United States Patent Office 3,664,835 Patented May 23, 1972

3,664,835

PHOTOGRAPHIC PRODUCT, COMPOSITION AND PROCESS COMPRISING AN ANHYDRO DIHYDRO AMINO REDUCTONE DEVELOPING AGENT

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No Drawing. Filed Oct. 2, 1969, Ser. No. 863,363
Int. Cl. G03c 1/42, 5/30, 5/54
U.S. Cl. 96—3 21 Claims

ABSTRACT OF THE DISCLOSURE

Photographic developing agents which are anhydro dihydro reductone silver halide developing agents such as anhydro dihydro amino reductone silver halide developing agents provide reduced stain without loss of desired sensitometric properties at reduced concentrations in a diffusion transfer system. These can be used in combination with other photographic developing agents such as aminomethyl hydroquinone developing agents, cinnamic acid developing agents, lactone developing agents or developing agent precursors, and the like. They are specially useful in a black and white silver halide diffusion transfer process.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to photographic developing agents and to photographic products, processing compositions, especially developer compositions, and to processes employing such developing agents. In one of its aspects, the invention relates to anhydro dihydro reductone silver halide developing agents, such as anhydro dihydro amino reductone silver halide developing agents and photographic products, processes and/or processing compositions, especially those employed in diffusion transfer systems. In another of its aspects, the invention is directed to processing compositions such as viscous processing compositions designed for diffusion transfer systems containing the described developing agents.

Description of the prior art

In recent years diffusion transfer of photographic processes, compositions and elements has become well known. The main advantage of a diffusion transfer process is that the positive print can be produced in a single step without resort to separate processing steps. The diffusion transfer process in brief is characterized by the use of a photographic emulsion layer and an image receiver or precipitating layer contiguous to the emulsion layer. After exposure of the photographic emulsion layer, typically a processing composition, e.g. a developer composition, is applied between the exposed photographic emulsion layer and the image receiver or precipitating layer. The processing composition usually contains a silver halide solvent such as sodium thiosulfate which causes the unexposed silver salts usually silver halides to dissolve forming the silver complex which diffuses to the image receiver or precipitating layer where development nuclei or an image precipitating agent in that layer causes the silver to be precipitated from the silver complex imagewise. Development nuclei or precipitating agents can be present in the image receiving layer before contact with the complex silver or the nuclei can be formed in situ. Diffusion transfer photographic processes, elements and compositions for such processes are well known and described, for example, in U.S. Pat. 2,698,237 of Land issued Dec. 28, 1954 and U.S. Pat. 2,647,056 of Land issued July 28, 1953 as well as in U.S. Pat. 3,108,001 of Green issued

Oct. 22, 1963 and U.S. 3,345,166 of Land issued Oct. 3, 1967.

A processing composition employed in diffusion transfer processes normally contains a developing agent and is usually applied as a viscous fluid layer spread between the photographic layer and the image receiving layer.

The requirements for developing agents for diffusion transfer systems are very stringent and relatively few of the develiping agents which are satisfactory for general silver halide developing processes are satisfactory or sufficiently active for diffusion transfer systems. One of the diffusion transfer developing agents used more successfully is a 2,4-diaminophenol, such as 2,4-diaminophenol dihydrochloride, also known as Amidol. However, although such developing agents will produce a positive image they are subject to rapid oxidation which results in unsightly and objectionable dark oxidation products which stains the positive print.

Surprisingly developing agents which have been employed successfully in developing silver halide emulsions in general photographic processing have not provided the desired reduction in stain. This is illustrated in the following Examples 2, 3 and 4 in which it is demonstrated that 6-methoxy-2,4-diaminophenol hpdroquinone and tertiary butyl hydroquinone do not provide a desired reduction in stain.

Thus there has been a need for developing agents which provide desired sensitometric properties and developing action without objectionable stain or oxidation products in diffusion transfer systems.

Accordingly it is an object of the invention to provide improved photographic elements, compositions, and processes, especially diffusion transfer processes and photographic elements in compositions therefore employing the described developing agents which provide reduced stain without loss of desired sensitometric properties.

SUMMARY OF THE INVENTION

According to the invention, reduced stain, without loss of desired sensitometric properties, at reduced developing agent concentrations, is provided in diffusion transfer systems employing photographic products, elements, processing compositions and processes with an anhydro dihydro reductone silver halide developing agent. Combinations of anhydro dihydro reductone silver halide developing agents with other silver halide developing agents such as pyrimidine silver halide developing agent, aminomethyl hydroquinone developing agents, cinnamic acid developing agents and coumarin developing agents or developing agent precursors are especially suitable in the practice of the invention.

The described anhydro dihydro reductone silver halide developing agents in a diffusion transfer system are specially advantageous over reductone developing agents in general due to their unexpected properties of providing desired sensitometric properties at concentration significantly lower than those necessary for reductone silver halide developing agents in general.

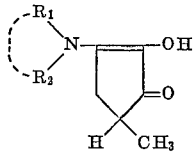
DESCRIPTION OF THE PREFERRED EMBODIMENT

A wide range of anhydro dihydro reductone silver halide developing agents which provide reduced stain without loss of desired sensitometric properties can be employed according to the invention. These include any anhydro dihydro reductone silver halide developing agents which provide desired developing activity and reduction of stain without adversely affecting desired maximum density, minimum density, photographic speed, gamma and other desired sensitometric properties. Typically, anhydro dihydro reductone silver halide developing agents

which are employed in the practice of the invention are anhydro dihydro amino reductone silver halide developing agents.

A wide variety of anhydro dihydro reductone silver halide developing agents can be employed in the practice of the invention. Suitable anhydro dihydro reductone silver halide developing agents include, for example, compounds of the formula:

(I)



wherein R_1 and R_2 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 Structure I, containing a nitrogen atom, preferably containing 5 to 6 carbon atoms in the nucleus, including, for example, the second nitrogen or an oxygen atom, e.g. morpholino, piperazino, pyrrolidino, piperidino and the like.

Suitable anhydro dihydro reductone silver halide developing agents include:

anhydro dihydro dimethylamino hexose reductone
anhydro dihydro diallylamino hexose reductone
anhydro dihydro di-n-butylamino hexose reductone
anhydro dihydro di-n-hexylamino hexose reductone
anhydro dihydro morpholino hexose reductone
anhydro dihydro piperazino di(hexose reductone)
anhydro dihydro pyrrolidino hexose reductone
anhydro dihydro piperidino hexose reductone
anhydro dihydro dimethylmorpholino hexose reductone
anhydro dihydro methylpiperidino hexose reductone
anhydro dihydro N-benzyl-N-methylamino hexose reductone

The described anhydro dihydro reductone silver halide developing 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 cyclic 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 mols 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 mol of water. The described dihydro anhydro hexose reductone compounds can be prepared from the described anhydro amino reductones by hydrogenation in the presence of a suitable catalyst such as Raney nickel. 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 mol of anhydrous D-glucose and 1.3 mols of piperidine are stirred together in absolute ethanol under nitrogen for about 15 minutes. The resulting mixture is then heated on a stream 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 to 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 anhydro dihydro reductone silver halide developing agents can be employed in the form of an acid salt such as a hydrochloride, sulfate or the like salt. An anhydro dihydro reductone silver halide developing agent as employed herein includes such compounds either in salt or in their nonsalt form.

The described anhydro dihydro reductone silver halide developing agents can be employed in the practice of the invention in a range of physical locations in a diffusion transfer photographic system. They can be employed in one or more layers of a photographic element and/or in a processing compoistion if desired. The optimum location will depend upon the desired image, processing condition and the like. For example, the described anhydro dihydro reductone silver halide developing agents can be employed in a processing composition, such as an aqueous alkaline developer solution or they can be incorporated into one or more layers of a photographic element, such as a photographic silver halide emulsion layer, a layer between the support and the silver halide emulsion layer, and/or an overcoat layer. Suitable diffusion transfer systems processes, processing compositions and elements therefor which can be employed in the practice of the invention are described for example in U.S. Pat. 2,352,014 of Rott issued June 20, 1944; U.S. 2,452,181 of Land issued Feb. 27, 1951; and U.S. 3,337,342 of Green issued Aug. 27, 1967. They can be used in so-called high speed diffusion transfer processes and compositions therefor as described, for example, in U.S. Pat. 3,326,683 of Land et al. issued June 20, 1967; or in other types of diffusion transfer systems processes and compositions therefor such as described in U.S. Pat. 2,857,274 of Land et al. issued Oct. 21, 1958; U.S. 3,020,155 of Yackel issued Feb. 6, 1962; U.S. 2,584,030 of Land issued Jan. 29, 1952; and U.S. 2,923,623 of Land issued Feb. 2, 1960. These references also describe typical photographic products suitable for diffusion transfer systems comprising in combination (a) a photographic element comprising a photographic silver halide layer; (b) a processing composition containing a silver halide solvent, typically in a rupturable container, and (c) an image receiving layer. Accordingly, one embodiment of the invention comprises in a photographic product comprising in combination (a) a photographic element comprising a photographic silver halide, (b) a processing compoistion containing a silver halide solvent, and (c) an image receiving layer, the improvement comprising an anhydro dihydro reductone silver halide developing agent. The described anhydro dihydro reductone silver halide developing agent can be employed, as described, in any suitable physical location such as in the photographic element, in the processing composition and/or in the image receiving layer or a layer contiguous thereto.

The developing agents described can be employed for developing an image in a wide range of photographic emulsions. They can be employed in such emulsions if desired. They photographic emulsions employed in the practice of the invention can be X-ray or other nonspectrally sensitized emulsions or they can contain spectral sensitizing dyes such as described in U.S. 2,526,632 of Brooker et al. issued Oct. 24, 1950 and U.S. 2,503,776 of Sprague issued Apr. 11, 1960. Spectral sensitizers which can be used include e.g. cyanines, merocyanines, complex (trinuclear) cyanines, complex(trinuclear)merocyanines, styryls and hemicyanines.

Various photographic silver salts can be used in the practice of the invention. These include photographic silver halides such as silver bromide, silver chloride, as well as mixed halides such as silver bromoiodide, silver chloroiodide and the like.

The photosensitive layers and/or image receiving layers which are employed in the practice of the invention can be coated on a wide variety of supports. Suitable supports include for example those generally employed for photographic elements, such as cellulose nitrate film, cellulose ester film, poly(vinyl acetal) film, polysyrene film, poly (ethylene terephthalate) film and related films or resinous materials, as well as papers such as paper supports coated with resinous materials, e.g. paper coated with alpha-olefin polymers particularly polymers of alpha-olefins containing 2 to 4 carbon atoms as exemplified by polyethylene, polypropylene, ethylenebutene copolymers or the like; as well as glass, metal and the like. The supports or layers coated on them, typically paper supports can contain fluorescent brightening agent, such as stilbenes, benzothiazoles, benzoxazoles and coumarins.

The photographic elements and image receiver layers employed in the practice of the invention typically contain binding materials suitable for photographic purposes. These include natural and synthetic binding materials generally employed for this purpose, e.g. gelatin, colloidal albumin, water-soluble vinyl polymers, cellulose derivatives, acrylamide polymers, polyvinyl pyrrolidone and the like. Mixtures of binding agents can also be used. The binding agents for an emulsion layer of a photographic element as described can also contain other dispersed polymerized vinyl compounds. Such compounds are described for example in U.S. 3,142,568 of Nottorf issued July 28, 1964; U.S. 3,193,383 of White issued July 6, 1965; U.S. 3,062,674 of Houck, Smith and Yudelson issued Nov. 6, 1962; and U.S. 3,220,844 of Houck, Smith and Yudelson issued Nov. 30, 1965, and include the water insoluble polymers of alkyl acrylates, and methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates and the like. The described elements can also contain stripping layers and/or antistatic layers, i.e. conducting layers.

Photographic emulsions employed in the practice of the invention can also contain speed increasing compounds such as quaternary ammonium compounds, polyethylene glycols or thioethers. Frequently, useful effects can be obtained by adding the described speed increasing compounds to the processing solutions instead of, or in addition to the photographic emulsions.

Photographic silver halide emulsions employed in the practice of the invention can be chemically sensitized using any of the well-known techniques in emulsion making, e.g. by digesting with naturally active gelatin or various sulfur, selenium, tellurium and/or noble metal sensitizers and/or reduction sensitizers. Combinations of sensitizers can be employed such as described in U.S. 3,297,446 of Dunn issued Jan. 10, 1967 and U.S. 3,408,196 of McVeigh issued Oct. 29, 1968.

The described developing agents employed in the practice of the invention can be employed in combination with addenda known in the art to be useful in processing photographic elements, especially those employed in photographic diffusion transfer systems. Various suitable addenda include hardeners, e.g. those set out in British 974,317; buffers which maintain desired developing activity and/or pH level; coating aids; plasticizers; and stabilizing agents, such as sodium sulfite.

The described developing agents employed in the practice of the invention can be used in colloid transfer processes and elements. They can also be used in photographic elements and/or in processing composition intended for use in monobath processing such as described in U.S. 2,875,048 of Haist et al. issued Feb. 24, 1959, and British 1,063,844 of Beavers et al. published Mar. 30, 1967. They can also be used in so-called web type processing such as described in U.S. 3,179,517 of Tregillus et al. issued Apr. 20, 1965.

The described developing agents employed in the practice of the invention can also be used to advantage in multilayer, single element diffusion transfer systems which utilize undeveloped silver halide in nonimage areas of a negative to form a positive by physical development of this silver onto a nuclei containing, contiguous, image receiving layer after which the upper layer is removed by scrubbing, washing, stripping or other suitable method. Processes of this type are described, for instance, in U.S. 3,020,155 of Yackel et al. issued Feb. 6, 1962.

Good results, evidenced by improved tone and desirable contrast are obtained in elements of this type when they are processed by use of a so-called external processing web containing the described developers of the invention in combination with a silver halide solvent and other processing or coating components dispersed in a vehicle and coated on a suitable support. Processing webs of this type are described, for example, in U.S. 3,179,517 of Tregillus et al., issued Apr. 20, 1965.

The developing agents employed in the practice of the invention can be employed if desired in photographic elements designed for stabilization type processing. For instance, they can be incorporated in one or more layers of a photographic element which is exposed, and then processed by contact with an alkaline development activator, and followed by stabilization with a suitable stabilizer, and such as with a thiocyanate or thiosulfate stabilizer, e.g. by contact with a thiocyanate or thiosulfate solution containing ammonium thiocyanate or sodium thiosulfate. They can be incorporated in the alkaline activator if desired. Such processes are described, for example, in U.S. 3,326,684 of Nishio et al. issued June 20, 1967; British 1,004,302 of Ilford published Sept. 15, 1965; French 1,516,556 of Fassbender; and in an article by H. D. Russell et al. in PSA Journal, volume 8, No. 50, pp. 59–62 entitled Stabilization Processing of Films and Papers.

The developing agents employed according to the invention can also be present in one or more layers of a photographic element designed for recording color images. For example, these compounds can be employed in one or more layers of a photographic element containing a photographic layer sensitive to the blue region of the spectrum, a photographic layer sensitive to the green region of the spectrum, and a photographic layer sensitive to the red region of the spectrum. Layers sensitive to the blue, green and red regions of the spectrum can contain any suitable sensitizing dyes. Photographic elements designed for recording color images in which the developing agents of the invention can be used are described, for example, in Mees The Theory of the Photographic Process, 3rd ed., 1966, pp. 382–396.

The developing agents employed in the practice of the invention can be employed in an element containing development nuclei or silver precipitating nuclei, e.g. an image receiver. As described, they can also be employed in photographic elements and/or processing compositions designed for use with an image receiver.

Development nuclei or silver precipitating agents which can be employed in diffusion transfer systems as described can be physical development nuclei or chemical precipitants including, for example, (a) heavy metals in colloidal form and salts of these metals; (b) salts of amines which form silver salts and/or (c) nondiffusing polymeric materials with functional groups capable of combining with silver amines.

Suitable development nuclei and/or silver image precipitating agents within the described classes include metals sulfides, selenides, polysulfides, polyselenides, thiourea and its derivates, stannous halides, silver, gold, platinum, palladium, and mercury, colloidal sulfur, aminoguanidine sulfate, aminoguanidine carbonate, arsenous oxide, sodium stannite, hydrazines, xanthates, and similar agents disclosed, for example, in U.S. Pat. 3,020,155 of Yackel issued Feb. 2, 1962. A nondiffusing polymeric silver precipitant or development nuclei such as polyvinylmercapto-

acetate can also be employed. A wide range of concentrations of development nuclei or silver precipitating agents can be employed. A concentration of the development nuclei or silver precipitant in the image receiving layer must be at least sufficient to insure the development of a positive image and sufficient removal of undeveloped silver salt from the light-sensitive layer to be processed. Usually the concentration of the developing agent as described is about 320 mg. per square foot of the layer containing the precipitants or development nuclei.

The developing agents employed in the practice of the invention can be employed in combination with any silver halide developing agent. The developing agents employed in the practice of the invention can be employed in such combinations as auxiliary developing agents or as the main component of the developing combination. Suitable silver halide developing agents which can be employed in combination with the described pyrimidine developing agents include, for example, polyhydroxybenzenes such as hydroquinone developing agents, e.g. hydroquinone, alkyl substituted hydroquinones as exemplified by tertiary butyl hydroquinone, methyl hydroquinone and 2,5-dimethylhydroquinone; catechol and pyrogallol; aminomethyl hydroquinone; chloro substituted hydroquinone such as chlorohydroquinone or dichlorohydroquinone; alkoxy substituted hydroquinone such as methoxyhydroquinone or ethoxyhydroquinone; amino phenol developing agents, such as 2,4-diaminophenols and methylaminophenols; pyrimidine developing agents; ascorbic acid developing agents such as ascorbic acid, ascorbic acid ketals, and ascorbic acid such as those described in U.S. Pat. 3,337,342 of Green issued Aug. 22, 1967; hydroxylamine; 3-pyrazolidone developing agents such as 1-phenyl-3-pyyrazolidone and 1-phenyl-4-methyl - 4-hydroxymethy-3-pyrazolidone, including those described in British Pat. 930,572 published July 3, 1963; and acyl derivatives of para aminophenol such as described in British Pat. 1,045,303 published Oct. 12, 1966. Such developing agents can be used alone or in combination. It is usually desirable to use other developing agents than aminophenol compounds because of the tendency of these compounds to cause stain.

The developing agents employed in the practice of the invention can be used in combination, for example, with the following compounds:

1-phenyl-3-pyrazolidone
hydroquinone
methyl hydroquinone
2,5-dimethyl hydroquinone
2,6-dimethyl hydroquinone
tertiary butyl hydroquinone
3,6-dihydroxy benzonorbornane
2,4-diamino-6-methyl phenyl dihydrochloride
4-phenyl catechol
tertiary butyl pyrocatechol
2,4-diaminophenol dihydrochloride
ascorbic acid
N-methyl-p-aminophenol sulfate
N,N'-ethylene di(oxymethyl)pyridinium perchlorate
7,14-diazo-6,15-dioxoeicosane-1,21-bis(pyridinium perchlorate)

The described compounds can, for instance, be incorporated in a photographic element employed in a diffusion transfer system as described which after exposure can be developed employing a processing composition containing a developing agent of the invention. One or more of the described combination of compounds can be in a photographic element and/or processing composition, e.g. a developer composition employed in the practice of the invention. For example, a photographic element can contain a 3-pyrazolidone developing agent and/or a 2,4-diaminophenol developing agent and/or polyhydroxybenzene developing agents and/or other described addenda and be developed employing a processing composition containing a developing agent of the invention, i.e. an anhydro dihydro reductone developing agent.

The developing agents employed in the practice of the invention can be employed in a photographic silver salt emulsion designed for diffusion transfer processing and/or in a processing composition designed for such processing. A typical processing composition employed in diffusion transfer systems is described, for example, in U.S. Pat. 3,120,795 of Land et al. issued Feb. 11, 1964.

Accordingly another embodiment of the invention is in a liquid photographic processing composition comprising (A) a silver halide solvent and (B) a silver halide developing agent, the improvement wherein said developing agent is an anhydro dihydro amino reductone silver halide developing agent.

This composition is typically employed in a combination of (a) a photographic element comprising a photographic silver salt layer, (b) a viscous processing composition comprising:

(1) a silver halide solvent,
(2) an alkaline development activator, and
(3) an anhydro dihydro amino reductone silver halide developing agent,

(c) an image receiving layer comprising development nuclei, especially palladium development nuclei, dispersed in a polymeric binder.

A processing composition employed in the practice of the invention is typically a viscous processing composition. A wide range of suitable viscosity can be employed. The viscosity is usually about 20 to about 100,000 centipoise. Various thickening agents are suitable in the described processing compositions and processes of the invention. Any of those commonly employed in diffusion transfer photographic systems can be employed as well as those employed in viscous monobaths. These include those described in U.S. Pat. 3,120,795 of Land et al. issued Feb. 11, 1964, such as hydroxyethylcellulose and carboxymethylcellulose.

Suitable viscous monobaths in which the described anhydro dihydro reductions silver halide developing agents can be employed are described, for example, in the Monobath Manual by Grant M. Haist (1966), and U.S. Pat. 3,392,019 of Barnes et al. issued July 9, 1968.

A wide range of silver halide solvents can be employed in the practice of the invention. Usually the silver halide solvent is sodium thiosulfate, however various organic silver halide complexing agents such as those described in Haist et al. Photographic Science and Engineering, vol. 5, page 198 (1961) and described in French Pat. 1,312,687, issued Nov. 12, 1962 and Belgian Pat. 606,559 of Ulrich et al. issued July 26, 1960 and similar agents can also be used.

Another embodiment of the invention comprises in a photographic diffusion transfer process comprising developing a latent image in a photographic silver salt layer and precipitating an image in an image receiver layer, the improvement comprising developing said latent image with an anhydro dihydro reductone silver halide developing agent. A photographic diffusion transfer process according to this invention is typically a black and white silver salt diffusion transfer system.

The described process is carried out at a pH which activates the described anhydro dihydro reductone silver halide developing agent. The activating pH is usually about 10 to about 14 with good results being obtained when the pH is above about 12. When the pH of the system is lowered to less than about 8, e.g. between 8 and 2, the developing activity stops. The optimum pH for any particular diffusion transfer system will be influenced by the particular photographic element, the desired image, various addenda employed in the processing composition, emulsion and image receiver, processing conditions and the like. Any development activator can be employed which provides the desired pH. Typical development ac-

tivators which can be employed are alkaline metal hydroxide such as sodium hydroxide, potassium hydroxide or lithium hydroxide as well as organic development activators such as amines, e.g. 2-aminoethanol, 2-methylaminoethanol, 2-dimethylaminoethanol, 2-ethylaminoethanol, 2-diethylaminoethanol, 2,2'-diiminodiethanol, 5-diethylamino-2-pentanol, and the like.

A photographic process according to the invention accordingly can comprise the steps of exposing a photographic element comprising a photographic silver salt layer to form a latent image therein, developing the resulting latent image with a processing composition as described at a pH of about 12 to about 14 comprising an anhydro dihydro reductone silver halide developing agent, contacting undeveloped silver salts in the photographic silver salt layer with a silver halide solvent to form an imagewise distribution of a silver complex in the unexposed areas of the photographic silver salt layer, transferring at least part of the silver complex to an image receiver layer contiguous to the photographic silver complex in the presence of development nuclei, to form a visible image in the receiver layer.

Processing conditions, time of development and the like can vary depending on several factors such as the desired image, the particular components of the described photographic element, processing, composition and image receiver. Typical processing is carried out under normal atmospheric conditions and is completed within about 60 seconds, e.g. within about 10 seconds. Processing temperatures are typically about 20° C. to about 30° C. but elevated temperatures can be employed if desired such as temperatures up to about 50° C.

The described photographic element, receiving element and/or processing composition can also contain toning agents. Typical toning agents which can be employed include, for example, polyvalent inorganic salts as described in U.S. Pat. 2,698,236 of Land issued Dec. 28, 1954; silica as described in U.S. Pat. 2,698,237 or Land issued Dec. 28, 1954; and heterocyclic mercaptans such as mercaptoazoles, e.g. mercaptodiazoles, mercaptotriazoles, and mercaptotetrazoles.

The concentrations of developing agents used in the practice of the invention can vary over wide ranges depending on the particular photographic and physical variables present in the system. For example, the location of the developing agent in the system, and the photographic element, processing composition, the desired image, processing conditions and the like. Suitable concentrations also depend on the particular addendum present in the photographic element to be processed and/or in the processing compositions. Typically when a developing agent according to the invention is employed in a photographic element, it is employed in the concentration of about 0.01 to about 5 mol of developing agents per mol of silver present in the photographic element. When a developing agent as described is employed in a processing composition, the total concentration of developing agents in the system is typically about 0.01 to about 10, preferably 1 to about 5% by weight of the total developer composition.

It is often advantageous to have an antifoggant present in the processing compositions and/or photographic elements processed according to the invention. Suitable antifoggants include organic antifoggants, such as benzotriazole, benzimidazole, 2-mercaptobenzimidazole, nitroindazole, and mercaptotetrazole antifoggants. The developer compositions of the invention can contain inorganic antifoggants such as potassium bromide, potassium iodide and/or sodium bromide. The concentration of antifoggant in either the processing composition or photographic element can vary depending upon the desired image or the components present, processing conditions and the like. The processing composition typically contains less than about 2% by weight of the antifoggant and the antifoggant is usually in the range of about 0.01 to 2% by weight of the total processing composition.

Especially good results can be obtained in the practice of the invention when the described anhydro dihydro reductone silver halide developing agents are employed in combination with other silver halide developing agents such as hydroxycinnamic acid silver halide developing agents and/or lactone silver halide developing agent precursors and/or pyrimidine silver halide developing agents and/or aminomethyl polyhydroxybenzene silver halide developing agents. One or more of these developing agents according to the practice of the invention are suitable in a range of physical locations in the described diffusion transfer system. One or more can be employed in one or more layers of a photographic element and/or processing composition and/or in an image receiver employed therewith. For example, one or more of the described developing agents can be employed in the processing composition such as an aqueous alkaline developer solution and one or more can be incorporated in a layer of a photographic element such as in a silver salt emulsion layer, an overcoat layer, a layer between the emulsion layer and the support and/or some other layer contiguous to the silver salt to be developed. The described developing agents can be employed in such combinations as auxiliary developing agents or one or more can be used as the main components of the developing combination or developing precursor combination.

A wide variety of pyrimidine silver halide developing agents can be employed in combination with the described anhydro dihydro reductone silver halide developing agents according to the practice of the invention. Suitable pyrimidine silver halide developing agents include, for example:

4-amino-5,6-dihydroxy-2-methyl pyrimidine
2,5-dihydroxy-4,6-dimethyl pyrimidine
2-amino-4,5-dihydroxy pyrimidine
2-piperidino-4,5-dihydroxy-6-methyl pyrimidine
2,4-diamino-5-hydroxy-6-methyl pyrimidine
2,4-diamino-5-hydroxy pyrimidine
2,5-diamino-4,6-dihydroxy pyrimidine
2,4-dihydroxy-5,6-diamino pyrimidine
2,4,6-triphydroxy-5-amino pyrimidine
2,4,5,6-tetrahydroxy pyrimidine
2-methyl-4-amino-5,6-dihydroxy pyrimidine
2-amino-4,5-dihydroxy-6-methyl pyrimidine
2,4,5-trihydroxy-6-methyl pyrimidine
2,4,5-triamino pyrimidine

Pyrimidine silver halide developing agents are described, for example, in an article by R. W. Henn and S. V. Carpenter, Photographic Science and Engineering, No. 3, May-June, 1959, pages 135–139.

The described pyrimidine silver halide developing agents are typically in the form of an acid salt such as a hydrochloride, chloride, sulfate or the like. A pyrimidine silver halide developing agent as emloyed herein includes such compounds either in salt form or in their nonsalt form.

A wide range of cinnamic acid silver halide developing agents can also be employed in combination with the described anhydro dihydro reductone silver halide developing agents in the practice of the invention. Suitable cinnamic acid silver halide developing agents include for example:

Beta-4-dimethyl-2,5-dihydroxy cinnamic acid
4-methyl-2,5-dihydroxy cinnamic acid
6-bromo-4-methyl-2,5-dihydroxy cinnamic acid
2-hydroxy-5-amino cinnamic acid
Beta-methyl-2-hydroxy-4-methoxy-5-amino cinnamic acid
Beta-4-dimethyl-2-hydroxy-5-amino cinnamic acid
Beta-methyl-2,5-dihydroxy-4-methoxy cinnamic acid
2-hydroxy-5-methylamino cinnamic acid
4-t-butyl-2,5-dihydroxy cinnamic acid
2,5-dihydroxy cinnamic acid
2,5-dihydroxy-3,4,6-trimethyl cinnamic acid
2,3-dihydroxy cinnamic acid

Cinnamic acid silver halide developing agents in a diffusion transfer system are described for example in U.S. application Ser. No. 764,301 of Oftedahl, filed Oct. 1, 1968.

Typically the described cinnamic acid silver halide developing agents are derived from corresponding hydroxycoumarin and/or aminocoumarin developing agent precursors. Suitable aminocoumarin and/or hydroxycoumarin developing agent precursors which can be employed in the practice of the invention include for example:

8-hydroxy coumarin
6-hydroxy-5,7-dimethoxy coumarin
6-hydroxy-4,7-dimethyl coumarin
6-hydroxy-5,7-diethoxy-4-methyl coumarin
6-hydroxy coumarin
8-hydroxy-4-methyl coumarin
6-hydroxy-4-methyl coumarin
7-(benzyloxy)-6-hydroxy coumarin
6-hydroxy coumarin-5-sulfonic acid
6-hydroxy coumarin-5-sulfinic acid
4,6-dihydroxy coumarin
8-amino coumarin
6-amino coumarin
6-amino-5,7-dimethoxy coumarin
8-amino-4-methyl coumarin
6-amino-5,7-diethoxy-4-methyl coumarin
6-amino-8-hydroxy coumarin
6-hydroxy-8-amino coumarin
6,7-dihydroxy-4-methyl-3,4-dihydro coumarin
7,8-dihydroxy-4-methyl-3,4-dihydro coumarin

Further a wide variety of aminoalkylaydroquinone silver halide developing agents can be employed in combination with the described anhydro dihydro reductone silver halide developing agents in the practice of the invention. Suitable aminomethylhydroquinone developing agents which can be employed include for example:

2-morpholinomethyl hydroquinone
2-piperidinomethyl hydroquinone
2-pyrrolidinomethyl hydroquinone
2-methyl-5-(4-methylpiperazinomethyl) hydroquinone
2-pirimidinomethyl hydroquinone
2,5-bis-(dimorpholinomethyl) hydroquinone
2,5-bis-(dipiperazinomethyl) hydroquinone
2,5-bis-(dipiperidinomethyl) hydroquinone
2-methyl-5-morpholinomethyl hydroquinone
2-methyl-5-pyrrolidinomethyl hydroquinone
2-methyl-5-piperidinomethyl hydroquinone
2-methoxy-5-morpholinomethyl hydroquinone
2-methyl-5-bis(hydroxyethyl)aminomethyl hydroquinone
2-t-butyl-5-morpholinomethyl hydroquinone

These are typically employed in the form of their acid salts, such as their chloride, sulfate, or hydrochloride salts or alkali metal salts such as their sodium or potassium salts.

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

EXAMPLE 1

This illustrates an anhydro dihydro reductone silver halide developing agent in a diffusion transfer system according to the invention.

A processing composition is prepared by mixing the following components:

	G.
Sodium sulfite	60.0
Sodium thiosulfate pentahydrate	40.0
Sodium iodide	1.5
Sodium hydroxide	64.0
Hydroxyethyl cellulose (sold under the tradename Natrasol 250H by Hercules Powder Company, U.S.A.)	25.0
Anhydro dihydro piperidinohexose reductone	5.0
Water to 1 liter.	

The resulting processing solution is a viscous liquid.

A photographic element is prepared by coating a gelatin solution containing the silver halide developing agent, 2-methyl-5-morpholinomethyl hydroquinone on electron bombarded polyethylene coated paper at 240 mg. of gelatin per square foot at 50 mg. of developing agent per square foot. Over this layer is coated a coarse grained silver bromoiodide gelatino emulsion containing 5 mole percent iodide and a concentration of 125 mg. of silver per square foot and 320 mg. of gelatin per square foot. An image receiver is prepared by coating a water resistant paper support wtih palladium development nuclei dispersed in a polymeric binder.

The described photographic element is sensitometrically exposed. The processing composition as described is then squeezed between the photographic element and the image receiver and the resulting so-called sandwich is pressed together by running it between two rollers. After 20 seconds the so-called sandwich is pulled apart and the resulting image on the image receiver is observed for oxidation stain.

The same procedure is carried out with the exception that the described anhydro dihydro reductone silver halide developing agent is omitted from the described processing composition. The resulting developed image on the image receiver is employed as a control.

The relative speed of the control image on the image receiver is assigned the value of 100 and has a maximum density of 1.15. The image on the image receiver employing the described anhydro dihydro piperidino hexose reductone in the processing composition has a relative speed of 100 and a maximum density of 1.55. This illustrates that the described reductone silver halide developing agent provides increased maximum density without undesired loss of photographic speed. The image on the image receiver in both cases contains no stain.

EXAMPLE 2

This is a comparative example.

A processing composition is prepared by mixing the following components:

	G.
Potassium sulfite	50.0
Sodium thiosulfate pentahydrate	40.0
Potassium iodide	1.6
Potassium hydroxide	16.7
Sodium hydroxide	17.5
6-methoxy-2,4-diaminophenol dihydrochloride	30.0
Hydroxyethyl cellulose (Natrasol 250H sold by Hercules Powder Company, U.S.A.	30.0

The resulting processing solution is a viscous liquid.

A photographic element is prepared by coating a gelatino coarse grained silver bromoiodide photographic emulsion on a film support. An image receiver is prepared by coating a water resistant paper support with palladium development nuclei dispersed in a polymeric binder. The photographic element is sensitometrically exposed. The processing composition, as described, is then squeezed between the photographic element and the image receiver and the resulting so-called sandwich is pressed together by running it between two rollers. After 30 seconds the so-called sandwich is peeled apart and the resulting image on the image receiver is observed for oxidation stain. The positive image is produced which has heavy yellow or orange stain.

This demonstrates that the developing agent such as a 2,4-diaminophenol developing agent causes undesired oxidation stain as compared to the described developing agents employed in the practice of the invention.

EXAMPLE 3

This is a comparative example.

The procedure set out in Example 2 is repeated with the exception that hydroquinone is employed in place of the described 2,4-diaminophenol developing agent. The

resulting positive image contains heavy yellow or orange stain.

EXAMPLE 4

This is a comparative example.

The procedure set out in Example 2 is repeated with the exception that tertiary butyl hydroquinone is employed in place of the described 2,4-diaminophenol developing agent. The resulting positive image contains heavy yellow or orange stain.

EXAMPLE 5

This is a comparative example.

The procedure set out in Example 1 is repeated with the exception that piperidino hexose reductone is employed as a developing agent in place of the described anhydro dihydro piperidino hexose reductone and also at a concentration of 20.0 grams per liter of processing solution. The resulting positive image has a relative speed of 80 compared to the described control at a maximum density of 1.55.

This demonstrates that a higher concentration of piperidino hexose reductone is required in order to obtain the desired maximum density as compared to the described anhydro dihydro piperidino hexose reductone of Example 1.

EXAMPLES 6–12

The procedure set out in Example 1 is repeated with the exception that the following anhydro dihydro reductone silver halide developing agents are employed in place of the described anhydro dihydro piperidino hexose reductone. In each instance, similar results are obtained as set out in Example 1.

Example No.:	Developing agent
6	Anhydro dihydro dimethylamino hexose reductone.
7	Anhydro dihydro diallylamino hexose reductone.
8	Anhydro dihydro di-n-butylamino hexose reductone.
9	Anhydro dihydro di-n-hexylamino hexose reductone.
10	Anhydro dihydro morpholino hexose reductone.
11	Anhydro dihydro piperazino di(hexose reductone).
12	Anhydro dihydro pyrrolidino hexose reductone.

As described, usually the concentration of the developing agent is about 320 milligrams per square foot of the layer containing the precipitants or development nuclei or the concentration can be about 2 grams to about 50 grams per liter of processing solution, e.g. 5 grams to 20 grams per liter of processing solution.

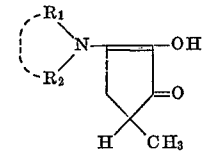
The supports or layers coated on them employed in the practice of the invention, typically paper supports, can contain acids, e.g. polymeric acids as described in U.S. Pat. 2,584,030 of Land issued Jan. 29, 1952, and U.S. Pat. 3,415,644 of Land issued Dec. 10, 1968.

It is often desirable to employ an antioxidant in a photographic element employed in the practice of the invention. This is typically in a layer containing a developing agent, as described. Typical antioxidants suitable for this purpose are sodium formaldehyde bisulfite and those described in U.S. Pat. 3,212,895 of Barbier et al. issued Oct. 19, 1965, and U.S. Pat. 3,418,132 of Kitze issued Dec. 24, 1968.

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 photographic product comprising in combination (a) a photographic element comprising a photographic silver salt, (b) a processing composition containing a silver halide solvent, and (c) an image receiving layer, said product containing a silver halide developing agent, the improvement wherein said developing agent is an anhydro dihydro amino reductone silver halide developing agent of the formula:



wherein R_1 and R_2 are each hydrogen, alkyl containing 1 to 5 carbon atoms, or, taken together, are atoms selected from the group consisting of carbon, hydrogen, oxygen and nitrogen atoms completing a 4 to 6 member heterocyclic nucleus.

2. A photographic product as in claim **1** wherein the anhydro dihydro amino reductone silver halide developing agent is present in the processing composition.

3. A photographic product as in claim **1** wherein the anhydro diyhdro amino reductone silver halide developing agent is present in the photographic element.

4. A photographic product as in claim **1** wherein the anhydro dihydro amino reductone silver halide developing agent is anhydro dihydro piperidino hexose reductone, anhydro dihydro morpholino hexose reductone, or anhydrodihydro pyrimidino hexose reductione.

5. A photographic product as in claim **1** wherein said photographic silver salt is photographic silver halide.

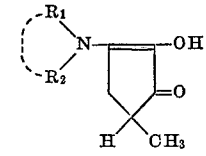
6. A photographic product as in claim **1** comprising an auxiliary silver halide developing agent.

7. A photographic product as in claim **1** comprising a hydroxy cinnamic acid silver halide developing agent.

8. A photographic product as in claim **1** comprising a lactone silver halide developing agent precursor.

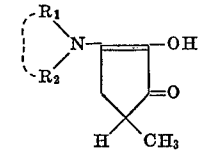
9. A photographic product as in claim **1** comprising a 3-pyrazolidone silver halide developing agent.

10. A photographic product comprising in combination (a) a photographic element comprising a photographic silver salt, (b) a processing composition containing a silver halide solvent, and (c) an image receiving layer, said product containing a silver halide developing agent, the improvement wherein said developing agent is an anhydro dihydro amino reductone silver halide developing agent of the formula:



wherein R_1 and R_2 are each hydrogen, alkyl containing 1 to 5 carbon atoms, or, taken together, are atoms completing a morpholino, piperazino, pyrrolidino, piperidino, dimethylmorpholino, methyl piperidino or pyrimidino heterocyclic nucleus.

11. In a liquid photographic processing composition comprising (a) a silver halide solvent and (b) a silver halide developing agent, the improvement wherein said developing agent is an anhydro dihydro amino reductone silver halide developing agent of the formula:



wherein R_1 and R_2 are each hydrogen, alkyl containing 1 to 5 carbon atoms, or, taken together, are atoms selected from the group consisting of carbon, hydrogen, oxygen

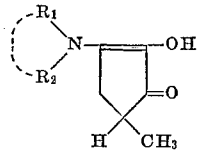
and nitrogen atoms completing a 4 to 6 member heterocyclic nucleus.

12. A liquid photographic processing composition as in claim **11** wherein said silver halide developing agent is anhydro dihydro piperidino hexose reductone, anhydro dihydro morpholino hexose reduction, or anhydro dihydro pyrimidino hexose reductone.

13. A liquid photographic processing composition as in claim **11** which is a monobath.

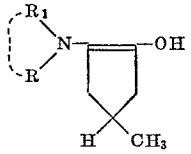
14. A liquid photographic processing composition as in claim **11** which is a viscous solution.

15. In a liquid photographic processing composition comprising (a) a silver halide solvent and (b) a silver halide developing agent, the improvement wherein said developing agent is an anhydro dihydro amino reductone silver halide developing agent of the formula:



wherein R_1 and R_2 are each hydrogen, alkyl containing 1 to 6 carbon atoms, or, taken together, are atoms completing a morpholino, piperazino, pyrrolidino, piperidino, dimethylmorpholino, methyl piperidino or pyrimidino heterocyclic nucleus.

16. In a photographic diffusion transfer process comprising developing a latent image in a photographic silver salt layer and precipitating an image in an image receiver layer, the improvement comprising developing said-latent image with an anhydro dihydro amino reductone silver halide developing agent of the formula:

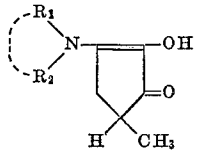


wherein R_1 and R_2 are each hydrogen, alkyl containing 1 to 5 carbon atoms, or, taken together, are atoms selected from the group consisting of carbon, hydrogen, oxygen and nitrogen atoms completing a 4 to 6 member heterocyclic nucleus.

17. A photographic diffusion transfer process as in claim **16** wherein said process is a black and white silver salt diffusion transfer process.

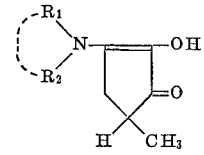
18. A photographic process as in claim **16** wherein said silver halide developing agent is anhydro dihydro piperidino hexone reductone, anhydro dihydro morpholino hexose reductone, or anhydro dihydro pyrimidino hexose reductone.

19. In a photographic diffusion transfer process comprising developing a latent image in a photographic silver salt layer and precipitating an image in an image receiver layer, the improvement comprising developing said latent image with an anhydro dihydro amino reductone silver halide developing agent of the formula:



wherein R_1 and R_2 are each hydrogen, alkyl containing 1 to 5 carbon atoms, or, taken together, are atoms completing a morpholino, piperazino, pyrrolidino, piperidino, dimethylmorpholino, methyl piperidino or pyrimidino heterocyclic nucleus.

20. A photographic process comprising the steps of exposing a photographic element comprising a photographic silver salt layer to form a latent image therein, developing the resultant latent image with a processing composition at a pH of about 12 to about 14 comprising an anhydro dihydro amino reductone silver halide developing agent of the formula:



wherein R_1 and R_2 are each hydrogen, alkyl containing 1 to 5 carbon atoms, or, taken together, are atoms completing a morpholino, piperazino, pyrrolidino, piperidino, dimethylmorpholino, methyl piperidino or pyrimidino heterocyclic nucleus, contacting undeveloped silver salts in the photographic silver salt layer with a silver halide solvent to form an imagewise distribution of a silver complex in the unexposed areas of the photographic silver salt layer, transferring at least part of the silver complex to an image receiver layer contiguous to the photographic silver salt complex in the presence of development nuclei, to form a visible image in the receiver layer.

21. A photographic process as in claim **20** wherein said anhydro dihydro amino reductone silver halide developing agent is anhydro dihydro piperidino hexose reductone, anhydro dihydro morpholino hexose reductone, or anhydro dihydro pyrimidino hexose reductone.

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"Treatment of Black and White Motion Picture Materials," Khaikin et al., U.S.S.R. 150,009, Sept. 14, 1962, Chemical Abstracts, vol. 58, p. 4086e.

JOHN T. GOOLKASIAN, Primary Examiner

D. J. FRITSCH, Assistant Examiner

U.S. Cl. X.R.

96—29, 61, 66, 76; 260—211, 268 MK, 247.7 A & K, 326.5 J, 294.7 J, 563 R

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,664,835 Dated May 23, 1972

Inventor(s) Mary J. Youngquist

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

In Column 2, line 9, "develiping" should read ---developing---.

In Column 2, line 24, "hpdroquinone" should read ---hydroquinone---.

In Column 3, line 71, "stream" should read ---steam---.

In Column 4, line 54, "compoistion" should read ---composition---.

In Column 7, lines 23-24, "aminomethyl hydroquinone" should read ---aminomethyl hydroquinones---.

In Column 7, line 33, "pyyrazolidone" should read ---pyrazolidone---.

In Column 8, line 41, "reductions" should read ---reductone---.

In Column 11, line 33, "aminoalkylaydroquinone" should read ---aminoalkylhydroquinone---.

In Column 11, line 43, "pirimidinomethyl" should read ---pyrimidinomethyl---.

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(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,664,835 Dated May 23, 1972

Inventor(s) Mary J. Youngquist

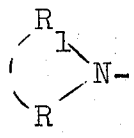
It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

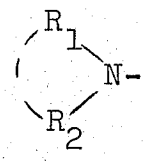
In the Claims:

In Column 15, line 6, "reduction" should read ---reductone---.

In Column 15, line 25, "6" should be ---5---.

In Column 15, lines 35-40, that portion of the formula reading

"  "

should read ---  ---.

In Column 15, line 52, "hexone" should read ---hexose---.

Signed and sealed this 5th day of December 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents