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3,531,290

DIRECT POSITIVE SILVER HALIDE EMULSIONS CONTAINING EXCESS HALIDE

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29 Claims

ABSTRACT OF THE DISCLOSURE

Direct positive silver halide photographic emulsions, in which the halide is at least 50 mole percent chloride, have on the surface thereof an electron acceptor or a halogen acceptor and sufficient bromide, or bromide together with iodide, to increase the speed of the silver halide grains.

This invention relates to photographic emulsions and methods for their preparation. In one aspect, it relates to improved direct positive photographic emulsions. In another aspect, it relates to improved processes for preparing direct positive photographic emulsions.

Fogged direct positive photographic silver halide emulsions described in the literature have slow speeds. It would be highly desirable to provide novel direct positive silver halide emulsions which exhibit increased speed, and processes for preparing such emulsions. It would also be desirable to provide direct positive emulsions which have high maximum density in unexposed areas.

Direct positive photographic emulsions comprising silver halide grains in which at least 50% of the halide is chloride are especially useful. These direct positive emulsions can be developed and processed very rapidly. Accordingly, this invention is directed to improved direct positive photographic silver halide emulsions in which the halide contains a substantial mole percent of chloride.

One object of this invention is to provide novel direct positive photographic silver halide emulsions.

Another object of this invention is to provide a process for preparing novel photographic silver halide direct positive emulsions.

A further object of this invention is to provide novel direct positive photographic silver halide emulsions which demonstrate increased speed and high density in unexposed areas.

Still another object of this invention is to provide processes for preparing novel direct positive photographic silver halide emulsions which exhibit increased speed and high density in unexposed areas.

Another object of this invention is to provide photographic elements comprising a support having coated thereon novel silver halide emulsions.

Other objects of this invention will be apparent from the disclosure herein and the appended claims.

In accordance with one embodiment of this invention, substantially uniformly fogged direct positive photographic emulsions are provided which comprise silver halide grains, the halide of the silver halide being at least 50 mole percent chloride, which silver halide grains have on the surface thereof an electron acceptor or a halogen acceptor, and a sufficient quantity of bromide to effectively increase the speed of said silver halide, said quantity of bromide being in addition to any bromide present in said grains as mixed silver halide.

In another embodiment of this invention, direct positive photographic emulsions of the type just described also have on the surface thereof a sufficient quantity of iodide

to effectively increase the maximum developable density in the unexposed areas of the emulsion, the quantity of iodide being in addition to any iodide present in the grains as mixed silver halide.

In still another embodiment of this invention, photographic elements are provided which comprise a support having coated thereon a novel silver halide emulsion of the type described herein.

In another embodiment of this invention, a process is provided for increasing the speed of a substantially uniformly fogged, direct positive emulsion comprising silver halide grains, the halide of the silver halide being at least 50 mole percent chloride, which includes contacting the surface of the grains with an electron acceptor or a halogen acceptor, and a sufficient quantity of a water soluble bromide salt to effectively increase the speed of said silver halide grains.

In a further embodiment of this invention, a process is provided for preparing direct positive silver halide emulsions as just described, but which further features contacting the silver halide grains with a sufficient quantity of a water soluble iodide salt to effectively increase the maximum developable density in unexposed areas of the emulsion.

In accordance with this invention, it has been found that direct positive photographic silver halide emulsions in which the halide of the silver halide is at least 50 mole percent chloride, will exhibit substantially increased speed if the surface of the silver halide grains is provided with a combination of bromide and either a halogen acceptor or an electron acceptor. It has further been found in accordance with this invention that the maximum developable density of the emulsions just described can be substantially increased by the further addition of iodide salt to the surface of said silver halide grains.

Any suitable water soluble bromide salt can be used in the practice of this invention. Typical useful bromide salts include the ammonium, potassium, sodium, lithium, cadmium and strontium bromide salts. In carrying out the processes of this invention, the water soluble bromide salt is added to the emulsion at a concentration sufficient to effectively increase the speed of the emulsion. This concentration can be varied over a considerable range. As a guide, it can be said that the addition of from about .01 to about 0.2 mole bromide salt per mole of silver produces useful increases in speed. Preferred concentration ranges for most emulsions are in the range of about .04 to about .09 mole bromide salt per mole of silver in the emulsion. Thus, potassium bromide can be added at concentrations of from about 1 to 20 grams, and preferably 4 to 9 grams, per mole of silver, with good results. Stated in another way, the surface of the silver halide grains of the invention can advantageously carry from about .01 to about 0.2 mole bromide per mole of silver, and preferably from about .04 to about .09 mole bromide per mole of silver. This concentration of bromide is, of course, in addition to any bromide present in the emulsion as mixed silver halide.

A wide variety of water soluble iodide salts can be used in the practice of this invention. Typical iodide salts include the ammonium, potassium, sodium, lithium, cadmium and strontium iodide salts. The quantity of iodide added to the emulsion should be sufficient to effectively increase the maximum developable density in the unexposed areas of the emulsion. This concentration can be varied over a wide range. As a suggested concentration, from about .002 to about .03 mole of water soluble iodide salt, per mole of silver, can be added in the process of the invention to obtain effective increases in maximum developable density. Especially good results are obtained when the water soluble iodide salt is added in the range of from about .003 to about .012 mole per mole of silver.

For example, potassium iodide can be added at from about .5 to 5 grams per mole of silver with good increases in maximum density. Stated another way, the silver halide emulsions of the invention can contain, on the surface thereof, from about .002 to about .03, and preferably from about .003 to about .012 mole iodide per mole of silver.

In accordance with the invention, the quantity of bromide, or bromide and iodide, present on the surface of the silver halide grains is in addition to any bromide or iodide present in the grains as mixed silver halide (such as that bromide or iodide present throughout the grains as silver chlorobromide, silver chloroiodide or silver chlorobromiodide).

The electron acceptors or halogen acceptors which give particularly good results in the practice of this invention can be characterized in terms of their polarographic half-wave 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 acceptors 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 acceptors 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 halfwave 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 voltometric 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.

Very good results are obtained with 2-aromatically substituted indole dyes, e.g., cyanine dyes containing an indole nucleus aromatically substituted in the 2-position, i.e., a cyanine dye containing a 2-aromatically substituted indole nucleus. Advantageously, such dyes also include a desensitizing nucleus in addition to the indole nucleus. The desensitizing nucleus is one which, when converted

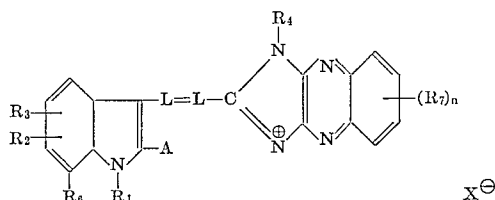
to a symmetrical carbocyanine dye and added to a silver chlorobromide emulsion containing 40 mole percent chloride and 60 mole percent bromide, at a concentration in the range of about 0.01 to about 0.2 g. of dye per mole of silver, causes, by electron trapping, at least an 80% loss in speed to blue radiation, and preferably more than a 90 or 95% loss in blue speed. One useful class of spectral sensitizing electron acceptors suitable for use in this invention has the following general formula:

A—L—B

where L represents a methine chain containing from 2 to 3 carbon atoms; A represents a 2-aromatically substituted indole nucleus attached to the methine chain through the 3-carbon atom of the indole nucleus; and B represents an organic heterocyclic nucleus, said nucleus being, where L represents a methine chain of 2 carbon atoms, a desensitizing nucleus to provide an unsymmetrical dimethine cyanine dye, and, where L represents a methine chain of 3 carbon atoms, B represents a 2-aromatically substituted indole nucleus attached to the methine chain through the 3-carbon atom of the indole nucleus. An especially useful desensitizing nucleus, where L is a methine chain containing 2 carbon atoms, is an imidazo[4,5-b]quinoxaline nucleus attached through the 2-carbon atom thereof to the methine chain. Spectral sensitizing electron acceptors of this type are dyes and can be prepared using any of the methods generally used for preparing such dyes. One convenient method involves refluxing, in a suitable solvent, a carboxaldehyde derivative of a 2-aromatically substituted indole with an alkyl substituted quaternary salt of a compound containing the desired desensitizing nucleus. For example, a 2-aromatically substituted indol-3-carboxaldehyde can be refluxed in a solvent such as acetic anhydride with a 2-alkylimidazo[4,5-b]quinoxalinium salt or a 2-alkylene pyrrolo[2,3-b]pyridine compound to provide the desired dye.

A preferred group of spectral sensitizing electron acceptors employed herein has the following general formula:

Formula I



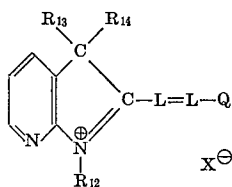
wherein L represents a methine linkage, e.g., $-\text{CH}=\text{}$, $-\text{C}(\text{CH}_3)=$, $-\text{C}(\text{C}_6\text{H}_5)=$, etc.; A represents an aromatic nucleus, such as a phenyl nucleus which can contain various groups, such as alkyl (e.g., methyl, ethyl, propyl, butyl, etc.), alkoxy (e.g., methoxy, ethoxy, propoxy, butoxy, etc.), halogen groups such as Br, Cl or F, aryl such as phenyl, or A can be a heterocyclic aromatic nucleus, preferably containing from 5 to 6 carbon atoms, and the hetero atom is preferably nitrogen, sulfur or oxygen; R_2 and R_3 each represents a hydrogen atom, a halogen atom such as Cl, Br or F, an alkyl or alkoxy substituent such as methyl, ethyl, propyl, butyl, methoxy, propoxy, hydroxy ethyl, etc.; or, R_2 and R_3 , taken together, represent the atoms necessary to complete a fused aromatic ring having 6 carbon atoms; R_1 represents an alkyl substituent (including substituted alkyl) preferably containing from 1 to 8 carbon atoms, including methyl, ethyl, propyl, butyl, octyl, sulfoalkyl such as sulfopropyl or sulfobutyl, sulfatoalkyl such as sulfatopropyl or sulfatobutyl, carboxyalkyl such as carboxyethyl or carboxybutyl and the like; R_4 and R_5 each represents an alkyl substituent (including substituted alkyl), preferably containing from 1 to 18 carbon atoms, including methyl, ethyl, propyl, isopropyl, butyl, sec-butyl, hexyl, dodecyl, octadecyl, benzyl, beta-phenylethyl, etc., sulfoalkyl such

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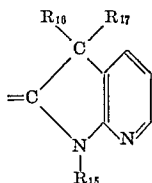
as sulfatobutyl; carboxyalkyl such as carboxyethyl and carboxybutyl; allyl; alkenyl such as propenyl and butenyl; alkynyl such as propargyl; cycloalkyl such as cyclobutyl and cyclohexyl; dialkylaminoalkyl such as dimethylaminoethyl and aryl such as phenyl, p-tolyl, o-tolyl, 3,4-dichlorophenyl, etc.; R_6 has the same meaning as R_2 or, taken together with R_1 , represents an alkylene group such as trimethylene or dimethylene; R_7 represents halogen, CN or NO_2 , n is an integer from 0 to 3, and, X represents an anion, preferably an acid anion such as chloride, bromide, iodide, p-toluenesulfonate, thiocyanate, sulfonate, methyl sulfate, ethyl sulfate, perchlorate, etc.

A related class of highly useful spectral sensitizing electron acceptors are pyrrolo[2,3-b]pyrido dyes, e.g., those having the following formula:

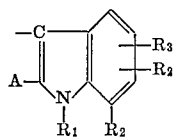
Formula IIA



wherein R_{12} , R_{13} and R_{14} each represents an alkyl group, such as methyl, ethyl, propyl or butyl, or an aryl group such as phenyl; L and X have the meaning given above; and Q represents a substituent selected from the group consisting of (1) $-\text{L}=\text{Q}_1$ wherein Q_1 represents the atoms necessary to complete a desensitizing nucleus to form a trimethine cyanine dye, such as a 6-nitrobenzthiazole nucleus, a 5-nitroindolenine nucleus, an imidazo[4,5-b]quinoxaline nucleus or a pyrrolo[2,3-b]pyrido nucleus, e.g.,



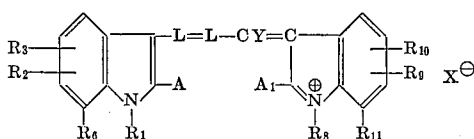
wherein R_{15} , R_{16} and R_{17} each represents the same groups given for R_{12} , R_{13} and R_{14} and (2) the atoms necessary to complete a desensitizing nucleus to form a dimethine cyanine dye, such as a pyrazole nucleus or a 2-aromatically substituted indole nucleus which is attached, through the 3-carbon atom thereof to the methine chain, e.g.,



wherein R_1 , R_2 , R_3 and R_6 have the same meanings given above.

Another useful group of spectral sensitizing electron acceptors have the following general formula:

Formula II



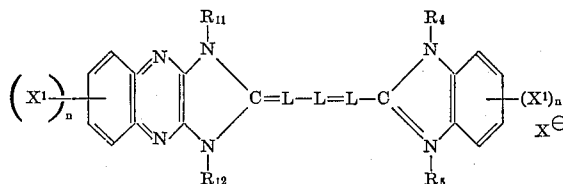
where X, L, A, R_1 , R_2 , R_3 and R_6 have the meanings given above; A_1 , R_8 , R_9 , R_{10} and R_{11} have the same values, respectively, as A, R_1 , R_2 , R_3 and R_6 ; and, Y represents a hydrogen atom, an aryl group, such as phenyl, an alkyl (e.g., methyl, ethyl, propyl or butyl) or alkoxy (e.g., methoxy, ethoxy or propoxy) substituted phenyl, or a heterocyclic aromatic group, such as a thiophene radical. Dyes of this type can be prepared

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using the method described in Coenen et al. U.S. Pat. 2,930,694, issued Mar. 29, 1960.

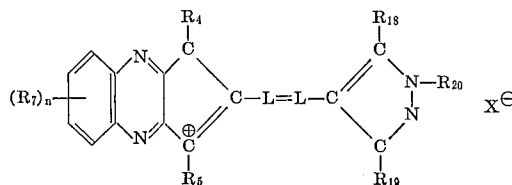
Symmetrical imidazo[4,5-b]quinoxaline trimethine cyanine dyes, wherein each nucleus is attached through the 2-carbon atom thereof to the methine chain, are useful electron acceptors in the practice of this invention. Typical of such dyes are those having the following general formula:

Formula III

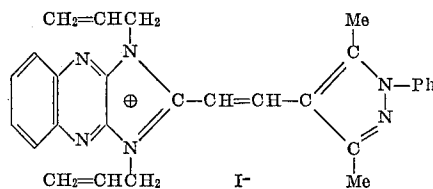


wherein X, L, R_4 and R_5 have the meanings given above, and R_{11} and R_{12} have the same values given for R_4 and R_5 , each X^1 is halogen such as Br, Cl and F and each n is an integer from 0 to 3. Dyes of this type can be prepared by the method described in Belgian Pat. 660,253, published Mar. 15, 1965.

Still another group of electron acceptors are pyrazolyl dyes, such as those having the following general formula:



wherein R_7 , n , R_4 , R_5 , L and X each have the meanings given in Formula I above, R_{18} and R_{19} each represents a substituent selected from the group consisting of hydrogen atom, an alkyl substituent, preferably containing 1 to 18 carbon atoms, as exemplified by methyl, butyl, octyl, dodecyl, octadecyl, an aryl substituent such as phenyl, p-tolyl, 3,4-dichlorophenyl, etc., and R_{20} has the same value as R_4 . Dyes of this type can be conveniently prepared by conventional techniques suitable for preparing such material. For example, a suitable method involves refluxing in a suitable solvent such as acetic anhydride, a 2-alkylimidazo[4,5-b]quinoxalinium salt with a pyrazole 4-carboxaldehyde. A typical dye of this type is 1,3-diallyl-2-[2-(3,5-dimethyl-1-phenyl-4-pyrazolyl) vinyl] - imidazo[4,5-b]quinoxalinium iodide which has the formula:

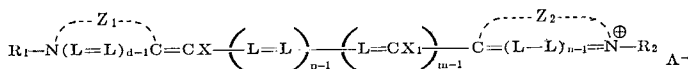
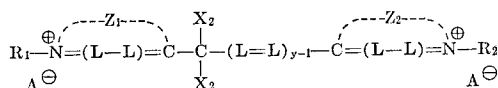


This dye can be prepared by refluxing 1,3-diallyl-2-methylimidazo[4,5-b]quinoxalinium p-toluenesulfonate with 3,5-dimethyl-1-phenyl-pyrazole - 4-carboxaldehyde in acetic anhydride for a suitable time, e.g., 10 minutes.

Still another class of useful spectral sensitizing electron acceptors are nitro-substituted dyes, such as the cyanine and merocyanine dyes in which at least one nucleus, and preferably two nuclei, contain desensitizing substituents such as NO_2 .

Some other specific electron acceptors which give outstanding results in the practice of this invention are the reaction product of a cyanine dye with a halogenating agent. Preferred electron acceptors of this type are those wherein a hydrogen atom of at least one methine group of the cyanine dye is replaced with a halogen atom having an atomic weight in the range of about

35 to about 127, i.e., chlorine, bromine or iodine atoms. In these compounds, one carbon atom linking the two nuclei thereof can carry two halogen atoms. Suitable halogen containing compounds can be represented by one of the following formulas:



wherein Z_1 and Z_2 each represents the non-metallic atoms necessary to complete a heterocyclic nucleus of the type used in cyanine dyes, such as a nucleus of the benzothiazole series (e.g., benzothiazole, 4-chlorobenzothiazole, 5-chlorobenzothiazole, 7-chlorobenzothiazole, 4-methylbenzothiazole, 5-methylbenzothiazole, 5-bromobenzothiazole, 4-phenylbenzothiazole, 5-phenylbenzothiazole, 6-phenylbenzothiazole, 4-methoxybenzothiazole, 5-methoxybenzothiazole, 5-iodobenzothiazole, 4-ethoxybenzothiazole, 5-ethoxybenzothiazole, 5-hydroxybenzothiazole, etc.); the naphthothiazole series (e.g., α -naphthothiazole, β -naphthothiazole, 5-methoxy- β -naphthothiazole, 5-ethyl- β -naphthothiazole, 8-methoxy- α -naphthothiazole, 7-methoxy- α -naphthothiazole, etc.); those of the benzoxazole series (e.g., benzoxazole, 5-chlorobenzoxazole, 5-methylbenzoxazole, 5-phenylbenzoxazole, 5-methoxybenzoxazole, 5-ethoxybenzoxazole, 5-hydroxybenzoxazole, etc.); those of the naphthoxazole series (e.g., α -naphthoxazole, β -naphthoxazole, etc.); those of the benzoselenazole series (e.g., benzoselenazole, 5-chlorobenzoselenazole, 5-methylbenzoselenazole, 5-hydroxybenzoselenazole, etc.); those of the naphthoselenazole series (e.g., α -naphthoselenazole, β -naphthoselenazole, etc.); those of the quinoline series including the 2-quinolines (e.g., quinoline, 3-methylquinoline, 5-methylquinoline, 7-methylquinoline, 8-methylquinoline, 6-chloroquinoline, 8-chloroquinoline, 6-methoxyquinoline, 6-hydroxyquinoline, 8-hydroxyquinoline, etc.); the 4-quinolines (e.g., quinoline, 6-methoxyquinoline, 7-methoxyquinoline, 8-methoxyquinoline, etc.); those of the isoquinoline series (e.g., the 1-isoquinolines, the 3-isoquinolines, etc.); each L represents a methine linkage as described above; X_2 represents a chlorine, bromine or iodine atom; X_1 and X each represents an atom selected from the group consisting of hydrogen, chlorine, bromine and iodine, at least one of X and X_1 being chlorine, bromine or iodine; R_1 and R_2 each represents alkyl, e.g., lower alkyl such as methyl, ethyl, propyl, isopropyl, butyl, secondary butyl, tertiary butyl, etc., a sulfo-alkyl group in which the alkyl group has from 1 to 4 carbon atoms, such as sulfomethyl, sulfoethyl, sulfopropyl, sulfobutyl, etc., and a carboxyalkyl group in which the alkyl group has from 1 to 4 carbon atoms such as carboxymethyl, carboxyethyl, carboxypropyl, carboxybutyl, etc.; A represents an acid anion such as chloride, bromide, iodide, p-toluenesulfonate, thiocyanate, methyl sulfate, ethyl sulfate, perchlorate, and the like; y represents an integer of from 1 to 3 and d, m, n, and p each represents a positive integer of from 1 to 2.

The halogen containing compounds described above can be prepared by halogenating a cyanine dye with chlorine, bromine or iodine. Any suitable halogenating agent may be used, such as aqueous alcoholic (e.g., methanol or ethanol) solutions of the halogen, N-chlorosuccinimide, N-bromosuccinimide, N-iodosuccinimide, or a commercially available halogen-pyrrolidone complex, such as a bromo-pyrrolidone complex sold by General Aniline and Film Corp. Using such halogenating agents causes replacement by halogen of a hydrogen atom in the methine chain. In carbocyanines, or dicar-

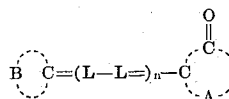
bocyanines, it is believed that halogen substitution occurs on a terminal carbon atom of the methine chain. As noted above, one linking carbon atom can carry two halogen atoms.

5 The compounds which accept electrons in the direct-

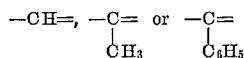
positive photographic silver halide emulsions and processes of this invention can be employed in widely varying concentrations. However, such compounds are preferably employed at concentrations in the range of about 100 milligrams to about 2 grams of electron acceptor per mole of silver halide. Best results are obtained using from 300 to 600 milligrams electron acceptor per mole of silver halide. Specific examples of suitable electron acceptors include;

- 1,1'-dimethyl-2,2'-diphenyl-3,3'-indolocarbo-
cyanine bromide;
- 2,2'-di-p-methoxyphenyl-1,1'-dimethyl-3,3'-indolocarbo-
cyanine bromide;
- 1,1'-dimethyl-2,2',8-triphenyl-3,3'-indolocarbo-
cyanine perchlorate;
- 1,3-diallyl-2-[2-(9-methyl-3-carbazolyl)vinyl]-imidazo
[4,5-b]quinoxalinium p-toluenesulfonate;
- 1,3-diethyl-1'-methyl-2'-phenyl imidazo[4,5-b]quinoxalino-3'-indolocarbo-
cyanine iodide;
- 1,1',3,3'-tetraethylimidazo[4,5-b]quinoxalino-
carbo-
cyanine chloride;
- 6-chloro-1'-methyl-1,2',3-triphenylimidazo[4,5-b]
quinoxalinocarbo-
cyanine chloride;
- 6-chloro-1'-methyl-1,2',3-triphenylimidazo[4,5-b]quinoxalino-3'-indolocarbo-
cyanine p-toluenesulfonate;
- 6,6'-dichloro-1,1',3,3'-tetraphenylimidazo[4,5-b]quinoxalino-3'-indolocarbo-
cyanine p-toluenesulfonate;
- 1,1',3,3'-tetramethyl-2-phenyl-3-indolopyrrolo[2,3-b]
pyridocarbo-
cyanine iodide;
- 1,1',3,3,3',3'-hexamethylpyrrolo[2,3-b]pyridocarbo-
cyanine perchlorate;
- 1,1',3,3-tetramethyl-5-nitro-2'-phenylindolocarbo-
cyanine iodide;
- 1,1',3,3,3',3'-hexamethyl-5,5'-dinitroindolocarbo-
cyanine p-toluenesulfonate;
- 3'-ethyl-1-methyl-2-phenyl-6'-nitro-3-indolothia-
carbo-
cyanine iodide;
- 5'-chloro-1,3'-dimethyl-2-phenyl-6'-nitro-3-indolocarbo-
cyanine p-toluenesulfonate;
- 5,5'-dichloro-3,3'-diethyl-6,6'-dinitrothiacarbo-
cyanine iodide;
- pinacryptol yellow,
- 5-m-nitrobenzylidenerhodanine,
- 5-m-nitrobenzylidene-3-phenylrhodanine,
- 1,3-diallyl-2-[2-(3,5-dimethyl-1-phenyl-4-pyrazolyl)vinyl]imidazo[4,5-b]quinoxalinium iodide,
- 3-ethyl-5-m-nitrobenzylidenerhodanine,
- 3-ethyl-5-(2,4-dinitrobenzylidene)rhodanine,
- 5-o-nitrobenzylidene-3-phenylrhodanine,
- 1',3-diethyl-6-nitrothia-2'-cyanine iodide,
- 6-chloro-4-nitro-benzotriazole,
- 6-amino-1-methyl-2-[1'-(methyl-6'-quinolinium)vinyl]quinolinium dichloride;
- 4-(p-n-amylphenoxyphenyl)-2,6-di(p-ethylphenyl)thiapyrylium perchlorate and the like.

A preferred class of halogen acceptors that can be used in the practice of this invention comprises the spectral sensitizing merocyanine dyes having the formula:



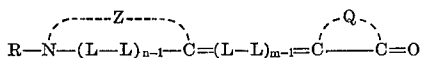
where A represents the atoms necessary to complete an acid heterocyclic nucleus, e.g., rhodanine, a 2-thiohydantoin and the like, B represents the atoms necessary to complete a basic nitrogen containing heterocyclic nucleus, e.g., benzothiazole, naphthiazole, benzoxazole and the like, each L represents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



and

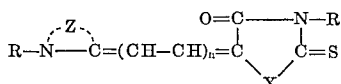
n is an integer from 0 to 2, i.e., 0, 1 or 2.

Halogen accepting merocyanine dyes which can be employed in the practice of this invention can also be represented by the formula:



where m represents an integer of from 1 to 3, R represents an alkyl group (including substituted alkyl) and preferably containing from 1 to 8 carbon atoms, such as methyl, ethyl, propyl, butyl, octyl, sulfoalkyl such as sulfopropyl or sulfobutyl, sulfatoalkyl such as sulfatopropyl or sulfatobutyl, or carboxyalkyl such as carboxyethyl or carboxybutyl, or an aryl group (including substituted aryl), e.g., phenyl, sulfophenyl, carboxyphenyl, tolyl and the like, each L represents a methine group, substituted or unsubstituted, n is a positive integer from 1 to 3, Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus containing from 5 to 6 atoms in the heterocyclic ring, e.g., a nucleus of the benzothiazole series, a nucleus of the benzoxazole series, a nucleus of the benzoselenazole series, a nucleus of the α -naphthothiazole series, a nucleus of the β -naphthothiazole series, a nucleus of the α -naphthoxazole series, a nucleus of the β -naphthoxazole series, a nucleus of the α -naphthoselenazole series, a nucleus of the β -naphthoselenazole series, a nucleus of the thiazoline series, a nucleus of the simple thiazole series (e.g., 4-methylthiazole, 4-phenylthiazole, 4-(2-thienyl)-thiazole, etc.), a nucleus of the simple selenazole series (e.g., 4-methylselenazole, 4-phenylselenazole, etc.) a nucleus of the simple oxazole series (e.g., 4-methylloxazole, 4-phenylthiazole, etc.) a nucleus of the quinoline series, a nucleus of the pyridine series, a nucleus of the 3,3-dialkylindolenine and the like, and Q represents the non-metallic atoms necessary to complete a heterocyclic nucleus containing 5 atoms in the heterocyclic ring, e.g., a rhodanine nucleus, a 2-thio-2,4(3,5)-oxazolidione nucleus, a 2-thiohydantoin nucleus, a 5-pyrazolone nucleus, etc.

A more preferred class of halogen accepting compounds which can be employed in the practice of this invention can be represented by the formula:



where each R represents an alkyl group (including substituted alkyl) and preferably containing from 1 to 8 carbon atoms, such as methyl, ethyl, propyl, butyl, octyl, sulfoalkyl such as sulfopropyl or sulfobutyl, sulfatoalkyl such as sulfatopropyl or sulfatobutyl, or carboxyalkyl such as carboxyethyl or carboxybutyl, or an aryl group (including substituted aryl), e.g., phenyl, sulfophenyl, carboxyphenyl, tolyl and the like, n is a positive integer from 1 to 2, Z represents the nonmetallic atoms necessary to complete a heterocyclic nucleus containing from 5 to 6 atoms in the heterocyclic ring, as defined in the previous formula, and X represents an oxygen atom, a sulfur atom, a selenium atom or a group of the formula



where R represents an alkyl group (including substituted alkyl) and preferably containing from 1 to 8 carbon atoms, such as methyl, ethyl, propyl, butyl, octyl, sulfo-

alkyl such as sulfopropyl or sulfobutyl, sulfatoalkyl such as sulfatopropyl or sulfatobutyl, or carboxyalkyl such as carboxyethyl or carboxybutyl, or an aryl group (including substituted aryl), e.g., phenyl, sulfophenyl, carboxyphenyl, tolyl and the like. Suitable procedures for preparing dyes employed in the practice of this invention are described in Brooker et al. U.S. Pats. 2,493,747 and 2,493,748, issued Jan. 10, 1950.

Specific examples of halogen accepting compounds which can be employed in the practice of this invention include:

- 3-carboxymethyl-5-[(3-ethyl-2-benzothiazolinyldene)-ethylidene]rhodanine;
- 3-ethyl-5-[(3-ethyl-2-benzothiazolinyldene)-ethylidene]rhodanine;
- 3-(2-dimethylaminoethyl)-5-[(4-(3-ethyl-2-benzothiazolinyldene)-2-butenyldene]rhodanine;
- 3-ethyl-5-[(3-ethyl-2-benzoxazolinyldene)-ethylidene]rhodanine;
- 3-carboxymethyl-5-[(3-ethyl-2-benzoxazolinyldene)-ethylidene]rhodanine;
- 3-carboxymethyl-5-[(3-methyl-2-thiazolidinyldene)-1-methylethylidene]rhodanine;
- 3-carboxymethyl-5-(3-ethyl-4-methyl-4-thiazolin-2-ylidene)rhodanine;
- 5-[(3-methyl-2-thiazolidinyldene)-1-methylethylidene]-3-(2-sulfoethyl)rhodanine;
- 3-ethyl-5-[1-(4-sulfobutyl)-4(1H)-pyridylidene]-rhodanine sodium salt;
- 3-ethyl-5-(1-ethyl-4(1H)-pyridylidene)rhodanine;
- 3-ethyl-5-[(3-ethyl-2-benzothiazolinyldene)ethylidene]-2-thio-2,4-oxazolidinedione;
- 3-carboxymethyl-5-[(3-ethyl-2-benzoxazolinyldene)-ethylidene]-2-thio-2,4-oxazolidinedione;
- 3-ethyl-5-[(3-ethylnaphtho[1,2-d]oxazolin-2-ylidene)-ethylidene]-2-thio-2,4-oxazolidinedione;
- 1-carboxymethyl-5-[(3-ethyl-2-benzothiazolinyldene)-ethylidene]-3-phenyl-2-thiohydantoin;
- 1-carboxymethyl-5-[(e-ethyl-2-benzoxazolinyldene)-ethylidene]-3-phenyl-2-thiohydantoin;
- 1-carboxymethyl-5-[(1-ethylnaphtho[1,2-d]thiazolin-2-ylidene)ethylidene]-3-phenyl-2-thiohydantoin;
- 3-heptyl-5-(1-methylnaphtho[1,2-d]thiazolin-2-ylidene)-1-phenyl-2-thiohydantoin;
- 5-[4-(3-ethyl-2-benzoxazolinyldene)-2-butenyldene]-1,3-diphenyl-2-thiohydantoin;
- 4-[(1-ethylnaphtho[1,2-d]thiazolin-2-ylidene)methyl-ethylidene]-3-methyl-1-(4-sulfophenyl)-2-pyrazolin-5-one;
- 1-ethoxycarbonylmethyl-5-[(1-ethylnaphtho[1,2-d]thiazolin-2-ylidene)ethylidene]-3-(4-nitrophenyl)-2-thiohydantoin;
- 5-[4-(3-ethyl-2-benzothiazolinyldene)-2-butenyldene]-3-heptyl-2-thio-2,4-oxazolidinedione;
- 5-[(1,3-diallylimidazo[4,5-b]quinoxalin-2(3H)-ylidene)ethylidene]-3-ethylrhodanine;
- 3-ethyl-5-(3-methyl-2-thiazolinyldene)ethylidene]-2-thio-2,4-oxazolidinedione;
- 5-[(3-(2-carboxyethyl)-2-thiazolinyldene)-ethylidene]-3-ethylrhodanine;
- 5-[(3-methyl-2-thiazolidinyldene)-1-methyl-ethylidene]-3-(2-morpholinoethyl)rhodanine;
- 5-[(3-(2-carboxyethyl)-2-thiazolidinyldene)-1-methyl-ethylidene]-3-carboxymethylrhodanine;
- 5-[(3-(2-carboxyethyl)-2-thiazolidinyldene)-1-methylethylidene]-3-(2-methoxyethyl)rhodanine;
- 3-(3-dimethyl aminopropyl)-5-[(3-methyl-2-thiazolidinyldene)ethylidene]rhodanine.

The halogen accepting compounds employed in the practice of this invention can be used in widely varying concentrations. However, the halogen accepting compounds are generally employed at concentrations in the range of about 200 mg. to about 1.0 g., preferably about 300 to about 600 milligrams per mole of silver halide.

If desired, the emulsions of the invention can be provided with a combination of electron acceptor and halogen acceptor.

In carrying out the process of this invention, we have found that highly useful increases in speed can be achieved when the water soluble bromide salt is added to the emulsion prior to the addition of the electron acceptor or halogen acceptor. However, the most pronounced increases in speed are achieved when the halogen acceptor or electron acceptor is added to the emulsion prior to the addition of the water soluble bromide salt. The increased speed obtained by this latter preferred sequence of addition does not require a holding period between the addition of halogen or electron acceptor and salt. Good speed increases are obtained by stirring the emulsion, adding halogen or electron acceptor and then adding the salt with continued stirring but without a holding period. However, a holding period can be used.

The direct positive silver halide emulsions useful herein can be uniformly fogged in any suitable manner, such as by light or with chemical fogging agents. Chemical fogging agents are preferred. Typical useful chemical fogging agents include reducing agents such as stannous chloride, formaldehyde, thiourea dioxide and the like. In preferred embodiments of this invention, the emulsion is fogged by the addition thereto of a reducing agent, such as thiourea dioxide, and a compound of a metal more electropositive than silver, such as a gold salt (e.g., potassium chloroaurate) as described in British Pat. 723,019 (1955).

Typical reducing agents that are useful in providing such emulsions include stannous salts, e.g., stannous chloride, hydrazine, sulfur compounds such as thiourea dioxide, phosphonium salts such as tetra(hydroxymethyl) phosphonium chloride, and the like. Typical useful metal compounds that are more electropositive than silver include gold, rhodium, platinum, palladium, iridium, etc., preferably in the form of soluble salts thereof, e.g., potassium chloroaurate, auric chloride, $(\text{NH}_4)_2\text{PdCl}_4$ and the like.

Useful concentrations of reducing agent and metal compound (e.g., metal salt) can be varied over a considerable range. As a general guideline, good results are obtained using about .05 to 40 mg. reducing agent per mole of silver halide, and 0.5 to 15.0 mg. metal compound per mole of silver halide. Best results are obtained at lower concentration levels of both reducing agent and metal compound.

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 Kodak DK-50 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

	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 l.	

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. patent application Ser. No. 448,467, filed Apr. 15, 1965, now 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 A below when the emulsion is coated at a silver coverage of 100 mg. per square foot. Such fogging can be effected 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, a sulfur 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 A

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 produce 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 application 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 Saubeneir 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.

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 U.S. patent application Ser. No. 609,794, filed Jan. 17, 1967, now abandoned and titled "Photographic Reversal Materials III." 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 one upon processing for six minutes at about 68° F. in Kodak DK-50 developer, 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 six minutes at about 68° F. in Kodak DK-50 developer 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 ten 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 silver halide emulsion on a support to give a maximum density of at least 1.0 upon processing for six minutes at about 68° F. in Kodak DK-50 developer and comparing the density of such a coating with an identical coating which is processed for six minutes at 68° F. in Kodak DK-50 developer 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 which contain at least 50 mole percent chloride, as exemplified by silver chloride, silver chlorobromide, silver chlorobromiodide, 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. In any case, the total chloride present as silver chloride or silver chlorohalide should be at least 50 mole percent of the total halide in the emulsion.

Silver halide grains having an average grain size less than about one micron, 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 U.S. patent application Ser. No. 609,778, filed Jan. 17, 1967, now abandoned and titled "Direct Positive Photographic Emulsions I." Such grains advantageously have a rather uniform diameter frequency distribution, as described and claimed in Illingsworth U.S. patent application Ser. No. 609,790, filed Jan. 17, 1967, now abandoned titled "Photographic Reversal Emulsions II." For example, at least 95%, by weight, of the photographic silver halide grains can have a diameter which is within about 40%, preferably within about 30% of the mean grain diameter. Mean grain diameter, i.e., average grain size, can be determined using conventional methods, e.g., as shown in an article by Trivelli and Smith entitled "Empirical Relations Between Sensitometric and Size-Frequency Characteristics in Photographic Emulsion Series" in *The Photographic Journal*, vol. LXXIX, 1949, pages 330-338. 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 five minutes at 68° F. in Kodak DK-50 developer 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 the preparation of the above photographic emulsions, the electron acceptors, halogen acceptor, 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 acceptors. 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, agaragar, 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 of the photographic element can also contain dispersed polymerized vinyl compounds. Such compounds are disclosed, for example, in U.S. Pats. 3,142,568; 3,193,386; 3,062,674 and 3,220,844 and includes the water insoluble polymers of alkyl acrylates and methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates and the like.

The novel emulsions of this invention may be coated on any suitable photographic support, such as glass, film base such as cellulose acetate, cellulose acetate butyrate, polyesters such as polyethylene terephthalate, paper, baryta coated paper, polyolefin coated paper, e.g., polyethylene or polypropylene coated paper, which may be electron bombarded to promote emulsion adhesion, to produce the novel photographic elements of the invention.

This invention will be further illustrated by the following examples. In these examples, the bromide and iodide salts are added subsequent to the halogen acceptor or electron acceptor, unless otherwise indicated.

Example 1 shows the substantial improvement in speed achieved in accordance with the invention when soluble bromide salts are added to a fogged direct positive emulsion in which the halide of the silver halide is at least 50% chloride, and which silver halide contains a halogen acceptor or an electron acceptor. The example also shows the improvement in maximum density obtained when iodide salts are employed in combination with bromide salts. This example further demonstrated that the use of bromide salt alone, i.e., in the absence of a halogen acceptor or an electron acceptor, fails to provide speed increases.

Example 1

A gelatin silver chloride having an average grain size of about 0.3 micron is prepared by adding an aqueous solution of potassium chloride and an aqueous solution of silver nitrate, simultaneously, to a rapidly agitated aqueous gelatin solution at a temperature of 70° C., over a period of about 35 minutes. The emulsion is chill-set, shredded and washed by leaching with cold water in the conventional manner. The emulsion is reduction-gold fogged by first adding 0.2 mg. of thiourea dioxide per mole of silver and heating for 60 minutes at 65° C. and then adding 4.0 mg. of potassium chloroaurate per mole of silver and heating for 60 minutes at 65° C. The emulsion is divided into several portions. Halogen acceptors, electron acceptors, potassium bromide and potassium iodide are added to various portions as shown in Table I. The emulsions obtained, along with control emulsions, are coated on cellulose acetate film supports at 100 mg. silver per square foot and 350 mg. gelatin per square foot, chill set and dried. The coatings are exposed on an intensity scale sensitometer, developed for three minutes at 65° C. in Kodak developer D-19, fixed, washed and dried with the following results. Speeds are read at 0.3 below Dmax. in all examples.

TABLE I

Halogen or electron acceptor (g./mole Ag)	KI g./mole Ag	KBr g./mole Ag	Relative clear speed	Dmax. in Unexposed area	Dmin. in exposed area
None			<0.15	1.1	1.05
Do	1.0		<0.15	1.33	1.36
Do		8.76	<0.15	1.27	1.25
Do	1.0	8.76	<0.15	1.25	1.12
I(1.5)			2.4	1.07	0.04
I(1.5)	1.0		0.54	1.41	0.07
I(1.5)		8.76	15.9	1.24	0.04
I(1.5)	1.0	8.76	11.0	1.27	0.05
II(1.0)			<0.15	1.19	0.84
II(1.0)	1.0		1.2	1.27	0.04
II(1.0)		8.76		0.11	0.04
II(1.0)	1.0	8.76	15.1	1.26	0.04
III(0.5)			1.1	1.32	0.80
III(0.5)	1.0		<0.15	1.25	1.07
III(0.5)		8.76	42.0	1.16	0.22
III(0.5)	10.	8.76	53.0	1.26	0.42

Example 2 demonstrates the preferred order of addition of halogen or electron acceptors prior to addition of the soluble bromide salt (or bromide and iodide salts). This order of addition results in even greater increases in speed than is achieved when the bromide salt (or bromide and iodide salts) are added to the emulsion prior to the addition of electron or halogen acceptors.

Example 2

An emulsion is prepared as in Example 1 except that the grains are allowed to grow to have an average size of about 0.7 micron. The emulsion is divided into several portions. Halogen or electron acceptors are added to portions of the emulsion both before and after the addition of the salts, with emulsion stirring, but no holding period, between the additions. The type and order of addition is indicated in Table II. These emulsions, along with controls, are coated, exposed and processed as in Example 1 except that coating is at 220 mg. silver per square foot and 425 mg. gelatin per square foot, and development is for 3.75 minutes in Kodak developer D-85. The results are shown in Table II. In this table, "Dye" refers to the halogen or electron acceptor.

TABLE II

Halogen or electron acceptor g./mole Ag	Order of addition	KI g./mole	KBr g./mole	Relative clear speed	D _{max.} in unexposed area	D _{min.} in exposed area
I(1.0)				0.21	1.34	0.93
I(1.0)	Dye first		8.76		0.16	0.04
I(1.0)	do.	1.0		8.7	1.34	0.27
I(1.0)	do.	1.0	8.76	363	1.17	0.07
I(1.0)	Salt first		8.76	22.0	0.54	0.13
I(1.0)	do.	1.0		1.3	1.42	0.21
I(1.0)	do.	1.0	8.76	60.0	0.78	0.22
I(1.0)	Dye first			0.76	1.32	0.67
III(0.5)	do.		4.38	240	0.74	0.08
III(0.5)	do.	1.0		0.63	1.46	1.0
III(0.5)	do.	1.0	4.38	138	1.20	0.08
III(0.5)	Salt first		4.38	331	1.48	0.8
III(0.5)	do.	1.0		0.95	1.51	1.0
III(0.5)	do.	1.0	4.38	60.0	1.46	0.09
III(0.5)	Dye first			58	1.50	0.63
IV(0.5)	do.		4.38	795	0.90	0.06
IV(0.5)	do.	1.0	4.38	120	1.66	0.15

Example 3 illustrates the practice of the invention using a direct positive emulsion of the type containing grains comprising a central core of a water insoluble silver salt containing centers which promote the deposition of photolytic silver and an outer shell covering the core comprising a fogged water insoluble silver salt that develops to silver without exposure.

Example 3

A gelatino silver chloride emulsion is prepared by simultaneously adding, over a period of about 20 minutes, 1000 ml. of a 4 molar silver nitrate aqueous solution and 1000 ml. of a 4 molar sodium chloride aqueous solution, to a well-stirred aqueous solution of 1000 ml. of 0.01 molar sodium chloride at 70° C. containing 40 grams of gelatin. Thereafter, 5000 ml. of water containing 280 grams of gelatin is added and the emulsion cooled. One-eighth of the resulting gelatino silver chloride emulsion (containing 0.5 mole percent silver chloride) is melted at 40° C., 100 mg. of the water-soluble iridium salt, potassium chloroiridite, dissolved in water are added, and the emulsion is heated to 70° C. This prepared emulsion constitutes the silver chloride core containing physical discontinuities that accept (or trap) electrons over which is coated a shell of silver chloride. The shell of silver chloride is formed by adding to the core emulsion 500 ml. of 4 molar silver nitrate aqueous solution and 500 ml. of 4 molar sodium chloride aqueous solution simultaneously over a period of 20 minutes. This silver chloride of this shell is reduction and gold fogged by adding 0.2 mg. thiourea dioxide per mole of silver, heating for 60 minutes

at 65° C., and then adding 4.0 mg. potassium chloroaurate per mole of silver and heating for 60 minutes at 65° C. 160 grams of gelatin, previously soaked in 340 ml. of water are then stirred in, and the emulsion cooled. During both additions of the silver nitrate and sodium chloride (i.e., to form both the core and the shell), the two solutions are added at approximately constant rates. Sufficient silver chloride is formed in the shell to give a ratio of 4 moles of shell silver chloride to 1 mole of core silver chloride. The resulting covered grain emulsion is melted, the gelatin content increased to 160 g. per mole of silver chloride, and water added to 4000 grams per mole of silver chloride. The emulsion obtained is divided into several portions and electron acceptors, halogen acceptors, potassium iodide and potassium bromide are added as indicated in Table III. The several emulsions are coated on a cellulose acetate film support at a coating rate of 180 mg. silver per square foot and 400 mg. gelatin per square foot, chill set and dried. The coatings are exposed and processed as described in Example 1, except that development is for 30 seconds in Kodak D-72 developer diluted with an equal volume of water. The results are shown in Table III.

TABLE III

Halogen or electron acceptor (g./mole Ag)	KI g./mole Ag	KBr g./mole Ag	Relative clear speed	D _{max.} in unexposed area	D _{min.} in exposed area
			71.0	1.78	0.06
		4.38	48.0	1.66	0.56
	1.0		50.0	1.58	0.06
	1.0	4.38	80.0	1.60	0.06
I(1.0)			<12.6	1.54	1.45
I(1.0)		4.38	550.0	1.12	0.03
I(1.0)	1.0		36.0	1.39	0.11
I(1.0)	1.0	4.38	759.0	1.39	0.03
V(1.0)			15.5	1.52	1.22
V(1.0)		4.38	398.0	1.46	0.02
V(1.0)	1.0		<12.0	1.40	1.32
V(1.0)	1.0	4.38	501.0	1.44	0.40
VI(1.0)			<12.0	1.32	1.30
VI(1.0)		4.38	302.0	1.10	0.03
VI(1.0)	1.0		<12.0	1.40	1.36
VI(1.0)	1.0	4.38	479.0	1.32	0.03
VII(1.0)			<12.0	1.24	1.16
VII(1.0)		4.38	32.0	0.34	0.03
VII(1.0)	1.0		27.5	1.54	1.01
VII(1.0)	1.0	4.38	1,450.0	1.16	0.03
VIII(1.0)			42.0	1.30	0.15
VIII(1.0)		4.38	302.0	1.26	0.04
VIII(1.0)	1.0		27.5	1.14	0.23
VIII(1.0)	1.0	4.38	501.0	1.28	0.06
IX(1.0)			<12.0	1.40	1.31
IX(1.0)		4.38	115.0	1.22	0.13
IX(1.0)	1.0		17.5	1.40	0.88
IX(1.0)	1.0	4.38	110.0	1.28	0.10
X(1.0)			<12.0	1.25	1.25
X(1.0)		4.38	15.9	0.56	0.26
X(1.0)	1.0		<12.0	1.26	1.18
X(1.0)	1.0	4.38	457.0	0.78	0.02
III(0.5)			501.0	1.29	0.05
III(0.5)		4.38	2,290.0	1.07	0.03
III(0.5)	1.0		603.0	1.27	0.08
III(0.5)	1.0	4.38	2,890.0	1.38	0.04

Examples 4 and 5 show the practice of this invention using a uniformly fogged silver chlorobromide emulsion, the halide of the silver chlorobromide being 90 mole percent chloride.

Example 4

An emulsion is prepared as described in Example 1, except that a sufficient quantity of potassium bromide is added during the precipitation to form a silver chlorobromide consisting of 90 mole percent chloride. The emulsion is divided into several portions and a halogen acceptor and an electron acceptor are added to various portions both with and without the addition of potassium bromide, as indicated in Table IV. The emulsions are coated on a cellulose acetate film support at the rate of 100 mg. silver per square foot and 370 mg. of gelatin per square foot. The coatings are chill set, dried, exposed and processed as described in Example 1, except that development is conducted for one minute. The results are shown in Table IV.

TABLE IV

Halogen or electron acceptor (g./mole Ag)	KBr g./mole Ag	Relative clear speed	D _{max.} in unexposed areas	D _{min.} in exposed areas
I(0.5)-----		7.3	1.48	0.06
I(0.5)-----	8.76	145.0	1.40	0.02
III(0.5)-----		100.0	1.58	0.80
III(0.5)-----	8.76	417.0	1.34	0.05

Example 5

A gelatin silver chlorobromide emulsion containing 90 mole percent chloride is prepared in a manner similar to the emulsion of Example 3, sufficient sodium bromide being added, along with sodium chloride, to form core and shell emulsions containing 90 mole percent chloride. The emulsion is split into several portions which are tested with an electron acceptor and a halogen acceptor, both with and without the addition of potassium bromide as indicated in Table V. The emulsions are coated and tested exactly as described in Example 4. The following results are obtained.

TABLE V

Halogen or electron acceptor (g./mole Ag)	KBr g./mole Ag	Relative clear speed	D _{max.} in unexposed areas	D _{min.} in exposed areas
I(0.5)-----		0.55	1.50	1.4
I(0.5)-----	4.38	7.6	1.34	0.04
III(0.5)-----		100.0	1.42	0.07
III(0.5)-----	4.38	263.0	1.17	0.07

Electron acceptors which are not dyes can be used in the practice of this invention. This is illustrated in Example 6.

Example 6

An emulsion prepared as described in Example 2 is divided into several portions and Compound I, which is an electron acceptor but not a dye, is added to various portions of the emulsion with and without the addition of potassium bromide. The emulsions are coated, exposed and processed as described in Example 2 with the following results.

TABLE VI

Electron acceptor (g./mole)	KI g./mole	KBr g./mole	Relative clear speed	D _{max.} in unexposed area	D _{min.} in exposed area
Cpd. I(0.5)-----			0.19	1.62	1.2
Cpd. I(0.5)-----		4.38		0.07	0.03
Cpd. I(0.5)-----	1.0	4.38	18.0	1.08	0.04

The halogen acceptors and electron acceptors employed in the above examples are identified below:

- Dye I—1,3-diethyl-1'-methyl-2'-phenylimidazo[4,5-b]-quinoxalino-3'-indolocarboxyanine iodide (an electron acceptor)
 Dye II—Pinacryptol yellow (an electron acceptor)
 Dye III—3-carboxymethyl-5-[(3-methyl-2(3)-thiazolinyldene)isopropylidene]rhodanine (a halogen acceptor)

Dye IV—3-ethyl-5-[1-(4-sulfobutyl)-4(1H)-pyridylidene]rhodanine sodium salt (a halogen acceptor)

Dye V—2-[2-(3,5-dimethyl-1-phenyl-4-pyrazolyl)-vinyl]-1,3-diphenylimidazo[4,5-b]quinoxalium iodide (an electron acceptor)

Dye VI—3-[(1,3-diethyl-2(1H)-imidazo[4,5-b]quinoxalinyldene)ethylidene]-2H-pyrido[1,2-a]pyrimidine-2,4-(3H)-dione (an electron acceptor)

Dye VII—3-ethyl-2-[(2-methyl-5-oxo-3-phenyl-3-isoxazolin-4-yl)vinyl]-o-nitrobenzothiazolium methylsulfate (an electron acceptor)

Dye VIII—1,1',3,3',3'-hexamethyl-5,5'-dinitroindocarbocyanine p-toluenesulfonate (an electron acceptor)

Dye IX—5,5'-dichloro-3,3-diethyl-6,6'-dinitrothiacarbocyanine iodide (an electron acceptor)

Dye X—3-[(3-ethyl-6-nitro-2-benzothiazolinyldene)ethylidene]-2H-pyrido[1,2-a]pyrimidine-2,4(3H)-dione (an electron acceptor)

Compound I—1,1'-diethyl-2,2'-cyanine chloride, dibrominated (i.e., the carbon atom joining the two nuclei carries two bromine atoms)

Results similar to those in Example 1 are obtained with a silver chloride emulsion fogged with high intensity light or with reducing agent alone, e.g., stannous chloride. Good results are also obtained when combinations of halogen acceptor with electron acceptor are used on the surface of the silver halide grains.

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 described hereinabove and in the appended claims.

I claim:

1. In a direct positive photographic emulsion comprising silver halide grains, the halide of said silver halide being at least 50 mol percent chloride, at least the outer shell of said grains being substantially uniformly fogged, said grains containing on the surface thereof a compound selected from the group consisting of:

- (1) an electron acceptor having an anodic polarographic half-wave potential and a cathodic polarographic half-wave potential, which, when added together, gives a positive sum, and
- (2) a halogen acceptor having an anodic polarographic half-wave potential less than 0.85 and a cathodic polarographic half-wave potential which is more negative than -1.0;

the improvement which comprises a sufficient quantity of halide on the surface of said silver halide grains to effectively increase the speed of said silver halide, said halide being selected from the group consisting of bromide and a mixture of bromide and iodide, and said quantity of halide being in addition to any halide present in said grains as mixed silver halide.

2. In a direct positive photographic emulsion comprising silver halide grains, the halide of said silver halide being at least 50 mol percent chloride, at least the outer shell of said grains being substantially uniformly fogged, said grains containing on the surface thereof a compound selected from the group consisting of:

- (1) an electron acceptor having an anodic polarographic half-wave potential and a cathodic polarographic half-wave potential, which, when added together, gives a positive sum, and
- (2) a merocyanine dye halogen acceptor having an anodic polarographic half-wave potential less than 0.85 and a cathodic polarographic half-wave potential which is more negative than -1.0;

the improvement which comprises a sufficient quantity of halide on the surface of said silver halide grains to effectively increase the speed of said silver halide, said halide being selected from the group consisting of bromide and a mixture of bromide and iodide, and said quantity of halide being in addition to any halide present in said grains as mixed silver halide.

3. A fogged direct positive photographic emulsion as defined in claim 2 wherein said halide comprises a quantity of bromide of from about .01 to about 0.2 mole per mol of silver.

4. A fogged direct positive photographic emulsion as defined in claim 2 wherein said halide is a mixture of bromide and iodide, the quantity of bromide is from about .01 to about 0.2 mole per mol of silver and the quantity of iodide is from about .002 to about .03 mole per mol of silver.

5. A fogged direct positive photographic emulsion as defined in claim 2 wherein said halide is a mixture of bromide and iodide, the quantity of bromide is from about .04 to about .09 mole per mol of silver and the quantity of iodide is from about .003 to about .012 mole per mol of silver.

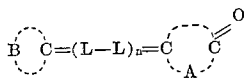
6. A fogged direct positive photographic emulsion as defined in claim 4 wherein said silver halide grains are chemically fogged and the halide of said silver halide is at least 80 mol percent chloride.

7. A fogged direct positive photographic emulsion as defined in claim 4 wherein said silver halide grains are fogged with the combination of a reducing agent and a compound of a metal more electropositive than silver; and, the halide of said silver halide is at least 80 mol percent chloride.

8. A fogged direct positive photographic emulsion as defined in claim 4 wherein said electron acceptor is a photographic sensitizing dye which spectrally sensitizes the emulsion so that the ratio of relative minus blue speed to relative blue speed is greater than 7.

9. A fogged direct positive photographic emulsion as defined in claim 4 wherein said compound is an electron acceptor, and is selected from the group consisting of a 2-aromatically substituted indole dye; an imidazo[4,5-b]quinoxaline dye; a pyrazolyl dye; a pyrrolo[2,3-b]pyrido dye; a nitro-substituted dye; and, the reaction product of a cyanine dye with a halogenating agent.

10. A fogged direct positive photographic emulsion as defined in claim 4 wherein said compound is a halogen acceptor, and has the following formula:



wherein n represents a value from 0 to 2; L represents a methine linkage; B represents the atoms required to complete a basic nitrogen containing heterocyclic nucleus; and, A represents the atoms required to complete an acidic heterocyclic nucleus.

11. A fogged direct positive photographic emulsion comprising silver halide grains substantially uniformly fogged with a combination of thiourea dioxide and potassium chloroaurate, the halide of said silver halide being at least 80 mol percent chloride, said grains containing on the surface thereof, as electron acceptor, 1,3-diethyl-1'-methyl-2'-phenylimidazo[4,5-b]quinoxalino-3'-indolocarboquinone iodide; and, the surface of said grains having thereon from about .04 to about .09 mole bromide per mol of silver and from about .003 to about .012 mole iodide per mol of silver, said bromide and iodide being in addition to any bromide or iodide present in said grains as mixed silver halide.

12. A fogged direct positive photographic emulsion comprising silver halide grains substantially uniformly fogged with a combination of thiourea dioxide and potassium chloroaurate, the halide of said silver halide being at least 80 mol percent chloride, said grains containing

on the surface thereof, as halogen acceptor, 3-carboxymethyl-5-[(3-methyl-2(3)-thiazolynylidene)isopropylidene]rhodanine; and, the surface of said grains having thereon from about .04 to about .09 mole bromide per mol of silver and from about .003 to about .012 mole iodide per mol of silver, said bromide and iodide being in addition to any bromide or iodide present in said grains as mixed silver halide.

13. In the process for increasing the speed of a substantially uniformly fogged, direct positive emulsion comprising silver halide grains, the halide of said silver halide being at least 50 mol percent chloride, at least the outer shell of said grains being substantially uniformly fogged, which process includes contacting the surface of said grains with a compound selected from the group consisting of:

(1) an electron acceptor having an anodic polarographic half-wave potential and a cathodic polarographic half-wave potential, which, when added together, gives a positive sum, and

(2) a halogen acceptor having an anodic polarographic half-wave potential less than 0.85 and a cathodic polarographic half-wave potential which is more negative than -1.0;

the improvement which comprises contacting the surface of said grains with a sufficient quantity of water-soluble halide salt to effectively increase the speed of said silver halide grains, said halide salt being selected from the group consisting of a bromide salt and a mixture of a bromide salt and an iodide salt.

14. In the process for increasing the speed of a substantially uniformly fogged, direct positive emulsion comprising silver halide grains, the halide of said silver halide being at least 50 mol percent chloride, at least the outer shell of said grains being substantially uniformly fogged, which process includes contacting the surface of said grains with a compound selected from the group consisting of:

(1) an electron acceptor having an anodic polarographic half-wave potential and a cathodic polarographic half-wave potential, which, when added together, gives a positive sum, and

(2) a merocyanine dye halogen acceptor having an anodic polarographic half-wave potential less than 0.85 and a cathodic polarographic half-wave potential which is more negative than -1.0;

the improvement which comprises contacting the surface of said grains with a sufficient quantity of water-soluble halide salt to effectively increase the speed of said silver halide grains, said halide salt being selected from the group consisting of a bromide salt and a mixture of a bromide salt and an iodide salt.

15. The process as defined in claim 14 wherein said compound is added to the emulsion prior to the addition of said halide salt.

16. The process as defined in claim 14 wherein said halide salt comprises a quantity of a bromide salt of from about .01 to about 0.2 mole per mol of silver.

17. The process as defined in claim 15 wherein said halide salt comprises a mixture of a bromide salt and an iodide salt, the concentration of said bromide salt being from about .01 to about 0.2 mole per mol of silver and the concentration of said iodide salt being from about .002 to about .03 mole per mol of silver.

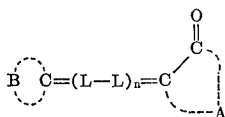
18. The process as defined in claim 15 wherein said halide salt comprises a mixture of a bromide salt and an iodide salt, the quantity of bromide salt being from about .04 to about .09 mole per mol of silver and said quantity of iodide salt being from about .003 to about .012 mole per mol of silver.

19. The process as defined in claim 17 wherein said compound is an electron acceptor, and said electron acceptor is a sensitizing dye which spectrally sensitizes the emulsion so that the ratio of relative minus blue speed to relative blue speed is greater than 7.

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20. The process as defined in claim 17 wherein said compound is an electron acceptor, and said electron acceptor is selected from the group consisting of a 2-aromatically substituted indole dye; an imidazo [4,5-b]quinoxaline dye; a pyrazolyl dye; a pyrrolo[2,3-b]pyrido dye; a nitro-substituted dye; and, the reaction product of a cyanine dye with a halogenating agent.

21. The process as defined in claim 17 wherein said compound is a halogen acceptor, and said halogen acceptor has the formula:



wherein n represents a value from 0 to 2; L represents a methine linkage; B represents the atoms required to complete a basic nitrogen containing heterocyclic nucleus; and, A represents the atoms required to complete an acidic heterocyclic nucleus.

22. The process for increasing the speed of a direct positive emulsion comprising silver halide grains substantially uniformly fogged with the combination of thiourea dioxide and potassium chloroaurate, the halide of said silver halide being at least 80 mol percent chloride, which comprises adding to said emulsion, as electron acceptor, 1,3-diethyl-1'-methyl-2'-phenylimidazo[4,5-b]quinoxalino-3'-indolocarbocyanine iodide, followed by the addition to said emulsion of from about .04 to about .09 mole potassium bromide per mol of silver and from about .003 to about .012 mole potassium iodide per mol of silver.

23. The process for increasing the speed of a direct positive emulsion comprising silver halide grains substantially uniformly fogged with a combination of thiourea dioxide and potassium chloroaurate, the halide of said silver halide being at least 80 mol percent chloride, which comprises adding to said emulsion, as halogen acceptor, 3-carboxymethyl - 5-[(3 - methyl-2(3)-thiazolylidene)isopropylidene]rhodanine, followed by the addition to said emulsion of from about .04 to about .09 mole potassium bromide per mol of silver, and from about .003 to about .012 mole potassium iodide per mol of silver.

24. The process as defined in claim 17 wherein said silver halide grains are chemically fogged and said silver halide is composed of at least 80 mol percent chloride.

25. The process as defined in claim 17 wherein said

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silver halide grains are fogged with a combination of a reducing agent and a compound of a metal more electropositive than silver, and said silver halide grains contain at least 80 mol percent chloride.

26. A direct positive, photographic emulsion in accordance with claim 2 which comprises fogged silver halide grains, said grains being 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 Kodak DK-50 developer, 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 Kodak DK-50 developer 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

27. A direct positive, photographic emulsion in accordance with claim 2 which comprises fogged silver halide grains, at least 95%, by weight, of said grains having a size which is within about 40% of the average grain size.

28. A photographic element comprising a support having coated thereon a direct positive photographic emulsion as defined in claim 2.

29. A photographic element comprising a support having coated thereon a direct positive photographic emulsion as defined in claim 4.

References Cited

UNITED STATES PATENTS

2,592,250	4/1952	Dovey et al.	96—94 X
3,314,796	3/1962	Gotze et al.	96—101
3,364,026	1/1968	Rees	96—101 X
3,367,778	2/1968	Berrimon	96—64

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