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3,583,870
**EMULSIONS CONTAINING A BIPYRIDINIUM
SALT AND A DYE**

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27 Claims

ABSTRACT OF THE DISCLOSURE

Direct positive emulsions are spectrally sensitized with a sensitizing methine or azacyanine dye and a bipyridinium salt.

This invention relates to novel photographic materials, and more particularly to a new class of direct positive photographic silver halide emulsions, and novel spectral sensitizing combinations for such materials.

It is known that direct positive images can be obtained with certain types of photographic silver halide emulsions. For example, photographic emulsions have been proposed for this purpose comprising an electron acceptor and silver halide grains that have been fogged with a combination of a reducing agent and a compound of a metal more electropositive than silver. One of the advantages of such direct positive emulsions is that the high-light areas of the images obtained with these materials are substantially free from fog. However, known materials of this type have not exhibited the high speed required for many applications of photography. Also, such known materials have not shown the desired sensitivity, especially to radiation in the green to red region of the spectrum. It is evident, therefore, that there is need in the art for improved direct positive photographic materials having both good speed and desirable sensitivity not only in the ultraviolet and blue region of the spectrum, but also extending to longer wavelength radiations.

It is, accordingly, an object of this invention to provide a new class of direct positive photographic silver halide emulsions having both good speed and desirable selective sensitivity to radiations extending from the ultraviolet and blue through to the longer wavelength regions of the spectrum.

Another object of this invention is to provide novel photographic elements comprising a support having thereon a novel emulsion layer of the invention.

Still another object of this invention is to provide novel spectral sensitizing combinations for direct positive emulsions.

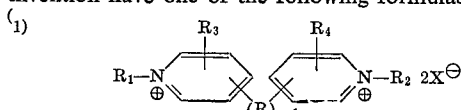
Other objects of this invention will be apparent from this disclosure and the appended claims.

I have now made the important discovery that direct positive silver halide emulsions are spectrally sensitized with the combination of a sensitizing methine or azacyanine dye and a bipyridinium salt. It was surprising to find that the combination of a sensitizing methine or azacyanine dye and a bipyridinium salt would effectively spectrally sensitize direct positive silver halide emulsions, because neither the sensitizing dye nor the bipyridinium salt will spectrally sensitize direct positive emulsions. It will be apparent that the present invention allows effective use in direct positive emulsions of the vast number of sensitizing methine and azacyanine dyes known to be useful in developing out emulsions.

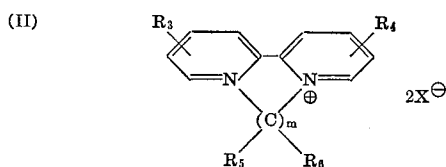
The bipyridinium salts useful herein have two pyridinium nuclei joined by a linkage which is attached to a carbon atom of each of said pyridinium nuclei. The two pyridinium nuclei can be joined by any suitable linkage, such as a single covalent bond, a vinylene linkage or

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an ethylene linkage. The bipyridinium salt advantageously has a polarographic reduction potential measurably below that of the dyes used in the invention. Typical bipyridinium salts which can be used in the practice of this invention have one of the following formulas:



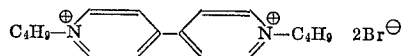
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wherein R₁-R₆, n, m and X represent the meanings given below. Preferred bipyridinium salts are the 1,1'-dialkyl-4,4'-bipyridinium salts, the best results being obtained with the 1,1'-diethyl, 1,1'-dipropyl or the 1,1'-dibutyl-4,4'-bipyridinium salts. Typical, specific useful bipyridinium salts are listed in Table 1 below.

TABLE 1

(A) 1,1'-dibutyl-4,4'-bipyridinium dibromide

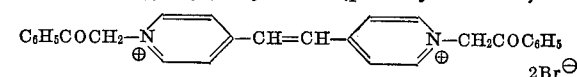


(B) 1,1'-dibutyl-4,4'-bipyridinium diperchlorate

(C) 1,1'-di(2-hydroxyethyl)-4,4'-bipyridinium dibromide

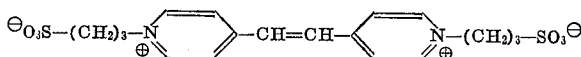
(D) 1,1'-diphenacyl-4,4'-bipyridinium dibromide

(E) 1,2-di(4-pyridyl)ethylene bis(phenacyl bromide)



(F) 1,2-di(4-pyridyl)ethylene bis(phenethobromide)

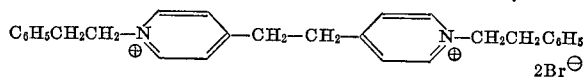
(G) Dianhydro-1,2-di[1-(3-sulfopropyl)-4-pyridyl]ethylene dihydroxide



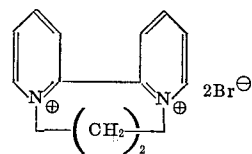
(H) 1,2-di(4-pyridyl)ethylene bis(methobromide)

(J) 1,1'-dimethyl-4,4'-bipyridinium dibromide

(K) 1,2-di(4-pyridyl)ethane bis(phenethobromide)



(L) 1,1'-ethylene-2,2'-bipyridinium dibromide



(M) 1,1'-tetramethylene-2,2'-bipyridinium dibromide

The bipyridinium salts that are useful in the invention, including those defined by Formulas I and II above, have been previously described in the prior art. See, for example, Fry et al. U.S. Pat. No. 3,035,917, patented May 22, 1962; Fry et al. U.S. Pat. No. 3,124,458, patented Mar. 10, 1964; and E. N. Mason and Sons Ltd. et al. British Pat. No. 714,290, dated Aug. 25, 1954.

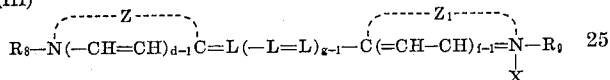
Any methine or azacyanine dye can be used in the practice of this invention which is a sensitizing dye. The term "methine" as used herein refers to dyes having the amidiniumion or amidic chromophoric system, and includes dyes having a zero methine chain length (i.e.,

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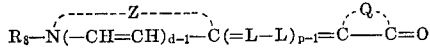
dyes in which the two nuclei are joined together without any methine linkage).

As used herein and in the appended claims, "sensitizing" dyes refers to those dyes which cause less than 80% loss in blue speed when added to gelatin silver chlorobromide emulsion containing 40 mole percent chloride and 60 mole percent bromide, at a concentration of from 0.01 to 0.2 gram dye per mole of silver, when the emulsion is sensitometrically exposed and developed three minutes in Kodak developer D-19 at room temperature. Advantageously, the sensitizing dyes are those which, when tested as just described, do not desensitize the test emulsion to blue radiation (i.e., cause less than about 5 to 10% loss of speed to blue radiation). Preferably the dye has a polarographic reduction potential which is measurably above the reduction potential of the bipyridinium salt. Merocyanine and cyanine sensitizing dyes are especially useful. Typical sensitizing dyes which can be used herein include cyanine dyes (Formula III), merocyanine dyes (Formula IV), hemicyanine bases (V) and hemicyanines (VI) and azacyanine dyes (Formula VII), represented by the following formulas:

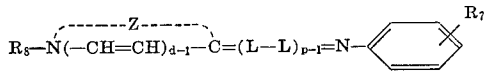
(III)



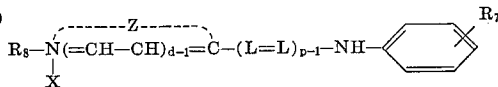
(IV)



(V)

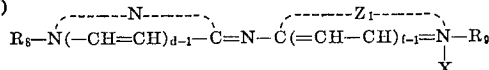


(VI)



and

(VII)



wherein n , d , f , g and p each represents a positive integer of from 1 to 2; m represents a positive integer of from 2 to 4; R represents a vinylene group ($-\text{CH}=\text{CH}-$) or an ethylene group ($-\text{CH}_2-\text{CH}_2-$); L represents a methine linkage, e.g., $-\text{CH}=\text{}$, $-\text{C}(\text{CH}_3)=$,



etc.; R_1 , R_2 , R_3 and R_9 each represents an alkyl group, including substituted alkyl, (preferably a lower alkyl containing from 1 to 4 carbon atoms), e.g., methyl, ethyl, propyl, isopropyl, butyl, hexyl, cyclohexyl, decyl, dodecyl, etc., and substituted alkyl groups, (preferably a substituted lower alkyl containing from 1 to 4 carbon atoms), such as a hydroxyalkyl group, e.g., β -hydroxyethyl, ω -hydroxybutyl, etc., an alkoxyalkyl group, e.g., β -methoxyethyl, ω -butoxybutyl, etc., a carboxyalkyl group e.g., β -carboxyethyl, ω -carboxybutyl, etc., a sulfoalkyl group, e.g., β -sulfoethyl, ω -sulfobutyl, etc., a sulfatoalkyl group, e.g., β -sulfatoethyl, ω -sulfatobutyl, etc., an aryloxy alkyl e.g., phenacyl acyloxyalkyl group, e.g., β -acetoxyethyl, γ -acetoxypropyl, ω -butyryloxybutyl, etc., an alkoxy carbonylalkyl group, e.g., β -methoxycarbonyl ethyl, ω -ethoxycarbonylbutyl, etc., or an aralkyl group, e.g., benzyl, phenethyl, etc., and the like; or, any aryl group, e.g., phenyl, tolyl, naphthyl, methoxyphenyl, chlorophenyl, etc.; R_3 and R_4 each represents a hydrogen atom, a lower alkyl group containing from 1 to 4 carbon atoms, e.g., methyl, butyl, etc., a lower alkoxy group containing from 1 to 4 carbon atoms, e.g., methoxy, butoxy, etc., or a halogen atom, e.g., chlorine or bromine; R_5 and R_6 each represents a hydrogen atom or a lower alkyl group containing from 1 to 4 carbon atoms, e.g., methyl, butyl, etc.; R_7

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represents a hydrogen atom, a lower alkyl group containing from 1 to 4 carbon atoms, e.g., methyl, butyl, etc., an acyl group, e.g., a saturated monobasic fatty acid containing from 2 to 5 carbon atoms, e.g., acetoxy, butyryloxy, etc., or a cyano group; X^\ominus represents an acid anion, e.g., chloride, bromide, iodide, sulfamate, thiocyanate, perchlorate, p-toluenesulfonate, methyl sulfate, ethyl sulfate, etc.; Z and Z_1 each represents the non-metallic atoms necessary to complete a 5- to 6-membered nitrogen containing heterocyclic nucleus of the type used in cyanine dyes such as those selected from the class consisting of

a thiazole nucleus (e.g., thiazole, 4-methylthiazole, 4-phenylthiazole, 5-methylthiazole, 5-phenylthiazole, 4,5-dimethylthiazole, 4,5-diphenylthiazole, 4-(2-thienylthiazole, etc.),

a benzothiazole nucleus (e.g., benzothiazole, 4-chlorobenzothiazole, 5-chlorobenzothiazole, 6-chlorobenzothiazole, 7-chlorobenzothiazole, 4-methylbenzothiazole, 5-methylbenzothiazole, 6-methylbenzothiazole, 5-bromobenzothiazole, 6-bromobenzothiazole, 4-phenylbenzothiazole, 5-phenylbenzothiazole, 4-methoxybenzothiazole, 5-methoxybenzothiazole, 6-methoxybenzothiazole, 5-iodobenzothiazole, 6-iodobenzothiazole, 4-ethoxybenzothiazole, 5-ethoxybenzothiazole,

a tetrahydrobenzothiazole nucleus, 5,6-dimethoxybenzothiazole, 5,6-dioxymethylenebenzothiazole, 5-hydroxybenzothiazole, 6-hydroxybenzothiazole, etc.),

a naphthothiazole nucleus, (e.g., naphtho[2,1-d]thiazole, naphtho[1,2-d]thiazole, 5-methoxynaphtho[2,3-d]thiazole, 5-ethoxynaphtho[1,2-d]thiazole, 8-methoxynaphtho[2,1-d]thiazole, 7-methoxynaphtho[2,1-d]thiazole, etc.),

a thionaphtheno-7',6',4,5-thiazole nucleus (e.g., 4'-methoxythianaphtheno-7',6',4,5-thiazole, etc.),

an oxazole nucleus (e.g., 4-methylloxazole, 5-methylloxazole, 4-phenylloxazole, 4,5-diphenylloxazole, 4-ethyloxazole, 4,5-dimethylloxazole, 5-phenylloxazole, etc.),

a benzoxazole nucleus (e.g., benzoxazole, 5-chlorobenzoxazole, 5-methylbenzoxazole, 5-phenylbenzoxazole, 6-methylbenzoxazole, 5,6-dimethylbenzoxazole, 4,6-dimethylbenzoxazole, 5-methoxybenzoxazole, 5-ethoxybenzoxazole, 5-chlorobenzoxazole, 6-methoxybenzoxazole, 5-hydroxybenzoxazole, 6-hydroxybenzoxazole, etc.)

a naphthoxazole nucleus (e.g., naphth[2,1-d]oxazole, naphth[1,2-d]oxazole, etc.),

a selenazole nucleus (e.g., 4-methylselenazole, 4-phenylselenazole, etc.),

a benzoselenazole nucleus (e.g., benzoselenazole, 5-chlorobenzoselenazole, 5-methoxybenzoselenazole, 5-hydroxybenzoselenazole, etc.)

a tetrahydrobenzoselenazole nucleus, a naphthoselenazole nucleus (e.g., naphtho[2,1-d]selenazole, naphtho[1,2-d]selenazole, etc.),

a thiazoline nucleus (e.g., thiazoline, 4-methylthiazoline, etc.),

a 2-pyridine nucleus (e.g., 2-pyridine, 5-methyl-2-pyridine, etc.),

a 4-pyridine nucleus (e.g., 4-pyridine, 3-methyl-4-pyridine, etc.),

a 2-quinoline nucleus (e.g., 2-quinoline, 3-methyl-2-quinoline, 5-ethyl-2-quinoline, 6-chloro-2-quinoline, 8-chloro-2-quinoline, 6-methoxy-2-quinoline, 8-ethoxy-2-quinoline, 8-hydroxy-2-quinoline, etc.),

a 4-quinoline nucleus (e.g., 4-quinoline, 6-methoxy-4-quinoline, 7-methyl-4-quinoline, 8-chloro-4-quinoline, etc.),

a 1-isoquinoline nucleus (e.g., 1-isoquinoline, 3,4-dihydro-1-isoquinoline, etc.),

a 3-isoquinoline nucleus (e.g., 3-isoquinoline, etc.),

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an imidazole nucleus (e.g., imidazole, 1-alkylimidazole, 1-alkyl-4-phenylimidazole, 1-alkyl-4,5-dimethylimidazole, etc.),

a benzimidazole nucleus (e.g., benzimidazole, 1-alkylbenzimidazole, 1-aryl-5,6-dichlorobenzimidazole, etc.),

a naphthimidazole nucleus (e.g., 1-alkyl-1H-naphth[1,2-d]imidazole, 1-aryl-3H-naphth[1,2-d]imidazole, 1-alkyl-5-methoxy-1H-naphth[1,2-d]imidazole, etc.), etc.;

and Q represents the non-metallic atoms required to complete a 5- to 6-membered ketomethylene heterocyclic nucleus of the type used in merocyanine dyes, typically containing a hetero atom selected from nitrogen, sulfur, selenium, and oxygen, such as

a 2-pyrazolin-5-one nucleus, e.g., 3-methyl-1-phenyl-2-pyrazolin-5-one, 1-phenyl-2-pyrazolin-5-one, 1-(2-benzothiazolyl)-3-methyl-2-pyrazolin-5-one, etc.;

an isoxazolone nucleus, e.g., 3-phenyl-5(4H)-isoxazolone, 3-methyl-5(4H)-isoxazolone, etc.;

an oxindole nucleus, e.g., 1-alkyl-2-oxindoles, etc.;

a 2,4,6-triketohexahydropyrimidine nucleus, e.g., barbituric acid or 2-thiobarbituric acid as well as their 1-alkyl (e.g., 1-methyl-1-ethyl, 1-propyl, 1-heptyl, etc.) or 1,3-dialkyl (e.g., 1,3-dimethyl, 1,3-diethyl, 1,3-dipropyl, 1,3-diisopropyl, 1,3-dicyclohexyl, 1,3-di(β -methoxyethyl), etc.) or 1,3-diaryl (e.g., 1,3-diphenyl, 1,3-di(p-chlorophenyl), 1,3-di(p-ethoxycarbonylphenyl), etc.) or 1-aryl (e.g., 1-phenyl, 1-p-chlorophenyl, 1-p-ethoxycarbonylphenyl), etc.) or 1-alkyl-3-aryl (e.g., 1-ethyl-3-phenyl, 1-n-heptyl-3-phenyl, etc.) derivatives;

a rhodanine nucleus (i.e., 2-thio-2,4-thiazolidinedione series), such as rhodanine, 3-alkylrhodanines, e.g., 3-ethylrhodanine, 3-allylrhodanine, etc., 3-carboxyalkylrhodanines, e.g., 3-(2-carboxyethyl)rhodanine, 3-(4-carboxybutyl)rhodanine, etc., 3-sulfoalkylrhodanines, e.g., 3-(2-sulfoethyl)rhodanine, 3-(3-sulfopropyl)rhodanine, 3-(4-sulfobutyl)rhodanine, etc., or 3-arylrhodanines, e.g., 3-phenylrhodanine, etc., etc.;

a 2(3H)-imidazo[1,2-a]pyridione nucleus;

a 5,7-dioxo-6,7-dihydro-5-thiazolo[3,2-a]pyrimidine nucleus, e.g., 5,7-dioxo-3-phenyl-6,7-dihydro-5-thiazolo[3,2-a]pyrimidine, etc.;

a 2-thio-2,4-oxazolidinedione nucleus (i.e., those of the 2-thio-2,4(3H,5H)-oxazolidinedione series) e.g., 3-ethyl-2-thio-2,4-oxazolidinedione, 3-(2-sulfoethyl)-2-thio-2,4-oxazolidinedione, 3-(4-sulfobutyl)-2-thio-2,4-oxazolidinedione, 3-(3-carboxypropyl)-2-thio-2,4-oxazolidinedione, etc.;

a thianaphthenone nucleus, e.g., 3-(2H)-thianaphthenone, etc.;

a 2-thio-2,5-thiazolidinedione nucleus (i.e., the 2-thio-2,5(3H,4H)-thiazolidinedione series), e.g., 3-ethyl-2-thio-2,5-thiazolidinedione, etc.;

a 2,4-thiazolidinedione nucleus, e.g., 2,4-thiazolidinedione, 3-ethyl-2,4-thiazolidinedione, 3-phenyl-2,4-thiazolidinedione, 3- α -naphthyl-2,4-thiazolidinedione, etc.;

a thiazolidinone nucleus, e.g., 4-thiazolidinone, 3-ethyl-4-thiazolidinone, 3-phenyl-4-thiazolidinone, 3- α -naphthyl-4-thiazolidinone, etc.;

a 2-thiazolin-4-one nucleus, e.g., 2-ethylmercapto-2-thiazolin-4-one, 2-alkylphenylamino-2-thiazolin-4-one, 2-diphenylamino-2-thiazolin-4-one, etc.;

a 2-imino-4-oxazolidinone (i.e., pseudohydantoin) nucleus;

a 2,4-imidazolidinedione (hydantoin) nucleus, e.g., 2,4-imidazolidinedione, 3-ethyl-2,4-imidazolidinedione, 3-phenyl-2,4-imidazolidinedione, 3- α -naphthyl-2,4-imidazolidinedione, 1,3-diethyl-2,4-imidazolidinedione, 1-ethyl-3-phenyl-2,4-imidazolidine-

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dione, 1-ethyl-3- α -naphthyl-2,4-imidazolidinedione, 1,3-diphenyl-2,4-imidazolidinedione, etc.;

a 2-thio-2,4-imidazolidinedione (i.e., 2-thiohydantoin) nucleus, e.g., 2-thio-2,4-imidazolidinedione, 3-ethyl-2-thio-2,4-imidazolidinedione, 3-(4-sulfobutyl)-2-thio-2,4-imidazolidinedione, 3-(2-carboxyethyl)-2-thio-2,4-imidazolidinedione, 3-phenyl-2-thio-2,4-imidazolidinedione, 3- α -naphthyl-2-thio-2,4-imidazolidinedione, 1,3-diethyl-2-thio-2,4-imidazolidinedione, 1-ethyl-3-phenyl-2-thio-2,4-imidazolidinedione, 1-ethyl-3- α -naphthyl-2-thio-2,4-imidazolidinedione, 1,3-diphenyl-2-thio-2,4-imidazolidinedione, etc.;

a 2-imidazolin-5-one nucleus, e.g., 2-propylmercapto-2-imidazolin-5-one, etc., etc.

(especially useful are nuclei wherein Q represents a heterocyclic nucleus containing 5 atoms in the heterocyclic ring, 3 of said atoms being carbon atoms, 1 of said atoms being a nitrogen atom, and 1 of said atoms being selected from the group consisting of a nitrogen atom, an oxygen atom, and a sulfur atom).

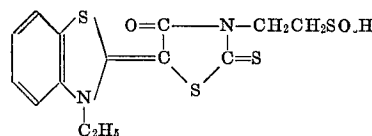
Typical useful cyanine dyes which can be used in the practice of this invention, and which are embraced by Formulas III to VII above, include the following:

TABLE 2

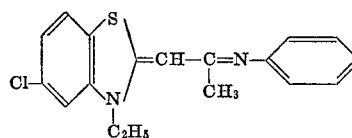
(Ia) 1,1'-diethyl-2,2'-cyanine chloride

(Ib) 1,1'-diethyl-2,2'-cyanine iodide

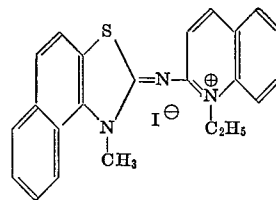
(II) 5-(3-ethyl-2-benzothiazolinyldene)-3- β -sulfoethylrhodanine



(III) 5-chloro-3-ethyl-2-(2-phenyliminopropylidene)benzothiazoline



(IV) 1'-ethyl-3-methyl-8-aza-4,5-benzothia-2'-cyanine iodide



(V) 2-[2-(4-acetylanilino)propenyl]-3-ethylbenzothiazolium chloride

(VI) 2-[2-(4-cyanoanilino)propenyl]-3-ethylbenzothiazolium chloride

(VII) 3-carboxymethyl-5-[(3-methyl-2-thiazolidinyldene)-1-methylethylidene]rhodanine

(VIII) 1-ethyl-2-[2-(p-tolylimino)propylidene]naphtho[1,2-d]thiazoline

(IX) Anhydro-5-chloro-3'-ethyl-3-(4-sulfobutyl)thiacyanine hydroxide

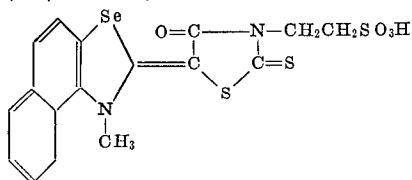
(X) 3,3'-dimethyl-9-phenyl-4,5; 4',5'-dibenzothiacarbocyanine chloride

(XI) 6,6'-dichloro-3,3'-diethylthiacarbocyanine iodide

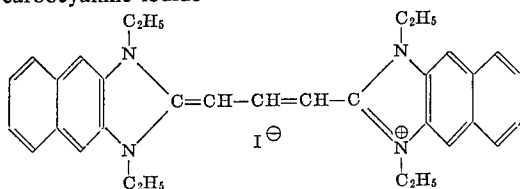
(XII) 3-carbomethyl-1,5-(3-ethyl-2-benzothiazolinyldene)rhodanine

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(XIII) 5-(1-methylnaphtho[1,2-d]selenazolin-2-ylidene)-3- β -sulfoethylrhodanine



(XIV) 1,1',3,3'-tetraethyl-1H-naphth[2,3-d]imidazolocarboyanine iodide



(XV) Anhydro-5-chloro-3'-methyl-3-(4-sulfobutyl)oxacyanine hydroxide

The various methine dye sensitizers of the invention including those defined by Formulas III to VII above are well known compounds in the photographic art. Pertinent patent references thereto include, for example, Larive et al., U.S. Pat. No. 2,921,067, patented Jan. 12, 1960; Jones, U.S. Pat. No. 2,977,229, patented Mar. 28, 1961; and Fix et al., U.S. Pat. No. 3,367,780, patented Feb. 6, 1968; White et al. U.S. 2,166,736, patented July 18, 1939, etc. The disclosure of these patents is incorporated herein by reference.

The proportions of bipyridinium salt and dye can vary widely, for example, in the ratios of about from 10:1 to 1:10. Preferably, I employ about 1 part of bipyridinium salt to from 1 to 10 parts of sensitizing dye on a weight basis. The images produced with the novel direct positive emulsions of the invention are clear and sharp, and of excellent contrast.

It will be apparent from the foregoing statement of the invention, that the bipyridinium salts of the invention are unique electron acceptors and that almost any of the cyanine dyes known to be spectral sensitizers for negative type emulsions can be combined therewith to produce by appropriate selections a multitude of direct positive emulsions having spectral sensitivities tailored to the requirements of the particular photographic application.

Useful combinations for practicing the invention may, if desired, also contain more than one cyanine dye as the sensitizing dye component. Advantageously, mixtures of cyanine dyes that have been proposed as "supersensitizing" combinations for negative type emulsions can also be employed for preparing the spectral sensitizing combinations of this invention, provided such cyanine dyes meet the aforementioned requirement as to their polarographic reduction potentials. Suitable combinations are disclosed in B. H. Carroll et al., U.S. Pat. No. 2,430,558.

In accordance with the preferred embodiment of the invention, novel and improved direct positive photographic silver halide emulsions are prepared by incorporating a spectral sensitizing combination of the invention into a suitable fogged silver halide emulsion. The emulsion can be fogged in any suitable manner, such as by light or with chemical fogging agents, e.g., stannous chloride, formaldehyde, thiourea dioxide, and the like. The emulsion may be 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, for example, 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)

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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, $(\text{NH}_4)_2\text{PdCl}_6$ 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.

The concentration of added spectral sensitizing combination can vary widely, e.g., from about 50 to 2000 mg. and preferably from about 200 to 1500 mg. per mole of silver halide in the direct positive emulsions.

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 liter.	

The spectral sensitizing combinations of this invention are also advantageously incorporated in 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. The dyes of the invention are incorporated, preferably, in the outer shell of such emulsions. 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 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

	G.
N-methyl-p-aminophenol sulfate	2.5
Ascorbic acid	10.0
Potassium metaborate	35.0
Potassium bromide	1.0
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 herein. Chemical sensitization techniques of the type described by Antoine Hautot and Henri Sauvenier 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 spectral sensitizing combinations of this invention are highly useful in high speed direct positive emulsions comprising fogged silver halide grains as described and claimed in Illingsworth U.S. patent application Ser. No. 619,936, filed Mar. 2, 1967, now Pat. No. 3,501,307 and titled "Photographic Reversal Materials Case C." 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 halide employed in the preparation of the photographic emulsions useful herein include any of the photographic silver halides as exemplified by silver bromide, silver iodide, silver chloride, silver chlorobromide, silver bromoiodide, silver chlorobromide, and the like. 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. 619,909, filed Mar. 2, 1967, now Pat. No. 3,501,306 and titled "Direct Positive Photographic Emulsions Case A." Such grains advantageously have a rather uniform diameter frequency distribution, as described and claimed in Illingsworth U.S. patent application Ser. No. 619,948, filed Mar. 2, 1967, now Pat. No. 3,501,305 and titled "Photographic Reversal Emulsions Case B." 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 preferred photographic silver halide emulsions comprise at least 50 mole percent bromide, the most preferred emulsions being silver bromoiodide emulsions, particularly those containing less than about ten mole percent iodide. The photographic silver halides can be coated at silver coverages in the range of about 50 to about 500 milligrams of silver per square of support.

The incorporation of photographic couplers or photographic coupler solvents (such as those described in Jelley et al. U.S. Pat. 2,322,027, issued June 15, 1943) in 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, prepared in various ways such as those described in Berriman U.S. Pat. 3,367,778, issued Feb. 6, 1968, improve incubation stability; especially improved is the great Dmax loss usually seen on incubation, with no loss in speed; this improvement is obtained when the emulsions are processed in black-and-white Elon-hydroquinone developers and color developers. A useful coupler solvent is di-n-butyl phthalate and useful couplers are cyan amidophenol couplers such as those described in U.S. Pat. 2,895,826 and the combination of an amidophenol coupler and a phenolic cyan coupler of the type described in U.S. Pat. 2,474,293.

The term "direct positive" as used herein and in the appended claims refers to those photographic silver halide emulsions which give reversal images when exposed to blue radiation or to longer wavelength radiation to which the emulsion has been spectrally sensitized. They are to be distinguished from special emulsions which do not reverse when exposed to blue radiation, and which give direct positive images only when exposed to longer wavelength radiation, such as red radiation (which emulsions are sometimes referred to as Herschel reversal emulsions).

In the preparation of the above photographic emulsions, the spectral sensitizing combinations of the invention are advantageously incorporated in the washed, finished silver halide emulsion and should, of course, be uniformly distributed throughout the emulsion. The methods of incorporating dyes and other 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 this purpose. The type of silver halide emulsions that can be sensitized with the invention 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, alginate 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 include 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 poly(ethylene 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.

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

A gelatin silver bromiodide emulsion (2.5 mole percent of the halide being iodide) and having an average grain size of about 0.2 micron is prepared by adding an aqueous solution of potassium bromide and potassium iodide, 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 chloraurate per mole of silver and heating for 60 minutes at 65° C. To separate portions of this emulsion, there are added solutions of either an electron acceptor (Compounds A to M) of the invention, and a cyanine dye (Dyes I to XII) of the invention or a spectral sensitizing combination (Compound and Dye) of the invention, in a suitable solvent, at concentrations per mole of silver as indicated in Table 3 hereinafter. The separate portions of emulsions are then coated on separate cellulose acetate film supports at a coverage of 100 mg. of silver and 400 mg. of gelatin per square foot of support.

A sample of each coating is then exposed on a Eastman 1b sensitometer using a tungsten light source and processed at 20° C. for 6 minutes in Kodak Developer D-19, which has the following composition:

	G.
N-methyl-p-aminophenol sulfate -----	2.0
Sodium sulfite (anhydrous) -----	90.0
Hydroquinone -----	8.0
Sodium carbonate (monohydrate) -----	52.5
Potassium bromide -----	5.0
Water to make 1.0 l.	

then fixed, washed and dried. The sensitometric results are set forth in Table 3 below.

TABLE 3

Ex. No.	Conc. of electron acceptor and of dye (mg./mole silver)	Density			Maximum sensitivity (nm.)
		Relative clear speed	Max. in unexposed areas	Min. in exposed areas	
1.....	Compound A (100).....	170	1.61	.13	440
2.....	(Dye Ib (350).....	1 NI	1.47	1.79	NI
	(Dye Ib (650) ²	575	1.49	.11	580
3.....	(Dye II (300).....	NI	1.47	1.80	NI
	(Dye II (650) ²	263	1.42	.23	470
4.....	(Dye III (300).....	NI	1.64	1.70	NI
	(Dye III (600) ²	468	1.49	.09	470
5.....	(Dye IV (300).....	NI	1.84	2.04	NI
	(Dye IV (600) ²	380	1.32	.08	470
6.....	(Dye V (600).....	NI	1.84	2.04	NI
	(Dye V (600) ²	263	1.76	.03	450
7.....	(Dye VI (300).....	NI	1.65	1.82	NI
	(Dye VI (600) ²	372	1.65	.16	468
8.....	(Dye VII (300).....	NI	1.69	2.11	NI
	(Dye VII (650) ²	209	1.39	.50	550
9.....	(Dye VIII (300).....	NI	1.68	1.94	NI
	(Dye VIII (300) ²	263	1.54	.26	470
10.....	(Dye IX (300).....	NI	1.70	1.88	NI
	(Dye IX (600) ²	525	1.58	.10	470
11.....	(Dye X (300).....	NI	1.33	1.60	NI
	(Dye X (300) ²	67	1.38	.42	680
12.....	(Dye XI (300).....	NI	1.63	1.90	NI
	(Dye XI (600) ²	123	1.49	.45	600
13.....	(Dye XII (300).....	NI	1.57	1.91	NI
	(Dye XII (300) ²	145	1.50	.48	470

¹ NI=No reversal image.

² Plus compound A (100).

Referring to above Table 3, it will be seen that none of the above dyes alone give reversal images with the fogged direct positive emulsion. However, when the various cyanine dyes are combined with the electron acceptor (Cpd. A in each case) highly satisfactory reversal images are obtained. Also, it will be noted that in all cases the maximum sensitivity peak is increased from 440 nm. (for Cpd. A) to as high as 680 nm. for Example 11 wherein Dye X and Cpd. A constitute the spectral sensitizing combination. Further, in most instances the relative clear speed is substantially greater than that obtained with Cpd. A alone. Particularly outstanding results are shown for Example 2 wherein the spectral sensitizing combination of Dye Ib and Cpd. A gives a relative speed of 575, densities of 1.49 and .11 for the unexposed areas, respectively, and a maximum sensitivity at 580 nm.

EXAMPLES 14-22

These examples illustrate spectral sensitizing combinations of the invention wherein the cyanine dye components in each example is 1,1'-diethyl-2,2'-cyanine chloride (Dye Ia herein) and wherein the electron acceptor component is varied (Cpds. B to M inclusive).

To 200 ml. of a 5% gel solution is added:

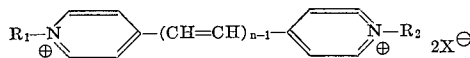
- (1) 20 grams of a silver-chloride emulsion containing one mole of silver and 30 g. of gelatin in 690 g. of emulsion.
- (2) 6 ml. of 7½% aqueous saponin solution.
- (3) 0.44 ml. of a 0.1% aqueous solution of gold chloride.
- (4) 0.044 ml. of a 0.1% aqueous solution of stannous chloride.
- (5) Hold the above mixture for 15 minutes at 40° C.
- (6) Add 0.2 ml. of 10% formaldehyde.

To separate 10 ml. portions of the above emulsion, there are added 1.5 ml. of an 0.1% aqueous solution of the dye 1,1'-diethyl-2,2'-cyanine chloride and 0.5 ml. of a 0.1% aqueous solution of the individual electron acceptor compounds indicated in the following Table 4. The final volume of each portion is then adjusted to 15 ml. with a 5% gelatin solution and coated .004"-wet thickness on a cellulose acetate support.

On drying the resulting coatings and exposing each for 30 seconds at 5 mm. on a modified Bausch and Lomb Spectrograph, followed by developing in Kodak developer D-19 (composition of which is given above), good speed and excellent direct positive images are obtained in each instance in the spectrally sensitized region up to about 590 nm. The relative minus blue speeds of each sample are determined by exposing the sample to white light filtered by Wratten No. 16 filter. A control containing the sensitizing dye but no bipyridinium salt has a relative minus blue speed of 100. The structure of the electron acceptor compounds employed in these examples are listed in Table 4 below.

TABLE 4

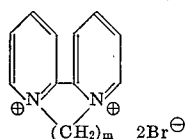
Formula I Type



Example No.	Compound of Table 1	R ₁ and R ₂	X [⊖]	n	Relative minus blue speed
Control.....	(Dye alone).....				100
14 ¹	B	-C ₄ H ₉	ClO ₄ [⊖]	1	3,160
15 ¹	C	-CH ₂ CH ₂ OH	Br [⊖]	1	3,160
16.....	D	-CH ₂ CO Ph	Br [⊖]	1	1,590
17.....	E	-CH ₂ CO Ph	Br [⊖]	2	3,160
18.....	F	-CH ₂ CH ₂ Ph	Br [⊖]	2	3,160
19.....	G	-(CH ₂) ₃ SO ₃ ^e		2	1,590
20.....	K	Ethane analog of compound of Example 18.			200

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Formula II Type



Example No.	Compound of Table 1	R ₁ and R ₂	X [⊖]	n	Relative minus blue speed
21	L	m is 2			1,590
22	M	m is 4			795

¹ A 0.6 log E speed increase in the blue region of the spectrum was observed with the dyed coating compared to the undyed coating containing the bipyridinium salt compound.

The following examples further illustrate the preparation of fogged, direct positive photographic emulsions and elements with the cyanine dyes of the invention.

EXAMPLE 25

To 9.0 pounds of a silver chloride gelatin emulsion containing an equivalent of 100 grams of silver nitrate is added 0.017 gram of the spectral sensitizing combination of above Example 2. The emulsion is coated on a non-glossy paper support, and is flashed with white light to give a density of 1.2 when developed in the following developer, diluted 1 part to 2 parts of water:

	Grams
N-methyl-p-aminophenol sulfate	3.1
Sodium sulfite, des.	45
Hydroquinone	12
Sodium carbonate, des.	67.5
Potassium bromide	1.9
Water to 1 liter.	

The light fogged material can be exposed to an image with light modulated by a Wratten No. 15 filter to give a direct positive image. Generally similar results are obtained when the spectral sensitizing combination of above Example 10 is used in place of the above combination.

By substituting other spectral sensitizing combinations of the invention into the procedure of the above examples, similar fogged direct positive photographic silver halide emulsions and photographic elements may be prepared.

The photographic silver halide emulsion and other layers present in the photographic elements made according to the invention can be hardened with any suitable hardener, including aldehyde hardeners such as formaldehyde, and mucochloric acid, aziridine hardeners, hardeners which are derivatives of dioxane, oxypolysaccharides such as oxy starch or oxy plant gums, and the like. The emulsion layers can also contain additional additives, particularly those known to be beneficial in photographic emulsions, including, for example, lubricating materials, stabilizers, speed increasing materials, absorbing dyes, plasticizers, and the like. These photographic emulsions can also contain in some cases additional spectral sensitizing dyes. Furthermore, these emulsions can contain color forming couplers or can be developed in solutions containing couplers or other color generating materials. Among the useful color formers are the monomeric and polymeric color formers, e.g. pyrazolone color formers, as well as phenolic, heterocyclic and open chain couplers having a reactive methylene group. The color forming couplers can be incorporated into the direct positive photographic silver halide emulsion using any suitable technique, e.g., techniques of the type shown in Jelley et al. U.S. Pat. 2,322,027, issued June 15, 1943, Fierke et al. U.S. Pat. 2,801,171, issued July 30, 1957, Fisher U.S. Pats. 1,055,155 and 1,102,028, issued Mar. 4, 1913 and June 30, 1914, respectively, and Wilmanns U.S. Pat. 2,186,849, issued Jan. 9, 1940. They can also be developed

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using incorporated developers such as polyhydroxybenzenes, aminophenols, 3-pyrazolidones, and the like.

Although the invention has been described in considerable detail with particular reference to certain preferred embodiments thereof, it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove, and as defined in the appended claims.

I claim:

1. A direct positive photographic silver halide emulsion containing a spectral sensitizing combination comprising a bipyridinium salt having two pyridinium nuclei joined by a linkage selected from a single covalent bond, a vinylene linkage and an ethylene linkage, which linkage is attached to a carbon atom of each of said pyridinium nuclei, and a sensitizing methine or azacyanine dye, said bipyridinium salt and said dye being present in an amount effective to spectrally sensitize said emulsion.

2. A direct positive photographic silver halide emulsion as defined in claim 1 wherein said sensitizing dye is selected from the group consisting of cyanine, merocyanine, azacyanine and hemicyanine dyes.

3. A photographic element comprising a support having thereon at least one layer containing a direct positive emulsion of claim 1.

4. A direct positive photographic silver halide emulsion as defined in claim 2 wherein said silver halide is present in the form of reduction and gold fogged silver halide grains.

5. 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 diameter which is within about 40% of the mean grain diameter.

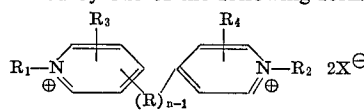
6. A direct positive photographic emulsion in accordance with claim 2 which comprises fogged silver halide grains, said grains being such that a test portion thereof, when coated as a photographic silver halide emulsion on a support to give a maximum density of at least about 1 upon processing for 6 minutes at about 68° F. in the following 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.	

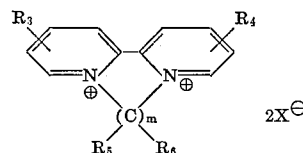
has a maximum density which is at least about 30% greater than the maximum density of an identical coated test portion which is processed for 6 minutes at about 68° F. in said developer after being bleached for about 10 minutes at about 68° F. in a bleach composition of:

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

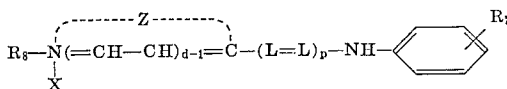
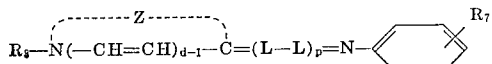
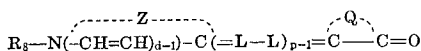
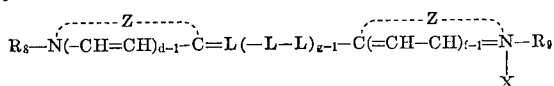
7. A direct positive photographic silver halide emulsion containing a spectral sensitizing combination comprising (1) a bipyridinium salt compound selected from those represented by one of the following formulas:



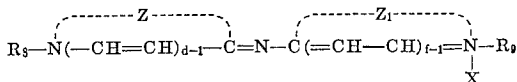
and



and (2) a methine dye selected from those represented by one of the following formulas:

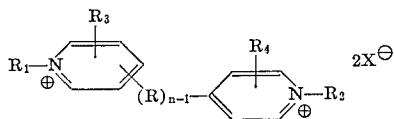


and

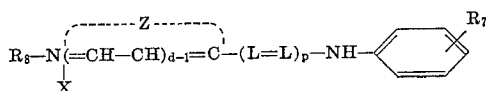
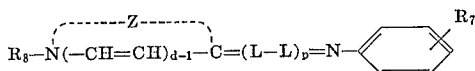
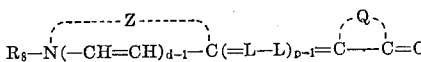
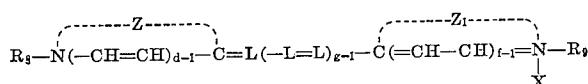


wherein n , d , f , g and p each represents a positive integer of from 1 to 2; m represents a positive integer of from 2 to 4; L represents a methine linkage; R represents a member selected from the group consisting of a vinylene group and a dimethylene group; R_1 , R_2 , R_8 and R_9 each represents a member selected from the group consisting of an alkyl group containing from 1 to 12 carbon atoms and an aryl group; R_3 and R_4 each represents a member selected from the group consisting of a hydrogen atom, an alkyl group containing from 1 to 4 carbon atoms, an alkoxy group containing from 1 to 4 carbon atoms and a halogen atom; R_5 and R_6 each represents a member selected from the group consisting of a hydrogen atom and an alkyl group containing from 1 to 4 carbon atoms; R_7 represents a member selected from the group consisting of a hydrogen atom, an alkyl group containing from 1 to 4 carbon atoms, an acyl group containing from 2 to 5 carbon atoms, and a cyano group; X represents an acid anion; Z and Z_1 each represents the non-metallic atoms necessary to complete a heterocyclic nucleus of the type used in cyanine dyes having from 5 to 6 atoms in the heterocyclic ring; and Q represents the non-metallic atoms necessary to complete a 5- to 6-membered heterocyclic nucleus of the type used in merocyanine dyes, said bipyridinium salt and said methine dye being present in an amount effective to spectrally sensitize said emulsion.

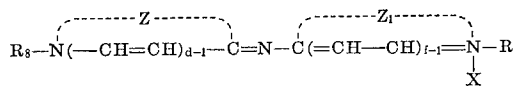
8. A direct positive photographic silver halide emulsion containing a spectral sensitizing combination comprising (1) a bipyridinium salt compound selected from those represented by the following formula:



and (2) a cyanine dye selected from those represented by one of the following formulas:



and



wherein n , d , f , g and p each represents a positive integer of from 1 to 2; L represents a methine linkage; R represents a member selected from the group consisting of a vinylene group and a dimethylene group; R_1 , R_2 , R_8 and R_9 each represents a member selected from the group consisting of an alkyl group containing from 1 to 12 carbon atoms and an aryl group; R_3 and R_4 each represents a member selected from the group consisting of a hydrogen atom, an alkyl group containing from 1 to 4 carbon atoms, an alkoxy group containing from 1 to 4 carbon atoms and a halogen atom; R_7 represents a member selected from the group consisting of a hydrogen atom, an alkyl group containing from 1 to 4 carbon atoms, an acyl group containing from 2 to 5 carbon atoms, and a cyano group; X represents an acid anion; Z and Z_1 each represents the non-metallic atoms necessary to complete a heterocyclic nucleus of the type used in cyanine dyes having 5 to 6 atoms in the heterocyclic ring; and Q represents the non-metallic atoms necessary to complete a 5- to 6-membered ketomethylene heterocyclic nucleus of the type used in merocyanine dyes, said dye and said bipyridinium salt being present in a weight ratio of 10:1 to 1:10 and the total weight of said bipyridinium compound and said dye being from 50 to about 200 mg. per mole of silver halide in said emulsion.

9. A direct positive emulsion in accordance with claim 8 wherein said n is 1.

10. A direct positive emulsion in accordance with claim 8 wherein each of said Z and Z_1 is selected from the group consisting of a thiazole nucleus and a quinoline nucleus.

11. A direct positive emulsion in accordance with claim 8 wherein said Q is a rhodanine nucleus.

12. A direct positive emulsion in accordance with claim 8 in which the said silver halide is present in the form of fogged silver halide grains.

13. A direct positive emulsion in accordance with claim 8 in which the said silver halide is present in the form of reduction and gold fogged silver halide grains.

14. A direct positive emulsion in accordance with claim 8 containing a photographic color former.

15. A direct positive photographic emulsion in accordance with claim 8 which comprises fogged silver halide grains, at least 95%, by weight, of said grains having a diameter which is within about 40% of the mean grain diameter.

16. A photographic element comprising a support having thereon at least one layer containing a direct positive emulsion of claim 8.

17. A photographic element comprising a support having thereon at least one layer containing a direct positive emulsion of claim 8.

18. A direct positive photographic emulsion in accordance with claim 8 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 the following developer:

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

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 said 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

19. A photographic element comprising a support having thereon at least one layer containing a direct positive emulsion of claim 15.

20. A fogged direct positive photographic silver halide emulsion containing a spectral sensitizing combination comprising (1) a bipyridinium salt compound selected from the group consisting of

1,1'-dibutyl-4,4'-bipyridinium dibromide;
1,1'-dibutyl-4,4'-bipyridinium diperchlorate;
1,1'-di(2-hydroxyethyl)-4,4'-bipyridinium dibromide;
1,1'-diphenacyl-4,4'-bipyridinium dibromide;
1,2-di(4-pyridyl)ethylene bis(phenacyl bromide);
1,2-di(4-pyridyl)ethylene bis(phenethobromide);
dianhydro-1,2-di[1-(3-sulfoethyl)-4-pyridyl]ethylene dihydroxide;
1,2-di(4-pyridyl)ethylene bis(methobromide);
1,1'-dimethyl-4,4'-bipyridinium dibromide;
1,2-di(4-pyridyl)ethane bis(phenethobromide);
1,1'-ethylene-2,2'-bipyridinium dibromide; and
1,1'-tetramethylene-2,2'-bipyridinium dibromide and

(2) a cyanine dye selected from the group consisting of

1,1'-diethyl-2,2'-cyanine chloride;
1,1'-diethyl-2,2'-cyanine iodide;
5-(3-ethyl-2-benzothiazolinyldiene)-3-β-sulfoethylrhodanine;
5-chloro-3-ethyl-2-(2-phenyliminopropylidene)benzothiazoline;
1'-ethyl-3-methyl-8-aza-4,5-benzothia-2'-cyanine iodide;
2-(4-acetylanilino)propenyl]-3-ethylbenzothiazolium chloride;
2-[2-(4-cyanoanilino)propenyl]-3-ethylbenzothiazolium chloride;
3-carboxymethyl-5-[(3-methyl-2-thiazolidinyldiene)-1-methylethylidene]rhodanine;
1-ethyl-2-[2-(p-tolylimino)propylidene]naphtho[1,2-d]thiazoline;
anhydro-5-chloro-3'-ethyl-3-(4-sulfobutyl)thiacyanine hydroxide;
3,3'-dimethyl-9-phenyl-4,5; 4',5'-dibenzothiacarbocyanine chloride;
6,6'-dichloro-3,3'-diethylthiacarbocyanine iodide;
3-carboxymethyl-5-(3-ethyl-2-benzothiazolinyldiene)rhodanine;
5-(1-methylnaphtho[1,2-d]selenazolin-2-ylidene)-3-β-sulfoethylrhodanine;
1,1',3,3'-tetraethyl-1H-naphtho[2,3-d]imidazolocarbo-cyanine iodide and
anhydro-5-chloro-3'-methyl-3-(4-sulfobutyl)oxa-cyanine hydroxide,

said bipyridinium salt and said methine dye being present in a weight ratio of 10:1 to 1:10 and the total weight of said bipyridinium salt and said dye being from 200 to 1500 mg. per mole of silver halide in said emulsion.

21. A direct positive photographic emulsion in accordance with claim 20 which comprises fogged silver halide grains, at least 95%, by weight, of said grains having a

diameter which is within about 40% of the mean grain diameter.

22. A photographic element comprising a support having thereon at least one layer containing a direct positive emulsion of claim 20.

23. A direct positive photographic emulsion in accordance with claim 20 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 the following developer:

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

20 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 said 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.
30 Water to 1 liter

24. A photographic element comprising a support having thereon at least one layer containing a direct positive emulsion of claim 21.

25. A photographic element comprising a support having thereon at least one layer containing a direct positive emulsion of claim 23.

26. A fogged, direct positive photographic silver halide emulsion containing a spectral sensitizing combination comprising 1,1'-dibutyl-4,4'-bipyridinium dibromide and a sensitizing methine or azacyanine dye in an amount effective to spectrally sensitize said emulsion.

27. A fogged, direct positive photographic silver halide emulsion containing a spectral sensitizing combination comprising 1,2 - di(4 - pyridyl)ethylene bis(phenacyl bromide) and a sensitizing methine or azacyanine dye in an amount effective to spectrally sensitize said emulsion.

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