United States Patent

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[54] PHOTOGRAPHIC ELEMENT AND PROCESS HAVING A LIGHT-SENSITIVE METAL COMPLEX

16 Claims, No Drawings

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[50] **Field of Search** 96/73, 66, 48 PD, 96, 78

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ABSTRACT: Light-sensitive photographic elements incorporating an azo dye and, as a physical development nuclei precursor, a light-sensitive component which is either a photoactivated metal oxide in combination with a water soluble silver salt or a heavy metal complex coated at a metal coverage of from about 0.5 mg/ft.^{2} to about 10 mg./ft.^{2} can be processed by dye bleach means to yield positive dye images. Preferred heavy metal complexes are silver-spectral sensitizing dye complexes. Processing comprehends forming an exposed imagewise metallic image by physical development including diffusion transfer means and then conventional dye bleaching to produce the final positive dye image.

PHOTOGRAPHIC ELEMENT AND PROCESS HAVING A LIGHT-SENSITIVE METAL COMPLEX

This invention relates to photography and in particular to novel photographic elements designed for use in dye-bleach systems and to the dye-bleach process associated therewith.

The selective destruction of azo 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).

Monochromatic silver dye-bleach photographic elements generally involve a support coated with a silver halide layer having in association therewith at least one azo dye. After an imagewise exposure, followed first by development in a black-and-white silver halide developer solution to produce a silver image in the areas of exposure, and then by treatment with an acidic or alkaline dye-bleaching solution, a positive azo dye image results on the support material.

A typical multicolor silver-dye-bleach element includes 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 azo dyes. After an imagewise exposure, there 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 typically 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, dye image is thereby produced which is photographically the converse of the initial silver image.

In known dye-bleach elements, however, each light-sensitive layer requires the presence of significant amounts of a silver salt, typically a silver halide, which imparts light sensitivity and also supplies a source of silver ions from which the photographic silver image necessary for dye bleaching is obtained. Inefficiencies in the system necessitate the use of excess amount of silver in order to achieve adequate sensitivity to light and also to promote the formation of a silver image which promotes advantageous bleaching.

Accordingly, it is an object of this invention to provide, for photographic dye-bleach purposes, a novel photographic element incorporating decreased amounts of a light-sensitive silver salt.

Another object of the present invention is to provide new photographic dye-bleach processes for the production of positive, colored azo dye images.

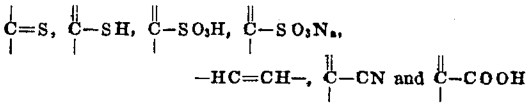
These and other objects of the instant invention will become apparent from a consideration of the following specification and appended claims.

The objects of this invention are accomplished with dye-bleach photographic elements comprising a support having coated thereon at least one layer comprising as a physical development nuclei precursor and at a heavy metal coverage of from about 0.5 mg./ft.^{2} to about 10 mg./ft.^{2}, a light-sensitive component which is either (a) a photoactivatable metal oxide in combination with a water soluble silver salt or (b) a heavy metal complex, and contiguous to said light-sensitive component at least one bleachable azo dye.

The subject photoactivatable metal oxides which are used in combination with a water soluble silver salt to provide silver physical development nuclei directly upon exposure to activating radiation include both photoconductors and nonphotoconductors, and are those metal oxides which will transfer and donate electrons to a reducible silver salt when activated by ultraviolet or actinic radiation. Typical such oxides are aluminum oxide, zinc oxide, titanium dioxide and antimony trioxide. The water-soluble silver salts which are combined with a photoactivatable metal oxide, receiving electrons from such oxides upon exposure and being reduced in the exposed areas to produce minute metallic silver specks which function as physical development nuclei, include salts of the more highly solubilizing anions such as silver nitrate, silver acetate and silver lactate.

The heavy metal complexes of the subject invention are light-sensitive and produce free metal nuclei directly upon exposure. These complexes can be heavy metal salts of either organic or inorganic acids and are preferably salts of low molecular weight acids such as a diazosulfonic acid, a sulfinic acid, a halogen acid like those of chlorine, bromine and iodine, or nitric acid. Suitable heavy metals include such heavy metals as silver, copper, chromium, cobalt, platinum and gold, with silver metal being especially preferred. The preparation of such complexes can be carried out as a displacement reaction between two reactive salts, sodium chloride and silver nitrate for example, to form the light-sensitive silver chloride complex. Such heavy metal complexes are sensitive to actinic and ultraviolet rays and will undergo photoreduction to produce minute free metallic specks or nuclei upon exposure to the noted activating radiation.

Alternatively, the heavy metal complexes of this invention can be visible light-sensitive species which are the complex reaction product of a water-soluble heavy metal salt and a spectral sensitizing dye. Preferred heavy metal spectral-sensitizing dye complexes are those of silver, and the complexes are prepared by combining a sensitizing dye and a water-soluble heavy metal salt. Particularly advantageous salts include those of the more highly solubilizing anions, and especially nitrate salts like silver nitrate. The subject heavy metal-sensitizing dye complexes are sensitive in general to the absorption spectra of the complexed sensitizing dye. Advantageous spectral sensitizing dyes include, for example, dyes of the type commonly used to spectrally sensitize photographic silver halide and and include such organic dyes as cyanine dyes, merocyanine dyes, oxonol dyes, hemicyanine dyes, styryl dyes, hemioxonal dyes, benzylidene dyes and the like. Such spectra sensitizers enter into complexes of varying strength with soluble silver salts such as silver nitrate. Particularly useful complex forming dyes include those of the types noted above which also exhibit functional groups like



$$>C{=}S,\quad >C(=)\text{—SH},\quad >C(=)\text{—SO}_3\text{H},\quad >C(=)\text{—SO}_3\text{Na},\quad \text{—HC}{=}\text{CH—},\quad >C(=)\text{—CN and } >C(=)\text{—COOH},$$

such as the cyanine dye anhydro-3-ethyl-9-methyl-3′-(3-sulfobutyl)-thiocarbocyanine hydroxide.

Preferred spectral sensitizing dyes of the instant invention are merocyanine dyes such as:

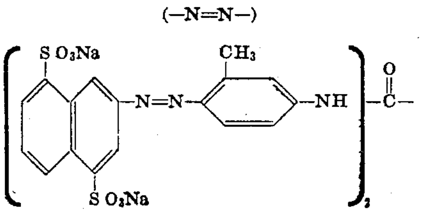
a. 3-carboxymethyl-5-[3-methyl-2-thiazolidinylidene)-ethylidene]rhodanine 420–560 mμ
b. 5-[(3-thiazolidinylidene)ethylidene]-rhodanine 460–570 mμ
c. 5-[(3-methyl-2-thiazolidinylidene)ethylidene]-2-thio-2,4-oxazolidinedione 400–560mμ
d. 3-ethyl-5-[(3-methyl-2-thiazolidinylidene)ethylidene]-2-thio-2,4-oxazolidinedione 430–540mμ
e. 1-methyl-5-[(3-methyl-2-thiazolidinylidene)ethylidene]-2-thiobarbituric acid 430–530 mμ
f. 3-carboxymethyl-5-[(3-ethyl-2-benzoxazolinylidene)-ethylidene]rhodanine 420–580 mμ
g. 5-(3-ethyl-2-benzoxazolinylidene)rhodanine 370–460 mμ

h. 5-[(3-ethyl-2-benzoxazolinylidene)ethylidene]-rhodanine 520–560 mμ

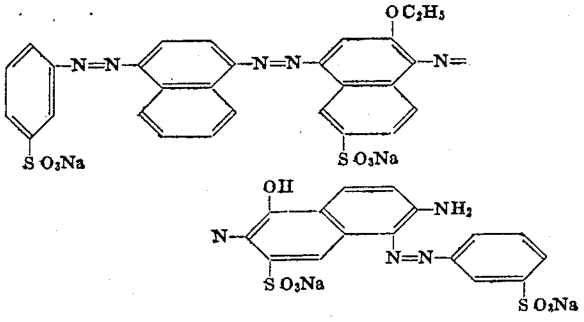
i. 3-ethyl-5-[(3-ethyl-2-benzoxazolinylidene)ethylidene]-1-phenyl-2-thiohydantoin 520–560 mμ

j. 1-carboxymethyl-5-[(3-ethyl-2-benzoxazolinylidene)-ethylidene]-3-phenyl-2-thiohydantoin 520–560 mμOther advantageous spectral sensitizing dyes include such dyes as those disclosed in French Pat. No. 1,453,635. Spectral sensitizers are typically rendered colorless by the processing solutions and so not form a part of the final positive dye image. Also, the spectral sensitizing dyes forming the visible light-sensitive heavy metal complexes are used in relatively small amounts. In certain instances, a photoactivatable metal oxide as recited herein can be present along with the subject heavy metal complexes to foster the more rapid photoreduction of nuclei.

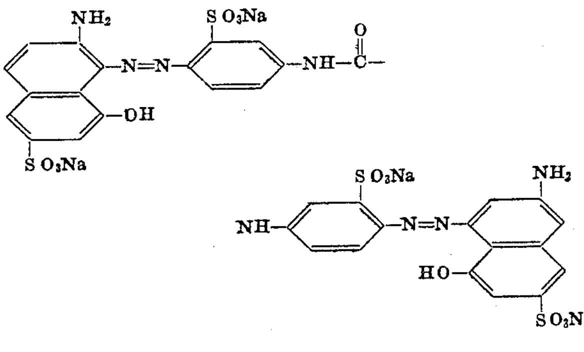
As noted herein, in the composite photographic elements of this invention, the subject light-sensitive components have in association therewith a bleachable azo dye. Such bleachable azo dyes can be positioned in the same layer as the subject physical development nuclei precursors or in layers adjacent thereto. Bleachable azo dyes include those dyes having at least one azo linkage (—N N—) such as monoazo, diazo, triazo, tetraazo and the like azo dyes which are reduced to a colorless form in the presence of a heavy metal image and a conventional dye-bleaching solution such as those described herein. Typical bleachable azo dyes include, for example, a yellow colored diazo dye having the formula:



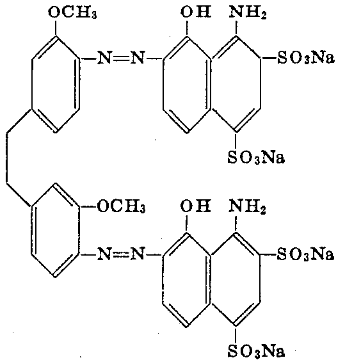
a cyan colored tetraazo dye having the formula:



a magenta colored diazo dye having the formula:



a blue colored diazo dye having the formula:



A wide variety of other bleachable azo dyes are well known to those skilled in the photographic dye-bleach arts. A composite photographic element can then be prepared by coating the light-sensitive component and accompanying azo dye on a support material and preferably dispersed in a hydrophilic carrier such as gelatin. The silver or other heavy metal coverage in such photographic elements can be considerably diminished from that amount which is typically present as the light-sensitive component in conventional dye-bleach photographic elements.

In preparing a photographic element of the subject invention, the choice of a support material can be extensively varied in accordance with usual practice. Conventional polymeric film supports, for example cellulose esters such as cellulose acetate butyrate and also other polymers like poly(ethylene terephtalate) and polystyrene are advantageously employed. Paper, including polyethylene and polypropylene coated paper, as well as titanium dioxide, zinc oxide and baryta pigmented paper, are also typical support materials. Other supports are well known to those skilled in the photographic dye-bleach arts.

The coating sequence and composition of individual coating solutions used to prepare the subject photographic dye-bleach elements are subject to wide variation. In one embodiment, the support can be coated with a first layer which includes the bleachable azo dye. The light-sensitive component is coated in a second layer which is separated from the support by and contiguous to the first azo dye layer. Such a method is particularly amenable to monochromatic elements. Alternatively, the light-sensitive component and bleachable azo dye can be intermixed and coated in a single layer which is especially advantageous in the production of multicolor elements where three light-sensitive layers, sensitized to red, green and blue light, respectively, are used to produce a full color positive dye image of an original subject. Also, where the light-sensitive component is a heavy metal complex, the reagents from which the complex is prepared, such as a soluble heavy metal salt and a spectral sensitizing dye, can be coated separately, whereupon the subject complex forms in the coated light-sensitive layer.

Typically, the active ingredients are dispersed in a hydrophilic binder material such as gelatin, polyvinyl alcohol, cellulose acetate and the like binders prior to coating in order to insure adequate adhesion and uniform dispersion of the active components.

In addition to the previously mentioned photoactivatable metal oxides, soluble silver salts, heavy metal complexes, bleachable azo dyes, spectral sensitizing dyes and hydrophilic binders, other addenda can be present in the coating solution. Where dye solubility or dye migration makes it advantageous, whether because of the dye characteristics or the type of dye-bleach system, a polymeric mordanting material can be used in the dye-containing layers to inhibit such dye wandering. Exemplary of such materials are cationic mordants like poly-(styrene-maleimide) mordants as described in U.S. Ser. No. 655,758, filed July 25, 1967 and presently copending herewith, poly-a-methyl-allyl-N-guanidyl ketimine glycolate, disclosed in U.S. Pat. No. 2,882,156 and the like. Such mordant materials are especially useful in multicolor elements of the subject invention. Other conventional photographic emulsion addenda such as antifoggants, hardeners, coating aids etc. can also be included in the coated layers of the subject elements. If desired, an organic reducing agent, such as a dihydroxy benzene compound like hydroquinone or an aminophenol like metol developing agent, a 3-pyrazolidone, as well as other reducing agents which are typically including in black-and-white photographic developer compositions, can be included in the coating composition. Such addenda work to simplify the process of development and allow processing without the use of conventional developer solutions.

Coating can be accomplished by a wide variety of means known to those skilled in the art, with doctor blade coating and hopper coating being typically employed techniques. As coated in any layer, either the heavy metal-sensitizing dye complex prepared with a water soluble heavy metal salt, the unsensitized heavy-metal complex or the water soluble silver salt which is coated in combination with a photoactivatable metal oxide, generally varies from about 0.5 mg/ft.^{2} to about 10 mg./ft.^{2} of heavy metal coverage. The bleachable azo dye is typically incorporated in an amount ranging from about 15 mg./ft.^{2} to about 60 mg./ft.^{2}, and the spectral sensitizers are generally present in smaller sensitizing amounts that are requisite to obtaining a desired degree of photosensitivity, e.g., about 0.01 mg./ft.^{2} to 2 mg./ft.^{2}. The hydrophilic binder material is generally present in an amount by weight of from about 200 % to about 400 % of the bleachable azo dye. Where a mordant is used, it is typically included in a weight ratio of from about 10 % to about 200 % of the bleachable azo dye. These amounts are merely illustrative, however, and more widely varying amounts can be used where desired, in accordance with usual practice.

A photographic element of the subject invention can be imagewise exposed to activating light radiation through an original pattern or to other subject matter, which exposure produces an imagewise-exposed pattern of minute heavy metal nuclei by photolytic reduction of the incorporated heavy metal salt. Subsequent to exposure, a silver or other metal image is formed in the exposed, nucleated areas by physical development, including diffusion transfer techniques wherein generally silver ions are obtained from a second and superposed element as well as typical physical development processes using silver ions or other heavy metal ions in the process bath.

Where physical development is employed to form the metallic silver image, the imagewise exposed photographic element is contacted with a physical developer solution for a period of time necessary to produce, in the exposed areas, a silver image which is sufficient to catalyze or effect the reductive dye bleaching. Conventional physical developer solutions contain heavy metal ions 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. 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 metallic ions such as silver, copper, iron, nickel and cobalt necessary to form a visible image at and in the vicinity of nucleating centers, the microscopic metal deposits created during the above-described exposure 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-chlorohydroquinone, 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.

When a metallic image, typically silver, is produced by diffusion transfer means, the imagewise exposed photographic element of this invention is generally contacted with a second photographic element having coated thereon a silver halide emulsion, which contacting is in the presence of a developer composition of the type used in silver halide processes. Typically, such conventional developer compositions used in diffusion transfer processing are similar to the physical developing compositions described above, except that no silver ion is required. If desired, the imagewise exposed element of this invention and the second element containing the silver halide can be immersed concurrently into the developer composition, or either or both elements can have the developer imbibed therein.

Upon the formation of an exposed, imagewise metallic 2image, the subject photographic element is treated with an an azo dye-bleaching solution which operates to reduce the azo dye to a colorless form in those areas bearing a photographic silver or other metal image. Conventional such bleaching solutions utilize an acid medium such as hydrochloric acid wherein the typically silver image is the reducing agent. Acidic bleaching solutions can also contain complex formers for silver ion (e.g. thiourea, mercaptans, benzimidazoles, etc.) to diminish the concentration of silver ion formed in the bleaching reaction. Additionally, where more rapid bleaching is desired, certain compounds such as phenazines like 2-hydroxy-3-aminophenazine, oxazines and sulfonated anthraquinones accelerate the bleach process catalytically. Typical of acidic bleaching solutions is one having the formula:

Concentrated HCL	100 ml.
Thiourea	125 g.
2-Hydroxy-3-aminophenazine	0.15 g.
Water to make	1 liter

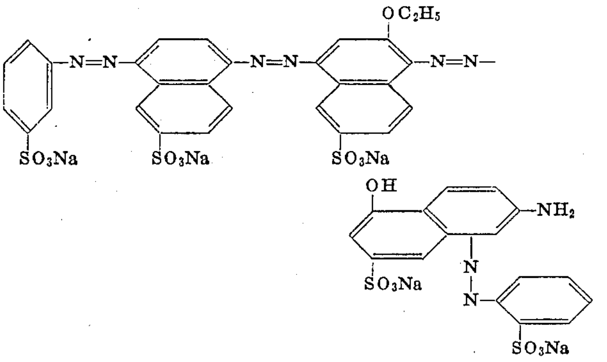
Other conventional dye-bleaching solutions are well known in the photographic art.

After bleaching, residual silver can be removed by treatment with typical photographic silver bleaching agents such as water-soluble ferricyanides, and excess silver halide can be eliminated by treatment with a conventional fixing or silver halide solubilizing agent such as thiosulfates, thiocyantes and mercaptans. Typical fixing agents include compounds like ammonium thiosulfate and the disodium salt of 2-mercapto-4-hydroxy-5-aminopyrimidine. A particularly preferred fixing agent is sodium thiosulfate. The result is an azo dye image which is also a positive reproduction of the original. Such an 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 by transmitted light such as by projection.

The invention has been described in considerable detail and is further illustrated by the following examples which include per preferred embodiments thereof.

EXAMPLE I

A light-sensitive photographic element is prepared by coating a cellulose acetate film support material with a first layer containing gelatin at a coverage of 184 mg./ft.^{2}, a cyan colored tetraazo dye having the formula:



at a coverage of 30 mg./ft.^{2} and a mordant material, poly(α-methylallyl-N-guanidyl ketimine glycolate) as described in U.S. Pat. No. 2,882,156, at a coverage of 63 mg./ft.^{2}. Over and contiguous to this first layer is coated a second layer containing gelatin at a coverage of 400 mg./ft.^{2}, silver (added as silver nitrate), at a silver coverage of 1.65 mg./ft.^{2} and 0.066 mg./ft.^{2} of the spectral sensitizer 1-carboxymethyl-5-{[3-ethyl-2-(3H)-benzoxazolylidene]-ethylidene}-3-phenylthiohydantoin. The element so prepared is imagewise exposed for 30 seconds to the tungsten light of a 500 watt, R2 photoflood lamp held about 15 inches from the exposing plane and is then immersed in a diffusion transfer developer composition having the formula:

Methylaminoethanol ·2 ($18.9\%\ SO_2$)	190.0 g.
4,4'-dimethyl-1-phenyl-3 -pyrazolidone	1.0 g.
Hydroquinone	11.6 g.
Sodium thiosulfate pentahydrate	60.0 g.
Potassium iodide	0.42 g.
Distilled H_2O to	1.0 liter

to which is added 10 cc. of a toner, 1% 5-methyl-3-piperidinylmethyl-2-thio-oxazolidine in methanol. After removal from the developer, the element is laminated for 3 minutes against a second photographic element having coated thereon a fine grained gelatino silver bromoiodide emulsion layer containing silver at a coverage of 363 mg./ft.^{2} and gelatin at a coverage of 1,080 mg./ft.^{2}. When the two are stripped apart, the azo-dye-containing element possesses a negative silver image corresponding to the previously imagewise exposed areas. The negative silver image-containing element is then immersed for 3 minutes at 60° C. in an azo-dye-bleaching solution containing:

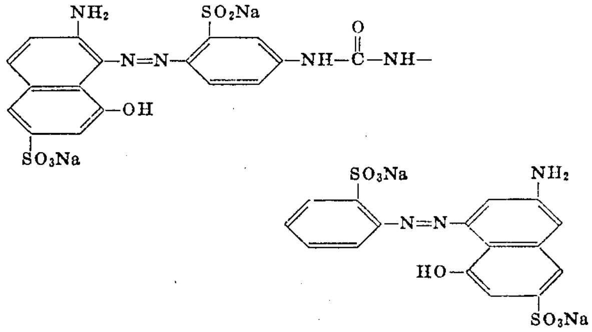
Sodium chloride	150 g.
Concentrated HCl	113 ml.
2-Hydroxy-3-aminophenazine—1% in acetic acid/H_2O (1:1)	30 ml.

This bleaching treatment causes the azo dye to be reduced to a colorless form in the areas where a silver image is present. Thereafter, treatment for 1 minute in a ferricyanide bleach removes remaining silver and for one minute in a sodium thiosulfate fixing solution removes remaining silver halide. The resulting processed photographic element exhibits a high density (D_{max}) positive cyan dye image with low stain (D_{min}) in the nonimage exposed areas.

EXAMPLE II

A light-sensitive photographic element is prepared by coating a cellulose acetate film support material with a red light-sensitive first layer containing gelatin at a coverage of 400

mg./ft.^{2}, silver (added as silver nitrate) at a silver coverage of 2.6 mg./ft.^{2}, the red light spectral sensitizer 5[(1-ethyl-2(1)-β-naphthothiazolylidene)-α-phenylethylidene]-3β-methoxyethyl-2-(3-β-methoxyethyl-4-oxo-2-thiono-5-thiazolidylidene)-4thiazolidone at a coverage of 0.071 mg./ft.^{2} and the cyan colored tetraazo dye of example I at a coverage of 35 mg./ft.^{2}. Over and contiguous to this first layer is coated a second layer which is sensitized to green light. This second layer is identical to the first layer except that a green light spectral sensitizer, 3-ethyl-5-(3-ethyl-2benzoxazolyidene-ethylidene)-1-phenyl-2-thiohydantoin is substituted for the red light spectral sensitizer and a magenta colored diazo dye having the formula:



is substituted for the cyan colored tetraazo dye of the first layer. The element which is so prepared is imagewise exposed to the light of a 500 watt R2 photoflood lamp through multicolor positive transparency. After exposure silver images are formed on the element by immersion for two minutes in a physical developer having the formula:

Part A

Water	800 cc.
Sodium sulfite	20 g.
Sodium isoascorbate	26 g.
Sodium carbonate monohydrate	50 g.
Octylphenoxyethoxy ethyldimethyl p-chlorobenzyl ammonium chloride (1% in water)	22 cc.
Water to make	1 liter
Adjust pH to 11.0	

Part B

Water	800 cc.
Sodium thiosulfate pentahydrate	30 g.
Silver chloride	5×10^{12} moles
Water to make	960 cc.
5-Methylbenzatriazole (1% in diluted potassium hydroxide)	40 cc.

wherein Parts A and B are mixed just prior to use. For making the silver chloride used in Part B. 42.4 g. of silver nitrate are dissolved to 900 cc. of water and 42.4 g. of potassium chloride are dissolved in a second 900 cc. of water. Then 90 cc. of each solution are mixed in 6 ounce bottles which are allowed to stand overnight, after which time the liquid is poured off. The contents of two such bottles is required to make the 5×10^{12} moles, since each contains 2.5×10^{12} moles of silver chloride. Once a silver image is formed on the element, it is treated as in example 1, but with an azo dye bleaching solution having the formula:

Concentrated HCl	100 ml.
Thiourea	125 g.

2-Hydroxy-3-aminophenazine	0.15 g.
Water to make	1 liter

It is also treated as in example I to remove excess silver and silver halide. After such processing, the element exhibits a two color, high density positive dye images which reproduce the red and green portions of the original.

EXAMPLE III

A light-sensitive photographic element is prepared according to the procedure of example I, except that an equimolar amount of sodium chloride is substituted for the spectral sensitizer 1-carboxymethyl-5-{[3-ethyl-2-(3H)-benzoxazolylidene]-ethylidene}-3-phenylthiohydantoin. Exposure is as described in example I, except that it is to the light of a mercury vapor lamp, rich in ultraviolet rays. After exposure, a silver image is produced in the exposed, nuclei bearing areas by diffusion transfer means as in example I, and dye bleaching is then accomplished in a like fashion. The resulting processed photographic element exhibits a positive cyan dye image of high quality, comparable to that noted in example I.

EXAMPLE IV

A light-sensitive photographic element is prepared by coating polyethylene-coated paper support material with a layer comprising the cyan-colored tetraazo dye described in example I at a coverage of 30 mg./ft.^{2,} gelatin at a coverage of 150 mg./ft.^{2,} titanium dioxide at a coverage of 300 mg./ft.^{2} and silver (added as silver nitrate) at a silver coverage of 10, mg./ft.^{2}. The composite element is exposed and developed as described in example I, after which bleaching is accomplished also as noted in example I. The resulting processed element exhibits a positive cyan dye image like that described in example I.

Although the invention has been described in considerable detail with reference to certain preferred embodiments thereof, it will be understood that variations and modifications can be effected without departing from the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

I claim:

1. A photographic element comprising a support having coated thereon at least one layer comprising, as a physical development nuclei precursor and at a heavy metal coverage of from about 0.5 mg./ft.^{2} to about 10 mg./ft.^{2}, a light-sensitive component selected from the group consisting of (a) a photoactivatable metal oxide in combination with a water soluble silver salt and (b) a [heavy metal complex] light-sensitive heavy metal complex that produces free metal nuclei directly on exposure, and contiguous to said light-sensitive component at least one bleachable azo dye.

2. A photographic element as described in claim 1, wherein said photoactivatable metal oxide is selected from the group consisting of zinc oxide, titanium dioxide, antimony trioxide and aluminum oxide, and wherein said water soluble silver salt coated at a silver coverage of from about 0.5 mg./ft.^{2} to about 10 mg./ft.^{2} is selected from the group consisting of silver nitrate, silver acetate and silver lactate.

3. A photographic element comprising, as a physical development nuclei precursor, a light-sensitive heavy metal complex that produces free metal nuclei directly on exposure, [serving as a physical development nuclei precursor,] coated at a metal coverage of from about 0.5 mg./ft.^{2} to about 10 mg./ft.^{2} and contiguous to said complex at least one bleachable azo dye.

4. A photographic element as described in claim 3 wherein said heavy metal complex is a heavy metal salt of a spectral sensitizing dye.

5. A photographic element comprising a support having coated thereon at least one layer comprising a light-sensitive silver-spectral sensitizing dye complex, serving as a physical development nuclei precursor, coated at a silver coverage of about 0.5 mg./ft^2 to about 10 mg./ft^2, and contiguous to said complex at least one bleachable azo dye.

6. A photographic element as described in claim 5 wherein the said azo dye is coated in a layer which is contiguous to the said light-sensitive layer.

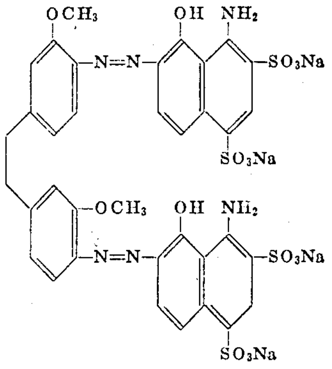
7. A photographic element as described in claim 5 wherein the support comprises poly(ethylene terephthalate).

8. A photographic element as described in claim 5 wherein the said azo dye is coated in a first layer contiguous to the said support and the said light-sensitive silver salt is coated in a second layer contiguous to said first azo dye layer.

9. A photographic element comprising a support having coated thereon at least one layer comprising a light-sensitive silver-merocyanine dye complex, serving as a physical development nuclei precursor, coated at a silver coverage of about 0.5 mg./ft.^{2} to about 10 mg./ft.^{2} and at a merocyanine dye coverage of about 0.01 mg./ft.^{2} to about 2 mg./ft.^{2}, and contiguous to said light-sensitive layer at least one azo dye bleachable in the dye-bleach process coated at a coverage of about 15 mg./ft.^{2} to about 60 mg./ft.^{2}.

10. A photographic element comprising a support having coated thereon:

a. a first layer comprising a cyan colored azo dye having the formula:



b. a second layer comprising a silver spectral sensitizing dye complex, serving as a physical development nuclei precursor, which is the reaction product of silver nitrate coated at a silver coverage of 1.65 mg./ft.^{2} and 1-carboxymethyl - 5 - {[3 - ethyl - 2 - (3H) - benzoxazolylidene] - ethylidene}-3-phenyl-2-thiohydantoin coated at a coverage of 0.066 mg./ft.^{2}.

11. A process for treating an imagewise exposed photographic element comprising a support having coated thereon at least one layer comprising, as a physical development nuclei precursor and at a heavy metal coverage of from about 0.5 mg./ft.^{2} to about 10 mg./ft.^{2}, a light-sensitive component selected from the group consisting of (a) a photoactivatable metal oxide in combination with a water soluble silver salt and (b) a heavy metal complex that produces free metal nuclei directly on exposure, and contiguous to said light-sensitive component at least one bleachable azo dye to produce photographic images, which process comprises sequentially contacting said photographic element with:

a. a combination comprising silver ions and a reducing agent for silver ions for a period of time sufficient to produce a silver image in the areas of exposure,

b. a bleaching solution for a period of time sufficient to reduce the azo dye to a colorless form in the areas bearing a silver image, and

c. an alkaline silver salt complexing composition for a period of time sufficient to remove unreduced silver salt.

12. A process as described in claim 11 wherein the said combination comprising silver ions and a reducing agent for silver ions is a photographic physical developer solution.

13. A process as described in claim **11** wherein the said combination comprising silver ions and a reducing agent for silver ions is a silver halide emulsion layer that has been treated with a photographic developer solution.

14. A process as described in claim **11** wherein the said bleaching solution has the formula:

Concentrated HCl	100.00 ml.
Thiourea	125.00 g.
2-Hydroxy-3-aminophenazine	0.15 g.
Water to make	1.00 liter

15. A process as described in claim **11** wherein excess silver is removed from the photographic element by treatment with a ferricyanide bleaching solution.

16. A process as described in claim **11** wherein the treated photographic element comprises a support having coated thereon at least one layer comprising a light-sensitive silver-spectral sensitizing dye complex, serving as a physical development nuclei precursor, coated at a silver coverage of about 0.5 mg./ft.^{2} to about 10 mg./ft.^{2}, and contiguous to said complex at least one bleachable azo dye.

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