention. After a suitable treatment, excess solution is permitted to drain off the coated support and the coating is dried to produce a composite, vacuum-deposited titanium dioxide photographic element which is spectrally sensitized to visible light.

When particulate titanium dioxide coated from solution in the presence of a binder material is used as the photosensitive component, the subject complex-forming ligands are typically included in the coating solution in such excess amounts as are described hereinabove, and the ultimate complex is then coated on the support. If it is preferred, however, complexing can be accomplished subsequent to coating the titanium dioxide according to the methods outlined for vacuum deposited titanium dioxide.

The choice of binder material is largely dependent upon the use to which the completed photographic element will be applied. Where the ultimate photographic image is a silver or other metallic image produced by conventional photographic techniques such as the physical development described herein, hydrophilic binders such as gelatin, polyvinyl alcohol and other water permeable polymers are particularly compatible with processing media which are typically aqueous solutions. The amount of binder material which is coated with the titanium dioxide can be widely varied in accordance with conventional practice. Typically, where hydrophilic binder materials are employed in the production of conventional photoimages, from about .05 to about 1 part by weight of polymeric binder per 1 part by weight of titanium dioxide is employed, but more extensive variations can be used if desired.

The subject elements and especially those incorporating crystalline titanium dioxide, such as the varieties of colloidal titanium dioxide, dispersed in a hydrophilic binder material, can be coated in layered fashion to provide a composite, multicolor photographic element having individual cyan, magenta and yellow hues sensitized by the subject complexes to record light of the red, green and blue portions of the spectrum respectively. When an element of this sort is imagewise exposed and processed utilizing dye-bleach techniques, a full color, positive image is obtained, with the image colors being provided by the unbleached colored complexes that originally served to spectrally sensitize the titanium dioxide to record red, green and blue light. As such, the need for bleachable dyes separate from and additional to the sensitizing, complex-forming ligands of this invention is avoided. Utilizing the spectral sensitizer as the bleachable component represents a distinct improvement in simplifying the composition of dye-bleach elements. Also,

due to the increased absorption of the subject sensitizing and bleachable complexing agents, problems of dye migration heretofore associated with conventional bleachable dyes are mitigated.

A photographic element coated and produced as described hereinabove can be stored under lighted conditions. If it is so stored, then immediately prior to exposure it must be dark adapted. Dark adaptation constitutes storing the titanium dioxide coated support under dark conditions for a time sufficient to raise the resistivity of the titanium dioxide to a point where the ratio of dark resistivity to light resistivity is sufficiently great to permit the development of a suitable dense photographic image. The length of this period of dark conditioning depends in part upon the intensity with which the element has been previously exposed and the intensity with which it will receive its intended imagewise exposure. Typically, however, dark adaptation of from about 10 to about 24 hours will insure adequate photographic response. Alternatively, storing the photographic element under conditions of elevated temperature may enhance photosensitivity.

The subject photographic elements which are described herein as being suited for the production of conventional photographic images by physical development means are typically exposed through an original pattern or to another imagewise pattern of light, producing a latent charge image corresponding to the exposed and unexposed areas. The presence of such a charge distribution renders the photographic element amenable to development. The titanium dioxide layers of the present photographic elements are sensitive to visible light radiation due to formation of the described colored complexes between titanium dioxide and the ligand compounds of this invention, and hence, exposing means which are rich in the particular absorption wave lengths of each complex are preferred. However, due to the natural sensitivity of titanium dioxide to ultraviolet rays, such an exposing means can also be employed.

Development of a latent image in such of the present photographic elements as are designed to produce a photographic silver or other metal image, is preferably a two-step physical development sequence. Initially, the imagewise exposed element is treated with a solution typically containing silver ions. Such a solution can be, for example, an aqueous solution of a silver salt such as silver nitrate, silver perchlorate, silver p-toluene sulfonate, etc., and treatment therewith produces microscopic deposits or development centers of metallic silver in the exposed areas. The treating technique can be by immersion, swabbing, spraying or any other means whereby sufficient solution contacts the exposed element.

Subsequent to the treatment with a solution preferably containing silver ions, the imagewise exposed photographic element is treated with a physical developer solution containing heavy metal ions in salt form and a reducing agent for the metal ions, and when the metal ion salt is substantially insoluble in water, a solvent for the metal ion salt, such as water-soluble thiosulfates, thiocyanates, etc., to produce a visible photographic image corresponding to the exposed areas having development centers. Typical physical developer solutions are well known (see Hornsky, *Basic Photographic Chemistry* (1956), 66, and Mees and James, ed., *The Theory of the Photographic Process*, 3rd ed. (1966), 329-331) and contain the silver ions necessary to form a visible image at and in the vicinity of nucleating centers, the microscopic metal deposits created during the above-described first step. Typical reducing agents used in the physical developer include, for example, polyhydroxy-substituted aryl compounds such as hydroquinones, catechols and pyrogallols; ascorbic acid derivatives; aminophenols; p-phenylenediamines, and the like developing agents used in the photographic art. Particular examples of reducing agents for physical developer solutions are 2-methyl-3-chlorohydro-

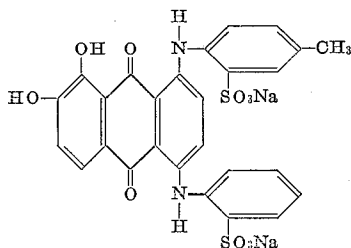
quinone, bromohydroquinone, catechol, 5-phenylcatechol, pyrogallol monomethyl ether (1-methoxy-2,3-dihydroxybenzene) and 5-methylpyrogallol monomethyl ether, isoascorbic acid, N-methyl-p-aminophenol, dimethyl-p-phenylene diamine, 4-amino-N,N-di(n-propyl) aniline and 6-amino-1-ethyl-1,2,3,4-tetrahydroquinoline. The completely developed element carries a visible image, typically metallic silver, corresponding to the exposed areas. As such, it is a negative reproduction of the original pattern, and when a negative serves as the original pattern, positive copies are obtained.

Subsequent to the formation of a metallic image, conventionally silver, as is described hereinabove, the subject element is then treated with a conventional dye-bleaching solution to render the colored complexes colorless in exposed areas, thereby preparing a positive, colored photographic image. Bleaching is effected by contacting the photographic element with an acidic or an alkaline bleaching solution for a period of time sufficient to effect the chemical reduction of the colored complexes to colorless forms. Typical alkaline bleaching solutions are reducing agents such as alkali metal hydroxides which have been activated by the addition of a metal salt, stannous salts for example. A preferred alkaline bleaching agent is sodium stannite, a combination of sodium hydroxide and stannous chloride. Typically, its concentration is such that the pH is advantageously in excess of about 11. Acidic bleaching solutions, wherein the developed silver image functions as the reducing agent, conventionally include an acid, a silver ion complex former such as thiourea, mercaptans and benzimidazoles and bleach catalysts like phenazines, oxazines and sulfonated anthraquinones. A generally used acidic bleaching solution includes acidic thiourea and has the formulation: concentrated HCl, 100 ml.; thiourea, 125 g.; 2-hydroxy-3-aminophenazine, .15 g.; and water to make 1 liter. After bleaching, any residual silver can be removed by treatment with a ferricyanide bleach or other silver bleaching agent and a conventional fixing agent such as sodium thiosulfate. In many instances, however, such as with the subject elements, the separate bleaching of residual silver and fixing of undeveloped silver halide can often be avoided. Where the amounts of silver halide and developed silver are not significantly in excess of the amount of bleachable dye, the action of the thiourea and phenazine bleach catalyst operates to remove both silver halide and residual silver by converting them to soluble complexes. The resultant photographic image is a high quality mono or multicolored image which is a positive reproduction of the original. Such image, if present on an opaque support, can be viewed in conventional fashion via reflected light. If the support is a transparent material, cellulose acetate or poly(ethylene terephthalate) for example, the final dye image is amenable to viewing via transmitted light such as by projection.

The following examples are included to further illustrate the present invention:

#### EXAMPLE 1

Colloidal titanium dioxide (20 g.) is dispersed in 100 ml. of distilled water. To 10 g. of this dispersion is added 5 ml. of a 1% by weight aqueous solution of a cyan-colored dye having the formula:



and known in the trade as Alizarin Veridine, Colour 75

Index 1084, to form a chelate complex between the dye and the titanium dioxide. To this dispersed complex is also added 8 ml. of a 10% by weight aqueous gelatin solution, 1.0 ml. of a 7.5% aqueous saponin solution and 0.25 ml. of 10% aqueous formaldehyde. The complete mixture is then coated at a .004 in. wet thickness on baryta-coated paper support to prepare a composite photographic element with spectral sensitivity out to 760 nm. All preparations are carried out under dark conditions, and any dark adaptation of the titanium dioxide is thereby avoided. The resultant photographic element is then exposed for 5 seconds through a line transparency to the light of a 500 watt tungsten photoflood lamp held at a distance of one foot from the exposing plane, after which it is immersed for 5 seconds in a 1% aqueous silver nitrate solution and rinsed with water for an additional 5 seconds, thereby producing minute silver nuclei in exposed areas of the element. Physical development for 2 minutes in a developer having a temperature of about 20° C. and the formula:

(1) Part A consists of—

Water—800 cc.

Sodium sulfite—20 g.

Sodium isoascorbate—26 g.

Sodium carbonate (monohydrate)—50 g.

Octyl phenoxy ethoxy ethyl dimethyl-p-chlorobenzyl ammonium chloride (1% in H<sub>2</sub>O)—20 cc.

(2) Part B consists of—

Water—800 cc.

Sodium thiosulfate .5H<sub>2</sub>O—30 g.

Silver chloride—5 × 10<sup>-2</sup> moles

Water to 960 cc.

5 methylbenzotriazole (1% in dilute potassium hydroxide)—40 cc.

(Parts A and B are mixed in equal portions just prior to use.)

forms a visible metallic silver image in exposed areas of the element. A positive, single-color cyan image is then produced by immersing the partially processed element for one minute in a dye-bleaching solution having the composition:

Concentration HCl—100 ml.

Thiourea—100 g.

2-hydroxy-3-aminophenazine—180 mg.

Water to make 1 liter.

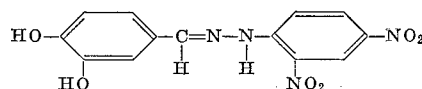
In those areas bearing a silver image, the above bleaching solution removes the silver image and converts the cyan-colored complex to a colorless form. Previously unexposed areas containing no silver image are unaffected, thereby producing a positive, cyan-colored image of the original line transparency.

#### EXAMPLE 2

A piece of poly(ethylene terephthalate) support is coated with a 100 mμ thick layer microcrystalline titanium dioxide produced by the vacuum deposition of titanium metal at 10<sup>-4</sup> torr. The titanium dioxide is rendered suitably photoactive by dark adaptation for 18 hours. The photographic element so produced is then treated with the dye solution of Example 1 and dried. Exposure and processing are as in Example 1, and a similar high quality cyan-colored positive image is obtained.

#### EXAMPLE 3

A photographic element is prepared according to the procedure of Example 1. Over and contiguous to the cyan-colored photosensitive layer is coated a second similar photosensitive layer, except that this second layer contains a colored chelate complex between titanium dioxide and a yellow colored dye having the formula:



which results in a coating having a spectral sensitivity range out to 490 nm. Exposure, development and bleaching are as in Example 1, and subsequent to the processing sequence and drying, a colored, positive photographic image of the line transparency remains on the support.

The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

I claim:

1. A dye-bleaching process for producing positive, colored photographic dye images on an imagewise exposed photographic element comprising a support having coated thereon at least one light-sensitive layer comprising a light-sensitive colored complex of titanium dioxide and an unsaturated organic ligand compound having at least one nitrogen-containing linkage and a polydentate chelating group comprising electron-donating atoms which are separated from each other on said organic ligand compound by 2-3 intervening atoms, which process comprises:

(a) physically developing a silver metal image on the imagewise exposed areas of said photographic element, and

(b) treating said photographic element with a photographic dye-bleaching solution for a period of time sufficient to render said colored complex colorless in the areas having a metallic silver image,

whereupon a positive, colored photographic image remains on said element.

2. A dye-bleaching process as described in claim 1 wherein physically developing a silver metal image on the imagewise exposed areas of said photographic element comprises sequentially treating said element with:

(a) a first solution comprising a silver ion-containing solution to produce development centers of metallic silver in the exposed areas, and

(b) a physical developer solution containing silver ions and a reducing agent for said silver ions to produce a visible metallic silver image in the exposed areas.

3. A dye-bleaching process as described in claim 2 wherein:

(a) said first solution comprises silver nitrate,

(b) said physical developer solution has a formula consisting of equal portions of Parts A and B, wherein:

(1) Part A consists essentially of—

Water—800 cc.

Sodium sulfite—20 g.

Sodium isoascorbate—26 g.

Sodium carbonate (monohydrate)—50 g.

Octyl phenoxy ethoxy ethyl dimethyl-p-chlorobenzyl ammonium chloride (1% in H<sub>2</sub>O)—20 cc.

Water to make 1 liter at a pH of 11.0, and

(2) Part B consists essentially of—

Water—800 cc.

Sodium thiosulfate .5H<sub>2</sub>O—30 g.

Silver chloride— $5 \times 10^{-2}$  moles

Water to 960 cc.

5-methylbenzotriazole (1% in dilute potassium hydroxide)—40 cc., and

(c) said photographic dye-bleaching solution consists essentially of:

Concentrated HCl—100 ml.

Thiourea—125 g.

2-hydroxy-3-aminophenazine—.15 g.

Water to make 1 liter.

4. A dye-bleaching process for producing positive, colored photographic dye images on an imagewise exposed photographic element comprising support having coated thereon at least one light-sensitive layer comprising a light-sensitive colored complex of titanium dioxide and an unsaturated organic ligand compound having at least one nitrogen-containing linkage selected from the

group consisting of an azo linkage, a hydrazo linkage, and a bivalent amino linkage and a polydentate chelating group comprising electron-donating atoms which are separated from each other on said organic ligand compound by 2-3 intervening atoms, which process comprises:

(a) physically developing a silver metal image on the imagewise exposed areas of said photographic element, and

(b) treating said photographic element with a photographic dye-bleaching solution for a period of time sufficient to render said colored complex colorless in these areas having a metallic silver image.

5. A dye-bleaching process as described in claim 4 wherein physically developing a silver metal image on the imagewise exposed areas of said photographic element comprises sequentially treating said element with:

(a) a first solution comprising a silver ion-containing solution to produce development centers of metallic silver in the exposed areas, and

(b) a physical developer solution containing silver ions and a reducing agent for said silver ions to produce a visible metallic silver image in the exposed areas.

6. A dye-bleaching process as described in claim 5 wherein:

(a) said first solution comprises silver nitrate,

(b) said physical developer solution has a formula consisting of equal portions of Parts A and B, wherein:

(1) Part A consists essentially of—

Water—800 cc.

Sodium sulfite—20 g.

Sodium isoascorbate—26 g.

Sodium carbonate (monohydrate)—50 g.

Octyl phenoxy ethoxy ethyl dimethyl-p-chlorobenzyl ammonium chloride (1% in H<sub>2</sub>O)—20 cc.

Water to make 1 liter at a pH of 11.0, and

(2) Part B consists essentially of—

Water—800 cc.

Sodium thiosulfate .5H<sub>2</sub>O—30 g.

Silver chloride— $5 \times 10^{-2}$  moles

Water to 960 cc.

5-methylbenzotriazole (1% in dilute potassium hydroxide)—40 cc., and

(c) said photographic dye-bleaching solution consists essentially of:

Concentrated HCl—100 ml.

Thiourea—125 g.

2-hydroxy-3-aminophenazine—.15 g.

Water to make 1 liter.

7. A dye-bleaching process for producing positive, colored photographic dye images on an imagewise exposed photographic element comprising a support having coated thereon a light-sensitive colored complex of titanium dioxide and an unsaturated organic ligand compound selected from the group consisting of 1,2-dihydroxy-5-(2-sodiumsulfophenyl)amido - 8 - (2 - sodiumsulfo-4-methylphenyl)amidoanthraquinone, and 4-(2,4-dinitrophenylhydrazonomethyl)pyrocatechol, which process comprises:

(a) physically developing a silver metal image on the imagewise exposed areas of said photographic element, and

(b) treating said photographic element with a photographic dye-bleaching solution for a period of time sufficient to render said colored complex colorless in these areas having a metallic silver image.

8. A dye-bleaching process as described in claim 7 wherein physically developing a silver metal on the imagewise exposed areas of said photographic element comprises sequentially treating said element with:

(a) a first solution comprising a silver ion-containing solution to produce development centers of metallic silver in the exposed areas,

(b) a physical developer solution containing silver ions and a reducing agent for said silver ions to pro-

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duce a visible metallic silver image in the exposed areas.

9. A dye-bleaching process as described in claim 8 wherein:

- (a) said first solution comprises silver nitrate,
- (b) said physical developer solution has a formula consisting of equal portions of Parts A and B, wherein:

(1) Part A consists essentially of—

- Water—800 cc.
- Sodium sulfite—20 g.
- Sodium isoascorbate—26 g.
- Sodium carbonate (monohydrate)—50 g.
- Octyl phenoxy ethoxy ethyl dimethyl-p-chlorobenzyl ammonium chloride (1% in H<sub>2</sub>O)—20 cc.

Water to make 1 liter at a pH of 11.0, and

(2) Part B consists essentially of—

- Water—800 cc.
- Sodium thiosulfate .5H<sub>2</sub>O—30 g.
- Silver chloride— $5 \times 10^{-2}$  moles
- Water to 960 cc.
- 5-methylbenzotriazole (1% in dilute potassium hydroxide)—40 cc., and

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(c) said photographic dye-bleaching solution consists essentially of:

- Concentrated HCl—100 ml.
- Thiourea—125 g.
- 2-hydroxy-3-aminophenazine—.15 g.
- Water to make 1 liter.

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U.S. Cl. X.R.

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