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PATENT SPECIFICATION (11) 1 591 176

(21) Application No. 42116/77 (22) Filed 10 Oct. 1977
(61) Patent of Addition to No. 1 542 913 dated 4 Nov. 1976
(31) Convention Application No. 730 912
(32) Filed 8 Oct. 1976 in
(33) United States of America (US)
(44) Complete Specification published 17 June 1981
(51) INT CL³ G03C 5/50, 5/54
(52) Index at acceptance G2C A6X C8X
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(19)

(54) FORMING PHOTOGRAPHIC REVERSAL DYE IMAGES

(71) We, EASTMAN KODAK COMPANY, a Company organized under the Laws of the State of New Jersey, United States of America of 343 State Street, Rochester, New York 14650, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of forming photographic reversal dye images.

In our Application No. 45977/76 (Serial No. 1,542,913) there is claimed a method of forming a photographic reversal dye image comprising

developing with a first developer solution an imagewise exposed photographic material comprising a support and at least one photosensitive silver halide emulsion layer to produce a first silver image,

poisoning said first silver image as a catalyst for the dye-forming reaction below,

rendering the undeveloped silver halide remaining in the emulsion layer developable,

developing the undeveloped silver halide with a second developer solution to produce a reversal silver image which is catalytic for the dye-forming reaction below, and

treating the material with a solution of a peroxide oxidising agent in the presence of a dye image-generating reducing agent and, if necessary for dye formation, a colour coupler to produce a dye image corresponding to the reversal silver image.

We now provide a method similar to that claimed in 1,542,913 in which dye images are formed from redox dye releasers (RDR'S).

According to the present invention there is provided a method of forming a photographic reversal dye image comprising

developing with a first developer solution an imagewise exposed photographic material comprising a support and at least one photosensitive silver halide emulsion layer having associated therewith a non-diffusible redox dye releaser to produce a first silver image,

poisoning said first silver image as a catalyst for the dye-forming reaction below,

rendering the undeveloped silver halide remaining in the emulsion layer developable,

developing the undeveloped silver halide with a second developer solution to produce a reversal silver image which is catalytic for the dye-forming reaction below, and

treating the material with a solution of a peroxide oxidising agent in the presence of a cross-oxidising developing agent to produce a diffusible dye image corresponding to the reversal silver image, and

thereafter removing the diffusible dye from the layer in which it was released either by receiving it on a dye image-receiving layer or by washing with an aqueous liquid.

Redox dye-releasers are non-diffusible compounds which upon reaction with a cross-oxidising developing agent with or without subsequent hydrolysis release a diffusible dye. The mobile dye can be transferred to a receiver to form a dye image or simply washed out of the photographic element so that the immobile redox dye-releaser which remains in the photographic element forms a retained dye image. Typical redox dye-releasers are disclosed, for example, in British Specification 1,405,662 and *Research Disclosure,* 15157 and 15162, both published November 1976.

In a preferred mode of practising the present invention a silver halide emulsion photographic element of a type used in producing multicolour images is employed which differs from the conventional incorporated colour coupler element described in Specification 1,542,913 by having a redox dye-releasing compound in place of the colour coupler in each of the emulsion layers or in a separate layer adjacent thereto, such that a yellow dye can be released from the blue recording emulsion layer or a layer adjacent thereto; a magenta dye can be released from the green recording emulsion layer or a layer adjacent thereto and a cyan dye can be released from the red recording emulsion layer or a layer adjacent thereto. Processing can be undertaken as described in Specification 1,542,913 for the incorporated colour coupler photographic element, except that in this instance in place of the colour-developing agent it is necessary to employ a cross-oxidising developing agent. The cross-oxidising developing agent reacts with the peroxide oxidising agent in the presence of the catalytic silver image surface to form oxidised developing agent. This oxidised developing agent then cross-oxidises the redox dye-releaser, thereby regenerating the developing agent and causing an image dye to be released directly or upon hydrolysis. The released dye may then be transferred to a receiving layer to form a transferred dye image if desired.

It should be noted that while the retained and transferred dye images are complementary they are both reversals of the retained and transferred dye images, respectively, which would be produced by using the first developed silver image as a redox catalyst.

The light-sensitive silver halide layers used in elements processed in accordance with this invention are most preferably coated at silver coverages of up to 30 mg silver/ft^2 (325 mg/m^2), such as from 0.1 to 30 mg/ft^2 (1.0—325 mg/m^2) and more preferably from 1 to 25 mg silver/ft^2 (10—270 mg/m^2). Especially good results are obtained with coverages of from 2 to 15 mg/ft^2 of silver (20—160 mg/m^2) for the green- and red-sensitive layers of a multilayer colour film.

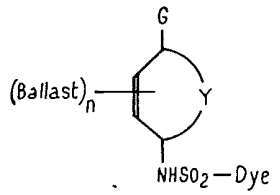
Advantageously, the redox dye-releasers employed in a multicolour element are selected so that they will give a good neutral dye image. Preferably, the released cyan dye has its major visible light absorption between 600 and 700 nm (that is, in the red third of the visible spectrum), the released magenta dye has its major absorption between 500 and 600 nm (that is, in the green third of the visible spectrum), and the released yellow dye has its major absorption between 400 and 500 nm (that is, in the blue third of the visible spectrum). Particularly useful elements comprise a support having coated thereon red-, green- and blue-sensitive silver halide emulsion layers containing, respectively, cyan, magenta and yellow redox dye-releasing compounds.

The light-sensitive silver halides are generally coated in the colour-providing layer units in the same layer with the RDR. However, they can be coated in separate adjacent layers as long as the RDR is effectively associated with the respective silver halide emulsion layer to provide for immediate dye-releasing reactions to take place before substantial cross-oxidising-developer oxidation reaction products diffuse into adjacent colour-providing layer units.

Exemplary redox-releasers useful in the practice of the present process and their synthesis and incorporation into photographic elements are, described for example, in Canadian Patent 602,607, British Specification 1,405,662, U.S. Patents 3,698,897, 3,728,113, 3,725,062, 3,443,939, 3,443,940, 3,443,941 and 3,390,380.

Exemplary of preferred RDR's are those of the sulphonamide type, which may be represented by the following general formula:

(I)



wherein

Dye is the radical of a dye or dye precursor,

Ballast is a photographically inert organic ballasting radical of such molecular size and configuration as to render the compound nondiffusible during development in an alkaline processing composition;

G is OR or NHR_1 wherein R is hydrogen or a hydrolyzable moiety and R_1 is hydrogen or a substituted or unsubstituted alkyl or cycloalkyl group of 1 to 22 carbon

atoms, e.g. methyl, ethyl, hydroxyethyl, propyl, butyl, secondary butyl, *tert*-butyl, cyclopropyl, 4-chlorobutyl, cyclobutyl, 4-nitroamyl, hexyl, cyclohexyl, octyl, decyl, octadecyl, docosyl, benzyl or phenethyl (when R_1 is an alkyl group of a greater than 6 carbon atoms, it can serve as a partial or sole *Ballast* group);

Y represents the atoms necessary to complete a benzene or naphthalene nucleus or a 5 to 7 membered heterocyclic ring, e.g. pyrimide.

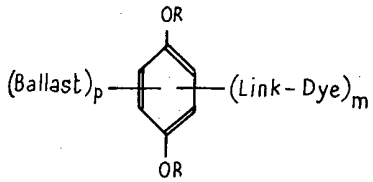
n is 0 or 1 and is 1 when G is OR or when R_1 is hydrogen or an alkyl group of less than 8 carbon atoms.

When Y completes a naphthalene nucleus, *Ballast* may be attached to either ring thereof.

In addition to Ballast, the nucleus completed by Y in the above formula may have groups or atoms attached thereto such as the halogens, alkyl, aryl, alkoxy, aryloxy, nitro, amino, alkylamino, arylamino, amido, cyano, alkylmercapto, keto, carboalkoxy, heterocyclic groups.

Exemplary hydroquinone-type RDR's which may be used in the present invention are represented by the following formula:

(II)



wherein:

each R represents hydrogen or a hydrolyzable moiety;

Ballast and *Dye* are as defined above,

Link is a S, O, or SO_2 linking group, and

m and p are each 1, 2 or 3, m + p being from 2 to 4.

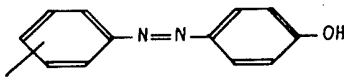
The nature of the ballast group (*Ballast*) in the above formulae may be widely varied as long as it confers nondiffusibility to the compounds. Typical ballast groups include long-chain alkyl radicals linked directly or indirectly to the compound as well as aromatic radicals of the benzene and naphthalene series indirectly attached or fused directly to the benzene nucleus. Useful ballast groups generally have at least 8 carbon atoms such as substituted or unsubstituted alkyl group of 8 to 22 carbon atoms, an amide radical having 8 to 30 atoms or a keto radical having 8 to 30 carbon atoms.

As previously mentioned, *Dye* in the above formlae represents a dye or dye precursor radical. Such radicals are preferably of the azo, azomethine, azopyrazolone, indoaniline, indophenol, anthraquinone, triarylmethane, alizarin or metal complex dye series but may also be radicals of dye precursors such as a leuco dye, a "shifted" dye which shifts hypsochromically or bathochromically when subjected to a different environment such as a change in pH or reaction with a material to form a complex. These dye radicals may contain a solubilizing group if desired.

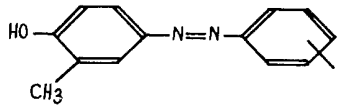
The following groups may represent the group *DYE* in the above formulae:

YELLOW DYE GROUPS.

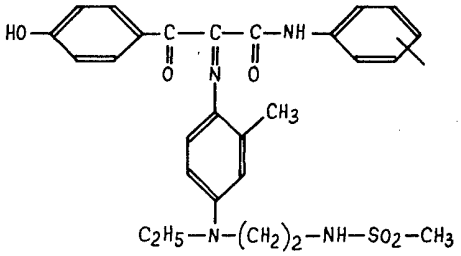
YDG—1 4-Hydroxyphenylazophenylene.



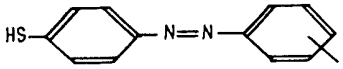
YDG—2 3-Methyl-4-hydroxyphenylazophenylene.



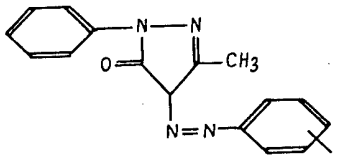
YDG—3.



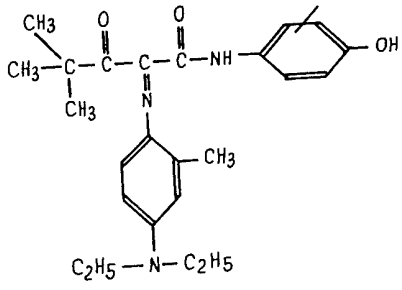
YDG—4 p-Sulphhydrylphenylazophenylene.



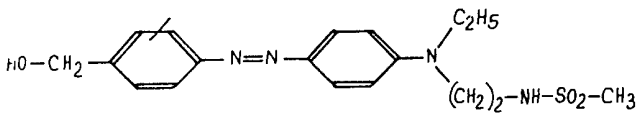
YDG—5.



YDG—6.

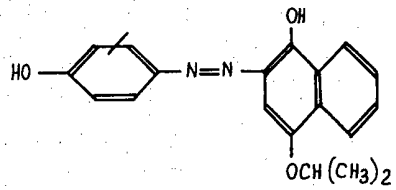


YDG—7.

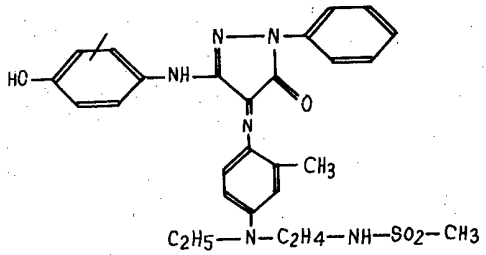


MAGENTA DYE GROUPS.

MDG—1.

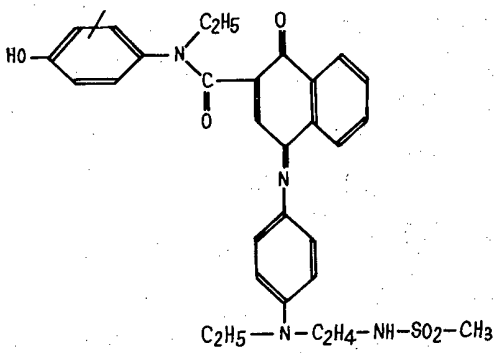


MDG—2.

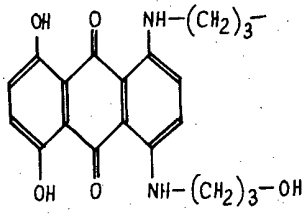


CYAN DYE GROUPS.

CDG—1.



CDG—2.



When dye precursor moieties are employed in the RDR's instead of dyes, they are converted to dyes by means well known to those skilled in the art, e.g., oxidation, either in the photosensitive element, in a processing composition or in a dye image-receiving layer to form a visible dye. Such techniques are disclosed, for example, in British Patents 1,157,501; 1,157,502; 1,157,503; 1,157,504; 1,157,506; 1,157,507; 1,157,508; 1,157,509; 1,157,510; and U.S. Patents 2,774,668; 2,698,798; 2,698,244; 2,661,293 and 2,559,643.

In using the photographic element containing an RDR, it is preferred that the developer composition employed in the first development step be substantially free of a cross-oxidizing developing agent. A cross-oxidizing developing agent is one which upon oxidation in developing silver halide to silver will react with the RDR so that it

releases dye directly or upon hydrolysis. However, where a photographic element contains both a low silver halide coating weight and an RDR any developing agent may be employed in the first development step, since release of dye will be negligible.

Particularly preferred noncross-oxidising developing agents include ascorbic acid and certain derivatives of pyrimidine such as those described in U.S. Patent 3,672,891. Particularly preferred are 5-amino derivatives of pyrimidine and 5-hydroxy derivatives of pyrimidine, especially 2-methyl-4-amino-5-hydroxy-pyrimidine-6-one.

It is recognized that specific developing agents are able to be either cross-oxidizing or noncross-oxidising in developer compositions differing solely in their pH values. It is known that cross-oxidizing silver halide developing agents cease to be cross-oxidizing at lower pH values, although the particular pH value at which a specific developing agent ceases to cross-oxidize varies from one developing agent to another. The appropriate pH for a developer composition employed in the first step of this invention may be readily determined merely by developing a sample of an exposed photographic element containing a silver halide emulsion layer and associated therein an RDR of the type defined above. If a dye is observed in the developer composition or in the photographic element being processed, another quantity of developer composition can be made up differing by having a somewhat lower pH and a second sample can be processed therein. If a dye is again observed, the above procedure can be repeated until a pH is reached at which development of the sample ceases to produce observable dye.

The photographic developers employed in the practice of this invention may include, in addition to conventional developing agents, other conventional components as described in Specification 1,542,913.

The methods of poisoning the first developed silver image as a catalyst described in Specification 1,542,913 may also be employed in the present process. In particular it is preferred that the first developer contains a halide ion in sufficient concentration to poison the first silver image. For example the first developer solution may contain from 1 to 30, preferably from 1 to 15 gms/litre of bromide ion or from 1×10^{-6} to 1 gm, especially from 1 mg to 1 gm/litre, particularly 10 mg/litre of iodide ion.

The treatments between the two developing steps described in Specification 1,542,913 may also be employed herein.

In the second development step the developer composition may be identical to that employed in the first development step where the developer ingredients are incorporated initially entirely in the developer composition. Any catalyst poison which may be present is preferably maintained at a concentration below that disclosed above to be effective. Generally, we prefer that the second developer composition be at least initially substantially completely free of any substance which will poison the developing silver as a redox amplification catalyst.

Catalyst poison initially present in the photographic element or picked up in the first development step will typically be adsorbed to the surface of the first developed silver and will not contaminate the additional silver formed in the second development step. Further, introducing unadsorbed poison into the second developer can be avoided by leaching in processing solutions between the first and second development steps e.g., in an intervening stop and/or wash bath.

Where it is desirable to render developable the silver halide grains not developed in the first development step through the use of a nucleating agent, a conventional nucleating agent may be incorporated in the second developer composition. Exemplary nucleating agents are referred to in Specification 1,542,913.

While any conventional concentration of developing agent(s) may be employed, typically the first and second developer solutions will contain from 1 to 20, most typically from 2 to 10, grams per litre.

In one form of this invention, after forming an imagewise distribution of unpoisoned catalyst silver during the second development, the photographic element being processed is transferred to a redox amplification bath containing a peroxide oxidizing agent. The amplification bath may take the form of conventional redox amplification baths containing a peroxide oxidizing agent of the type disclosed in U.S. Patents 3,674,490 and 3,776,730. The bath may also take the form of that disclosed in British Patent 1,329,444 or "Image Amplification Systems", Item No. 11660 of *Research Disclosure*, No. 116, December 1973. These redox amplification baths are aqueous solutions containing a peroxide oxidizing agent.

The peroxide oxidizing agents employed in the practice of the invention may be chosen from peroxide oxidizing agents which are known to require the presence of a catalyst surface to oxidize a dye-image-generating reducing agent. Peroxide oxidizing agents of this type include water-soluble compounds containing a peroxy

group, such as inorganic peroxide compounds or salts of peracids. For example, perborates, percarbonates or persilicates and, particularly, hydrogen peroxide, may be employed as peroxide oxidizing agents in the practice of the invention as well as organic peroxide compounds such as benzoyl peroxide, percarbamide and addition compounds of hydrogen peroxide and aliphatic acid amides, polyalcohols, amines and acylsubstituted hydrazines. It is preferred to employ hydrogen peroxide, since it is highly active and easily handled in the form of aqueous solutions. Peroxide oxidizing agent concentrations of from 0.001 mole to 0.5 mole per litre of amplification bath are preferred.

The redox amplification bath preferably contains a cross-oxidizing developing agent (often referred to in this type of application as an electron transfer agent). Exemplary cross-oxidizing developing agents are described in the patents referred to above disclosing RDR's and their use. The preferred developing agents useful as cross-oxidizing developing agents are pyrazolidones, for example, 1-phenyl-3-pyrazolidone, 1-phenyl-4,4-dimethyl-3-pyrazolidone and 4-hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidone.

Redox dye-releasers are similar to color-developing agents employed in combination with cross-oxidizing developing agents in that redox dye-releasers react through an intermediate redox couple provided by a cross-oxidizing silver halide developing agent. In this redox couple the silver halide developing agent reacts with the peroxide oxidizing agent on a catalytic surface to form oxidized developing agent. The oxidized developing agent then reacts with the redox dye-releaser and is regenerated. The oxidized redox dye-releaser then usually hydrolyzes in the aqueous alkaline medium provided by the amplification bath to release diffusible dye.

The term "nondiffusible" used herein has the meaning commonly applied to the term in colour photography and denotes materials which for all practical purposes do not migrate or wander through photographic hydrophilic colloid layers, such as gelatin, during processing in aqueous alkaline solutions. The term "diffusible" means the opposite to the above.

The best results can be obtained by maintaining the amplification bath within the alkaline pH ranges heretofore employed with photographic silver halide emulsions used to form dye images using RDR's. Preferred alkalinity for the amplification bath is at least 8, most preferably from 10 to 14. The amplification bath is typically maintained alkaline using activators of the type described above in connection with the developing steps of the process.

Other addenda known to facilitate image-dye formation in alkaline photographic developer solutions with specific RDR's may also be included in the amplification bath. Where lower pH alkaline amplification baths are being employed in combination with RDR-containing photographic elements, the mobility of the released dye can be enhanced by incorporating amino acids or combinations of amines and aliphatic carboxylic acids. Exemplary useful compounds include ω-amino acids, such as 2-aminoacetic acid, 4-aminobutyric acid, 6-aminohexanoic acid, 11-aminoundecanoic acid and 12-aminododecanoic acid. Such released dye solubilizers can be present in the amplification bath in concentrations of from 0.1 to 60 grams per litre, preferably from 1 to 20 grams per litre.

The foregoing description of the process may be termed a sequential mode of practising the invention in that separate second development and amplification baths are employed. Stop and rinsing steps of a conventional character may, if desired, be employed between the second development and the amplification step. Where it is desired to view the dye image within the photographic element being processed, it is contemplated that stop, bleach and rinse steps of a conventional nature may be performed after removing the photographic element from the amplification bath. Where low levels of silver are present, as can be made possible through redox amplification of the dye image, very little, if any difference may be observed as between photographic elements which have been bleached and those which have not been bleached to remove silver.

In an alternative, preferred, mode of practising the process, the second development and amplification steps can be accomplished in a combined second development and amplification bath. In a simple form, this may be accomplished merely by adding one or more peroxide oxidizing agents of the type and in the concentrations described above to one of the second development baths described above. In a specific preferred form, the combined second development and amplification bath is comprised of an aqueous alkaline solution having a pH of at least 8, preferably in the range of from 10 to 14. In addition, the combined bath contains at least one cross-oxidizing silver halide developing agent and at least one peroxide oxidizing agent. A single cross-

oxidizing developing agent can, of course, serve as both the second silver halide developing agent and the cross-oxidizing developing agent. Where the photographic element contains a silver haloiodide in its emulsion layer, it is essential that the second development and amplification steps be performed using a combined second development and amplification bath. Otherwise the silver developed during the second development step would be poisoned as a catalyst for the redox amplification reaction. While it has been observed that silver haloiodides can be developed in a combined second development and amplification bath and that an amplified dye image can be obtained using a peroxide oxidizing agent, the exact mechanism that permits this to occur has not been determined.

Since a redox dye-releaser forms a complementary pattern of diffusible and non-diffusible dye forms, the diffusible form must be separated from the non-diffusible forms in order for a visible image to be produced. A transferred image may be formed by allowing the diffusible form to diffuse to an image receiving layer. The retained dye image is formed once the mobile form has diffused from or been washed from the photographic element. Washing is most easily accomplished using an aqueous alkaline solution having a pH of at least 8, most preferably from 10 to 14. Conventional image receivers and dye transfer procedures as disclosed in the dye-developer and RDR patents cited above may be employed in the practice of the process.

The practice of the invention can be better appreciated by reference to the following Example:

Example.

(A) A photographic element having a transparent film support and a gelatino-silver halide emulsion layer coated thereon containing a redox dye-releaser was prepared. The emulsion coating contained the ingredients set forth below in Table 1. Unless otherwise stated, all coating weights are reported parenthetically in terms of g/metre^2. Silver halide coating weights are reported in terms of silver. Unless otherwise stated, all processing and processing solutions are at 24°C.

Table 1.

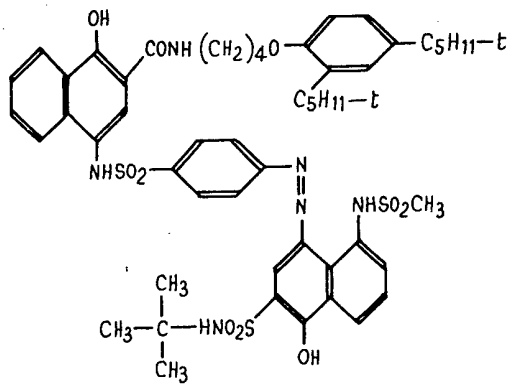
Photographic Element 6—A.

Gelatino-Silver Halide Emulsion Layer: Silver Halide (0.11); Gelatin (2.15); RDR* (0.65).

Transparent Cellulose Triacetate Film Support.

The silver halide employed was monodisperse, sulphur and gold chemically sensitized cubic grain silver bromide having a mean grain size of 0.2 micron.

*RDR.



(B) The photographic element was exposed with a white light source through a graduated-density test object having 21 equal density steps ranging from 0 density at Step 1 to a density of 3.0 at Step 21. The exposed element was then divided into eight (8) samples which were developed for 1 minute in a noncross-oxidizing developer (Kodak (trade mark) Developer D.19 whose composition is given in Table 2 of Specification 1,542,913), but with the substitution of 4 mg of potassium iodide per litre of developer for the potassium bromide.

(C) Four of the samples were then immersed for 30 seconds, 1 minute and 2 minutes and 4 minutes, respectively, in a cross-oxidizing developer solution of the composition set forth below in Table 3.

Table 3.
Cross-Oxidizing Developer.

Potassium hydroxide	56.0 g
Diaminopropanol tetraacetic acid	2.0 g
4-Hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidone	0.5 g
1.4% *tertiary*-Butylamine borane solution	5.5 ml
Water to 1 litre.	

The samples were then immersed for 1 minute in a stop bath formed by a solution of 1 percent by weight acetic acid in water. The samples were immersed for 2 minutes in a bleach-fix bath of the composition set forth in Table 4.

Table 4.
Bleach-Fix Bath.

Ammonium thiosulphate	132.0 g
Sodium bisulphate	13.0 g
Ammonium ferric ethylenediamine tetraacetic acid (0.18 M solution)	65.6 g
Ethylenediamine tetraacetic acid (EDTA)	6.56 g
Ammonium hydroxide (28% solution)	27.9 g
Water to 1 litre, pH 6.8.	

The samples were washed for 2 minutes in water, then immersed for 2 minutes in a solution containing 5 grams per litre of 1-hexadecylpyridinium chloride in water to shift the dye to a photographically more acceptable hue, washed for 1 minute in water and dried. In the samples immersed in the cross-oxidizing developer for 30 seconds, 1 minute, 2 minutes and 4 minutes, magenta dye images remained having density ranges of 1.8 to 1.9; 1.7 to 1.8; 1.4 to 1.6 and 0.9 to 1.1, respectively. It is apparent that insufficient dye had been released by the redox dye-releaser in each case to permit images of useful contrast to be formed.

(D) The procedure of (C) above was repeated using the four remaining samples of the photographic element, except that 10 ml of 30 percent by weight hydrogen peroxide was added to the cross-oxidizing developer to convert it to a combined developer-amplification bath. A negative dye image of excellent contrast was produced in each instance. The sample immersed for 30 seconds in the combined developer-amplification bath produced a negative magenta image ranging in dye density from 0.4 to 1.9 indicating that the sample had not developed for sufficient time in the cross-oxidizing developer to produce a desirably low minimum density in unexposed areas. The samples immersed in the cross-oxidizing developer bath for 1, 2 and 4 minutes gave satisfactory negative images having dye density ranges of 0.3 to 1.9; 0.25 to 1.75; and 0.2 to 1.6, respectively. If the released dye had been transferred to a conventional receiver, such as a mordant layer, it is apparent that a complementary positive transferred image would have been formed.

WHAT WE CLAIM IS:—

1. A method of forming a photographic reversal dye image comprising

developing with a first developer solution an imagewise exposed photographic material comprising a support and at least one photosensitive silver halide emulsion layer having associated therewith a non-diffusible redox dye releaser to produce a first silver image,

poisoning said first silver image as a catalyst for the dye-forming reaction below,

rendering the undeveloped silver halide remaining in the emulsion layer developable,

developing the undeveloped silver halide with a second developer solution to produce a reversal silver image which is catalytic for the dye-forming reaction below, and

treating the material with a solution of a peroxide oxidising agent in the presence of a cross-oxidising developing agent to produce a diffusible dye image corresponding to the reversal silver image, and

thereafter removing the diffusible dye from the layer in which it was released either by receiving it on a dye image-receiving layer or by washing with an aqueous liquid.

2. A method as claimed in Claim 1 in which the silver images are subsequently removed from the photographic material by bleaching and fixing or by bleach-fixing.

3. A method as claimed in Claim 1 or 2 in which the first silver image is poisoned as it is formed.

4. A method as claimed in any of Claims 1—3 in which the developing agent in the first developer solution is a non-cross-oxidising developing agent.

5. A method as claimed in Claim 3 or 4 in which the first developer contains a halide ion in sufficient concentration to poison the first silver image.

6. A method as claimed in Claim 4 in which the first developer solution contains bromide ion in a concentration of from 1 to 30 gms/litre.

7. A method as claimed in Claim 4 in which the first developer solution contains iodide ion in a concentration of from 1×10^{-6} to 1 gm/litre.

8. A method as claimed in Claim 4 in which the first developer solution contains iodide ion in a concentration of from 1 mg to 1 gm/litre.

9. A method as claimed in any of Claims 1—8 in which the cross-oxidising developing agent is a pyrazolidone.

10. A method as claimed in any of Claims 1—9 in which the second developer solution is combined with the solution of the peroxide oxidising agent.

11. A method of forming a reversal dye image according to Claim 1 substantially as described herein and with reference to the Example.

12. A photographic material containing a dye image obtained by the method of any of Claims 1—11.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1981.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.