United States Patent

[11] 3,615,615

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[21] Appl. No. **28,041**
[22] Filed **Apr. 13, 1970**
[45] Patented **Oct. 26, 1971**

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Continuation-in-part of application Ser. No. 828,064, Apr. 28, 1969.

[54] **PHOTOGRAPHIC EMULSIONS INCLUDING REACTIVE QUATERNARY SALTS**
31 Claims, No Drawings

[52] **U.S. Cl.** **96/109,** 96/107, 96/64

[51] **Int. Cl.** **G03c 1/34,** G03c 5/24, G03c 1/28

[50] **Field of Search** 96/107, 64, 109

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ABSTRACT: Reactive N-substituted, cyclammonium quaternary salts, wherein the N-substituent includes alkyl radicals whose terminal carbon atom is additionally substituted with a radical such as a formyl radical, an acetal or thioacetal radical including cyclic acetals and cyclic thioacetals, or a hydrazono radical which is itself optionally substituted, are useful photographic emulsion addenda such as antifoggants and nucleating agents in silver halide reversal emulsions, as well as being useful dye intermediates.

PHOTOGRAPHIC EMULSIONS INCLUDING REACTIVE QUATERNARY SALTS

This application is a continuation-in-part of U.S Ser. No. 828,064 filed Apr. 28, 1969.

The present invention relates to photography and more particularly to novel compounds and addenda that are useful in photographic elements and processes, especially to reactive, N-substituted, cyclammonium quaternary salts.

An object of the present invention is to provide new heterocyclic quaternary salt photographic addenda.

Still another object of the present invention is to provide new heterocyclic quaternary salt nucleating agents for photographic reversal emulsions.

These and other objects of the instant invention will become additionally apparent from a reading of the following specification and appended claims.

The objects of this invention are accomplished with silver halide emulsions containing heterocyclic quaternary salts including those quaternary salts comprising a heterocyclic nucleus containing a heterocyclic ring of five to six atoms including a quaternary nitrogen atom, which quaternary nitrogen atom has substituted thereon a radical having the formula $-(CH_2)_n-R$ wherein:

a. n represents a positive integer of from 2 to 6, and

b. R represents a member selected from:

1. a formyl radical,

2. a radical having the formula

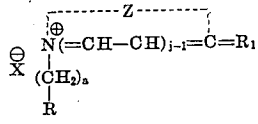


wherein T_1 and T_2, when taken alone, each represents a member selected from an alkoxy radical and an alkylthio radical, and T_1 and T_2, when taken together, represent the atoms necessary to complete a cyclic acetal selected from five- and six-membered cyclic oxyacetals and cyclic thioacetals, or

3. a hydrazonoalkyl radical.

The subject quaternary salts also include heterocyclic quaternary salts comprising a heterocyclic nucleus containing a heterocyclic ring of five to six atoms including a quaternary nitrogen atom and from four to five additional atoms of which from three to four atoms are carbon atoms and wherein the remaining additional atom is selected from the group consisting of carbon, nitrogen, oxygen, sulfur and selenium atoms. The quaternary nitrogen atom is substituted as described hereinabove.

Advantageously included within the subject invention are quaternary salts having the formula



wherein:

a. Z represents the atoms necessary to complete a heterocyclic nucleus containing a heterocyclic ring of five to six atoms including the quaternary nitrogen atom, with the additional atoms of said heterocyclic ring being selected from carbon, nitrogen, oxygen, sulfur and selenium,

b. j represents a positive integer of from 1 to 2,

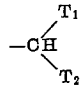
c. a represents a positive integer of from 2 to 6,

d. $X^{\ominus}$ represents an acid anion,

e. R represents a member selected from:

1. a formyl radical,

2. a radical having the formula



wherein T_1 and T_2, when taken alone, each represents a member selected from an alkoxy radical and an alkylthio radical, and T_1 and T_2, when taken together, represent the atoms necessary to complete a cyclic radical selected from cyclic oxyacetals and cyclic thioacetals having from five to six atoms in the heterocyclic acetal ring, and

3. a 1-hydrazonoalkyl radical, and

f. R_1 represents either a hydrogen atom, an alkyl radical, an aralkyl radical, an alkylthio radical or an aryl radical such as phenyl and naphthyl, and including substituted aryl radicals.

Exemplary heterocyclic nuclei completed by those atoms represented by Z are such nuclei as, for example, an indole nucleus, an imidazole nucleus, an oxazole nucleus, a thiazole nucleus, a selenazole nucleus, or a quinoline nucleus including members of the indole series like indole, indolenine, etc.; those of the imidazole series such as benzimidazole compounds like 5-chlorobenzimidazole and also including compounds of the naphthimidazole series; those of the thiazole series such as thiazole, 4-methylthiazole, 4-phenylthiazole, 5-methylthiazole, 5-phenylthiazole, 4,5-dimethylthiazole, 4,5-diphenylthiazole, 4-(2-thienyl)thiazole, etc.; those of the benzothiazole series like benzothiazole, etc.; 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, tetrahydrobenzothiazole, 5,6-dimethoxybenzothiazole, 5-hydroxybenzothiazole, 6-hydroxybenzothiazole, etc.; those of the naphthothiazole series such as α-naphthothiazole, 8-methoxy-α-naphthothiazole, 7-methoxy-α-naphthothiazole, naphtho[2,1-d]thiazole, etc.; those of the thionaphtheno-7′,6′, 4,5-thiazole series like 4′-methoxythionaphtheno-7′,6′, 4,5-thiazole, etc., those of the oxazole series such as 4-methyloxazole, 5-methyloxazole, 4-phenyloxazole, 4,5-diphenyloxazole, 4-ethyloxazole, 4,5-dimethyloxazole, 5-phenyloxazole, etc.; those of the benzoxazole series like 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, etc.; those of the naphthoxazole series such as α-naphthoxazole; those of the selenazole series like 4-methylselenazole, 4-phenylselenazole, etc.; those of the benzoselenazole series like benzoselenazole, 5-chlorobenzoselenazole, 5-methoxybenzoselenazole, 5-hydroxybenzoselenazole, tetrahydrobenzoselenazole, etc.; those of the naphthoselenazole series such as α-naphthoselenazole; and those of the quinoline series such as quinoline, lepidine, etc.

The acid anions represented by $X^{\ominus}$ include a wide variety of such anions including halide anions like bromide, chloride and iodide, as well as additional anions, e.g., sulfates including sulfate, hydrosulfate, and lower alkyl sulfates like methylsulfate and ethylsulfate, aromatic sulfonates such as p-toluene sulfonate and benzenesulfonate, acid anions derived from carboxylic acids like acetate, trifluoroacetate, propionate and a wide variety of other anions including anions such as, for example, perchlorate, cyanate, thiocyanate, sulfamate, benzoate, etc.

Of the radicals represented by R, included are formyl and additional radicals as described herein having the formula

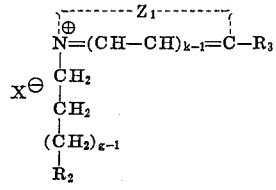


wherein each of T_1 and T_2, when taken alone, represents either an alkoxy radical typically having from one to six carbon atoms in the alkoxy chain or an alkylthio radical preferably

having from one to six carbon atoms in the alkyl chain thereof and, when taken together, represent the atoms necessary to complete a cyclic acetal which is either a five- or six-membered cyclic oxyacetal or cyclic thioacetal radical such as 1,3-dithiolan-2-yl, 1,3-dioxolan-2-yl, 1,3-dithian-2-yl, 1,3-dioxan-2-yl and the like radicals; and 1-hydrazonoalkyl radicals including such substituted 1-hydrazonoalkyl radicals as a thiosemicarbazonomethyl radical, a phenylhydrazonomethyl radical like phenthydrazonomethyl, p-tolylhydrazonomethyl and p-sulfophenylhydrazonomethyl, a benzothiazol-2-yl hydrazonomethyl radical, an N-phenylcarbamoylhydrazonomethyl radical, 1-phenylhydrazonoethyl, 1-phenylhydrazonopropyl, 1-(p-tolylhydrazono)ethyl, 1-(2-benzothiazolyhydrazono)-propyl, 1-(N-phenylcarbamoylhydrazono)butyl, 1-(p-toluenesulfonylhydrazono)ethyl, 1-(p-sulfophenylhydrazono)propyl and the like 1-hydrazonoalkyl radicals.

As employed herein, the terms alkyl radical, alkoxy radical and alkylthio radical include aliphatic, branched and straight chain alkyl, alkoxy and alkylthio radicals typically having from one to six carbon atoms in the alkyl moiety such as alkyl radicals like methyl, ethyl, propyl, isopropyl, n-butyl, tert-butyl, amyl, hexyl, etc., alkoxy radicals such as methoxy, ethoxy, propoxy, n-butoxy, tert-butoxy, and the like alkoxy radicals, and alkylthio radicals like methylthio, ethylthio, tert-butylthio, hexylthio, etc. Lower alkyl, alkoxy and alkylthio radicals have from one to four carbon atoms in the alkyl moiety, and they can be substituted or unsubstituted radicals. The term aralkyl radical defines alkyl radicals such as those described elsewhere herein having an aryl radical like phenyl or naphthyl substituted on the alkyl moiety. Exemplary aralkyl radicals include such radicals as benzyl, phenylethyl, 2-phenylpropyl, naphthylethyl, phenylbutyl and the like.

Of the reactive cyclammonium quaternary salts described herein, especially advantageous salts include those having the formula:



wherein:

a. Z_1 represents the nonmetallic atoms necessary to complete a heterocyclic nucleus such as those described elsewhere herein as completed by Z atoms,
b. *k* represents a positive integer of from 1 to 2,
c. *g* represents a positive integer of from 1 to 5,
d. $X^{\ominus}$ represents an acid anion such as those described hereinabove,
e. R_2 represents either a formyl radical or a radical having the formula

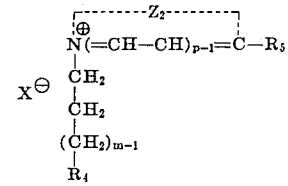


wherein T_3 and T_4, when taken alone, each represents either an alkoxy radical or an alkylthio radical and T_3 and T_4, when taken together, represent the atoms necessary to complete a cyclic acetal selected from five- and six-membered cyclic oxyacetals and cyclic thioacetals, and

f. R_3 represents either a hydrogen atom, an alkyl radical, an aralkyl radical, an alkylthio radical or an aryl radical. Reactive quaternary salts of the invention include such compounds as:

3-(2-formylethyl)- 2-methylbenzothiazolium bromide,
3-(3,3-dimethoxypropyl)- 2-ethylbenzimidazolium chloride,
3-(3,3-diethoxypropyl)- 2-methylbenzothiazolium iodide,
1-(2-formylethyl) lepidinium bromide,
1-[2-(1,3-dithian-2-yl)ethyl]-2-ethylquinolium iodide,
3-(3,3-diethoxypropyl)-2-methylbenzothiazolium perchlorate,
5-chloro-3-(2-formylethyl)-2-methylbenzoselenazolium bromide,
3-[3,3-di(ethylthio)propyl]-2-methylbenzothiazolium iodide,
3-[3,3-di(ethylthio)propyl]-2-methylbenzothiazolium p-toluene sulfonate,
1-(2-formylethyl)lepidinium bromide,
3-(3-formylpropyl)-2-ethylbenzimidazolium hydrosulfate,
3-(6,6-diethoxy-n-hexyl)-2-methylnaphtho[2,1-d]thiazolium bromide,
3-[3,3-di(methylthio)propyl]-2-methylbenzothiazolium iodide,
3-(2-formylethyl)-2-methylbenzoselenazolium bromide,
3-(3,3-diethylthiopropyl)-2-ethylbenzoxazolium bromide,
3-[2(1,3-dithiolan-2-yl)ethyl]-2-methylbenzothiazolium iodide,
3-[2-(1,3-dioxan-2-yl)ethyl]-2-methylbenzoselenazolium bromide,
3-(5-formylpentyl)-2-ethylbenzoselenazolium bromide,
3-(2-formylethyl)-2-methylnaphtho[2,1-d]thiazolium bromide,
3-(3,3-diethoxypropyl)-2-ethylthionaphtho[2,3-d]thiazolium methylsulfate,
3-[3-(1,3-dioxolan-2-yl)propyl]-1-ethyl-2-phenylbenzimidazolium perchlorate,
3-(2-formylethyl)-2-methylnaphtho[2,3-d]thiazolium bromide,
3-[3,3-di(propylthio)propyl]-2-p-tolylbenzothiazolium benzoate,
5-chloro-3-(2-formylethyl)-2-methylbenzothiazolium bromide,
3-(2-formylethyl)-5-methoxy-2-methylbenzothiazolium bromide,
3-(2-formylethyl)-5,6-dimethoxy-2-methylbenzothiazolium bromide.

Other useful quaternary salts of the subject invention include hydrazonoalkyl-substituted salts having the formula:



wherein:

a. Z_2 represents the nonmetallic atoms necessary to complete a heterocyclic nucleus such as those described elsewhere herein as completed by Z atoms,
b. *p* represents a positive integer of from 1 to 2,
c. *m* represents a positive integer of from 1 to 5,
d. R_4 represents a 1-hydrazonoalkyl radical,
e. R_5 represents a substituent as defined for R_1, and
f. $X^{\ominus}$ represents an acid anion.

Exemplary hydrazonoalkyl radicals useful herein are, for example, those having the formula M—NH—N=CH— wherein M represents an aryl radical such as phenyl or naphthyl which can be substituted with such substituents as hydroxy, alkyl, amino radicals like alkylamino, arylamino, heterocyclic amino, alkoxy, aryloxy, such amido radicals as acyloxy amido arylcarbonamido, alkylcarbonamido, heterocyclic carbonamido, arylsulfonamido, alkylsulfonamido and heterocyclic sulfonamido.

Especially advantageous hydrazonoalkyl-substituted quaternary salts of this invention include such salts as those described hereinabove wherein *m* is 1, R_5 represents a methyl radical and R_4 represents a hydrazonoalkyl such as:

a. a phenylhydrazonomethyl radical,
b. a p-tolylhydrazonomethyl radical,
c. a p-sulfophenylhydrazonomethyl radical,
d. a thiosemicarbazonomethyl radical,
e. a 2-benzothiazolylhydrazonomethyl radical,
f. a p-carboxyphenylhydrazonomethyl radical,
g. a p-toluenesulfonylhydrazonomethyl radical,
h. a p-chlorophenylhydrazonomethyl radical,
i. a p-nitrophenylhydrazonomethyl radical,
j. an N-phenylcarbamoylhydrazonomethyl radical,
k. a 2,4-di(methylsulfo)phenylhydrazonomethyl radical,
l. a 2,4-dinitrophenylhydrazono radical, or
m. a 3-quinolylhydrazonomethyl radical,
n. a 1-phenylhydrazonoethyl radical,
o. a 1(p-tolylhydrazono)ethyl radical,
p. a 1-(p-sulfophenylhydrazono)propyl radical,
q. a 1-thiosemicarbazonobutyl radical,
r. a 1-(2-benzothiazolylhydrazono)ethyl radical,
s. a 1-(p-carboxyphenylhydrazono)pentyl radical,
t. a 1-(p-toluenesulfonylhydrazono)ethyl radical,
u. a 1-(p-chlorophenylhydrazono)propyl radical,
v. a 1-(p-nitrophenylhydrazono)propyl radical,
w. a 1-(N-phenylcarbamoylhydrazono)butyl radical,
x. a 1-[2,4-bis(methylsulfonyl)phenylhydrazono]propyl radical,
y. a 1-(2,4-dinitrophenylhydrazono)ethyl radical, and the like.

Exemplary hydrazonoalkyl substituted quaternary salts of the invention include such compounds as, for example:

3-[3-(2-benzothiazolylhydrazono)propyl]-2-methylbenzothiazolium iodide,
3-[3-(p-carboxyphenylhydrazono)propyl]-2-methylbenzoxazolium chloride,
3-[3-(p-carboxyphenylhydrazono)propyl]-2-methylbenzothiazolium bromide,
2-methyl-3-[3-(p-toluenesulfonylhydrazono)propyl]naphtho[2,1-d]thiazolium iodide,
3-[3-(p-chlorophenylhydrazono)propyl]-2-methylnaphtho-[2,1-d]thiazolium bromide,
3-[3-(p-carboxyphenylhydrazono)propyl]-2-ethylnaphtho [2,1-d]thiazolium bromide,
2-methyl-3-[(-p-nitrophenylhydrazono)propyl]naphtho [2,1-d]thiazolium iodide,
2-methyl-3-[3-(N-phenylcarbamoylhydrazono)propyl]naphtho[2,1-d]thiazolium iodide,
3-[3-(2,4-dimethylsulfonylphenylhydrazono)propyl]-2-methylnaphtho[2,1-d]thiazolium bromide,
3-[3-(p-carboxyphenylhydrazono)propyl]-2-benzylbenzoselenazolium-p-toluene sulfonate,
2-benzyl-3-[3-(phenylhydrazono)propyl]benzothiazolium acetate,
3-[3-(p-carboxyphenylhydrazono)propyl]-2-methylbenzothiazolium bromide,
3-[3-(p-carboxyphenylhydrazono)propyl]-5-chloro-2-methylbenzothiazolium bromide,
2-methyl-3-[3-(phenylhydrazono)propyl]benzothiazolium benzene sulfonate,
2-ethyl-[3-(p-sulfophenylhydrazono)propyl]benzothiazolium iodide,
2-methyl-3-[3-(p-sulfophenylhydrazono)propyl] benzothiazolium iodide,
2-methyl-3-[3-(thiosemicarbazono)propyl]benzothiazolium bromide,
2-methyl-3-[3-(thiosemicarbazono)propyl]benzothiazolium hydrosulfate,
2-methyl-3-[3-(phenylhydrazono)propyl]benzothiazolium iodide,
2-methyl-3-[3-(phenylhydrazono)propyl]benzothiazolium thiocyanate,
2-methyl-3-[3-(p-tolylhydrazono)propyl]benzothiazolium iodide,
2-methyl-3-[3-(p-sulfophenylhydrazono)propyl] benzothiazolium chloride,
2-methyl-3-[3-(thiosemicarbazono)propyl]benzothiazolium perchlorate,
2-methyl-3-[3-(phenylhydrazono)propyl]benzothiazolium benzene sulfonate,
2-methyl-3-[3-(p-tolylhydrazono)propyl]benzothiazolium acetate,
2-methyl-3-[3-(p-sulfophenylhydrazono)propyl] benzothiazolium propionate,
2-methyl-3-[3-(2-benzothiazolyhydrazono)propyl]benzothiazolium cyanate,
5,6-dichloro-1-ethyl-2-methyl-3-[3-(p-sulfophenylhydrazono)propyl]benzimidazolium bromide,
1-(p-carboxyphenylhydrazonopropyl)-2,3,3-trimethyl-3H-indolium bromide,
5,6-dichloro-3-[3-(2-benzothiazolylhydrazono)propyl]-1-ethyl-2-methylbenzimidazolium bromide,
5,6-dichloro-2-methyl-3-[3-(3-quinolylhydrazono)propyl]-1-ethylbenzimidazolium bromide,
5-chloro-2-methyl-3-[3-(p-tolylhydrazono)propyl]benzoselenazolium bromide,
2-methyl-3-[3-(p-toluenesulfonylhydrazono)propyl]benzothiazolium bromide,
2-methyl-3-[3-(p-tolylhydrazono)propyl]benzothiazolium bromide,
3-[3-(2,4-dinitrophenylhydrazono)propyl]benzothiazolium bromide,
5,6-dichloro-1-ethyl-2-methyl-3-[3-(p-tolylhydrazono)propyl]benzimidazolium bromide,
5,6-dichloro-1-ethyl-2-methyl-3-[3-(p-nitrophenylhydrazono)propyl]benzimidazolium bromide,
3-[3-(p-carboxyphenylhydrazono)propyl]-5-methoxy-2-methylbenzothiazolium bromide,
2-methyl-1-[3-(p-carboxyphenylhydrazono)propyl]-1H-benz[e]indolium bromide,
3-[3-(p-carboxyphenylhydrazono)propyl]-5,6-dimethoxy-2-methylbenzothiazolium bromide,
3-[3-(p-carboxyphenylhydrazono)propyl]-2-methylnaphtho[2,3-d]thiazolium bromide,
3-[3-(2-benzothiazolylhydrazono)butyl]-2-methylbenzothiazolium iodide,
3-[3-(p-carboxyphenylhydrazono)pentyl]-2-methylbenzoxazolium chloride,
3-[3-(p-carboxyphenylhydrazono)hexyl]-2-methylbenzothiazolium bromide,
2-methyl-3-[3-(p-toluenesulfonylhydrazono)-butyl]naphtho[2,1-d]thiazolium iodide,
3-[3-(p-chlorophenylhydrazono)heptyl]-2-methylnaphtho-[2,1-d]thiazolium bromide,
3-[3-(p-carboxyphenylhydrazono)butyl]-2-ethylnaphtho-[2,1-d]thiazolium bromide,
2-methyl-3-[3-(p-nitrophenylhydrazono)propyl]naphtho-[2,1-d]thiazolium iodide,
2-methyl-3-[3-(N-phenylcarbamoylhydrazono)pentyl]naphtho-[2,1-d]thiazolium iodide,
3-[3-[2,4-bis(methylsulfonyl)phenylhydrazono]hexyl]-2-methylnaphtho[2,1-d]thiazolium bromide,
3-[3-(p-carboxyphenylhydrazono)butyl]-2-benzylbenzoselenazolium p-toluene sulfonate,
2-methyl- 3-[(3-phenylhydrazono)butyl]benzothiazolium acetate,
3-[3-(p-carboxyphenylhydrazono)pentyl]-2-methylbenzothiazolium bromide,
3-[3-(p-carboxyphenylhydrazono(butyl]-5-chloro-2-methylbenzothiazolium bromide,
3-[3-(phenylhydrazono)hexyl]benzothiazolium benzenesulfonate,
2-ethyl-[3-(p-sulfophenylhydrazono)butyl]benzothiazolium iodide,
2-methyl-3-[3-(p-sulfophenylhydrazono)pentyl] benzothiazolium iodide,

2-methyl-3-[3-(thiosemicarbazono)heptyl]benzothiazolium bromide,
2-methyl-3-[3-(thiosemicarbazono)hexyl]benzothiazolium hydrosulfate,
2-methyl-3-[3-(phenylhydrazono)butyl]benzothiazolium iodide,
2-methyl-3-[3-(phenylhydrazono)pentyl]benzothiazolium thiocyanate,
2-methyl-3-[3-(p-tolylhydrazono)heptyl]benzothiazolium iodide,
2-methyl-3-[3-(p-sulfophenylhydrazono)butyl] benzothiazolium chloride,
2-methyl- 3-[3-(thiosemicarbazono)pentyl]benzothiazolium perchlorate,
2-methyl-3-[3-(phenylhydrazono)butyl]benzothiazolium benzenesulfonate,
2-methyl-3-[3-(p-tolylhydrazono)pentyl]benzothiazolium acetate,
2-methyl-3-[3-(p-sulfophenylhydrazono)butyl] benzothiazolium propionate,
2-methyl-3-[3-(2-benzothiazolylhydrazono)butyl]benzothiazolium cyanate,
5,6-dichloro-1-ethyl-2-methyl-3-[3-(p-sulfophenylhydrazono)pentyl]benzimidazolium bromide,
5,6-dichloro-3-[3-(2-benzothiazolylhydrazono)butyl]-1-ethyl-2-methylbenzimidazolium bromide,
5,6-dichloro-2-methyl-3-[3-(3-quinolylhydrazono)propyl]-1-ethylbenzimidazolium bromide,
5-chloro-2-methyl- 3-[3-(p-tolylhydrazono)hexyl]benzoselenazolium bromide,
2-methyl-3-[3-(p-toluenesulfonylhydrazono)butyl] benzothiazolium bromide,
2-methyl-3-[3-(p-tolylhydrazono)pentyl]benzothiazolium bromide,
3-[3-(2,4-dinitrophenylhydrazono)hexyl]benzothiazolium bromide,
5,6-dichloro-1-ethyl-2-methyl-3-[3-(p-tolylhydrazono)butyl]-benzimidazolium bromide,
5,6-dichloro-1-ethyl-2-methyl-3-[3-(p-nitrophenylhydrazono)pentyl]benzimidazolium bromide,
3-[3-(p-carboxyphenylhydrazono)butyl]-5-methoxy-2-methylbenzothiazolium bromide,
3-[3-(p-carboxyphenylhydrazono)pentyl]-5,6-dimethoxy-2-methylbenzothiazolium bromide, and
3-[3-(p-carboxyphenylhydrazono)hexyl]-2-methylnaphtho[2,3-d]thiazolium bromide,
1-[3-(p-carboxyphenylhydrazono)propyl]-2-methylquinolium iodide.

The subject quaternary salts are conveniently prepared by reacting a cyclammonium hydrosalt compound with another compound containing an active double-bond system such as ethylenic unsaturation between the first and second carbon atoms of an aliphatic molecule or radical.

The reaction medium can be an inert organic solvent that exhibits moderate polarity and dissolves both reagents, but which is not a solvent for the quaternary salt reaction product. Advantageous solvents include organic solvents having moderate polarity such as acetonitrile and dimethyl acetamide. No reaction catalysts are generally required and the reaction temperature is conventionally variable from about 20°C. to about 30° C., although wider reaction temperatures can be employed so long as the reagents remain in solution and are not subjected to heating in excess of their decomposition temperatures. The reaction products precipitate from solution and can then be purified by such conventional means as solvent washing or sequential crystallization.

The hydrazonoalkyl-substituted quaternary salts of the invention can be synthesized in a similar fashion and under like reaction conditions, but using a two-step reaction sequence in the first step of which a cyclammonium base hydrosalt is reacted with a compound containing an activated double-bond system and preferably having the formula:

$$CH_2=CH-(CH_2)_{m-1}-T_5$$

wherein m represents an integer having a value of from 1 to about 5 and T_5 represents either a formyl radical, an acetyl radical or a propionyl radical, to prepare an intermediate compound which is then reacted with a hydrazine compound to produce the composite hydrazonoalkyl-substituted quaternary salts of this invention. Exemplary hydrazine compounds include such species as, for example, phenylhydrazine, p-tolylhydrazine, p-sulfophenylhydrazine, thiosemicarbazide, benzothiazol-2-ylhydrazine, p-carboxyphenylhydrazine, p-tolylsulfohydrazine, p-chlorophenylhydrazine, p-nitrophenylhydrazine, N-phenylcarbamoylhydrazine, 2,4-di(methylsulfo)phenylhydrazine, p-carboxyphenylhydrazine or p-sulfophenylhydrazine. The preparation of the subject-reactive quaternary salts is described in the Lincoln and Heseltine U.S. Pat. application Ser. No. 819,946 titled REACTIVE QUATERNARY SALTS AND THEIR PREPARATION, filed Apr. 28, 1969, and pending concurrently herewith.

The conveniently prepared, reactive quaternary salts of this invention are useful as photographic addenda in silver halide photographic emulsions and especially in gelatino-silver halide emulsions as, for example, antifoggants, etc., and as chemical intermediates in, for example, the production of photographic dyestuffs. The subject salts have utility in both conventional negative type, developing out silver halide emulsions as well as in direct-positive silver halide emulsions. An exemplary dye condensation to prepare a symmetrical photographic sensitizing dye is the reaction of a subject quaternary salt with a stoichiometric excess amount (molar) of a reagent such as diethoxymethyl acetate, 1,3,3-trimethoxypropene and the like. Unsymmetrical photographic dyes can be prepared by reacting the quaternary salts of this invention with a dye intermediate such as p-dimethylaminobenzaldehyde, 5-acetanilidomethylene-3-ethylrhodanine, 3-ethylmercaptobenzothiazolium ethylsulfate, etc. The dyes so prepared are useful in photographic elements either as spectral sensitizers for a photosensitive species such as silver halide or serving alternative functions wherein organic dyestuffs are advantageously employed.

Silver halide emulsions into which the quaternary salts of this invention are advantageously incorporated typically contain other chemical addenda such as, for example, carrier vehicles, spectral sensitizing dyes, coating aids, brighteners, hardeners, developing agents and the like addenda. Desirable carrier vehicles include any of the hydrophilic, water-permeable binding materials suitable for this purpose. Suitable materials include gelatin, colloidal albumin, polyvinyl compounds cellulose derivatives, acrylamide polymers and the like, alone or in combination and mixture The binding agents for the emulsion layer of the photographic element can also contain dispersed polymerized vinyl compounds. Certain of such compounds are disclosed, for example, in U.S. Pat. Nos. 3,142,568 of Nottorf issued July 28, 1964; 3,193,386 of White issued July 6, 1965; 3,062,672 of Houck et al., issued Nov. 6, 1962; and 3,220,844 of Houck et al., issued Nov. 30, 1965; and include the water-insoluble polymers and latex copolymers of alkyl acrylates and methacrylates, acrylic acid sulfoalkyl acrylates or methacrylates and the like.

Spectral sensitizing dyes useful in sensitizing the silver halide emulsions employed in this invention are described in, for example, U.S. Pat. Nos. 2,526,632 of Brooker and White issued Oct. 24, 1950 and 2,503,776 of Sprague issued Apr. 11, 1950. Spectral sensitizers which can be used are the cyanines, merocyanines, complex (trinuclear) cyanines, complex (trinuclear) merocyanines, styryls and hemicyanines.

The photographic silver halide emulsions or coatings disclosed herein can also contain nonionic, anionic and/or amphoteric coating aids. Some useful coating aids include, for example, saponin, alkyl-substituted aryl oxy alkylene ethyl sulfonates of the type described in U.S. Pat. No. 2,600,831 issued June 17, 1952, maleopimarates of the type described in U.S.

Pat. No. 2,823,123, issued Feb. 11, 1958, taurine derivatives of the type described in U.S. Pat. No. 2,739,891 issued on Mar. 27, 1956, and alkyl aminopropionates of the type described in U.S. Pat. No. 3,133,816 issued May 19, 1964. Typical of still other good coating aids and surfactants which can be employed in the emulsions of this invention include the alkylphenoxy poly(hydroxyalkylene oxides) such as alkylphenoxy poly(glycidols) having from about five to about 12 glycidol units, for example, such as those disclosed in British Pat. No. 1,022,878 issued Mar. 16, 1966, to Olin Mathieson.

Advantageous brighteners typically include compounds containing at least one heterocyclic five- or six-membered ring such as derivatives of stilbene, stilbenetriazole, triazine stilbene, coumarin, triazinylamino coumarin, oxazole, benzidene, benzimidazole, benzothiazole, benzoxazole, pyrazoline, naphthalic acid imide, etc. Exemplary brighteners include such compounds as those described in U.S. Pat. No. 2,933,390 and in U.S. Pat. No. 3,406,070.

As well as including the above-mentioned addenda, the silver halide emulsions employed in this invention can be hardened with any suitable hardener or combinations such as, e.g. formaldehyde, mucochloric acid, glutaraldehyde, maleic dialdehyde, aldehyde hardeners, aziridine hardeners, hardeners which are derivatives of dioxane, vinyl sulfones, oxypolysaccharides such as oxystarch, oxy plant gums, inorganic hardeners such as chromium salts, and the like. Developing agents of the types suitable for inclusion in a silver halide emulsion are described hereinbelow.

The subject hydrazonoalkyl-substituted quaternary salts are especially advantageous as incorporated nucleating agents or fogging agents in silver halide reversal or direct positive emulsions utilized in photographic elements designed for reversal processing to prepare direct positive photographic images without an intermediate developed negative image. Typical of such direct positive emulsions are those that form latent images predominantly inside the silver halide grains.

The photographic emulsions generally used in reversal processes are gelatino silver halide emulsions such as silver bromide, silver bromoiodide or silver chlorobromide emulsions. They need not contain sensitizing dyes although certain of such dyes can be added to reversal emulsions to widen spectral sensitization. Advantageous sensitizing dyes would include those described in U.S. Pat. No. 2,497,876, especially between column 2, line 15, and column 4, line 20. Internal latent image-forming emulsions are typically undigested or if digested, the digestion is carried out without the use of surface chemical sensitizers. An emulsion of this type, known as Burton's emulsion is described in Wall "Photographic Emulsions," 1927, pp. 52 and 53. A further type of suitable reversal emulsion is an internal latent image emulsion described in Davey and Knott, U.S. Pat. No. 2,592,250.

An internal latent image-forming emulsion can be prepared by first forming in one or more stages silver salt grains consisting at least partly of a silver salt which is more soluble in water than silver bromide, subsequently converting at least part of the grains to silver bromide or silver bromoiodide, ripening, preferably in the absence of ammonia, and then either washing out some of the soluble salts or washing out the whole of the soluble salts, followed by the addition of soluble salts such as soluble chloride, bromide or iodide to prepare a composite silver chlorobromide, bromoiodide or chlorobromoiodide reversal emulsion. Suitable silver chlorobromide internal image emulsions also can be prepared by simultaneously adding an aqueous solution of silver nitrate and an aqueous solution containing potassium chloride and potassium bromide to an agitated aqueous gelatin solution as described in example 4 of Luckey et al., U.S. Pat. No. 2,996,382.

An "internal latent image" type of silver halide emulsion can be defined as one which, when a test portion is exposed to a light intensity scale for a fixed time up to about 1 second and developed for 4 minutes at 20° C., in an ordinary "surface" developer, one which develops an image only on the surface of the grains of an "internal latent image emulsion," which developer type is exemplified by one having the formula:

p-hydroxyphenylglycine	10 g.
sodium carbonate (crystals)	100 g.
water to	1 l.

exhibits a maximum density not greater than one-fifth the maximum density obtained when the same emulsion is equally exposed and developed for 3 minutes at 20° C., in an "internal" type developer, one which develops an image inside the grains of an "internal latent image emulsion," which developer type is exemplified by one having the formula:

hydroquinone	15 g.
monomethyl-p-aminophenol sulfate	15g.
sodium sulfite (anhyd)	50 g.
potassium bromide	10 g.
sodium hydroxide	25 g.
sodium thiosulfate (crystals)	20 g.
water to	1 l.

Preferably the maximum density obtained with the "surface" developer is not greater than one-tenth the maximum density obtained when the same emulsion is developed in the "internal" type developer. Stated conversely, an "internal latent image" emulsion, when developed in an "internal type developer" exhibits a maximum density at least five and preferably at least 10 times the maximum density obtained when the emulsion is exposed in the same way and developed in a "surface" developer.

The subject quaternary salts that operate advantageously as nucleating agents or fogging agents in internal latent image-forming (reversal) emulsions are conveniently added to a silver halide reversal emulsion, such as, for example, those described in U.S. Pat Nos., 2,566,180 or 2,592,250 in amounts designed to produce adequate fog in the form of minute surface development sites which foster the production of direct-positive images upon development. The subject quaternary salt nucleating agents appear to be more tightly adsorbed to the silver halide grain surface than are previously known fogging agents, such as the hydrazine compounds of Ives, U.S. Pat. No. 2,588,982, since lesser amounts are required. With the utilization of a diminished amount of fogging agent, desired sensitometric characteristics are preserved since less fogging agent is released into developer solutions.

Generally, concentrations of from about 75 to about 1,500 mg. of the subject fogging agents per mole of silver in the silver halide emulsion are useful with from about 90 to about 1,200 mg. nucleating agent per mole of silver being preferred. These ratios are according to conventional practice, however, and with either particular reversal emulsions, fogging agents of varying chemical activity, or varying processing conditions, more widely varying fogging agent concentrations can be advantageously used.

To prepare direct-positive photographic elements that can be reversal processed, an internal latent-image-forming silver halide emulsion such as described hereinabove, and also containing a nucleating agent of this invention is coated onto a typical photographic support material and dried. The reversal or direct positive silver halide emulsions utilized in the photographic or light-sensitive elements of the invention are to be distinguished from emulsions containing silver halide grains that have substantial surface sensitivity and form latent images when exposed to light on the surface thereof. Advantageous support materials include conventional photographic film base materials like cellulose esters such as cellulose acetate, cellulose triacetate, cellulose acetate butyrate, etc. poly-α-olefins like polyethylene and polypropylene, polycarbonates, polyesters such as poly(ethylene terephthalate) as well as metals such as zinc and aluminum and paper including polyethylene and polypropylene coated papers. Other support materials that are suitably used herein are known in the art.

The nucleating agents of the invention can be used in reversal color as well as black-and-white silver halide emulsions. The preparation of color reversal photographic elements is conveniently accomplished by employing cyan, magenta and yellow color-forming couplers contiguous to silver halide emulsion layers capable of recording light substantially complementary in color to the color of dye produced with the respective couplers on color development as described in U.S. Pat. Nos. 3,227,550 and 3,227,552. Spectral sensitizing dyes can be used to sensitize the silver halide in the usual manner. In a multilayer element, the red-recording emulsion layer can contain a coupler such as 5-(p-amylphenoxy benzene sulfonamino)-1-naphthol, the green-recording emulsion layer, a coupler like 2-cyanoacetyl-5-(p-sec.amylbenzoylamino) coumarone and the blue-recording emulsion layer, a coupler such as N-amyl-p-benzoylacetamino benzenesulfonate. Additional couplers are well known in the art. If desired, the color couplers can be incorporated into the developer solution, as described in Mannes et al., U.S. Pat. No. 2,252.718 and Glass et al., U.S. Pat. No. 2,507,154, such an arrangement necessitating multiple exposures and color-developing steps.

After an imagewise exposure, the direct positive photographic elements containing the subject nucleating agents are immersed in a conventional surface developer solution having relatively low solvent action on silver halide whereupon a positive photographic image is formed. Such surface developers can advantageously contain image-enhancing compounds which increase maximum image density and lower minimum image density such as the benzotriazoles described in Stauffer, U.S. Pat. No. 2,497,917.

If color images are to be prepared, the developer solution typically contains a p-phenylenediamine color developing agent such as a 4-amino-N-dialkylaniline like those described in Mees, "The Theory of the Photographic Process," 3rd Ed. (1961) pp. 294–295. With a color developer, one or more colored dye images are produced depending upon the construction of the particular photographic element. In polychromatic color elements, cyan, magenta and yellow dye images are typically produced in the red-sensitive, green-sensitive and blue-sensitive layers, respectively. Remaining silver is first converted to a soluble silver salt and removed in the usual way by treatment with a fixing agent such as sodium thiosulfate.

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

EXAMPLE 1

The quaternary salt, 3-(2-formylethyl)-2-methylbenzothiazolium bromide, is added to a conventional negative-type, developing-out gelatino silver bromoiodide photographic emulsion at a concentration of 0.6 g. per mole of silver halide. The composite emulsion is then coated onto a subbed polyethylene terephthalate) film support and dried in the usual manner to prepare a photographic element. A control element is prepared in a like fashion, but without the quaternary salt addendum. A portion of each element is exposed through a neutral density step wedge in an Eastman model 1 B sensitometer. After exposure, the elements are developed for about 2 minutes at 20° C., in a photographic developing solution having the composition:

p-methylaminophenol	3 g.
sodium sulfite (dessicated)	45 g.
hydroquinone	12 g.
sodium carbonate (monohydrate)	80 g.
potassium bromide	2 g.
water to make	2 l.

and then fixed by treatment for about 3 minutes at 20° C., in a fixing bath having the composition:

sodium thiosulfate	240 g.
sodium sulfite (dessicated)	15 g.
acetic acid (28%)	48 ml.
boric acid crystals	7.5 g.
potassium alum	15 g.
water to make	1 l.

The residual fog for each element is tabulated as follows:

	Fog	
	Initial	After two-week, 45° C.; 85% Relative Humidity Incubation Period
Control	0.19	1.08
Element with addendum compound	0.29	0.81

From the table, it is observed that the subject quaternary salt compound exhibits antifogging properties when used as an addendum in photographic silver halide emulsions. Seven additional elements are prepared in a like fashion, except that

3-(3,3-diethoxypropyl)-2-methylbenzothiazolium iodide,
1-[2-(1,3-dithian-2-yl)ethyl]-2-ethylquinolium iodide,
5-chloro-3-(2-formylethyl)-2-methylbenzoselenazolium bromide,
3-[3,3-di(ethylthio)propyl]-2-methylbenzothiazolium iodide,
3-[2-(1,3-dithiolan-2-yl)ethyl]-2-methylbenzothiazolium iodide,
3-[2-(1,3-dioxan-2-yl)ethyl]-2-methylbenzoselenazolium bromide, and
3-[3-(1,3-dioxolan-2-yl)propyl]-1-ethyl-2-phenyl-benzimidazolium bromide

are used in lieu of the 3-(2-formylethyl)-2-methylbenzothiazolium bromide. Exposure and processing are in a like fashion and commensurate results are obtained. Typical concentrations of the subject addenda for antifoggant purposes are about 0.001 to 10 g. of such addenda per mole of silver halide.

EXAMPLE 2

A photographic element (control) is prepared by coating a cellulose acetate support with a gelatino-silver bromoiodide reversal emulsion prepared as described in Davey and Knott, U.S. Pat. No. 2,592,250. After coating and drying, the element is exposed in an Eastman model 1B sensitometer. Subsequent to exposing, the element is developed for about 3 minutes at 20° C., in a developing solution having the formula:

p-methylaminophenol	3 g.
sodium sulfite (dessicated)	45 g.
hydroquinone	12 g.
sodium carbonate (monohydrate)	80 g.
potassium bromide	2 g.
water to make	2 l.

and the developed positive image is stabilized by treatment for about 3 minutes at 20° C., with a fixing bath having the formula:

sodium thiosulfate	240 g.
sodium sulfite (dessicated)	15 g.
acetic acid (28%)	48 ml.
boric acid crystals	7.5 g.
potassium alum	15 g.
water to make	1 l.

A second element (element2) is prepared, exposed and processed in like fashion, with the exception that the subject quaternary salt fogging agent, 2-methyl-3-[(3-phenylhydrazono)propyl]benzothiazolium bromide, is added to the emulsion in a concentration of 200 mg./mole of silver. A reversal image is obtained with element 2. Pertinent photographic date is summarized as follows:

	Relative Speed	Dmax.	Dmin.	Gamma
Control	100	0.10	0.04	0.05
Element 2	3,720	1.44	0.15	1.57

As can be observed, the hydrazonomethyl quaternary salt of the invention functioned as an efficient nucleating agent in reversal emulsions.

EXAMPLE 3

Three direct positive photographic elements (designated A, B and C) are prepared by coating a polyethylene-coated paper support material with a photosensitive layer containing:

Element A	Coverage
Internal image gelatino-silver chlorobromoiodide emulsion prepared as described in U.S. Pat. No. 2,592,250	30 mg. silver/ft.²
	200 mg./ft.²
Dye-forming coupler: 2-[α-(4'-tert.-amylphenoxy)-n-butyrylamino]-5-methyl-1-phenol	30 mg./ft.²
Formyl-4-phenylhydrazine	19.4 mg./ft.²
Element B	
As element A except in lieu of formyl-4-phenylhydrazine is substituted 2-methyl-3-(3-phenylhydrazonopropyl)benzothiazolium	0.027 mg./ft.²
Element C	
As element A except in lieu of 4-phenylhydrazine is substituted 2-methyl-3-[3-(p-tolylhydrazono)propyl]benzothiazolium bromide	0.027 mg./ft.²

The above three coated elements are dried and exposed through a neutral density step wedge in an Eastman model 1 B sensitometer. After exposure, each element is processed for about 2 minutes and at a temperature of 20° C., in a developing solution having the composition:

distilled water	1 l.
benzyl alcohol	12 ml.
sodium sulfite	1.5 g.
potassium bromide	1.0 g.
potassium carbonate	55 g.
5-nitrobenzimidazole	0.005 g.
4-amino-3-methyl-N-ethyl-β-(methanesulfonamide)-ethylaniline sesquisulfate hydrate	7 g.

pH is adjusted to 11.3with sodium hydroxide. After development, the elements are treated for about 3 minutes and at a temperature of 20° C., with a combination bleaching and fixing "blix" solution to remove developed silver an residual silver salts. The composition of the "blix" solution is

potassium ferricyanide	35 g.
sodium acetate	20 g.
1,8-dihydroxy-3,6-dithiaoctane	25 g.
acetic acid (glacial)	3 ml.
water to	1l.

(Adjusted to pH of 5.0 with aceitic acid.)

Subsequent to treatment in the "blix" solution, the elements are washed and dried, whereupon the processed elements exhibit a positive colored dye image. Second and third sets of elements A and C are prepared and processed in like fashion, except that the developing solution is adjusted to pH 11.15 in the second set and pH 10.0 in the third set. The photographic densities obtained from the processed elements are summarized in tabular form.

	Developing Solution pH			
	11.3		11.15	10.0
	Dmax.	Dmin.	Dmax.	Dmax.
Element A	2.36	0.18	2.29	0.44
Element B	2.32	0.25		
Element C	2.28	0.24	2.30	2.02

Using the hydrazono-substituted quaternary salts of the invention (elements B and C), advantageous positive image dye density is preserved at lower developer pH values than those obtained with related nucleating agents of the art (e.g. element A). This preservation is maintained with other known internal image emulsions, couplers and processing solutions.

EXAMPLE 4

A direct-positive photographic element is prepared as element A of example 3, except that the dye-forming coupler is deleted, in lieu of formyl-4-phenylhydrazine is substituted 2-methyl-3-[3-(p-sulfophenylhydrazono)propyl]benzothiazolium bromide at a coverage of 0.027 mg./ft.² and the spectral sensitizing dye anhydro-5,5' -**dichloro**-9-ethyl-3,3'-**di**(3-sulfopropyl)oxacarbocyanine hydroxide sodium salt is added at a coverage of 30 mg./ft.². After drying, the composite element is exposed and processed as in example 2 to yield a reversal silver image of a quality commensurate with that of element 2 in example 2.

EXAMPLE 5

A direct positive photographic element is prepared as in example 4 except that a like amount of 1-(p-carboxyphenylhydrazono)propyl-2,3,3-trimethyl-3trimethyl-3H-indolium bromide is employed as the nucleating agent in lieu of 2-methyl-3-[3-(p-sulfophenylhydrazono)propyl]benzothiazolium bromide. Exposure and processing are as in example 4 and a silver reversal image of commensurate quality is produced.

EXAMPLE 6

Two direct positive photographic elements are prepared as in example 4 except that like amounts of 2 -methyl- 3 -[3-p-toluenesulfonylhydrazono)pentyl]naphtho [2,1-d]thiazolium iodide and 2-methyl-3-[3-(p-sulfonphenylhydrazono)pentyl]benzothiazolium iodide respectively are employed as the nucleating agents. Exposure and processing are as in example 4, and a silver reversal image of commensurate quality is produced.

The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

We claim:

1. A negative-type silver halide emulsion containing from 0.001 to 10 grams per mole silver halide of a heterocyclic quaternary salt comprising a heterocyclic nucleus containing a heterocyclic ring of five to six atoms including a quaternary nitrogen atom, said quaternary nitrogen atom having substituted thereon a single radical having the formula $-CH_2)_n-$ R wherein:

a. *n* represents a positive integer of from 2 to 6, and

b. R represents a member selected from the group consisting of:

1. a formyl radical,

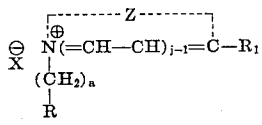
2. a radical having the formula



wherein T_1 and T_2, when taken alone, each represents a member selected from the group consisting of an alkoxy radical and an alkylthio radical, and T_1 and T_2, when taken together, represent the atoms necessary to complete a cyclic acetal selected from the group consisting of cyclic oxyacetals and cyclic thioacetals having from five to six atoms in the heterocyclic acetal ring, and

3. a 1-hydrazonoalkyl radical.

2. A negative-type silver halide emulsion containing from 0.001 to 10 grams per mole silver halide of a quaternary salt having the formula:



wherein:

a. Z represents the atoms necessary to complete a heterocyclic nucleus containing a heterocyclic ring of five to six atoms including the quaternary nitrogen atom, with the additional atoms of said heterocyclic ring being selected from the group consisting of carbon, nitrogen, oxygen, sulfur and selenium,

b. *j* represents a positive integer of from 1 to 2,

c. *a* represents a positive integer of from 2 to 6,

d. $X^{\ominus}$ represents an acid anion,

e. R represents a member selected from the group consisting of:

1. a formyl radical,

2. a radical having the formula



wherein T_1 and T_2, when taken alone, each represents a member selected from the group consisting of an alkoxy radical and an alkylthio radical, and T_1 and T_2, when taken together represent the atoms necessary to complete a cyclic acetal selected from the group consisting of cyclic oxyacetals and cyclic thioacetals having from five to six atoms in the heterocyclic acetal ring, and

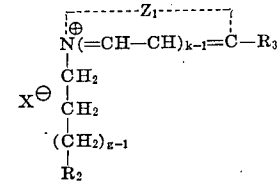
3. a 1-hydrazonoalkyl radical, and

f. R_1 represents a member selected from the group consisting of a hydrogen atom, a lower alkyl radical, an aralkyl radical, an alkylthio radical and an aryl radical.

3. A silver halide emulsion containing a quaternary salt as described in claim 2 wherein R_1 represents a methyl radical and $X^{\ominus}$ represents a halide anion.

4. A silver halide emulsion containing a quaternary salt as described in claim 2 wherein *a* represents an integer having a value of 2.

5. A negative-type silver halide emulsion containing from 0.001 to 10 grams per mole silver halide of a quaternary salt having the formula:



wherein:

a. Z_1 represents the atoms necessary to complete a heterocyclic nucleus containing a heterocyclic ring of five to six atoms including the quaternary nitrogen atom, with the additional atoms of said heterocyclic ring being selected from the group consisting of carbon, nitrogen, oxygen, sulfur and selenium,

b. *k* represents a positive integer of from 1 to 2,

c. *g* represents a positive integer of from 1 to 5,

d. $X^{\ominus}$ represents an acid anion,

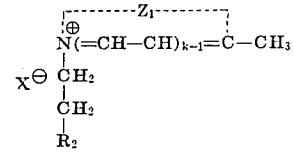
e. R_2 represents a member selected from the group consisting of a formyl radical and a radical having the formula



wherein T_3 and T_4, when taken alone, each represents a member selected from the group consisting of an alkoxy radical and an alkylthio radical and T_3 and T_4, when taken together, represent the atoms necessary to complete a cyclic acetal selected from the group consisting of oxyacetals and cyclic thioacetals having from five to six atoms in the heterocyclic acetal ring, and

f. R_3 represents a member selected from the group consisting of a hydrogen atom, a lower alkyl radical, an aralkyl radical, an alkylthio radical, and an aryl radical.

6. A negative-type silver halide emulsion containing from 0.001 to 10 grams per mole silver halide of a quaternary salt having the formula:



wherein:

a. Z_1 represents the atoms necessary to complete a heterocyclic nucleus containing a heterocyclic ring of five to six atoms including the quaternary nitrogen atom, with the additional atoms of said heterocyclic ring being selected from the group consisting of carbon, nitrogen, oxygen, sulfur and selenium,

b. *k* represents a positive integer of from 1 to 2,

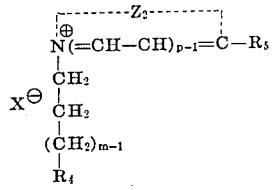
c. $X^{\ominus}$ represents a halogen anion,

d. R_2 represents a monovalent radical selected from the group consisting of a formyl radical and a radical having the formula:



wherein T_3 and T_4, when taken alone, each represents a member selected from an alkoxy radical and an alkylthio radical having from one to four carbon atoms, and T_3 and T_4, when taken together, represent the atoms necessary to compete a cyclic acetal radical selected from a 1,3-dithiolan-2-yl radical, a 1,3-dioxolan-2-yl radical, a 1,3-dithian-2-yl radical and a 1,3-dioxan-2-yl radical.

7. A direct positive silver halide emulsion containing a nucleating amount of a quaternary salt having the formula:



wherein:

a. Z_2 represents the atoms necessary to complete a heterocyclic nucleus containing a heterocyclic ring of five to six atoms including the quaternary nitrogen atom, with the additional atoms of said heterocyclic ring being selected from the group consisting of carbon, nitrogen, oxygen, sulfur and selenium,

b. *p* represents a positive integer of from 1 to 2,

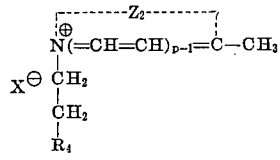
c. *m* represents a positive integer of from 1 to 5,

d. R_4 represents a 1-hydrazonoalkyl radical,

e. R_5 represents a member selected from the group consisting of a hydrogen atom, a lower alkyl radical, an aralkyl radical, an alkylthio radical and an aryl radical, and

f. X represents an acid anion.

8. A direct positive silver halide emulsion containing a nucleating amount of quaternary salt having the formula:



wherein:

a. Z_2 represents the atoms necessary to complete a heterocyclic nucleus containing a heterocyclic ring of five to six atoms including the quaternary nitrogen atom, with the additional atoms of said heterocyclic ring being selected from the group consisting of carbon, nitrogen, oxygen, sulfur and selenium,

b. *p* represents a positive integer having a value of from 1 to 2,

c. X represents an acid anion, and

d. R_4 represents a 1-hydrazonoalkyl radical.

9. A direct positive silver halide emulsion containing a quaternary salt as described in claim **8** wherein X represents a halide anion and wherein the 1-hydrazonalkyl radical represented by R_4 is selected from the group consisting of:

a. a phenylhydrazonomethyl radical,
b. a p-tolylhydrazonomethyl radical,
c. a p-sulfophenylhydrazonomethyl radical,
d. a thiosemicarbazonomethyl radical,
e. a 2-benzothiazolyhydrazonomethyl radical,
f. a p-carboxyphenylhydrazonomethyl radical,
g. a p-tolylsulfohydrazonomethyl radical,
h. a p-chlorophenylhydrazonomethyl radical,
i. a p-nitrophenylhydrazonomethyl radical,
j. an N-phenylcarbamoylhydrazonomethyl radical,
k. a 2,4-di(methylsulfo)phenylhydrazonomethyl radical,
l. a 2,4-dinitrophenylhydrazonomethyl radical,
m. a 3-quinolylhydrazonomethyl radical,
n. a 1-(phenylhydrazono)ethyl radical,
o. a 1-(phenylhydrazono)propyl radical,
p. a 1-(p-tolyhydrazono)ethyl radical,
q. a 1-(2-benzothiazolylhydrazono)propyl radical,
r. a 1-(N-phenylcarbamoylhydrazono)butyl radical,
s. a 1-(p-toluenesulfonylhydrazono)ethyl radical, and
t. a 1-(p-sulfophenylhydrazono)propyl radical.

10. A negative-type silver halide emulsion containing from 0.001 to 10 grams per mole silver halide of the quaternary salt 3-(2-formylethyl)-2-methylbenzothiazolium bromide.

11. A negative-type silver halide emulsion containing from 0.001 to 10 grams per mole silver halide of the quaternary salt 3-(3,3-diethoxypropyl)-2-methylbenzothiazolium iodide.

12. A negative-type silver halide emulsion containing from 0.001 to 10 grams per mole silver halide of the quaternary salt 3-(3,3-diethylthiopropyl)-2-methylbenzothiazolium iodide.

13. A negative-type silver halide emulsion containing from 0.001 to 10 grams per mole silver halide of the quaternary salt 3-(2-formylethyl)-2-methyllepidinium bromide.

14. A negative-type silver halide emulsion containing from 0.001 to 10 grams per mole silver halide of the quaternary salt 3-[2(1,3-dithiolan-2-yl)ethyl]-2-methylbenzothiazolium iodide.

15. A negative-type silver halide emulsion containing from 0.001 to 10 grams per mole silver halide of the quaternary salt 3-[2-(1,3-dithian-2-yl)ethyl]-2-ethylquinolium iodide.

16. A negative-type silver halide emulsion containing from 0.001 to 10 grams per mole silver halide of the quaternary salt 3-[2-(1,3-dioxan-2-yl)ethyl]-2-methylbenzoselenazolium bromide.

17. A direct-positive silver halide emulsion containing a nucleating amount of the quarternary salt 2-methyl-3-[3-(thiosemicarbazono)propyl]benzothiazolium bromide.

18. A direct-positive silver halide emulsion containing a nucleating amount of the quarternary salt 2-methyl-3-[(3-phenylhydrazono)propyl]benzothiazolium bromide.

19. A direct positive silver halide emulsion containing a nucleating amount of the quaternary salt 2-methyl-3-[3-(p-tolyhydrazono)propyl]benzothiazolium bromide.

20. A direct-positive silver halide emulsion containing a nucleating amount of the quarternary salt 2-methyl-3-[3-(p-sulfophenylhydrazono)propyl]benzothiazolium bromide.

21. A direct-positive silver halide emulsion containing a nucleating amount of the quarternary salt 2-methyl-3-[3-(2-benzothiazolylhydrazono)propyl]benzothiazolium iodide.

22. A direct positive silver halide emulsion containing a nucleating amount of the quaternary salt 3-[3-(4-carboxyphenylhydrazono)propyl]benzothiazolium bromide.

23. A direct positive silver halide emulsion containing a nucleating amount the quaternary salt 2-ethyl-3-[(4-sulfophenylhydrazono)propyl]benzothiazolium chloride.

24. A direct positive silver halide emulsion containing a nucleating amount of the quaternary salt 1-[3-(p-carboxyphenylhydrazono)propyl]-4-methylquinolium iodide.

25. A direct positive silver halide emulsion containing a nucleating amount of the quaternary salt 2-methyl-3-[3-(p-toluenesulfonylhydrazono)butylh-naphtho-[2,1-d]thiazolium iodide.

26. A direct positive silver halide emulsion containing a nucleating amount of the quaternary salt 3-[3-(p-sulfophenylhydrazono)pentyl]benzothiazolium iodide.

27. A silver halide emulsion as described in claim **7** wherein the emulsion has a dye-forming coupler compound contiguous thereto.

28. A silver halide emulsion as described in claim **7** wherein the quaternary salt is present at a concentration of from about 75 mg. to about 1,500 mg. per mole of silver halide in said emulsion.

29. A direct-positive silver halide emulsion that forms a latent images predominantly inside the silver halide grains containing, as a nucleating agent, a nucleating amount of a quaternary salt selected from the group consisting of:

a. 2-methyl-3-(3-thiosemicarbazonopropyl)benzothiazolium bromide,
b. 2-methyl-3-(3-phenylhydrazonopropyl)benzothiazolium iodide,
c. 2-methyl-3-[3-(p-tolylhydrazonopropyl)]benzothiazolium iodide,
d. 2-methyl-3-[3-(p-sulfophenylhydrazonopropyl)]benzothiazolium bromide,
e. 2-methyl-3-[3-(2-benzothiazolylhydrazonopropyl)]benzothiazolium iodide,
f. 3-[3-(4-carboxyphenylhydrazono)propyl]-2-ethylbenzothiazolium bromide,
g. 2-benzyl-3-[3-(4-sulfophenylhydrazono)propyl]benzothiazolium chloride,
h. 2-methyl-3-[3-(p-toluenesulfonylhydrazono)butyl]naphtho[2,1-d]thiazolium salt, and
i. 2-methyl-3-[3-(p-sulfophenylhydrazono)pentyl]benzothiazolium iodide.

30. A silver halide emulsion as described in claim **31** wherein the emulsion is a gelatin emulsion.

31. A silver halide emulsion as described in claim **1** wherein the silver halide is silver bromoiodide.

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