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3,667,958

PHOTOSENSITIVE AND THERMOSENSITIVE ELEMENTS, COMPOSITIONS AND PROCESSES

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27 Claims

ABSTRACT OF THE DISCLOSURE

A reducing agent combination of a polyhydroxybenzene reducing agent with a reducing agent which is a hydroxylamine, a reductone and/or a hydrazine, in a photosensitive and thermosensitive element, composition and/or process employing an oxidation-reduction image forming combination provides greater image discrimination or resolution, with an increase in relative speed and improved black tone. Such a reducing agent combination can be employed in an image reproduction sheet in which a radiation sensitive heavy metal salt can be reduced to free metal and form the image components in an oxidation reduction reaction combination by producing a visible color change with an organic silver salt.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to photosensitive and thermosensitive elements employing an improved oxidation-reduction image forming combination. In one of its aspects it relates to a particular combination of reducing agents in such an image forming combination. In another of its aspects it relates to a photosensitive and thermosensitive composition containing such a combination of reducing agents. A further aspect of the invention relates to a method of developing a latent image in a photosensitive and thermosensitive element containing such an oxidation-reduction image forming combination and a described reducing agent combination.

Description of the state of the art

Photosensitive and thermosensitive elements containing an oxidation-reduction image forming combination provide images after exposure with so-called dry processing with heat. These elements and processes are described, for example, in U.S. Pat. 3,152,904 of Sorensen et al. issued Oct. 13, 1964. For example, (1) an organic silver salt which is an oxidizing agent, (2) an organic reducing agent and a low concentration of photographic silver halide are provided in a photosensitive element. After exposure, the resulting latent image is developed by heating the element. Methods of this type are also described, for example, in French Pat. 1,441,619 and Belgian Pat. 705,872, as well as U.S. Pat. 3,392,020 of Yutzy et al., issued July 9, 1968.

While many reducing agents have been employed in elements wherein an oxidation-reduction image forming combination of an oxidizing agent and a reducing agent, especially with a toning agent in the presence of a catalyst, some of these have not provided desired tone, increased maximum density satisfactorily, reduced background print-out to a desired extent, or provided desired image discrimination or resolution. For example, a hydroquinone reducing agent which has been employed in such a combination has not provided a sufficiently dense black image, e.g. desired maximum density, and moreover the background of the developed image is not desirably clean,

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that is undesired print-out in the background areas of the print occurs. This is demonstrated in following comparative Example 2.

Accordingly, there has been a continuing need to provide reducing agents in photosensitive and thermosensitive elements, compositions and processes employing an oxidation-reduction image forming combination as described which provide greater image discrimination or resolution, with an increase in relative speed and improved black tone.

SUMMARY OF THE INVENTION

It has been found, according to the invention, that in a photosensitive and thermosensitive oxidation-reduction image forming combination of (a) an oxidizing agent and (b) a reducing agent, a reducing agent combination of (1) a polyhydroxybenzene reducing agent with (2) a reducing agent which is a hydroxylamine, a reductone or a hydrazine, provides greater image discrimination or resolution, with an increase in relative speed and improved black tone. These properties are provided in a process of developing a latent image in a photosensitive and thermosensitive element, as described herein by heating the element to about 70° C. to about 250° C.

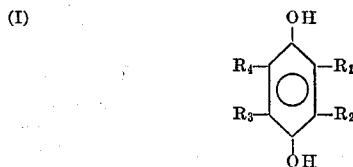
DETAILED DESCRIPTION OF THE INVENTION

Accordingly, one embodiment of the invention is: in a photosensitive and thermosensitive element comprising a support and an oxidation-reduction image forming combination of (a) an oxidizing agent and (b) a reducing agent the improvement comprising a reducing agent combination of (1) a polyhydroxybenzene reducing agent with (2) a reducing agent which is a hydroxylamine, a reductone and/or a hydrazine, as herein described.

A range of hydroxylamine, reductone, and/or hydrazine reducing agents can be employed in the practice of the invention.

A range of polyhydroxybenzene reducing agents can be employed as described, according to the invention. These include any polyhydroxybenzene reducing agent, especially a hydroquinone reducing agent, which has desired reducing properties in combination with the described hydroxylamine, reductone and/or hydrazine reducing agents without adverse effects on the desired sensitometric properties of the photosensitive and thermosensitive elements.

A suitable hydroquinone reducing agent useful in the practice of the invention is, for example, a compound of the formula:



wherein R₁, R₂, R₃ and R₄ are each hydrogen, alkyl, especially alkyl containing 1 to 5 carbon atoms, e.g. methyl, ethyl, propyl, butyl and pentyl; hydroxyl, i.e. —OH, preferably no more than one of R₁, R₂, R₃ and R₄ being hydroxyl; halo, especially chloro, bromo or iodo; alkoxy, especially alkoxy containing 1 to 5 carbon atoms, e.g. methoxy, ethoxy, propoxy, butoxy and pentoxy; or aryl, especially aryl containing 6 to 20 carbon atoms, e.g. phenyl, tolyl or xylyl.

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Typical hydroquinone reducing agents, as described, are, for example, hydroquinone and/or the following hydroquinones:

t-butyl	bromo
2,5-dimethyl	methoxy
2,6-dimethyl	ethyl
methyl	phenyl
chloro	

A suitable hydroxylamine reducing agent useful according to the invention is, for example, a compound of the formula:

(II)



wherein R_5 is hydroxyalkyl, especially hydroxyalkyl containing 1 to 5 carbon atoms, such as hydroxymethyl; hydroxyethyl, hydroxypropyl, hydroxybutyl, and hydroxypentyl; R_6 and R_7 are each hydrogen, hydroxyl or alkyl, especially alkyl containing 1 to 3 carbon atoms, e.g. methyl, ethyl or propyl.

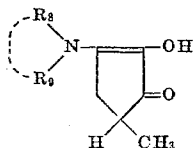
Typical hydroxylamine reducing agents which can be used in the practice of the invention are, for example:

2-aminoethanol,
2-methylaminoethanol,
2-ethylaminoethanol,
2-dimethylaminoethanol,
2-diethylaminoethanol, and/or
bisethoxyethylhydroxylamine.

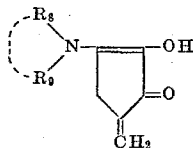
Combinations of hydroxylamine reducing agents, as described, can be employed, if desired.

A range of reductone reducing agents can be employed, as described, according to the invention. These include reductone reducing agents, for example, of the formulas:

(III)



(IV)



wherein R_8 and R_9 are each hydrogen, alkyl, especially alkyl containing 1 to 5 carbon atoms such as methyl, ethyl, propyl and pentyl, or atoms completing a heterocyclic nucleus, as denoted by the broken line in Structures III and IV containing a nitrogen atom, preferably containing 4 to 6 carbon atoms in the nucleus, including, for example, a second nitrogen or an oxygen atom, e.g. morpholino, piperazino, pyrrolino, hexamethyleneimino, piperidino and the like.

Suitable reductone reducing agents include the following amino hexose reductones, anhydro amino hexose reductones and/or anhydro dihydro amino hexose reductones:

dimethylamino
diallylamino
di-n-butylamino
di-n-hexylamino
morpholino
piperazino di(hexose reductone)
pyrrolidino
piperidino
dimethylmorpholino
methylpiperidino

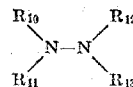
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The described anhydro dihydro reductone reducing agents are typically prepared from the corresponding anhydro hexose reductone compounds which in turn are typically prepared from corresponding amino hexose reductones. A typical method of preparing the described amino hexose reductones and anhydro amino hexose reductones is set out in U.S. Pat. 2,936,308 of Hodge issued May 10, 1960. Such compounds are typically prepared from sugars especially D-glucose although other reducing sugars such as D-galactose, D-fructose, L-sorbose or the like can be used. A typical method of preparing the starting amino hexose reductones comprises heating in a reaction medium, substantially free of water, a hexose reducing sugar and an aliphatic or cycle secondary amine in the presence of an acidic reductone forming catalytic agent such as phosphoric acid, boric acid, acetic acid, succinic acid or the like. The removal of 3 moles of water results during the formation of the amino hexose reductone. The described anhydro amino hexose reductone can be prepared by heating the hydrochloride salts of the amino hexose reductones further in the presence of strong acids such as sulfuric acid, acetic anhydride, zinc chloride and the like to remove another mole of water. The described anhydro dihydro hexose reductone compounds can be prepared from the described anhydro amino reductones by hydrogenation in the presence of a suitable hydrogenation catalyst such as Raney nickel catalyst. The preparation of anhydro dihydro piperidino hexose reductone is typical of the preparation of the class of compounds employed in the practice of the invention. One mole of anhydrous D-glucose and 1.3 moles of piperidine are stirred together in absolute ethanol under nitrogen for about 15 minutes. The resulting mixture is then heated on a steam bath and stirred until the solution becomes homogeneous. Then a solution of glacial acetic acid in absolute ethanol is added dropwise to the solution. The resulting solution is stirred and refluxed under nitrogen for about 12 hours. It is then cooled and the crystals which are formed are filtered, washed and recrystallized, such as from ethanol. The resulting piperidino hexose reductone is dehydrated with a butanol solution of anhydrous hydrogen chloride in form the intermediate anhydro piperidino hexose reductone. This product is then hydrogenated in ethanol over a suitable catalyst, such as Raney nickel, to form the desired anhydro dihydro piperidino hexose reductone. The resulting product can be purified if desired such as by recrystallization from a suitable solvent, e.g. ethanol.

The described reductone reducing agents can be employed in the form of a salt, especially an acid salt, e.g. a hydrochloride, sulfate or the like salt. A reductone reducing agent as employed herein includes such compounds either in salt form or in their nonsalt form.

A suitable hydrazine reducing agent useful according to the invention is a compound of the formula:

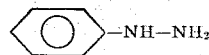
(V)



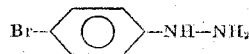
wherein at least two of R_{10} , R_{11} , R_{12} and R_{13} are hydrogen and when less than four of R_{10} , R_{11} , R_{12} and R_{13} are hydrogen the remaining R's are individually aryl, especially aryl containing 6 to 20 carbon atoms, such as phenyl, tolyl, naphthyl and xylol, or acyl, especially acyl containing 1 to 5 carbon atoms, such as acetyl and formyl.

Suitable hydrazine reducing agents include:

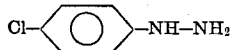
phenylhydrazine



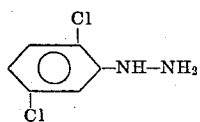
p-bromophenylhydrazine



5
p-chlorophenylhydrazine



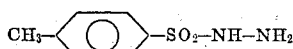
2,5-dichlorophenyl hydrazine



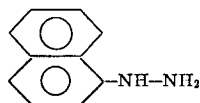
p-tolylhydrazine



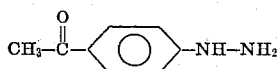
p-tolyl sulfonyl hydrazine



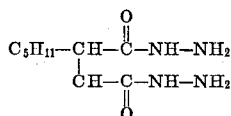
α -naphthylhydrazine



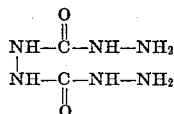
p-acetylphenylhydrazine



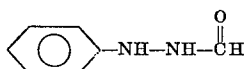
n-amyl succinyl dihydrazide



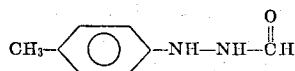
hydrazine dicarboxylic dihydrazide



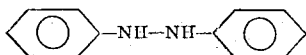
formyl phenylhydrazine



formyl - 4 - methylphenylhydrazine also known as 1-formyl-2-(4-methylphenyl)hydrazine



hydrazobenzene



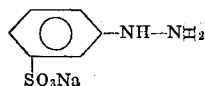
p-hydrazinobenzoic acid



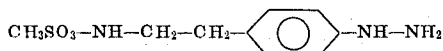
p-hydrazinobenzene sulfonic acid sodium salt



phenylhydrazine-m-sulfonic acid sodium salt



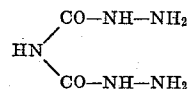
p-[p-(methylsulfonylamido)ethyl]phenyl hydrazine



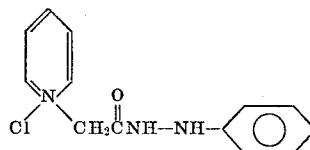
6
p-methylsulfonylamido phenylhydrazine



5 diamino biuret

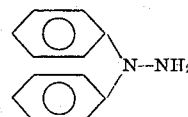


10 β -phenyl acethydrazido pyridinium chloride



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N,N-diphenyl hydrazine



20

25 p-diphenyl hydrazine



p,p'-dihydrazino-diphenyl dihydrochloride

30 $\text{HCl} \cdot \text{NH}_2\text{-NH-} \text{C}_6\text{H}_4\text{-C}_6\text{H}_4\text{-NH-NH}_2 \cdot \text{HCl}$

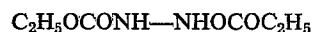
4-p-phenylene disemicarbazide

35 $\text{NH}_2\text{-NH-C(=O)-NH-C}_6\text{H}_4\text{-NH-C(=O)-NH-N}$

hydrazine dihydrochloride



40 N,N'-dicarbethoxyhydrazine



salicylhydrazide

45 $\text{HO-C}_6\text{H}_4\text{-C(=O)-NN-NH}_2$

1-naphthylhydrazine-4-sulfonic acid

50 $\text{HO}_3\text{S-C}_6\text{H}_3\text{(NH-NH}_2\text{)-C}_6\text{H}_4\text{-SO}_3\text{H}$

1-naphthylhydrazine-6-sulfonic acid

55 $\text{HO}_3\text{S-C}_6\text{H}_3\text{(NH-NH}_2\text{)-C}_6\text{H}_4\text{-SO}_3\text{H}$

60

2-naphthylhydrazine-7-sulfonic acid

4-bromo-1-naphthyl hydrazine-7-sulfonic acid

2-naphthylhydrazine-6-sulfonic acid

2-naphthylhydrazine-4,8-disulfonic acid

65 2-naphthylhydrazine-5,7-disulfonic acid

2-naphthylhydrazine-6,8-disulfonic acid

N-(β -hydroxy- γ -hydrazinopropyl) piperidine

N-(β -hydrazinoethyl) piperidine

N-(γ -diethylamino- β -hydraxypropyl)-hydrazine dioxalate

70 γ -aminopropylhydrazine oxalate

The compounds within Structure V, as described, are compounds which have a hydrazino ($\text{H}_2\text{N-NH-}$), or hydrazo (-NH-NH-) moiety. These are employed herein and described as hydrazine compounds, i.e. hy-

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drazine reducing agents. Combinations of these hydrazine reducing agents can be employed if desired.

The described reducing agents can be employed in a photosensitive and thermosensitive element containing a silver-dye complex, a silver halide developing agent, a source of silver for physical development, especially silver behenate or silver stearate and a binder, especially polyvinyl butyral. Suitable silver-dye complexes are set out in U.S. Pat. 3,446,610 of Gilman et al. issued May 27, 1969. The silver-dye complex is a reaction product of silver ions, e.g. silver nitrate in aqueous solution, with a spectral sensitizing dye which upon exposure to radiation forms active sites for physical development. Typical sensitizing dyes include cyanines, merocyanines, oxonols, hemicyanines, hemioxonols, styryls and benzylidenes. A typical photosensitive and thermosensitive element containing such a silver-dye complex comprises a support having a layer containing a silver-merocyanine dye complex, silver behenate, a reducing agent combination as described, and a binder, such as cellulose acetate, polyvinyl acetate or polyvinyl butyral. The photosensitive and thermosensitive element can contain a stabilizing agent such as an organic acid stabilizing agent, e.g. phthalic acid, salicylic acid or benzoic acid.

The described elements can comprise a silver salt of an organic acid, as an oxidizing agent. The silver salt of the organic acid should be resistant to darkening under illumination to prevent undesired deterioration of a developed image. An especially suitable class of silver salts of organic acids is represented by the water insoluble silver salts of long-chain fatty acids which are stable to light. Compounds which are suitable silver salts include silver behenate, silver stearate, silver oleate, silver laurate, silver hydroxystearate, silver caprate, silver myristate, and silver palmitate. Other suitable oxidizing agents are silver 5-nitrosalicylaldoxime, silver-5-chlorosalicylaldoxime, silver benzoate, silver phthalazinone, silver benzotriazole, silver saccharin, silver-4'-n-octadecyloxydiphenyl-4-carboxylic acid, silver-ortho-aminobenzoate, silver acetamidobenzoate, silver furoate, silver camphorate, silver p-phenylbenzoate, silver phenyl acetate, silver salicylate, silver meta-nitrobenzoate, silver butyrate, silver terphthalate, silver phthalate, silver acetate, and silver acid phthalate. Oxidizing agents which are not silver salts can be employed if desired, such as zinc oxide, gold stearate, mercuric behenate, auric behenate, and the like.

Other organic reducing agents can be employed in the practice of the invention with the described combination of reducing agents to provide a desired developed image. Such reducing agents are typically silver halide developing agents. Suitable silver halide developing agents or organic reducing agents include, for example, methylhydroxy naphthalene; phenylenediamine developing agents; methylgallate; aminophenol developing agents, such as 2,4-diaminophenols and methylaminophenols; ascorbic acid developing agents such as ascorbic acid, ascorbic acid ketals and ascorbic acid derivatives such as those described in U.S. Pat. 3,337,342 of Green issued Aug. 22, 1967; 3-pyrazolidone developing agents such as 1-phenyl-3-pyrazolidone and 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone including those described in British Pat. 930,572 published July 3, 1963; hydroxytetrone acid, and hydroxytetroneimide developing agents; and the like.

It is preferable to employ a catalyst for the described oxidation-reduction image forming combination. An especially suitable catalyst is photographic silver halide.

Accordingly a preferred embodiment of the invention is: in a photosensitive and thermosensitive element comprising a support and an oxidation-reduction image forming combination of (a) an oxidizing agent and (b) a reducing agent, the improvement comprising a reducing agent combination of (1) a polyhydroxybenzene reducing agent with (2) a reducing agent which is a hydroxylamine, a reductone and/or a hydrazine, as described, and a cata-

lyst, especially photographic silver halide, for the oxidation-reduction image forming combination.

The described element can contain a photographic salt as the described catalyst, especially a photographic silver salt. Suitable photographic silver salts include silver chloride, silver bromide, silver bromoiodide, silver chlorobromoiodide or mixtures thereof. The photographic silver halide can be coarse or fine-grain, very fine grain emulsions being particularly useful. The emulsion containing the photographic silver halide can be prepared by any of the well-known procedures in the photographic art, such as single-jet emulsions, double-jet emulsions, such as Lippmann emulsions, ammoniacal emulsions, thiocyanate or thioether ripened emulsions, such as those described in U.S. Pat. 2,222,264 of Nietz et al. issued Nov. 14, 1940; U.S. Pat. 3,320,069 of Illingsworth issued May 15, 1967 and U.S. Pat. 3,271,157 of McBride issued Sept. 6, 1966. Surface image silver halide emulsions can be used or internal image silver halide emulsions such as those described in U.S. Pat. 2,592,250 of Davey et al. issued Apr. 8, 1952; U.S. Pat. 3,206,313 of Porter et al. issued Sept. 14, 1965; U.S. Pat. 3,367,778 of Berriman et al. issued Feb. 6, 1968; and U.S. Pat. 3,447,927 of Bacon et al. issued June 3, 1969. If desired, mixtures of surface and internal image silver halide emulsions can be used as described in U.S. Pat. 2,996,382 of Luckey et al. issued Apr. 15, 1961. Negative type emulsions can be used or direct positive silver halide emulsions such as those described in U.S. Pat. 2,184,013 of Leermakers issued Dec. 19, 1939; U.S. Pat. 2,541,472 of Kendall et al. issued Feb. 13, 1951; U.S. Pat. 3,367,778 of Berriman et al. issued Feb. 6, 1968; British Pat. 723,019; French Pat. 1,520,821; U.S. Pat. 2,563,785 of Ives issued Aug. 7, 1951; U.S. Pat. 2,456,953 of Knott et al. issued Dec. 21, 1968; and U.S. Pat. 2,861,885 of Land issued Nov. 25, 1958. The silver halide emulsion can be a regular grain emulsion such as described in Klein and Moisar, *Journal of Photographic Science*, volume 12, No. 5, September-October (1964) pages 242-251.

The silver halide emulsions employed in the practice of the invention can be unwashed or washed to remove soluble salts. In the latter case the soluble salts can be removed by chill setting and leaching or the emulsion can be coagulation washed.

The silver halide employed in the practice of the invention can be sensitized with chemical sensitizers, such as with reducing agents; silver, selenium, or tellurium compounds; gold, platinum, or palladium compounds; or combinations of these. Suitable procedures are described, for example in U.S. Pat. 1,623,499 of Shepard issued Apr. 5, 1927; U.S. Pat. 2,399,083 of Waller et al. issued Apr. 23, 1946; U.S. Pat. 3,297,447 of McVeigh issued Jan. 10, 1967; and U.S. Pat. 3,297,446 of Dunn issued Jan. 10, 1967.

Photographic silver halide employed in the practice of the invention can be protected against the production of fog and can be stabilized against loss of sensitivity during keeping. Suitable antifoggants and stabilizers, e.g. used alone or in combination include, for example, thiazolium salts; azaindenes, mercury salts as described, for example, in U.S. Pat. 2,728,663 of Allen et al. issued Dec. 27, 1955; urazoles; sulfocatechols; oximes described, for example, in British Pat. 623,448; nitron; nitroindazoles; polyvalent metal salts described, for example, in U.S. Pat. 2,839,405 of Jones issued June 17, 1958; platinum, palladium and gold salts described, for example, in U.S. Pat. 2,566,263 of Trivelli et al. issued Aug. 28, 1951 and U.S. Pat. 2,597,915 of Yutzky et al. issued May 27, 1952.

A photosensitive and thermosensitive element and emulsions described and used in the practice of the invention can contain various colloids alone or in combination as vehicles, binding agents and in various layers. Suitable materials are typically hydrophobic but hydrophilic materials can also be employed. They are transparent or trans-

lucent and include both naturally-occurring substances such as proteins, for example, gelatin, gelatin derivatives, cellulose derivatives, polysaccharides such as dextran, gum arabic and the like; and synthetic polymeric substances such as water-soluble polyvinyl compounds like poly(vinyl pyrrolidone), acrylamide polymers and the like. Other synthetic polymeric compounds which can be employed include dispersed vinyl compounds such as in latex form and particularly those which increase dimensional stability of photographic materials. Suitable synthetic polymers include those described in U.S. Pat. 3,142,586 of Nottorf issued July 28, 1964; U.S. Pat. 3,193,386 of White issued July 6, 1965; U.S. Pat. 3,062,674 of Houck et al. issued Nov. 6, 1962; U.S. Pat. 3,220,844 of Houck et al. issued Nov. 30, 1965; U.S. Pat. 3,287,289 of Ream et al. issued Nov. 22, 1966; and U.S. Pat. 3,411,911 of Dykstra issued Nov. 19, 1968. Effective polymers include water-insoluble polymers of alkyl acrylates and methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates, and those which have cross-linking sites which facilitate hardening or curing as well as those having recurring sulfobetaine units as described in Canadian Pat. 774,054. Preferred high molecular weight materials and resins include polyvinyl butyral, cellulose acetate butyrate, polymethyl methacrylate, poly(vinyl pyrrolidone), ethyl cellulose, polystyrene, polyvinyl chloride, chlorinated rubber, polyisobutylene, butadiene styrene copolymers, vinyl chloride-vinyl acetate copolymers, copolymers of vinyl acetate, vinyl chloride and maleic acid, polyvinyl alcohol, and high molecular weight ethylene oxide polymers.

The photosensitive and thermosensitive layers and other layers of an element employed in the practice of the invention and described herein can be coated on a wide variety of supports. Typical supports include cellulose nitrate film, cellulose ester film, poly(vinylacetal) film, polystyrene film, poly(ethylene terephthalate) film, polycarbonate film and related films or resinous materials, as well as glass, paper, metal and the like. Typically a flexible support is employed, especially a paper support which can be partially acetylated or coated with baryta and/or an alpha olefin polymer, particularly a polymer of an alpha olefin containing 2 to 10 carbon atoms such as polyethylene, polypropylene, ethylene-butene copolymers and the like.

The photosensitive and thermosensitive and other hardenable layers of an element used in the practice of this invention can be hardened by various organic or inorganic hardeners, alone or in combination, such as aldehydes, and blocked aldehydes, ketones, carboxylic and carbonic acid derivatives, sulfonate esters, sulfonyl halides and vinyl sulfonyl ethers, active halogen compounds, epoxy compounds, aziridines, active olefins, isocyanates, carbodiimides, mixed-function hardeners and polymeric hardeners such as oxidized polysaccharides like dialdehyde starch and oxyguarum and the like.

The photosensitive and thermosensitive elements used in the practice of the invention can contain antistatic or conducting layers. Such layers can comprise soluble salts such as chlorides, nitrates and the like, evaporated metal layers, ionic polymers such as those described in U.S. Pat. 2,861,056 of Minsk issued Nov. 18, 1958 and U.S. patent 3,206,312 of Sterman et al. issued September 14, 1965 or insoluble inorganic salts such as those described in U.S. patent 3,428,451 of Trevoy issued February 18, 1969. The photographic and thermosensitive elements can also contain antihalation materials and antihalation dyes.

The photosensitive and thermosensitive layers or other layers employed in the practice of the invention can contain plasticizers and lubricants. Suitable plasticizers and lubricants include, for example, polyalcohols such as glycerine and diols described, for example, in U.S. patent 2,960,404 of Milton et al. issued Nov. 1, 1966; fatty acids or esters such as those described in U.S. patent 2,588,765 of Robijns issued Mar. 11, 1952; U.S. patent 3,121,060 of Duane issued Feb. 11, 1964; and silicone

resins such as those described in British patent 955,061.

The photosensitive and thermosensitive layers or other layers employed in the practice of the invention can contain surfactants such as saponin; anionic compounds such as alkyl aryl sulfonates described, for example in U.S. patent 2,600,831 of Baldisieffen issued June 17, 1962; amphoteric compounds such as those described in U.S. patent 3,133,816 of Ben-Ezra issued May 19, 1964; and adducts of glycidol and an alkyl phenol such as those described in British patent 1,022,878.

If desired, the photosensitive and thermosensitive elements employed in the practice of the invention can contain matting agents such as starch, titanium dioxide, zinc oxide, silica, polymeric beads including beads described, for example, in U.S. Pat. 2,992,101 of Jelley et al. issued July 11, 1961 and U.S. Pat. 2,701,245 of Lynn issued Feb. 1, 1955.

The photosensitive and thermosensitive elements employed in the practice of the invention can contain brightening agents including stilbenes, triazines, oxazoles, and coumarin brightening agents. Water-soluble brightening agents can be used such as those described in German Pat. 972,067 and U.S. Pat. 2,933,390 of McFall et al. issued April 19, 1960 or dispersions of brighteners can be used such as those described in German Pat. 1,150,274; U.S. Pat. 3,406,070 of Oetiker et al. issued October 15, 1968; and French Pat. 1,530,244.

The various layers including the photosensitive and thermosensitive layers of an element employed in the practice of the invention can contain light-absorbing material and filter dyes such as those described in U.S. Pat. 3,253,921 of Sawdey issued May 31, 1966; U.S. Pat. 2,274,782 of Gaspar issued Mar. 3, 1942; U.S. Pat. 2,527,583 of Silberstein et al. issued Oct. 31, 1956; and U.S. Pat. 2,956,879 of VanCampen issued Oct. 18, 1960. If desired, the dyes can be mordanted, for example, as described in U.S. Pat. 3,282,699 of Jones et al. issued Nov. 1, 1966.

The photosensitive and thermosensitive layers used in the practice of the invention can be coated by various coating procedures including dip coating, airknife coating, curtain coating or extrusion coating using hoppers such as described in U.S. Pat. 2,681,294 of Beguin issued June 15, 1954. If desired, two or more layers can be coated simultaneously such as by the procedures described in U.S. Pat. 2,761,791 of Russell issued Sept. 4, 1956 and British Pat. 837,095.

If described, the photographic silver halide can be prepared in situ in the photosensitive and thermosensitive coatings of an element employed in the practice of the invention. Such a method is described, for example, in U.S. Pat. 3,457,075 of Morgan et al. issued July 22, 1969. For example, a dilute solution of a halogen acid such as hydrochloric acid can be applied to the surface of a thin coating containing an organic silver salt, such as silver behenate, on a suitable substrate followed by removal of the solvent if desired. Silver halide is thus formed in situ throughout the surface of the coating of the organic silver salt.

The photographic silver halide can be prepared on the oxidizing agent such as silver behenate or silver stearate or other organic silver salt prior to application of the silver halide on the support employed. This is also described in U.S. Pat. 3,457,075 of Morgan et al. issued July 22, 1969, for example, a halogen acid such as hydrochloric acid or hydrobromic acid can be mixed with an organic silver salt in a suitable reaction medium. A halide salt more soluble than the organic silver salt can be added to a suspension of the organic silver salt to form the silver halide. A suitable reaction medium includes water or other solutions which do not interfere with the reaction.

Spectral sensitizing dyes can be used conveniently to confer additional sensitivity to the photosensitive and thermosensitive elements employed in the practice of the invention. For instance, additional spectral sensitization

can be obtained by treating the silver halide with a solution of a sensitizing dye in an organic solvent or the dye can be added in the form of a dispersion as described in British Pat. 1,154,781. The dye can either be added to the emulsion as a final step or at some earlier stage.

Sensitizing dyes useful in sensitizing silver halide are described, for example, in U.S. Pat. 2,526,632 of Brooker et al. issued October 24, 1950; U.S. Pat. 2,503,776 of Sprague issued April 11, 1950; U.S. Pat. 2,493,748 of Brooker et al. issued Jan. 10, 1950; and U.S. Pat. 3,384,486 of Taber et al. issued May 21, 1968. Spectral sensitizers which can be used include the cyanines, merocyanines, complex (trinuclear or tetranuclear) merocyanines, complex (trinuclear or tetranuclear) cyanines, holopolar cyanines, styryls, hemicyanines such as enamines, hemicyanines, oxonols and hemioxonols. Dyes of the cyanine classes can contain such basic nuclei as the thiazolines, oxazolines, pyrrolines, pyridines, oxazoles, thiazoles, selenazoles, and imidazoles. Such nuclei can contain alkyl, alkylene, hydroxyalkyl, sulfoalkyl, carboxyalkyl, aminoalkyl, and enamine groups that can be fused to carbocyclic or heterocyclic ring systems either unsubstituted or substituted with halogen, phenyl, alkyl, haloalkyl, cyano, or alkoxy groups. The dyes can be symmetrical or unsymmetrical and can contain alkyl, phenyl, enamine or heterocyclic substituents on the methine or polymethine chain.

The merocyanine dyes can contain the basic nuclei described as well as acid nuclei such as thiohydantoins, rhodanines, oxazolidenediones, thiazolidenediones, barbituric acids, thiazolineones, and malononitrile. These acid nuclei can be substituted with alkyl, alkylene, phenyl, carboxyalkyl, sulfoalkyl, hydroxyalkyl, alkoxyalkyl, alkylamino groups, or heterocyclic nuclei. Combinations of these dyes can be used, if desired. In addition supersensitizing addenda which do not adsorb visible light may be included such as, for instance, ascorbic acid derivatives, azaindenes, cadmium salts, and organic sulfonic acid as described in U.S. Pat. 2,933,390 of McFall et al. issued Apr. 19, 1960 and U.S. Pat. 2,937,089 of Jones et al. issued May 17, 1960.

The sensitizing dyes and other addenda used in the practice of the invention can be added from water solutions or suitable organic solvent solutions can be used. The compounds can be added using various procedures including, for example, those described in U.S. Pat. 2,912,343 of Collins et al. issued Nov. 10, 1959; U.S. Pat. 3,342,605 of McCrossen et al. issued Sept. 19, 1967; U.S. Pat. 2,996,287 of Audran issued Aug. 15, 1961; and U.S. Pat. 3,425,835 of Johnson et al. issued Feb. 4, 1969.

A range of concentration of dye can be employed in the practice of the invention. The desired concentration will be influenced by the desired spectral sensitivity, other components in the system, the desired image, processing conditions and the like. Typically a concentration of the described sensitizing dye is about 0.05 to about 1 milligram per square foot of the described photosensitive and thermosensitive element, usually about 0.1 milligram per square foot of dye being employed.

It is often necessary to employ a so-called toner in the described photosensitive and thermosensitive elements according to the invention in order to obtain a desirable black image. Various toners can be employed for this purpose. Typically a heterocyclic organic toning agent containing at least two hetero atoms in the heterocyclic ring of which at least one is a nitrogen atom is employed. These are described, for example, in U.S. Pat. 3,080,254 of Grant issued March 5, 1963. Suitable toners include, for example, phthalazone, phthalic anhydride, 2-acetyl phthalazinone, 2-phthalyl phthalazone. Other suitable toners are described, for example, in U.S. Pat. 3,446,648 of Workman issued May 27, 1969. Photosensitive and thermosensitive elements which are suitable for processing with heat according to the practice of the invention can provide a developed image by physical development, such as described in U.S. Pat. 3,457,075 of Morgan et al. issued July

22, 1969. Other elements of this type are described, for example, in U.S. Pat. 3,429,706 of Shepard et al. issued February 25, 1969 and U.S. Pat. 3,152,904 of Sorensen et al. issued October 13, 1964. In elements, as described, typically a support is provided with a light-stable organic silver salt oxidizing agent, an organic reducing agent, and photographic silver salt, especially silver halide, which provides a photographic and heat-sensitive element. A visible image on the photosensitive and thermosensitive element can be produced within a few seconds after exposure by heating the element to moderately elevated temperatures.

Accordingly, one embodiment of the invention is: a photosensitive and thermosensitive element, comprising a support,

- (a) silver behenate,
- (b) hydroquinone,
- (c) a reducing agent which is a hydroxylamine, a reductone and/or a hydrazine, as described,
- (d) photographic silver halide, and
- (e) polyvinyl butyral.

Another embodiment of the invention is: in a photosensitive and thermosensitive composition comprising an oxidation-reduction image forming combination of (a) an oxidizing agent with (b) a reducing agent, the improvement comprising (1) a polyhydroxybenzene reducing agent, as described, with (2) a reducing agent which is a hydroxylamine, a reductone or a hydrazine, as described. This composition can be an emulsion. It is especially useful containing a catalyst, such as photographic silver halide, for the described oxidation-reduction image forming combination. It is also especially suitable containing a toning agent, as described.

The photosensitive and thermosensitive composition can comprise, for example, an oxidation-reduction image forming combination comprising

- (a) silver behenate
- (b) hydroquinone
- (c) a reducing agent which is a hydroxylamine, a reductone, and/or a hydrazine, as described,
- (d) photographic silver halide, and
- (e) polyvinyl butyral.

After exposure of the described photosensitive and thermosensitive element, e.g. to actinic radiation, the resulting latent image is developed merely by heating the element. Accordingly another embodiment of the invention is: a process of developing a latent image in a photosensitive and thermosensitive element comprising a support and an oxidation-reduction image forming combination comprising (a) an oxidizing agent with (b) a reducing agent combination comprising (1) a polyhydroxybenzene reducing agent, as described, with (2) a reducing agent which is a hydroxylamine, a reductone, and/or a hydrazine as described, comprising heating the element to about 70° C. to about 250° C. A temperature of about 75° C. to about 100° C. is usually suitable for developing a desired image. By increasing or decreasing the time of heating, a higher or lower temperature within the described range can be employed. A developed and stable image is typically produced within a few seconds such as about 1 to about 60 seconds, e.g. about 1 to about 30 seconds.

Processing is usually carried out under ambient conditions of temperature, pressure and humidity. Temperatures, pressures and humidity outside normal atmospheric conditions can be employed if desired; however, normal atmospheric conditions are preferred.

Various means can be employed in providing the necessary heating of the described photosensitive and thermosensitive elements. The heating means can be a simple hot plate, iron or the like.

In some cases, if desired, an element can be prepared wherein the described silver halide can be in one layer and other components in other layers contiguous to the silver

halide layer. For example, an element can comprise a support, a layer containing photographic silver halide, and a layer containing other components of the element, e.g. a so-called processing composition layer. Such a processing composition is, for example,

- (a) an oxidizing agent, especially silver behenate and/or silver stearate,
- (b) a polyhydroxybenzene reducing agent, as described, and
- (c) a reducing agent which is a hydroxylamine, a reductone, and/or a hydrazine reducing agent, as described.

Typically a binder is employed with this composition, e.g. polyvinyl butyral.

Other addenda known to be useful in photosensitive and thermosensitive elements, such as described in British Pat. 1,161,777 published Aug. 20, 1969 and U.S. Pat. 3,152,904 of Sorensen et al. issued Oct. 13, 1964 can be employed in the practice of the invention.

The concentration of the described reducing agents which is suitable in a photosensitive and thermosensitive element according to the invention can vary. This depends on the particular reducing agents employed, other components of the element, the processing time and temperature, desired image and the like.

The ratio of polyhydroxybenzene reducing agent to hydroxylamine agent can be, typically, about 1:1 to about 9:1 parts by weight. The concentration of the total combination of polyhydroxybenzene reducing agent with hydroxylamine reducing agent is typically about 5 milligrams per square foot to about 50 milligrams per square foot of support, e.g. about 15 milligrams per square foot. It is often desirable to maintain the ratio of polyhydroxybenzene reducing agent to hydroxylamine reducing agent at nearer 9:1 to avoid any undesirable stain.

The ratio of polyhydroxybenzene reducing agent to reductone reducing agent can be, typically, about 9:1 to about 1:9 parts by weight, e.g. about 1:1 to about 9:1. The concentration of the total combination of polyhydroxybenzene reducing agent with reductone reducing agent is about 5 to about 50 milligrams per square foot of support, e.g. about 15 milligrams per square foot.

The ratio of polyhydroxybenzene reducing agent to hydrazine reducing agent can be, typically, about 9:1 to about 1:9 parts by weight, e.g. about 1:1 to about 9:1. The concentration of the total combination of polyhydroxybenzene reducing agent with hydrazine reducing agent is about 5 to about 50 milligrams per square foot, e.g. about 15 milligrams per square foot.

The concentration range of oxidizing agent, as described, is typically about 5 to about 100 milligrams per square foot of support. This will vary depending on several factors, such as the particular oxidizing agent, the reducing agent combination, the desired image, temperature employed, total concentration of silver in the element, and the like.

The process of the invention can be carried out within a wide pH range, but is usually carried out at about pH 7.

The following examples are included for a further understanding of this invention.

EXAMPLE 1

This illustrates the invention.

A dispersion is made by mixing the following components:

Silver behenate—3.5 g.
Behenic acid—3.9 g.
Polyvinyl butyral—1.25 g.
Acetone—25.0 ml.
Toluene—25.0 ml.
Cadmium iodide—0.183 g.

The mixture is mixed in a ball mill for 12 hours. The liquid from the mixture is drained and the mixture is rinsed with 25 milliliters of acetone. The volume of the

mixture is then brought to 75 milliliters with acetone. This is designated as dispersion Z.

A 10% by weight reducing agent solution is prepared by mixing bisethoxyethylhydroxylamine with acetone. This is designated as reducing agent solution A.

A melt is prepared by mixing 75.0 milliliters of dispersion Z with 100.8 milliliters of a solvent containing 50% by volume acetone and 50% by volume toluene. This is designated as melt C.

A 1.0% by weight reducing agent solution is prepared by mixing hydroquinone with acetone. This is designated as reducing agent solution D.

0.94 milliliter of reducing agent solution A (bisethoxyethylhydroxylamine in acetone), 0.94 milliliter of reducing agent solution D (hydroquinone in acetone) and 4.4 milliliters of melt C are mixed together. The resulting composition is designated as composition E.

4.5 milliliters per square foot of composition E is coated on a paper support containing a resin coating. The resulting coating contains 15 milligrams of silver per square foot. The coating is dried under atmospheric conditions to provide a photosensitive and thermosensitive element.

The resulting photosensitive and thermosensitive element is designated as Element 1 and is sensitometrically exposed, using a step tablet, with tungsten light (120 watt light bulb in a contact printer) for 0.25 second.

The side of Element 1 opposite the described photosensitive coating is held in contact with a heated metal block at 85° C. for 5 seconds.

The resulting developed image has a maximum density of 1.19, a minimum density of 0.18 and a brown-black tone. The number of visible steps developed, which indicates the degree of image discrimination or resolution obtained, is 9. Nine visible steps developed is desirable image discrimination or resolution. The number of steps developed is rated from 9 as very good to 1 as very poor.

EXAMPLE 2

This is a comparative example.

The procedure set out in Example 1 is repeated with the exceptions that reducing agent solution A is omitted (bisethoxyethylhydroxylamine in acetone) and 1.88 milliliters of reducing agent solution D (hydroquinone in acetone) is employed in place of 0.94 milliliter of reducing agent solution D.

The resulting developed image has a maximum density of 0.31, a minimum density of 0.09 and an orange tone. The number of visible steps developed is 7.

This demonstrates the surprising increase in maximum density and improved black tone provided by a combination of reducing agents according to the invention as set out in Example 1.

EXAMPLE 3

This is a comparative example.

The procedure set out in Example 1 is repeated with the exceptions that reducing agent solution D (hydroquinone in acetone) is omitted and 1.88 milliliters of reducing agent solution A (bisethoxyethylhydroxylamine in acetone) is employed in place of reducing agent solution D.

The resulting developed image has a maximum density of 0.17 and a minimum density of 0.14. The image was insufficient to determine tone. Only one visible image step is developed.

This further demonstrates the surprising increase in maximum density and improved black tone provided by a combination of reducing agents according to the invention as set out in Example 1.

EXAMPLE 4

The procedure set out in Example 1 is repeated with the exception that in place of reducing agent solution A 0.94 milliliter of a solution is employed containing 1.0% by weight piperidino hexose reduction in a solvent which

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is 50% by volume methanol and 50% by volume acetone. This provides a combination of hydroquinone with piperidino hexose reduction in the element. Also, the element, after sensitometric exposure, is placed in contact with a heated block at 95° C. for two seconds.

The resulting developed image has a maximum density of 1.2, a minimum density of 0.20 and a black tone. The number of visible image steps developed is 9.

EXAMPLE 5

This is a comparative example.

The procedure set out in Example 1 is repeated with the exception that reducing agent solution A is omitted and 1.88 milliliters of reducing agent solution D (hydroquinone in acetone) is employed in place of 0.94 milliliter of reducing agent solution D. Also the element is placed in contact with a heated block at 95° C. for 5 seconds.

The resulting developed image has a maximum density of 0.88, a minimum density of 0.19 and a brown tone. The number of visible image steps developed is 9.

This demonstrates the surprising increase in density with improved black tone employing a combination of reducing agents according to the invention.

EXAMPLE 6

This is a comparative example.

The procedure set out in Example 1 is repeated with the exception that reducing agent solutions D and A are omitted and 1.88 milliliters of a solution is employed containing 1.0% by weight piperidino hexose reductone in a solvent which is 50% by volume methanol and 50% by volume acetone. Also, the element, after sensitometric exposure, is placed in contact with a heated block at 95° C. for 5 seconds.

The resulting developed image has a maximum density of 0.87, a minimum density of 0.14 and a brown tone. The number of visible image steps developed is 9.

EXAMPLE 7

The procedure set out in Example 1 is repeated with the exception that formyl-4-methylphenyl hydrazine is employed in place of bisethoxyethylhydroxylamine. Also the element is placed in contact with a heated block at 95° C. for 3 seconds.

The resulting developed image has a maximum density of 0.89, a minimum density of 0.17 and a brown tone. The number of visible image steps developed is 9.

EXAMPLE 8

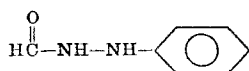
This is a comparative example.

The procedure set out in Example 7 is repeated with the exception that reducing agent solutions A and D are omitted and 1.88 milliliters of a 1.0% by weight solution of formyl-4-methylphenyl hydrazine in acetone is employed. Also, after exposure, the element is placed in contact with a heated block at 95° C. for 5 seconds.

The resulting developed image has a maximum density of 0.81, minimum density of 0.28 and a brown tone. The number of visible steps developed is 8.

EXAMPLE 9

The procedure set out in Example 1 is repeated with the exception that formylphenyl hydrazine which is believed to have the formula:



is employed in place of bisethoxyethylhydroxylamine. Also the element is placed in contact with a heated block at 95° C. for 2 seconds.

The resulting developed image has a maximum density of 1.12, a minimum density of 0.18, and a brown-black tone. The number of visible steps developed is 9.

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EXAMPLE 10

This is a comparative example.

The procedure set out in Example 9 is repeated with the exception that reducing agent solutions A and D are omitted and 1.88 milliliters of a 1.0% by weight solution of formylphenylhydrazine in acetone is employed. Also, after exposure, the element is placed in contact with a heated block at 95° C. for 7 seconds.

The resulting developed image has a maximum density of 0.77, a minimum density of 0.19 and a brown tone. The number of visible steps developed is 8.

EXAMPLE 11

This is a comparative example.

The procedure set out in Example 10 is repeated with the exception that 1-phenyl-3-pyrazolidone is employed in place of formylphenylhydrazine. Also, the element is placed in contact with a heated block for 5 seconds at 85° C.

The resulting developed image has a maximum density of 0.87, a minimum density of 0.31 and a brown tone. The number of visible steps developed is 9.

EXAMPLE 12

This is a comparative example.

The procedure set out in Example 10 is repeated with the exception that para-aminophenol is employed in place of formylphenyl hydrazine. Also, the element is placed in contact with a heated block for 5 seconds at 85° C.

The resulting developed image has a maximum density of 1.18, a minimum density of 0.35 and a brown-black tone. The number of visible steps developed is 7.

EXAMPLE 13

This is a comparative example.

The procedure set out in Example 10 is repeated with the exception that t-butyl hydroquinone is employed in place of formylphenyl hydrazine. Also, the element is placed in contact with a heated block for 5 seconds at 85° C.

The resulting developed image has a maximum density of 0.75, a minimum density of 0.20 and orange-brown tone. The number of visible steps developed is 8.

EXAMPLE 14

The procedure set out in Example 1 is repeated with the exception that t-butyl hydroquinone is employed in place of hydroquinone.

The resulting developed image has a maximum density of 1.26, a minimum density of 0.22 and black tone. The number of visible steps developed is 9.

EXAMPLE 15

The procedure set out in Example 4 is repeated with the exception that t-butyl hydroquinone is employed in place of hydroquinone.

The resulting developed image has a maximum density of 1.17, a minimum density of 0.19 and a brown-black tone. The number of visible steps developed is 9.

EXAMPLE 16

This is a comparative example.

The procedure set out in Example 2 is repeated with the exception that pyrocatechol is employed in place of hydroquinone.

The resulting developed image has a maximum density of 0.53, a minimum density of 0.12 and orange-brown tone. The number of visible steps developed is 7.

EXAMPLE 17

The procedure set out in Example 1 is repeated with the exceptions that pyrocatechol is employed in place of hydroquinone and the element is heated, after exposure, by contact with a heated block at 95° C. for 2 seconds.

The resulting developed image has a maximum density of 1.21, a minimum density of 0.10 and a black tone. The number of visible steps developed is 9.

EXAMPLE 18

The procedure set out in Example 4 is repeated with the exception that pyrocatechol is employed in place of hydroquinone and the element is heated, after exposure, to 95° C. for 2 seconds.

The resulting developed image has a maximum density of 1.10, a minimum density of 0.20 and brown-black tone. The number of visible steps developed is 9.

EXAMPLE 19

The procedure set out in Example 7 is repeated with the exception that pyrocatechol is employed in place of hydroquinone and the element, after exposure, is heated to 95° C. for 2 seconds.

The resulting developed image has a maximum density of 1.11 and a minimum density of 0.24 and brown-black tone. The number of visible steps developed is 9.

EXAMPLE 20

This is a comparative example.

The procedure set out in Example 1 is repeated with the exception that alpha-naphthol is employed in place of hydroquinone, and the element, after exposure, is heated by placing the element in contact with a heated block at 95° C. for 15 seconds.

The resulting developed image has a maximum density of 0.79, a minimum density of 0.28 and a brown tone. The number of visible steps developed is 6.

EXAMPLES 21-32

Similar results to those in Example 4 are obtained employing the following reductone reducing agents in place of piperidino hexose reductone:

Example 21: anhydro dihydro piperidino hexose reductone

Example 22: anhydro piperidino hexose reductone

Example 23: anhydro dihydro dimethylamino hexose reductone

Example 24: anhydro dimethylamino hexose reductone

Example 25: anhydro dihydro morpholino hexose reductone

Example 26: anhydro morpholino hexose reductone

Example 27: anhydro dihydro pyrrolidino hexose reductone

Example 28: anhydro pyrrolidino hexose reductone

Example 29: anhydro dihydro methylpiperidino hexose reductone

Example 30: methylpiperidino hexose reductone

Example 31: pyrrolidino hexose reductone

Example 32: morpholino hexose reductone

EXAMPLES 33-36

Similar results to those in Example 1 are obtained employing the following hydroxylamine reducing agents in place of bisethoxyethylhydroxylamine:

Example 33: 2-aminoethanol

Example 34: 2-methylaminoethanol

Example 35: 2-ethylaminoethanol

Example 36: 2-dimethylaminoethanol

EXAMPLES 37-40

Similar results to those in Example 7 are obtained employing the following hydrazine reducing agents in place of formyl-4-methylphenyl hydrazine:

Example 37: phenylhydrazine

Example 38: p-bromophenylhydrazine

Example 39: p-tolylhydrazine

Example 40: α-naphthylhydrazine

The invention has been described in detail with particular reference to 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. In a photosensitive and thermosensitive element comprising a support and an oxidation-reduction image-forming combination of (a) an oxidizing agent and (b) a reducing agent, and a catalyst for said oxidation-reduction image-forming combination the improvement comprising a reducing agent combination of (1) a polyhydroxybenzene reducing agent with (2) a reducing agent which is bisethoxyethylhydroxylamine, an amino reductone or a formylphenyl hydrazine.

2. A photosensitive and thermosensitive element as in claim 1 wherein said reducing agent combination comprises hydroquinone with bisethoxyethylhydroxylamine.

3. A photosensitive and thermosensitive element as in claim 1 wherein said reducing agent combination comprises hydroquinone with piperidino hexose reductone.

4. A photosensitive and thermosensitive element as in claim 1 wherein said reducing agent combination comprises hydroquinone with formylphenyl hydrazine.

5. A photosensitive and thermosensitive element as in claim 1 wherein said polyhydroxybenzene reducing agent is pyrocatechol.

6. A photosensitive and thermosensitive element as in claim 1 wherein said oxidizing agent is silver behenate.

7. A photosensitive and thermosensitive element as in claim 1 comprising a toning agent.

8. A photosensitive and thermosensitive element as in claim 1 comprising a catalyst which is photographic silver halide for said oxidation-reduction image forming combination.

9. A photosensitive and thermosensitive element comprising a support,

(a) silver behenate,

(b) hydroquinone,

(c) a reducing agent which is bisethoxyethylhydroxylamine, an amino reductone or a formylphenyl hydrazine,

(d) photographic silver halide, and

(e) polyvinyl butyral.

10. In a photosensitive and thermosensitive composition comprising an oxidation-reduction image-forming combination of (a) and oxidizing agent with (b) a reducing agent and a catalyst for said oxidation-reduction image-forming combination the improvement comprising a reducing agent combination of (1) a polyhydroxybenzene reducing agent with (2) a reducing agent which is bisethoxyethylhydroxylamine, an amino reductone or a formylphenyl hydrazine.

11. A photosensitive and thermosensitive composition as in claim 10 wherein said reducing agent combination is hydroquinone with bisethoxyethylhydroxylamine.

12. A photosensitive and thermosensitive composition as in claim 10 wherein said reducing agent combination is hydroquinone with piperidino hexose reductone.

13. A photosensitive and thermosensitive composition as in claim 10 wherein said reducing agent combination is hydroquinone with formylphenyl hydrazine.

14. A photosensitive and thermosensitive composition as in claim 10 wherein said polyhydroxybenzene reducing agent is pyrocatechol.

15. A photosensitive and thermosensitive composition as in claim 10 comprising a toning agent.

16. A photosensitive and thermosensitive composition as in claim 10 comprising:

(a) silver behenate,

(b) hydroquinone,

(c) a reducing agent which is bisethoxyethylhydroxylamine, and amino reductone or a formylphenyl hydrazine,

(d) photographic silver halide, and

(e) polyvinyl butyral.

17. A process of developing a latent image in a photosensitive and thermosensitive element comprising a sup-

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port and an oxidation-reduction image forming combination comprising (a) an oxidizing agent with (b) a reducing agent combination comprising (1) polyhydroxybenzene reducing agent with (2) a reducing agent which is bisethoxyethylhydroxylamine, an amino reductone or a formylphenyl hydrazine and a catalyst for said oxidation-reduction image-forming combination, comprising heating said element to about 70° C. to about 250° C.

18. A process of developing a latent image in an exposed photosensitive and thermosensitive element as in claim 17 wherein said reducing agent combination is hydroquinone with bisethoxyethylhydroxylamine.

19. A process of developing a latent image in an exposed photosensitive and thermosensitive element as in claim 17 wherein said reducing agent combination is hydroquinone with piperidino hexose reductone.

20. A process of developing a latent image in an exposed photosensitive and thermosensitive element as in claim 17 wherein said reducing agent combination is hydroquinone with formylphenyl hydrazine.

21. A process of developing a latent image in an exposed photosensitive and thermosensitive element as in claim 17 wherein said element comprises a toning agent.

22. A process of developing a latent image in an exposed photosensitive and thermosensitive element as in claim 17 wherein said element comprises a support,

(a) silver behenate,

(b) hydroquinone,

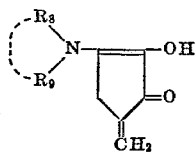
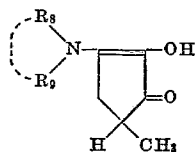
(c) a reducing agent which is bisethoxyethylhydroxylamine an amino reductone or a formylphenyl hydrazine,

(d) photographic silver halide, and

(e) polyvinyl butyral.

23. A process as in claim 17 wherein said element is heated for about 1 to about 30 seconds.

24. In a photosensitive and thermosensitive element comprising a support having thereon an oxidation-reduction image forming combination of (a) an oxidizing agent and (b) a reducing agent and photosensitive silver halide, the improvement comprising a reducing agent combination of (1) a polyhydroxybenzene reducing agent with (2) an amino reductone reducing agent of the formula:

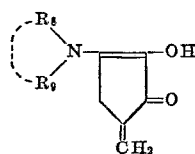
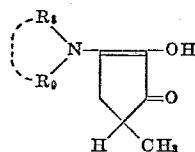


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wherein R_8 and R_9 are each hydrogen, alkyl containing 1 to 5 carbon atoms, or when taken together complete a heterocyclic nucleus which is morpholino, piperazino, pyrrolino, hexamethyleneimino, piperidino, dimethylmorpholino or methylpiperidino.

25. A photosensitive and thermosensitive element as in claim 24 wherein said amino reductone reducing agent is piperidino hexose reductone.

26. In a photosensitive and thermosensitive composition comprising an oxidation-reduction image forming combination of (a) an oxidizing agent and (b) a reducing agent and photosensitive silver halide, the improvement comprising a reducing agent combination of (1) a polyhydroxybenzene reducing agent with (2) an amino reductone reducing agent of the formula:



wherein R_8 and R_9 are each hydrogen, alkyl containing 1 to 5 carbon atoms, or when taken together complete a heterocyclic nucleus which is morpholino, piperazino, pyrrolino, hexamethyleneimino, piperidino, dimethylmorpholino or methylpiperidino.

27. A photosensitive and thermosensitive composition as in claim 26 wherein said amino reductone reducing agent is piperidino hexose reductone.

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U.S. Cl. X.R.

117—36.8; 250—65.1

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,667,958 Dated June 6, 1972

Inventor(s) Francis J. Evans

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 62, "reuctones" should read
---reductones---.

Column 4, line 6, "redutcones" should read
---reductones---.

Column 5, line 68, that part of the formula
reading:

$-N\equiv_2$ should read $-NH_2$

Column 6, line 35, that part of the formula reading:

$-N$ should read $-NH_2$

Column 6, line 45, that part of the formula reading:

NN should read NH

Column 6, line 69, that part of the formula reading
"hydraxypropyl" should read ---hydroxypropyl---.

Column 11, line 13, "merocyanies" should read
---merocyanines---.

Column 11, line 68, "phthalazione" should read
---phthalazinone---.

Column 11, line 69, "phthalazione" should read
---phthalazinone---.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,667,958 Dated June 6, 1972

Inventor(s) Francis J. Evans

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 12, lines 23-24, "photosentive" should read ---photosensitive---.

Column 13, line 10, "hydroxyamine" should read ---hydroxylamine---.

In the Claims:

Column 18, line 70, "and" should read ---an---.

Column 19, lines 1-2, "combinatio" should read ---combination---.

Signed and sealed this 6th day of February 1973.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents