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FOGGED, DIRECT-POSITIVE SILVER HALIDE EMULSION CONTAINING NITRON

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ABSTRACT OF THE DISCLOSURE

This invention relates to direct-positive, silver halide, photographic elements. In one aspect, at least one layer of said element contains nitron. In another aspect, an over-layer containing light-insensitive silver chloride is used to provide more uniform photographic characteristics in used developers. In still another aspect, improved direct-positive silver halide grains are prepared by reducing a portion of the water-soluble silver salt before admixture with the water-soluble halide to precipitate the silver halide grains.

This invention relates to direct-positive, fogged silver halide emulsions. In one aspect, this invention relates to direct-positive silver halide elements comprising at least one layer which contains nitron. In another aspect, this invention relates to a direct-positive photographic element which comprises at least one direct-positive silver halide emulsion layer and at least an overcoat layer and/or an interlayer in said element which contains nitron. In still another aspect, this invention relates to a process for fogging direct-positive emulsions and the products produced thereby.

It is known in the prior art to make direct-positive, fogged silver halide emulsions. Emulsions of this type can be used in photographic elements to provide positive images upon exposure and chemical development. In many of the prior direct-positive elements, image characteristics upon development were highly dependent upon development conditions, length of use of the developer solutions, etc. The formation of a yellow fog is especially prevalent when the developing solution has been extensively used. Density and contrast changes also occur with used developers as opposed to fresh developing solutions. Therefore, improved direct-positive photographic elements and processes for making direct-positive emulsions would be desirable to provide direct-positive elements which demonstrate better image properties under a wide variety of exposure and development conditions.

We have now found that fogged, direct-positive silver halide emulsions can be made with improved photographic properties. In one aspect, we have found that nitron can be used in overcoats, gelatin interlayers and/or silver halide emulsion layers in direct-positive elements to prevent the formation of yellow physical development fog. In another aspect, we have found that direct-positive photographic elements comprising fogged silver halide grains and at least one layer containing nitron can be processed after exposure in either fresh developer or extensively used developer to obtain substantially uniform sensitometric characteristics in the photographic element. In another aspect, we have found that a silver chloride overlayer which preferably contains an excess of chloride ions on the direct-positive element provides more uniform image properties without substantial effects due to length of use of the developer, such as occurs when bromine ions build up in the developer. In still another aspect of this invention, we have found that a portion of the silver nitrate used in the precipitation of the direct-positive silver

halide can be reduced with a reduction agent such as thiourea dioxide, stannous chloride and the like to provide improved direct-positive emulsions.

In a preferred embodiment, the direct-positive emulsions used in combination with layers which contain nitron are direct-positive-blue-sensitive, chemically fogged silver halide emulsions.

In another preferred embodiment, the direct-positive emulsions comprise halogen-accepting compounds.

In another preferred embodiment, the direct-positive emulsions comprise electron-conducting compounds which are sometimes referred to as desensitizers.

In one preferred embodiment of this invention, the direct-positive photographic elements comprise layers which contain nitron. Generally, the nitron is utilized at a concentration of about 100 milligrams to about 2 grams per mole of silver halide in the element and preferably from about 300 milligrams to about 1 gram. Nitron is generally known in the trade to be 1,4-diphenyl-3,5-endoanilino-4,5-dihydro-1,2,4-triazole or 3,5,6-triphenyl-2,3,5,6-tetraazabicyclo[2.1.1]hex-1-ene.

The preferred direct-positive silver halide emulsions of this invention are blue-sensitive. It is understood that blue-sensitive means that the direct-positive composition will provide a reversal image when exposed with light in the 350- to 500-millimicron range of the electromagnetic spectrum. The silver halide compositions can also be spectrally sensitized so as to form reversal images when exposed in other regions of the spectrum such as the red and green regions. However, they all have the property of being capable of forming a reversal image when exposed with light in the blue region of the spectrum. Generally, these emulsions have high photographic speed compared to compositions such as conventional Hershel reversal emulsions.

Typical blue-sensitive-direct-positive silver halide emulsions which can be used in combination with nitron in photographic elements with improved properties include those disclosed in Berriman, U.S. Pat. 3,367,778, issued Feb. 6, 1968; Illingsworth, Belgian Pats. 695,355 through 695,366, all of which were granted Sept. 11, 1967; and Allentoff and Fogler, Belgian Pat. 689,233, granted Jan. 13, 1967. In one embodiment, the silver halide emulsions can comprise silver halide grain centers which promote the deposition of photolytic silver. In one embodiment of the invention, the sites for deposition of photolytic silver are provided by reducing a portion of the water-soluble silver salt such as silver nitrate before admixture in the reaction vessel with the water-soluble halide such as, for example, potassium bromide. Reduction of the silver nitrate can take place with any common reducing agent such as, for example, stannous chloride, thiourea dioxide, formalin, alkaline arsenite and the like. In this embodiment, it is also advantageous to add small amounts of polyvinyl pyrrolidone to the silver nitrate before reduction to obtain high contrast and maximum density with a small silver halide coverage ratio.

Typical direct-positive silver halide compositions which can be characterized by the above definitions and which are useful in this invention are: (1) emulsions comprising silver halide grains having internal centers which promote the deposition of photolytic silver and an outer region or shell of a fogged insoluble silver salt and preferably a halogen-conducting compound in said emulsion or (2) an emulsion which comprises fogged silver halide grains and an organic compound which accepts electrons, said grains being such that a test portion thereof, when coated as a photorgraphic silver halide emulsion on a support to give a maximum density of at least about 0.5 upon processing for 5 minutes at about 68° F. in Developer A (formula at end of specification), has a maximum density

which is at least about 30% greater than the maximum density of an identical coated test portion which is processed for 6 minutes at about 68° F. in Developer A after being bleached for about 10 minutes at about 68° F. in a bleach composition of:

Potassium cyanide—50 mg.
Acetic acid (glacial)—3.47 cc.
Sodium acetate—11.49 g.
Potasium bromide—119 mg.
Water to 1 liter

This invention can be practiced with direct-positive emulsions of the type in which a silver halide grain has a water-insoluble silver salt center and an outer shell composed of a fogged water-insoluble silver salt that develops to silver without exposure. These emulsions can be prepared in various ways, such as those described in Berriman, U.S. Pat. 3,367,778, issued Feb. 6, 1968. For example, the shell of the grains in such emulsions may be prepared by precipitating over the core grains a light-sensitive, water-insoluble silver salt that can be fogged and which fog is removable by bleaching. The shell is of sufficient thickness to prevent access of the developer used in processing the emulsions of the invention to the core. The silver salt shell is surface fogged to make it developable to metallic silver with conventional surface image developing compositions. The silver salt of the shell is sufficiently fogged to produce a density of at least about 0.5 when developed for 6 minutes at 68° F. in Developer B below when the emulsion is coated at a silver coverage of 100 mg. per square foot. Such fogging can be affected by chemically sensitizing to fog with the sensitizing agents described for chemically sensitizing the core emulsion, high-intensity light and the like fogging means well-known to those skilled in the art. While the core need not be sensitized to fog, the shell is fogged. Fogging by means of a reduction sensitizer, a noble metal salt such as gold salt plus a reduction sensitizer, high pH and low pAg silver halide precipitating conditions, and the like can be suitably utilized. The shell portion of the subject grains can also be coated prior to fogging.

Developer B

N-methyl-p-aminophenol sulfate—2.5 g.
Ascorbic acid—10.0 g.
Potassium metaborate—35.0 g.
Potassium bromide—1.0 g.
Water to 1 liter
pH of 9.6

Before the shell of water-insoluble silver salt is added to the silver salt core, the core emulsion is first chemically or physically treated by methods previously described in the prior art to product centers which promote the deposition of photolytic silver, i.e., latent image nucleating centers. Such centers can be obtained by various techniques as described in the Berriman patent referred to above. Silver salt cores containing centers attributable to a metal of Group VIII of the Periodic Table, e.g., palladium, iridium or platinum and the like, are especially useful since these centers also appear to function as electron acceptors. Chemical sensitization techniques of the type described by Antoine Hautot and Henri Saubenier in Science et Industries Photographiques, vol. XXVIII, January 1957, pages 1 to 23, and January 1957, pages 57 to 65, are particularly useful. Such chemical sensitization includes three major classes, namely, gold or noble metal sensitization, sulfur sensitization, such as by a labile sulfur compound, and reduction sensitization, e.g., treatment of the silver halide with a strong reducing agent which introduces small specks of metallic silver into the silver salt crystal or grain.

In another embodiment, the silver halide emulsions can comprise silver halide grains having centers which promote the deposition of photolytic silver which are either sufficiently small or sufficiently buried within the crystal as to be not accessible to initiate development to a visible image. Silver halide grains of this type can be provided by either using very low concentrations of the sensitizing agent throughout the precipitation or adding the sensitizing agent to the precipitation medium during the initial part of the precipitation whereby the concentration of the sensitizing agent will be lowered significantly by occlusion of the agent in the grains so that continued precipitation would result in lowered concentration of centers for promoting deposition of photolytic silver in the outer regions of each grain.

The practice of this invention is particularly suitable for high-speed direct-positive emulsions comprising fogged silver halide grains and a compound which accepts electrons, as described and claimed in Illingsworth, patent application Ser. No. 619,909 and titled "Photographic Reversal Materials III" now U.S. Pat. 3,501,306, issued Mar. 17, 1970. The fogged silver halide grains of such emulsions are such that a test portion thereof, when coated as a photographic silver halide emulsion on a support to give a maximum density of at least about 1 upon processing for 6 minutes at about 68° F. in Developer A, has a maximum density which is at least about 30% greater than the maximum density of an identical coated test portion which is processed for 6 minutes at about 68° F. in Developer A after being bleached for about 10 minutes at about 68° F. in a bleach composition of:

Potassium cyanide—50 mg.
Acetic acid (glacial)—3.47 cc.
Sodium acetate—11.49 g.
Potassium bromide—119 mg.
Water to 1 liter

The grains of such emulsions will lose at least about 25% and generally at least about 40% of their fog when bleached for 10 minutes at 68° F. in a potassium cyanide bleach composition as described herein. This fog loss can be illustrated by coating the silver halide grains as a photographic silvver halide emulsion on a support to give a maximum density of at least 1.0 upon processing for 6 minutes at about 68° F. in Developer A and comparing the density of such a coating with an identical coating which is processed for 6 minutes at 68° F. in Developer A after being bleached for about 10 minutes at 68° F. in the potassium cyanide bleach composition. As already indicated, the maximum density of the unbleached coating will be at least 30% greater, generally at least 60% greater, than the maximum density of the bleached coating.

The silver halides employed in the preparation of the photographic emulsions useful in this invention include any of the photographic silver halides as exemplified by silver chloride, silver bromide, silver bromoiodide, silver chlorobromide, silver chlorobromoiodide, and the like. Emulsion blends, e.g., blends of silver chloride and silver chlorobromide, can be used. Also, the core of the silver halide grain can be composed of silver halide of different composition than that in the outer shell of the grain.

Silver halide grains having an average grain size less than about 2 microns, preferably less than about 0.5 micron, give particularly good results. The silver halide grains can be regular and can be any suitable shape such as cubic or octahedral, as described and claimed in Illingsworth, patent application Ser. No. 619,948, and titled "Direct-Positive Photographic Emulsions I," now U.S. Pat. 3,501,305, issued Mar. 17, 1970. Such grains advantageously have a rather uniform size frequency distribution, as described and claimed in Illingsworth, patent application Ser. No. 619,936, titled "Photogaphic Reversal Emulsions II," now U.S. Pat. 3,501,307, issued Mar. 17, 1970. For example, at least 95%, by weight, of the photographic silver halide grains are within about 40%, preferably within about 30%, of the mean grain size. Average grain size can be determined using conventional methods, e.g., as shown in an article by Trivelli and Smith entitled "Empirical Relations Between Sensi-

tometric and Size-Frequency Characteristics in Photographic Emulsion Series" in The Photographic Journal, vol. LXXIX, 1949, pages 330–338, and "Methods of Particle-Size Analysis," ASTM Symposium on Light Microscopy, by Loveland, 1953, pages 94–122. The fogged silver halide grains in these direct-positive photographic emulsions of this invention produce a density of at least 0.5 when developed without exposure for 5 minutes at 68° F. in Developer A when such an emulsion is coated at a coverage of 50 to about 500 mg. of silver per square foot of support. The photographic silver halides can be coated at silver coverages in the range of about 50 to 500 milligrams of silver per square foot.

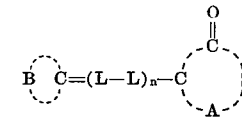
In preferred embodiments of this invention, electron acceptors and halogen conductors (sometimes referred to as halogen acceptors) are present in the direct-positive emulsions.

The electron acceptors or halogen conductors which give particularly good results in the practice of this invention can be characterized in terms of their polarographic halfwave potentials, i.e., their oxidation reduction potentials determined by polarography. The electron acceptors useful herein have an anodic polarographic potential and a cathodic polarographic potential which, when added together, give a positive sum. The halogen conductors useful herein have an anodic polarographic potential less than 0.85 and a cathodic polarographic potential which is more negative than −1.0. Preferred halogen conductors have an anodic polarographic potential less than 0.62 and a cathodic polarographic potential which is more negative than −1.3. Cathodic measurements can be made with a 1×10^{-4} molar solution of the electron acceptor in a solvent, for example, methanol which is 0.05 molar in lithium chloride using a dropping mercury electrode with the polarographic half-wave potential for the most positive cathodic wave being designated E_c. Anodic measurements can be made with 1×10^{-4} molar aqueous solvent solution, for example, methanolic solutions of the electron acceptor which are 0.05 molar in sodium acetate and 0.005 molar in acetic acid using a carbon paste of pyrolytic graphite electrode, with the voltammetric half peak potential for the most negative anodic response being designated E_a. In each measurement, the reference electrode can be an aqueous silver—silver chloride (saturated potassium chloride) electrode at 20° C. Electrochemical measurements of this type are known in the art and are described in New Instrumental Methods in Electrochemistry, by Delahay, Interscience Publishers, New York, 1954; Polarography, by Kolthoff and Lingane, 2nd edition, Interscience Publishers, New York, N.Y., 1952; Analytical Chemistry, 36, 2426 (1964) by Elving; and Analytical Chemistry, 30, 1576 (1958) by Adams. Signs are given according to IUPAC, Stockholm Convention 1953.

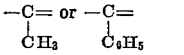
Advantageously, these electron acceptors used herein also provide spectral sensitization such that the ratio of minus blue relative speed to blue relative speed of the emulsion is greater than 7, and preferably greater than 10, when exposed to a tungsten light source through Wratten No. 16 and No. 35 plus 38A filters respectively. Such electron acceptors can be termed "spectrally sensitizing electron acceptors." However, electron acceptors can be used which do not spectrally sensitize the emulsion.

An especially useful class of electron acceptors which can be used in the direct-positive photographic silver halide emulsions and processes of this invention are cyanine dyes, such as the imidazo[4,5-b]quinoxaline dyes. Dyes of this class are described in Brooker and Van Lare Belgian Pat. 660,253, issued Mar. 15, 1965. In these dyes, the imidazo[4,5-b]quinoxaline nucleus is attached, through the 2-carbon atom thereof, to the methine chain. Typical good electron-acceptor dyes used in direct-positive emulsions are disclosed in Illingsworth and Spencer, Belgian Pat. 695,364, granted Sept. 11, 1967.

A preferred class of halogen-conducting compounds useful in this invention is characterized by an anodic halfwave potential which is less than 0.62 and a cathodic halfwave potential which is more negative than −1.3. A preferred class of halogen conductors that can be used in the practice of this invention comprises the spectral sensitizing merocyanine dyes having the formula:



where A represents the atoms necessary to complete an acid heterocyclic nucleus, e.g., rhodanine, 2-thiohydrantoin and the like, B represents the atoms necessary to complete a basic nitrogen-containing heterocyclic nulceus, e.g., benzothiazole, naphthothiazole, benzoxazole and the like, each L represents a methine linkage, e.g., —CH=,



and n is an integer from 0 to 2, i.e., 0, 1 or 2. Typical halogen-conducting compounds are disclosed in Wise, Belgian Pat. 695,361, granted Sept. 11, 1967.

In the preparation of the above photographic emulsions, the electron acceptors, halogen conductors, bromide and iodide salts are advantageously incorporated in the washed, finished silver halide emulsion and should, of course, be uniformly distributed throughout the emulsion. The methods of incorporating such addenda in emulsions are relatively simple and well-known to those skilled in the art of emulsion making. For example, it is convenient to add them from solutions in appropriate solvents, in which case the solvent selected should be completely free from any deleterious effect on the ultimate light-sensitive materials. Methanol, isopropanol, pyridine, water, etc., alone or in admixtures, have proven satisfactory as solvents for the electron acceptors and halogen conductors. The type of silver halide emulsions that can be sensitized with these dyes include any of those prepared with hydrophilic colloids that are known to be satisfactory for dispersing silver halides, for example, emulsions comprising natural materials such as gelatin, albumin, agar-agar, gum arabic, alginic acid, etc., and hydrophilic synthetic resins such as polyvinyl alcohol, polyvinyl pyrrolidone, cellulose ethers, partially hydrolyzed cellulose acetate, and the like. The binding agents for the emulsion layer can also contain dispersed polymerized vinyl compounds such as disclosed, for example, in U.S. Pats. 3,142,568, 3,193,386, 3,062,674 and 3,220,-844, and include the water-insoluble polymers of alkyl acrylates and methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates and the like.

The overlayers are generally very effective in maintaining constant reproducibility of image properties with used developers when silver halide direct-positive emulsions are used in the element wherein a predominant amount of the halide is bromide. The overlayer preferably contains chloride ions or silver chloride, but generally any silver compounds more soluble than silver bromide including silver ferrocyanides can be utilized as they will be displaced by bromide. When the overlayer is a silver compound, it is preferably desensitized to light. Typical desensitizers useful for this purpose include rhodium ammonium chloride, 1-phenyl-5-mercaptotetrazole, methyl benzotriazole, 4-nitro-6-chlorobenzotriazole and the like. Useful concentrations of these desensitizers are from about 0.1 to 0.5 percent per mole of silver.

The overlayers and silver halide layers of this invention can be hardened by any acceptable means known in the photographic art; however, aldehyde hardeners such as formaldehyde and mucochloric acid are preferred. The overlayers can be coated at any suitable concentration to provide the necessary stability in image properties, but they are preferably coated at about 7 to

about 15 mg./dm.^{2} of the ingredient to be reduced by the bromide ions.

This invention can be further illustrated by the following examples.

EXAMPLE 1

A silver halide direct-positive emulsion is prepared by adding an aqueous solution containing 170 g. of silver nitrate which have been partially reduced to an aqueous solution containing 131 g. of potassium bromide and 2.25 g. of potassium iodide. The precipitate is decanted, washed, gelatin added, chilled and set. This emulsion has fog specks distributed throughout the grains as a result of the partial reduction of the silver nitrate.

To separate aliquot portions of the emulsion are added 0.127 g. of diphenylamino-5-[(3 - ethyl - 2(3H) - benzoxasolylidene)-ethylene]-5-isothiohydantoin (also known as 2 - diphenylamino-5-[(3-ethyl-2-benzoxazolinylidene) ethylidene]-2-thiazolin-4-one) in methanol solution. A solution containing .0018 g. of potassium chloroaurate, a gelatin solution and a mucochloric acid solution are also added. To one of the portions is added an aqueous solution containing .0012 g. of nitron.

The emulsions are coated on a support and dried. Respective samples of the emulsions are then exposed in a sensitometer and developed in a hydroquinone-1-phenyl-3-pyrazolidone developer containing sodium bisulfite and methoxy polyethylene glycol.

The samples containing the nitron contain no noticeable yellow physical development fog, while the control sample containing no nitron contains substantial yellow physical development fog.

Samples of the exposed control emulsion and the emulsion containing nitron are then developed in the samples of the above developer which contains respectively 8 g., 14 g., 18 g. and 28 g. of sodium bromide per liter to approximate conditions of using extensively used developers. When the amount of bromide is increasing, the D_{max} of nitron-containing samples is slightly decreasing, whereas in control samples without nitron, D_{max}, gamma and yellow fog are highly increasing.

It is apparent that the nitron represses the solvent action of extensively used developers which contain higher concentrations of bromide ions.

Similar results are obtained when nitron is used in an overlayer on the emulsion or in a gelatin interlayer within the layer arrangement.

Similar results are also obtained when the dyes diphenylamino - 5-[(3-ethyl-2(3H)-benzothiazolylidene)ethylene]-5-isothiohydantoin and [3-ethyl-2(3H)-benzoxaoylidene ethylidene] - 3 - phenyl-1-carboxymethyl-2-thiohydantoin (also known as 1-carboxymethyl-5-[(3-ethyl-2-benzoxazolinylidene) ethylidene] - 3 - phenyl-2-thiohydantoin) are utilized in the emulsion.

EXAMPLE 2

A fogged silver halide, direct-positive emulsion containing silver halide grains having silver bromide outer layers or shells is prepared according to Allentoff and Fogler, U.S. Ser. No. 582,262, filed Sept. 27, 1966, now U.S. Pat. 3,477,852, issued Nov. 11, 1969. To one portion of the emulsion is added 650 milligrams per mole of silver of nitron. Another portion served as a control.

Samples of the coated emulsion are exposed on a sensitometer and developed for 2¾ minutes in Kodak D–85 developer containing 1 g. of hypo per liter. The control sample produces a high degree of yellow fog, whereas the sample containing nitron has no apparent yellow fog.

The background density is measured through a blue filter to give an indication of yellow stain. The control sample has a density of 0.15 while the sample containing 650 mg. of nitron per mole of silver has a density of 0.10.

EXAMPLE 3

A fogged direct-positive silver chlorobromide gelatin emulsion is prepared as described in Example 5 of Litzerman, U.S. Ser. No. 618,354, filed Feb. 24, 1967, now U.S. Pat. 3,531,290, issued Sept. 29, 1970, containing 80 g. of gelatin/mole of silver halide. To this emulsion are added 80 g. of copoly(methyl acrylate-sulfopropyl acrylate-2-aceto-acetoxy ethyl methacrylate); 500 mg. of a halogen acceptor dye, 3-ethyl-5-[1-(4-sulfobutyl)-4-(1H)-pyridylidene]-rhodanine sodium salt; and 1 g. of potassium iodide/mole of silver halide. Formaldehyde is added as a hardener, and part of the emulsion is coated on a polyethylene terephthalate support. To a second part of the emulsion, 1.5 g. of nitron is added and the emulsion coated on a similar support. Both emulsions are coated at a coverage of 450 mg. of silver and 300 mg. of gelatin/ft.^{2}. A sample of each coating is exposed on an intensity scale sensitometer and processed for 1¾ minutes in an amine developer of the type described in Example 1 of Masseth, U.S. application Ser. No. 661,532 (Developer A), now U.S. Pat. 3,573,914, issued Apr. 6, 1971, fixed, washed and dried using a roller transport continuous processing machine. The following results are obtained.

Nitron	Relative speed	Gamma	$D_{max.}$	$D_{min.}$
Absent	100	7.1	5.09	.04
Present	105	6.8	5.0	.01

EXAMPLE 4

A silver chloride emulsion is made by mixing, over a period of 1 minute at 35° C., a gelatin solution containing 100 g. of silver nitrate with an aqueous gelatin solution containing 150 g. of sodium chloride and 0.01 g. of a mixture of rhodium and ammonium chloride. The emulsion is neutralized to a pH of 5.6 and a phthalated gelatin solution is added. The emulsion is coagulated by lowering the pH, then decanted and taken up in a gelatin solution. Mucochloric acid (0.5 g.), nitron (1 g.) and 1-phenyl-5-mercaptotetrazole (0.1 g.) are added to the emulsion.

The above chloride emulsion is then coated at a coverage of 10 mg. of silver per dm.^{2} over an X-ray duplicating direct-positive emulsion which has a gelatin overlayer.

The X-ray duplicating film having a fogged direct-positive emulsion is processed in a developer containing various concentrations of bromide ion simulating the build-up of bromide during extensive processing.

	Conc. of $Br^{\ominus}$ in developer, g.	Rel. speed	Contrast	$D_{max.}$	$D_{min.}$
With overlayer	9	100	1.30	1.9	0.2
	13	68	1.40	1.95	0.2
	15	63	1.20	1.95	0.2
Without overlayer	9	40	1.35	2.15	0.2
	13	12	2.20	2.3	0.2
	15	10	2.35	2.3	0.2

The maximum image density of the elements having chloride overcoats is much more stable and the relative speed and gamma of the photographic element is much more stable as compared with the element without the chloride overcoat.

Similar results are obtained when silver ferricyanide is used in the overlayer in place of silver chloride.

As used herein, and in the appended claims, "fogged" refers to emulsions containing silver halide grains which produce a density of at least 0.5 when developed, without exposure, for 5 minutes at 68° F. in Developer A having the composition set forth below, when the emulsion is coated at a silver coverage of 50 mg. to 500 mg. per square foot.

Developer A

	G.
N-methyl-p-aminophenol sulfate	2.5
Sodium sulfite (anhydrous)	30.0
Hydroquinone	2.5
Sodium metaborate	10.0
Potassium bromide	0.5
Water to make 1.0 liter.	

Although the invention has been described in considerable detail with particular reference to certain prefererd embodiments thereof, variations and modifications can be effected within the spirit and scope of the invention.

We claim:

1. A direct-positive photographic element which comprises a support having thereon at least one layer containing a fogged direct-positive silver halide emulsion and at least one layer containing 100 mg. to about 2 g. of. nitron per mole of silver in said element.

2. A direct-positive element according to claim 1 wherein said direct-positive silver halide emulsion layer contains nitron.

3. A direct-positive element according to claim 1 wherein the silver nitrate used to make said direct-positive silver halide emulsion is partially reduced prior to precipitating said silver halide.

4. A direct-positive element according to claim 1 wherein said direct-positive emulsion is a blue-sensitive-direct-positive silver halide emulsion containing silver halide grains which have been chemically fogged.

5. A direct-positive element according to claim 1 wherein the halide of said silver halide is predominantly bromide and wherein said element comprises an overlayer

which contains chloride ions, silver chloride or silver ferrocyanides the ions of which are displaced by bromide ions.

6. A fogged, direct-positive photographic element which comprises a support having thereon at least one layer containing a fogged, direct-positive silver halide emulsion and at least one layer containing about 100 mg. to about 1 g. of nitron per mole of silver in said element.

7. A direct-positive element according to claim 1 wherein the halide of said silver halide is predominantly bromide and wherein said element comprises an overlayer which contains chloride ions, or a silver compound more soluble than silver bromide having ions which are displaceable by bromide ions.

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