

[54] SURFACE DEVELOPMENT PROCESS UTILIZING AN INTERNAL IMAGE SILVER HALIDE EMULSION CONTAINING A COMPOSITE NUCLEATING AGENT-SPECTRAL SENSITIZING POLYMETHINE DYE

[75] Inventors: John Spence, Honeoye Falls; Donald E. Janssen, Rochester, both of N.Y.

[73] Assignee: Eastman Kodak Company, Rochester, N.Y.

[22] Filed: Feb. 12, 1971

[21] Appl. No.: 115,128

Related U.S. Application Data

[63] Continuation of Ser. No. 85,705, Oct. 30, 1970, abandoned.

[52] U.S. Cl.96/64, 96/130, 96/137, 96/139, 96/107

[51] Int. Cl.G03c 5/24

[58] Field of Search.....96/64, 130, 137, 139, 107

[56]

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Primary Examiner—J. Travis Brown

Assistant Examiner—Won H. Louie, Jr.

Attorney—R. W. Hampton, J. R. Frederick and D. M. De Leo

[57]

ABSTRACT

Polymethine dyes, including cyanine, carbocyanine, dicarbocyanine, merocyanine and styryl dyes, are useful in direct positive photographic image-forming processes when included in a light-sensitive silver halide internal image emulsion. These dyes are N-substituted with alkyl groups whose terminal carbon atom is additionally substituted with 1-hydrazonoalkyl groups. They function both as spectral sensitizers and as nucleating agents.

11 Claims, No Drawings

**SURFACE DEVELOPMENT PROCESS UTILIZING
AN INTERNAL IMAGE SILVER HALIDE
EMULSION CONTAINING A COMPOSITE
NUCLEATING AGENT-SPECTRAL SENSITIZING
POLYMETHINE DYE**

This application is a continuing application of U.S. Ser. No. 85,705, filed Oct. 30, 1970 now abandoned.

This invention relates to photography and particularly to process for preparing direct positive photographic images.

Dyestuffs, including certain polymethine cyanine dyes, carbocyanine dyes, dicarbocyanine dyes, merocyanine dyes and styryl dyes, are known in the art and known to be useful as spectral sensitizing dyes for photographic silver halide.

Heretofore, however, conventional spectral sensitizing dyes have often been characterized by a lack of compatibility with other included components of complex silver halide emulsions. As an example, it is thought that in emulsions where chemical components additional to the dye, e.g., nucleating agents, are desirably absorbed to the silver halide grain surface there is competition between these compounds and the spectral sensitizing dye for position on the grain surface. To overcome the low adsorption it is generally necessary to employ higher chemical concentrations, and this can cause undesirable sensitometric effects such as contamination of processing solutions, image staining and the like. Additionally, it is thought that the low adsorption of nucleating agents promotes agitation sensitivity and inhibits desirable image formation. It is desirable then to provide spectral sensitizing dyes that also possess additional functional capabilities, i.e., as nucleating agents in direct positive emulsions, or the like. In this manner, the second chemical component, which is thought to compete with the dye for a position on the silver halide grain, can be decreased in concentration or deleted since the dye can either assist in performing its function or assume it completely. Also, building multiple functions into a spectral sensitizing dye enables one to simplify coating formulations and thereby produce photographic elements more conveniently.

Accordingly, it is an object of this invention to provide novel direct positive photographic processes using bifunctional polymethine cyanine, carbocyanine, dicarbocyanine, merocyanine and styryl dyes.

Another object of the present invention is to provide new direct positive photographic processes using decreased concentrations of nucleating agents and having a decreased agitation sensitivity.

Still an additional object of the instant invention is to provide novel direct-positive photographic image forming processes that employ internal image emulsions containing polymethine dyes including cyanine, carbocyanine, dicarbocyanine, merocyanine and styryl dyes that are composite spectral sensitizing dyes and nucleating agents.

Yet additional objects of this invention will become apparent from a reading of the following specification and appended claims.

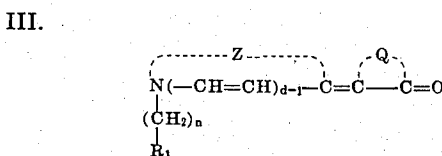
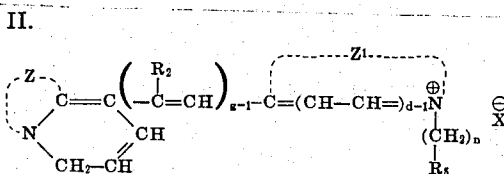
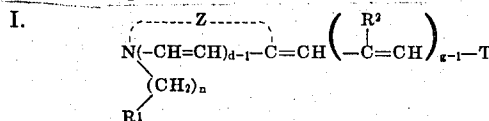
The objects of this invention are accomplished with a photographic image-forming process for the preparation of direct positive images on an imagewise exposed photographic element comprising a support having coated thereon at least one layer including a light-sensi-

tive photographic silver halide emulsion that forms latent images predominantly inside the silver halide grains, the emulsions comprising silver halide grains having a predominant amount of light-sensitivity in the internal portion of the grain, and at least one composite nucleating agent-spectral sensitizing polymethine dye comprising two terminal nuclei including at least one heterocyclic nucleus of the type used in cyanine dyes, the nucleus having a nitrogen atom joined to a polymethine carbon chain linkage intervening the terminal nuclei and including at least one nuclear carbon of the heterocyclic nucleus, the nitrogen atom having substituted thereon a member having the formula $+CH_2 \rightarrow_n R$ wherein R represents a 1-hydrazonoalkyl radical, which process comprises contacting the imagewise exposed photographic element with a surface type photographic developer and thereby producing a visible photographic image in the unexposed areas of said element.

1-Hydrazonoalkyl radicals as represented herein include radicals having a hydrazone moiety substituted on the one carbon atom of an alkyl radical. Such radicals can be unsubstituted or further substituted to provide 1-hydrazonoalkyl radicals such as a thiosemicarbazonoalkyl radical, a phenylhydrazonoalkyl radical like phenylhydrazonomethyl, 1-phenylhydrazonopropyl, p-tolylhydrazonomethyl and 1-(p-sulfophenylhydrazono)ethyl, a 2-benzothiazolylhydrazonomethyl radical and the like 1-hydrazonoalkyl radicals.

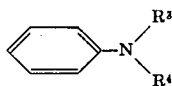
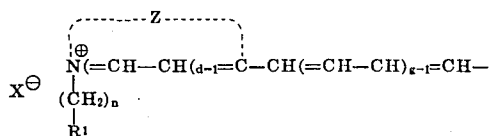
Polymethine dyes, as defined herein, include polymethine dyestuffs having an amidinium-ion system such as cyanine dyes including simple cyanine, carbocyanine, dicarbocyanine, etc., cyanine dyes wherein the prefix defines the length of the conjugated polymethine carbon bridge, as well as holopolar cyanines, hemicyanines, trinuclear cyanines, p-dialkylaminostyryl dyes and the like dye classes. Also included herein as defined by the term polymethine dyes are non-ionized, undissociated dyes containing the amidic system such as merocyanine dyes. Dyes of each of these two systems are conveniently designated herein as polymethine dyes since they exhibit a common characteristic, that being the presence of at least one nitrogen-containing heterocyclic nucleus which is joined to a conjugated polymethine carbon chain or linkage.

Exemplary polymethine dyes include dyes such as those having the formulas:



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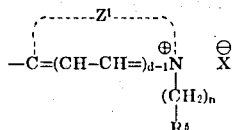
IV.



wherein:

- a. each of Z and Z¹ represents the non-metallic atoms necessary to complete a heterocyclic nucleus of the type used in the production of cyanine dyes,
- b. *d* represents a positive integer having a value of from 1 to 2,
- c. *n* represents an integer as defined above,
- d. *g* represents a positive integer having a value of from 1 to 3,
- e. T represents a member which is either:
 1. a heterocyclyl radical including a heterocyclic nucleus containing a nitrogen atom having substituted thereon a radical of the formula $\text{---CH}_2\text{---}_n\text{R}^5$ wherein *n* is as defined above and R⁵ is as defined below, and having in the heterocyclic nucleus the additional non-metallic atoms to complete a heterocyclic nucleus of the type used in the production of cyanine dyes, and
 2. a heterocyclidenemethyl radical having in the heterocyclic nucleus the non-metallic atoms, including the carbon atom of a keto group, necessary to complete a heterocyclic nucleus of the type used in merocyanine dyes, the keto group furnishing the carbonyl end of the amidic system.
- f. each of R¹ and R⁵ represents an organic substituent and at least one of R¹ and R⁵ represents a 1-hydrazonealkyl radical
- g. each of R², R³ and R⁴ represents either a hydrogen atom, an alkyl radical or an aryl radical, and preferably methyl, ethyl or phenyl,
- h. X[⊖] represents an anion including a wide variety of anions such as halide anions like bromide, chloride and iodide, as well as additional anions, e.g., sulfates including sulfate, hydrosulfate and lower alkylsulfates like methylsulfate, 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. and
- i. Q represents the non-metallic atoms necessary to complete a heterocyclic nucleus containing from 5 to 6 atoms in the heterocyclic ring, 3 to 4 of said atoms being carbon and 2 of said atoms being selected from nitrogen, oxygen or sulfur with at least one of said two atoms being nitrogen.

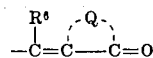
Of the polymethine dyes whose formulas are described hereinabove, advantageous members included are those wherein T represents a radical selected from a heterocyclyl radical having the formula



and

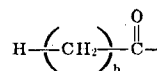
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a heterocyclidenemethyl radical having the formula:



wherein Z¹, *d*, R⁵, Q and X[⊖] are as defined above and wherein R⁶ represents a member selected from either a hydrogen atom, an alkyl radical or an aryl radical.

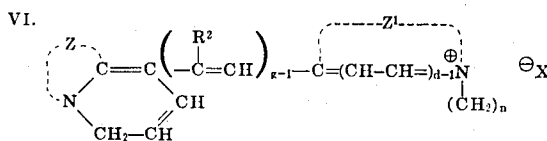
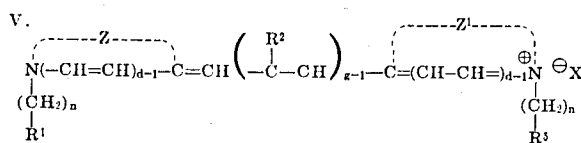
As defined herein, the term alkyl radical refers to straight and branched chain aliphatic radicals having from one to about 18 carbon atoms in the longest aliphatic chain (i.e., that chain which determines the radical nomenclature) such as methyl, ethyl, chloroethyl, phenethyl, propyl, isopropyl, n-butyl, isobutyl, tert-butyl, amyl, n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl, dodecyl, tetradecyl, pentadecyl, heptadecyl, octadecyl, and the like with alkyl radicals of from one to eight carbon atoms being preferred. The designation alkoxy radical, as that term is used herein, refers to alkoxy radicals having from one to about 18 carbon atoms in the aliphatic chain and including methoxy, ethoxy, propoxy, n-butoxy, isobutoxy, pentyloxy, octyloxy, decyloxy, dodecyloxy, pentadecyloxy, octadecyloxy and the like. Acyl radicals, as herein defined, include those having the formula



wherein *b* is an integer having a value of from 0 to about 18 and including such acyl radicals as formyl, acetyl, propionyl, hexanoyl, octanoyl, decanoyl, lauroyl, tridecanoyl, pentadecanoyl, stearoyl and the like. Preferred acyl radicals include those having from one to four carbon atoms and especially formyl. Aryl radicals are defined herein to include mono- and polycyclic aryl radicals having from six to 14 atoms in the nucleus, such as phenyl, p-tolyl, naphthyl, anthryl and the like. Heterocyclyl radicals useful herein include mono- and polycyclic radicals having from five to about 14 atoms, including at least one hetero atom, in the ring nucleus.

The alkyl, alkoxy, acyl, aryl and heterocyclyl radicals useful herein are also advantageously substituted with an additional wide variety of chemical substituents.

Of the useful polymethine dyes recited herein are included particularly advantageous cyanine carbo-cyanine and dicarbocyanine dyes having the formulas:



wherein:

- a. each of *n*, *d*, X, and R² are as previously defined.
- b. each of Z and Z¹ represent the non-metallic atoms necessary to complete a heterocyclic nucleus of the type used in the production of cyanine dyes,

and more particularly, a heterocyclic nucleus having therein at least one atom selected from either nitrogen, oxygen, sulfur or selenium,

- c. g represents a positive integer having a value of from 1 to 3,
- d. the organic substituent represented by each of R^1 and R^5 is selected from either
1. a hydrogen atom,
 2. a hydroxyl radical,
 3. a carboxyl radical,
 4. a cyano radical,
 5. an acyl radical,
 6. an acyloxy radical,
 7. an alkoxy radical,
 8. 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 containing from five to six atoms in the heterocyclic acetal ring,

9. a sulfo radical,
10. a 1-hydroxy-1-sulfoalkyl radical,
11. an aryl radical, and
12. a 1-hydrazonoalkyl radical selected from the group consisting of:
 - a 1-(thiosemicarbazono)alkyl radical,
 - a 1-(heterocyclhydrazono)alkyl radical,
 - a 1-(phenylhydrazono)alkyl radical,
 - a 1-(N-arylcabamoylhydrazono)alkyl radical,
 - a 1-(arylsulfonylhydrazono)alkyl radical, and at least one of the R^1 and R^5 represents a 1-hydrazonoalkyl radical.

The heterocyclic nuclei completed by Z and Z^1 atoms also include those containing a heterocyclic ring of from five to six atoms including a 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 either carbon, nitrogen, oxygen, sulfur or selenium atoms. The nitrogen atom is desirably substituted as described herein.

Exemplary heterocyclic nuclei completed by non-metallic Z and Z^1 atoms include those nuclei of the indole series such as indolenine; 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 like 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 such as 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, tetrahydrobenzothiazole, 5,6-dimethoxybenzothiazole, 5,6-dioxymethylenebenzothiazole, 5-hydroxybenzothiazole, 6-hydroxybenzothiazole, etc.; those of the naphthothiazole series like naphtho[2,1- d]thiazole, 8-methoxynaphtho[d]thiazole, 7-methoxynaphtho[2,1- d]thiazole etc.; those of the thionaphtheno-7', 6', 4,5-thiazole series such as 4-methoxythionaphtheno-7',6', 4,5-thiazole, etc.; those of the oxazole series for example, 4-methoxyoxazole, 5-methoxyoxazole, 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, 6-hydroxybenzoxazole, etc.; those of the naphthoxazole series such as naphtho[2,1- d]oxazole, etc.; those of the selenazole series, for example, 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 naphtho[2,1- d]selenazole; and those of the quinoline series such as quinoline, 4-methylquinoline, 5-ethylquinoline, 6-chloroquinoline, 8-chloroquinoline, 6-methoxyquinoline, 8-hydroxyquinoline, 7-methyl-4-quinoline, isoquinoline, etc.

Of the radicals described previously as represented by



especially desirable radicals include those wherein each of T^1 and T^2 , when taken alone, represents either an alkoxy or an alkylthio radical, each having from one to four carbon atoms. Other advantageous radicals of this type, but where T^1 and T^2 are taken together, include those wherein T^1 and T^2 represent the atoms necessary to complete a cyclic oxyacetal or thioacetal radical such as 1,3-dithiolan-2-yl, 1,3-dioxolan-2-yl, 1,3-dithian-2-yl or 1,3-dioxan-2-yl.

Additionally, the 1-hydroxy-1-sulfoalkyl include such members as those having alkyl radicals as are described elsewhere herein and preferably alkyl radicals having from one to two carbon atoms. It is also understood that in the case of particular dyes, the sulfo radical can be in its salt form. In merocyanine dyes, for example, the appropriate sulfo radical can be an alkali metal salt such as a sodiosulfo. Also, with certain cyanines having symmetrical 1-hydroxy-1-sulfoalkyl substitution, one such radical can exist in its salt form, i.e., as other than an internal salt, to form, for example, an alkali metal salt such as mono-sodium salt. Also, the

designation α -methine carbon atom refers to an extranuclear methine carbon atom that is directly attached to a methine carbon in a heterocyclic nucleus of the type used in cyanine dyes.

Included within the previously described range of useful 1-hydrazonoalkyl radicals are such particularly advantageous members as

- a. a phenylhydrazonomethyl radical,
- b. a p-tolyhydrazonomethyl 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-bis(methylsulfonyl)phenylhydrazonomethyl radical,
- l. a 2,4-dinitrophenylhydrazonomethyl radical,
- m. a 3-quinolyhydrazonomethyl radical,
- n. a 1-(phenylhydrazono)ethyl radical,
- o. a 1-(phenylhydrazono)propyl radical,
- p. a 1-(p-tolyhydrazono)ethyl radical,
- q. a 1-(2-benzothiazolyhydrazono)propyl radical,
- r. a 1-(N-phenylcarbamoylhydrazono)butyl radical,
- s. a 1-(p-toluenesulfonylhydrazono)ethyl radical, and
- t. a 1-(p-sulfophenylhydrazono)propyl radical.

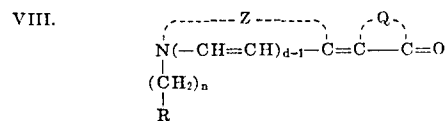
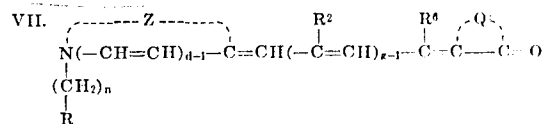
Especially desirable polymethine cyanine dyes, i.e., cyanine, carbocyanine, dicarbocyanine and the like dyes useful in the processes of the present invention are such dyes as:

- a. a 3,3'-bis(3-phenylhydrazonopropyl)thiacarbocyanine salt,
- b. a 3,3'-bis(3-phenylhydrazonopropyl)thiadicarbocyanine salt,
- c. a 3-ethyl-3'-(3-phenylhydrazonopropyl)oxathiacarbocyanine salt,
- d. a 3-(3-hydroxy-3-sulfopropyl)-3'-(3-phenylhydrazonopropyl)thiacarbocyanine salt,
- e. a 3-ethyl-9-methyl-3'-(3-phenylhydrazonopropyl)-thiacarbocyanine salt,
- f. a 3-ethyl-3'-(3-thiosemicarbazonopropyl)thiacyanine salt,
- g. a 1'-ethyl-3-(3-thiosemicarbazonopropyl)thia-2'-cyanine salt,
- h. a 3-ethyl-3'-(3-thiosemicarbazonopropyl)thiacarbocyanine salt,
- i. a 3-ethyl-3'-(3-thiosemicarbazonopropyl)oxathiacarbocyanine salt,
- j. a 3-ethyl-9-methyl-3'-(3-thiosemicarbazonopropyl)-thiacarbocyanine salt,
- k. a 3,3'-bis[3-(2-benzothiazolyhydrazono)propyl]-thiacarbocyanine salt,
- l. a 3-ethyl-9-phenyl-3'-[3-(2,4-dinitrophenylhydrazono)-propyl]selenacarbocyanine salt,
- m. a 3,3'-bis[3-(phenylcarbamoylhydrazono)butyl]-thiacarbocyanine salt,
- n. a 3,3'-bis(3-phenylhydrazonopentyl)benz[e]-indolo carbocyanine salt,
- o. a 3,3'-bis[3-(2-quinolyhydrazono)propyl]oxathiacarbocyanine salt,
- p. a 3-ethyl-3'-[3-(p-chlorophenylhydrazono)butyl]-1,1'-dimethylnaphth[1,2-d]imidazolocarbo-

cyanine salt, and

- q. a 1'-ethyl-4'-methyl-3{3-(p-toluenesulfonylhydrazono)butyl}-thia-a'-cyanine salt.

Other polymethine dyes useful in the processes of the subject invention include merocyanine dyes such as those having the formula:



wherein:

Z, g, n, d, R, R² and R⁶ are as defined above.

In the merocyanine dyes described herein, advantageous heterocyclic nuclei completed by the non-metallic atoms represented herein by Q include those of the thiazolone series, for example 2-thiazolin-4-one; those of the 2,4-thiazolidinedione series such as 2,4-thiazolidinedione, 3-alkyl-2,4-thiazolidinediones (e.g., 3-ethyl-2,4-thiazolidinedione, etc.) 3-phenyl-2,4-thiazolidinedione, 3-naphthyl-2,4-thiazolidinedione, etc., those of the 2-thio-2,4-thiazolidinedione (rhodanine) series, such as 3-alkyl-2-thio-2,4-thiazolidinedione (3-alkylrhodanines), (e.g., 3-ethyl-2-thio-2,4-thiazolidinedione (or 3-ethylrhodanine), 3-phenyl-2-thio-2,4-thiazolidinedione (3-phenylrhodanine), 3- α -naphthyl-2-thio-2,4-thiazolidinedione (3- α -naphthylrhodanine), 3-(1-benzothiazyl)-2-thio-2,4-thiazolidinedione(3-(1-benzothiazyl)rhodanine, etc., those of the 2-thio-2,5-thiazolidinedione series, such as 3-alkyl (e.g., 3-methyl, 3-ethyl, etc.)-2-thio-2,5-thiazolidinediones, etc., those of the 2-alkylmercapto-2-thiazolin-4-one series, such as 2-ethylmercapto-2-thiazolin-4-one, etc., those of the thiazolidinone series, such as 4-thiazolidinone or its 3-alkyl (e.g., ethyl, etc.), 3-phenyl or 3- α -naphthyl derivatives, those of the 2-alkylphenylamino-2-thiazolin-4-one series (e.g., 2-ethylphenylamino-2-thiazolin-4-one, etc.), those of the 2-diphenylamino-2-thiazolin-4-one series; those of the 2-thiazolin-5-one series, such as 2-ethylthio-2-thiazolin-5-one, 2-benzylthio-2-thiazolin-5-one, etc. those of the oxazolone series, for example: those of the 2-thio-2,4-oxazolidinedione series, such as 3-alkyl-2-thio-2,4-oxazolidinediones (e.g., 3-ethyl-2-thio-2,4-oxazolidinedione, etc.), those of the 2-imino-4-oxazolidinone(pseudohydantoin) series, etc.; those of the 2-oxazolinone-5-series, such as 2-phenyl-2-oxazolin-5-one, 2-ethyl-2-oxazolin-5-one, etc., those of the 2-isoxazolin-5-one series, such as 3-phenyl-2-isoxazolin-5-one, etc., those of the imidazolone series, for example: those of the hydantoin series, such as hydantoin, or its 3-alkyl-(e.g., ethyl, propyl, etc.), 3-phenyl or 3- α -naphthyl derivatives as well as its 1,3-dialkyl (e.g., 1,3-diethyl, etc.), 1-alkyl-3-phenyl (e.g., 1-ethyl-3-phenyl, etc.), 1-alkyl-3-naphthyl (e.g., 1-ethyl-3- α -naphthyl, etc.), 1,3-diphenyl, etc., derivatives, those of the 2-thio-hydantoin series, such as 2-thiohydantoin, or its 3-alkyl (e.g., 3-ethyl, etc.) 3-phenyl or 3-naphthyl derivatives as well as its 1,3-dialkyl (e.g., 1,3-diethyl, etc.), 1-alkyl-3-phenyl (e.g., 1-ethyl-3-phenyl, etc.), 1-alkyl-3-naphthyl (e.g., 1-ethyl-3- α -naphthyl), 1,3-diphenyl, etc., derivatives, those of the 2-alkylmercap-

to-2-imidazolin-5-one series, such as 2-n-propylmercapto-2-imidazolin-5-one; those of the thionaphthenone series, such as 2(3H)-benzothiophenone or 3(2H)-benzothiophenone; those of the pyrazolone series, such as 2-pyrazolin-5-one or its 1-alkyl (e.g., methyl, ethyl, etc.) 1-phenyl, 1-naphthyl (e.g., 1- α -naphthyl), 3-alkyl (e.g., methyl, ethyl, etc.), 3-phenyl, 3-naphthyl (3- α -naphthyl), 1-alkyl-3-phenyl (e.g., 1-methyl-3-phenyl, etc.), 3-alkyl-1-phenyl (e.g., 3-methyl-1-phenyl, etc.), 1,3-dialkyl (e.g., 1,3-dimethyl, etc.), 1,3-diphenyl, etc., derivatives; those of the oxindole series, such as 3(2H)-indolinone, and like five-membered heterocyclic nuclei; those of the 2,4,6-triketohexahydropyrimidine series, for example, (2,4,6-triketohexahydropyrimidine) {barbituric acid}, 2-thio-2,4,6-triketohexahydropyrimidine {2-thiobarbituric acid} as well as their 1-alkyl (e.g., 1-ethyl, etc.), or 1,3-dialkyl (1,3-diethyl, etc.) derivatives.

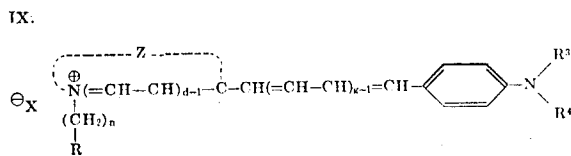
Especially advantageous merocyanine dyes include those wherein the heterocyclic nucleus completed by the atoms represented by Z is either an indole nucleus, an imidazole nucleus, an oxazole nucleus, a thiazole nucleus, a selenazole nucleus, or a quinoline nucleus, and wherein the heterocyclic nuclei completed by atoms represented by Q is either a thiazolone nucleus, a 2-thio-2,4-thiazolidinedione nucleus, a 2-thio-2,5-thiazolidinedione nucleus, a 2-alkylmercapto-2-thiazolin-4-one nucleus, a thiazolidin-one nucleus, e.g., 4-thiazolidinone, a 2-alkylphenylamino-2-thiazolin-4-one nucleus, a 2-diphenylamino-2-thiazolin-4-one nucleus, a 2-thiazolin-5-one nucleus, a 2-thio-2,4-oxazolinedione nucleus, a pseudohydantoin nucleus, a 2-oxazolin-5-one nucleus, a 2-isoxazolin-5-one nucleus, a hydantoin nucleus, a 2-thiahydantoin nucleus, a 2-alkylmercapto-2-imidazolin-5-one nucleus, a benzothiophenone nucleus, a 2-pyrazolin-5-one nucleus, a oxindole nucleus, a (2,4,6-triketohexahydropyrimidine) barbituric acid nucleus, and a 2-thiobarbituric acid and wherein n represents a positive integer having a value of 2.

Preferred merocyanine dyes useful in the process of this invention include such dyes as:

- a. 3-ethyl-5-{{3-((3-(N-phenylcarbonylhydrazono)-hexyl))-2-benzothiazolinylidene}ethylidene} rhodanine
- b. 3-ethyl-5-{{3-((3-p-nitrophenylhydrazonopropyl))-2-benzothiazolinylidene}ethylidene} rhodanine
- c. 5-{{3-((3-(2-benzothiazolylhydrazono)butyl))-2-benzothiazolinylidene}ethylidene}-3-ethylrhodanine
- d. 3-ethyl-5-{{3-((3-quinolyldiazonopropyl))-2-benzoselenazolinylidene}ethylidene} rhodanine
- e. 3-ethyl-5-{{3-((3-thiosemicarbazonopropyl))-2-benzothiazolinylidene}ethylidene} rhodanine
- f. 3-ethyl-5-{{3-((3-phenylhydrazonopropyl)benzothiazolinylidene}ethylidene} rhodanine
- g. 3-ethyl-1-phenyl-5-{{3-((3-phenylhydrazonobutyl))-2-benzothiazolinylidene}-2-thiohydantoin
- h. 1,3-diethyl-5-{{3-((3-thiosemicarbazonopropyl))-2-benzothiazolinylidene}ethylidene} barbituric acid
- i. 3-ethyl-5-{{3-((2-formylethyl))-2-benzoselenazolinylidene} rhodanine

- j. 5-[[3-((3,3-dimethoxypropyl))-2-benzothiazolinylidene]-3-ethyl-1-phenyl-2-thiohydantoin
- k. 1,3-diethyl-5-[[3-((3-p-sulfophenylhydrazonopropyl))-2-benzothiazolinylidene]-2-thiobarbituric acid
- l. 5-[[3-((3-hydroxy-3-sulfopropyl))-2-benzothiazolinylidene]-3-phenylrhodanine

Other polymethine dyes useful in this invention include styryl dyes such as those having the formula:



wherein Z, X, d, n, g, R, R³ and R⁴ are as defined above. Especially advantageous styryl dyes include those wherein n is 2, wherein the heterocyclic nuclei completed by the atoms represented by Z is either an indole nucleus, an imidazole nucleus, an oxazole nucleus, a thiazole nucleus, a selenazole nucleus or a quinoline nucleus such as those described hereinabove, and wherein the hydrazonomethyl radical represented by R is either a thiosemicarbazonomethyl radical, a phenylhydrazonomethyl radical, a p-tolylhydrazonomethyl radical, a p-sulfophenylhydrazonomethyl radical and a 2-benzothiazolyl radical.

Preferred styryl dyes include such dyes as:

- a. a 2-p-dimethylaminostyryl-3-((3-thiosemicarbazonopropyl)benzothiazolium salt,
- b. a 2-p-dimethylaminostyryl-3-((3-phenylhydrazono) benzothiazolium salt,
- c. a 2-p-diethylaminostyryl-3-[[3-((p-sulfophenylhydrazono)propyl)]benzothiazolium salt,
- d. a 2-p-diphenylaminostyryl-3-[[3-((p-chlorophenylhydrazono)propyl)]benzothiazolium salt,
- e. a 2-p-dimethylaminostyryl-3-[[3-((2,4-dinitrophenylhydrazono)butyl)]benzothiazolium salt, and
- f. a 2-p-dimethylaminostyryl-3-[[3-((N-phenylcarbonylhydrazono)hexyl)]benzothiazolium salt.

A wide variety of other useful polymethine merocyanine and styryl dyes, having an extensive range of 1-hydrazonoalkyl substituents, such as those recited elsewhere herein can be used in the present process.

The polymethine dyes of this invention, including cyanine, merocyanine and styryl dyes, are prepared from N-substituted cyclammonium quaternary salts.

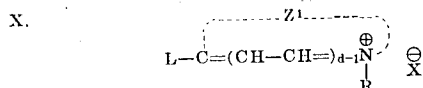
Preparation of these reactive cyclammonium quaternary salts is comprehensively described in the Lincoln and Heseltine application entitled REACTIVE QUATERNARY SALTS AND THEIR PREPARATION, Ser. No. 28,041, filed Apr. 13, 1970 now U.S. Pat. No. 3,615,615. Their synthesis is conveniently effected by the reaction of a hydro salt of a heterocyclic alkyl base with an aliphatic organic compound having ethylenic unsaturation between the first and second carbon atoms. The reaction medium is advantageously an inert solvent that exhibits moderate polarity and dissolves both the acid anion and the quaternary salt reagents, but which is not a solvent for the reaction product. Exemplary of such media are such solvents 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, e.g., reflux conditions, so long as the reagents remain in solution and are not subjected to heating in excess of their decomposition temperatures. The reaction products either precipitate from solution spontaneously or can be precipitated such as by addition of ether and can then be purified by such conventional means as solvent washes or crystallization. As a specific example, 3-(2-formylethyl)-2-methylbenzoselenazolium bromide is prepared by reacting 2-methylbenzoselenazolium hydrobromide and acrolein in dimethylacetamide as a solvent. The reaction is carried out at about 20°C (room temperature) and the reaction product is obtained as a precipitate.

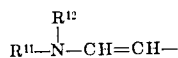
The herein described quaternary salts can be utilized to prepare polymethine dyes including cyanine, carbocyanine, dicarbocyanine, merocyanine and styryl dyes. Such dye preparations are conventionally accomplished by means of typical dye condensation reactions.

Cyanine dyes described above which are free from an N- α alkenylene bridge can be prepared by reacting a cyclammonium quaternary salt, such as one of Ser. No. 28,041, mentioned above, with a suitable agent. Symmetrical cyanine dyes are conveniently prepared by reacting the quaternary salt with an ortho ester such as diethoxymethylacetate, diethoxyethyl acetate, ethyl orthoformate, ethyl orthoacetate, ethyl orthopropionate, 1,3,3-trimethoxypropene, etc. By suitably substituting the ortho ester, for example as noted previously, carbon atoms of the conjugated methine chain can be advantageously substituted with a variety of substituents such as alkyl radicals, and aryl radicals like those described above.

Symmetrical and non-symmetrical cyanine dyes are prepared by reacting the quaternary salt with an intermediate such as one having the formula:



wherein d , R , Z^1 and X are as described above and L represents either a vinyl radical itself substituted with either a halogen atom such as chlorine, an alkyl or arylmercapto group (e.g., methylmercapto, ethylmercapto, phenylmercapto and additionally with alkyl or aryl radicals, etc.) or represents the group

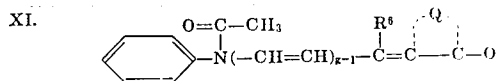


wherein R^{11} represents an acyl radical such as acetyl, propionyl, butyryl, benzoyl, etc. (e.g., an acyl group having from two to seven carbon atoms), and R^{12} represents either a hydrogen atom, an alkyl radical or an aryl radical such as those described hereinabove.

These reactions used to prepare the cyanine dyes are advantageously accelerated by heating the reaction

mixture, with temperatures varying from room temperature to reflux temperature of the reaction mixture being satisfactory. The reactions can be carried out in the presence of an inert diluent such as nitrobenzene, ethanol, n-propanol, butyrolacetone, acetonitrile, chloroform, dimethylformamide, pyridine, acetic anhydride, dimethylacetamide, etc. After dye formation, the resultant product is typically obtained and purified by filtration and recrystallization from an inert diluent such as an alcohol like methanol or ethanol.

Merocyanine dyes useful in the processes of this invention are conveniently prepared by condensing a quaternary salt as mentioned previously with an intermediate having the formula:



wherein Q , g and R^6 are as previously defined. The condensations can advantageously be carried out in the presence of a basic condensing agent, e.g., the organic tertiary amines, such as triethylamine, tri-n-propylamine, triisopropylamine, tri-n-butylamine, etc., N-methylpiperidine, N-ethylpiperidine, N,N-dimethylaniline, N,N-diethylaniline, etc. The condensations can advantageously be effected in the presence of an inert solvent, e.g., ethanol, n-propanol, isopropanol, 1,4-dioxane, pyridine, quinoline, etc. Heating accelerates the condensations and temperatures varying from room temperature to the reflux temperature of the solvent in the reaction mixture are used. Simple merocyanine dyes are prepared in a similar fashion but preferably wherein the reactive substituent on the quaternary salt is desirably alkylthio, arylthio, halo or sulfo, and wherein the intermediate is the ketomethylene compound of formula XII.

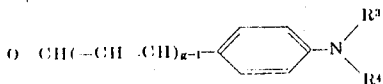
The merocyanine dyes described herein are also produced advantageously by reacting the cyclammonium quaternary salt with N,N'-diphenylformamidine, α -anilinoacrolein anil hydrochloride, or glutaconaldehyde dianilide hydrochloride and then refluxing with acetic anhydride to make the 3-acetanilidomethylene, the 3-acetanilidobutadienyl, or the acetanilidohexatrienyl derivative respectively of the salt of Formula XII which is then condensed with the ketomethylene intermediate having the formula:



wherein Q is as defined previously. This condensation reaction is advantageously carried out in the presence of any of the basic condensing agents listed previously, in an inert solvent and at temperatures between room temperature and the reflux temperature of the solvent in the reaction mixture.

The styryl dyes useful in the processes of our invention are conveniently prepared by condensing the quaternary salt with an intermediate used to produce a styryl dye, said intermediate being an aldehyde having the formula:

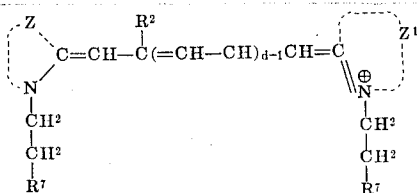
XIII.



wherein R^3 , R^4 and g are as described previously. This condensation is advantageously effected in the presence of a basic condensing agent, such as a piperidine, or others as described previously, and in the presence of an inert solvent, such as have been described for the merocyanine synthesis. Heat accelerates the reaction which is conveniently carried out between room temperature and the reflux temperature of the solvent.

In addition to the cyanine dyes whose preparations are described hereinabove, such dyes which include an N,α -alkenylene bridge are advantageously prepared for use in the subject processes. These N,α -alkenylene dyes are prepared from preformed dyes such as those having the formula:

XIV.



wherein Z , Z^1 , d , g , R^2 , R , X^\ominus and T are as previously defined and wherein R^7 represents either a formyl radical, a dialkoxymethyl radical or a dialkylthiomethyl radical. Preparation is accomplished by heating the preformed, purified dye in an organic solvent medium such as, for example, butyrolactone, acetic acid, dimethylformamide, etc., at a temperature above about 50°C . and below the decomposition temperatures of the reagent or resultant cyclized N,α -alkenylene dye. Advantageously, reflux conditions can be utilized. The cyclized dye so obtained is typically purified by filtration, drying and washing.

The dyes of the present process are useful in spectrally sensitizing photographic silver halide emulsions such as internal image emulsions when incorporated therein. The dyes are especially useful for extending the spectral sensitivity of emulsions such as silver chloride, silver chlorobromide, silver bromide, silver bromoiodide and silver chlorobromoiodide emulsions using a hydrophilic colloid carrier such as gelatin, its water-soluble derivatives, polyvinyl alcohol, its water-soluble derivatives and copolymers, water-soluble vinyl polymers, such as polyacrylamide, imidized polyacrylamide, etc., and other water-soluble film-forming materials that form water-permeable coatings, such as colloidal albumin, water-soluble cellulose derivatives like ethylanolamine cellulose acetate, etc.

The binding agents (carriers) for the emulsion layer of a photographic element can also contain dispersed polymerized vinyl compounds. Certain 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 of latex copolymers of alkyl acrylates and methacrylates, acrylic acid sulfoalkyl acrylates or methacrylates and the like. To prepare emulsions sensitized with one or more of the dyes described herein, it

is only necessary to disperse the dye or dyes in the emulsions. The methods of incorporating dyes in emulsions are simple and well known to those skilled in the art. In practice, it is convenient to add the dyes to the emulsion in the form of a solution in a suitable solvent. Methanol, ethanol, propanol, etc., acetone and pyridine are used to advantage. The dyes are advantageously incorporated in the finished washed emulsions, and should be uniformly distributed throughout the emulsions.

To prepare a hydrophilic colloid-silver halide emulsion sensitized with one or more of the dyes described herein, one can employ the following procedure. A quantity of dye is dissolved in a suitable solvent, such as an alcohol, acetone, pyridine, etc., and a volume of this solution, which may be diluted with water, containing the dye, is slowly added to, for example, a gelatino-silver halide emulsion, with stirring. Stirring is continued until the dye is uniformly dispersed in the emulsion to inhibit undesirable chemical or physical effects.

The above statements are only illustrative, as it will be apparent that the dyes can be incorporated in photographic emulsions by any of the other methods customarily employed in the art, e.g., by bathing a plate or film upon which an emulsion is coated in a solution of the dye in an appropriate solvent. However, bathing methods are ordinarily not to be preferred. Emulsions sensitized with the dyes can be coated on suitable supports to prepare composite photographic elements. Typical supports include cellulose nitrate film, cellulose ester film, poly(vinyl acetal) film, polystyrene film, poly(ethylene terephthalate) film, polycarbonate film and related films or resinous materials, as well as glass, paper, metal and the like. Typically, a flexible support is employed, especially a paper support, which can be partially acetylated or coated with baryta and/or an alphaolefin polymer, particularly a polymer of an alpha-olefin containing two to 10 carbon atoms such as polyethylene, polypropylene, ethylenebutene copolymers and the like.

In certain instances, the emulsions used with this invention can be sensitized with chemical sensitizers, such as with reducing agents; sulfur, selenium or tellurium compounds; gold, platinum or palladium compounds; or combinations of these. Suitable procedures are described in Porter James & Lowe, U.S. Pat. No. 3,206,313.

The silver halide emulsions sensitized by the dyes of this invention can also be protected against the production of fog and can be stabilized against loss of sensitivity during keeping. Suitable antifoggants and stabilizers each used alone or in combination include thiazolium salts described in Staud U.S. Pat. No. 2,131,038 and Allen U.S. Pat. No. 2,694,716; the azaindenes described in Piper U.S. Pat. No. 2,886,437 and Heimbach U.S. Pat. No. 2,444,605; the mercury salts as described in Allen U.S. Pat. No. 2,728,663; the urazoles described in Anderson U.S. Pat. No. 3,287,135; the sulfocatechols described in Kennard U.S. Pat. No. 3,236,652; the oximes described in Carroll et al. British Pat. No. 623,448; nitron; nitroindazoles; the mercaptotetrazoles described in Kendall et al. U.S. Pat. No. 2,403,927; Kennard et al. U.S. Pat. No. 3,266,897 and Luckey et al. U.S. Pat. No. 3,397,987; the polyvalent metal salts described in

Jones U.S. Pat. No. 2,839,405; the thiuronium salts described in Herz U.S. Pat. No. 3,220,839; the palladium, platinum and gold salts described in Trivelli U.S. Pat. No. 3,566,263 and Damschroder U.S. Pat. No. 2,597,915.

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 photographic silver halide emulsions or coatings disclosed herein can also contain non-ionic, anionic and/or amphoteric coating aids. Some useful coating aids include, for example, saponin, alkyl substituted aryloxy 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. 2,832,123, issued Feb. 11, 1958, taurine derivatives of the type described in U.S. Pat. No. 2,739,891 issued 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 emulsions of the type described herein include the alkylphenoxy poly(hydroxyalkylene oxides) such as alkylphenoxy poly(glycidols) having from about 5 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

To prepare such photographic elements as are described herein, at least one silver halide emulsion of the disclosed type and containing at least one of the dyes used in this invention is coated onto a typical photographic support material and dried. Coating can be accomplished by a wide variety of techniques including hopper coating, flow coating, etc. Advantageous support materials include conventional photographic film base materials such as those described elsewhere herein.

The dyes described herein, bearing 1-hydrazonoalkyl substitution, are especially advantageous when used in silver halide internal image emulsions (i.e., those silver halide emulsions which form latent images predominantly inside the silver halide grains and which have a predominant amount of radiation sensitivity in the internal portion of the silver halide grains). More specifically, internal image emulsions include those having silver halide grains wherein a predominant amount of the sensitivity is internal to the grains. Such internal image-forming emulsions are those which, when measured according to normal photographic techniques by coating a test portion of the emulsion on a transparent support, exposing to a light intensity scale having a fixed time between 1×10^8 and 1 second, bleaching 5 minutes in a 0.3 percent potassium ferricyanide solution at 65°F. and developing for about 5 minutes at 65°F. in Developer B below (an "internal-type" developer), have a sensitivity, measured at a density of

0.1 above fog, greater than the sensitivity of an identical test portion which has been exposed in the same way and developed for 6 minutes at 68°F. in Developer A below (a "surface-type" developer), e.g., one having no substantial silver halide solvent action.

DEVELOPER A

10	N-methyl-p-aminophenol sulfate	0.31 g.
	Sodium sulfite, desiccated	39.6 g.
	Hydroquinone	6.0 g.
	Sodium carbonate, desiccated	18.7 g.
	Potassium bromide	0.86 g.
	Citric acid	0.68 g.
	Potassium metabisulfite	1.5 g.
15	Water to make 1 liter	

DEVELOPER B

20	N-methyl-p-aminophenol sulfate	2.0 g.
	Sodium sulfite, desiccated	90.0 g.
	Hydroquinone	8.0 g.
	Sodium carbonate, monohydrate	52.5 g.
	Potassium bromide	5.0 g.
	Sodium thiosulfate	10.0 g.
	Water to make 1 liter	

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 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.

Still another advantageous method of preparing an internal image emulsion is described in McBride, U.S. Pat. No. 3,271,157 wherein a water-soluble silver salt and a water-soluble halide are reacted to precipitate the silver halide under acidic conditions. The pH of the silver halide precipitation is typically less than 6 and preferably less than 5. Such acids as phosphoric, trifluor-acetic, hydrobromic, hydrochloric, sulfur and nitric are typically utilized in the silver halide precipitating media to maintain acidic conditions. An excess of water-soluble halide is more generally used. The pAg during the silver halide precipitation is more generally about 8 to 10. The present silver halide emulsions can be washed after precipitation such as by the methods described in U.S. Pat. Nos. 2,614,929 and 2,618,556. The silver halide grains of the emulsions of

the invention generally have an average grain size of about 0.1 to 10 microns, and more generally about 0.5 to 2 microns, in diameter.

Although silver halide emulsions are generally made with an equivalent or slight excess of halide ion present, it is desirable to add additional water-soluble halide, particularly iodide, to the silver halide emulsion after its precipitation but before it is coated. More generally, about 0.1 to 50 mole percent, and preferably about 1 to 10 mole percent of water-soluble halide based on the silver halide in the emulsion are present in these emulsions. Illustrative water-soluble halides include the ammonium, lithium, magnesium, potassium, and sodium halide salts.

When incorporated into internal image emulsions suitable for reversal processing to prepare a directly developed positive photographic image without an intermediate developed negative image, the 1-hydrazonoalkyl substituted dyes described herein are advantageous as a composite spectral sensitizer-nucleating agent. Conventionally, at least one hydrazonoalkyl dye is added, typically as a solution and with stirring, to a silver halide reversal emulsion of the internal image type mentioned above such as, for example, those described in U.S. Pat. Nos. 2,566,180 or 2,592,250. The dye is added in an amount designed to produce adequate fog in the form of minute surface development sites, thereby fostering the production of direct positive images upon development. The subject dyes 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. As such, advantageous nucleation is obtained with the utilization of a diminished amount of fogging agent. As a result, desirable sensitometric characteristics are more easily preserved since less fogging agent is released into developer solutions. Additionally, tight adsorption to the silver halide grain appears to decrease agitation sensitivity of the emulsion. By agitation sensitivity is meant the tendency to develop an image of lower density when the processing solution is agitated by stirring or the like.

Generally, nucleating amounts of from about 50 to about 1,500 mg. of the subject fogging agents per mole of silver in the silver halide emulsion are useful with from about 200 to about 500 mg. 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, e.g., higher concentrations, can be advantageously used. Subsequent to the addition of at least one of the hydrazonoalkyl or acyl substituted dyes described herein, the internal image emulsion can be coated on a support material as described herein to prepare a light-sensitive photographic element capable of producing direct positive images upon imagewise exposure and suitable chemical processing.

The nucleating or fogging hydrazonoalkyl substituted dyes used in 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 coupler con-

tiguous to silver halide emulsion layers capable of recording light substantially complementary in color to the color of dye produced with respective couplers on color development as described in U.S. Pat. Nos. 3,227,550 and 3,227,552. Spectral sensitizing dyes such as the present nucleating dyes or other sensitizers either alone or in combination 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-amylyphenoxy 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-amy-p-benzoylacetamino benzene sulfonate. 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 dyes are immersed in a conventional surface developer solution having relatively low solvent action on silver halide whereupon a positive, black and white, photographic silver 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. (1966) 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.

In addition to their advantageous use as nucleating agents in direct positive elements, the hydrazonoalkyl substituted dyes described herein are desirable as halogen acceptors in internal image emulsions which are useful as light-developable, direct-print photographic emulsions. A detailed presentation of their use in direct print emulsions appears in an application of Lincoln and Heseltine entitled DYESTUFFS AND SPECTRAL SENSITIZERS FOR SILVER HALIDE, filed concurrently and presently copending herewith. Generally, these internal image emulsions are similar to those described above in conjunction with the direct positive processing sequence. They are distinguished, however, as regards the process for preparing these internal image emulsions since the photographic requirements of direct positive and direct print uses demand different photographic and chemical capabilities for specific emulsion formulations. Direct positive elements are chemically developed with a processing bath

to produce an image. The developing-out type of photographic element, as the name implies, requires that the exposed material be chemically developed and fixed in order to provide a stable visible image. The print-out type of photographic element develops on exposure and requires no solution development step. The print-out type is generally much slower than the developing-out type, and the images tend to be less stable.

Especially useful internal image silver halide emulsions for direct print include those described in McBride, U.S. Pat. No. 3,271,157, which are prepared in the presence of lead ions. Lead ions can be used in the precipitation or formation of the silver halide used in the emulsions useful herein. Water-soluble lead salts are typically added with a water-soluble silver salt to an appropriate water-soluble halide to precipitate a lead-silver halide. The amount of lead used in the described silver halide internal image emulsions generally ranges from about 0.01 to 5 mole percent based on the silver. The use of such lead ions in the formation of the silver halide facilitates the reduction of background density (D_{min}) while exhibiting increased image density (D_{max}) when exposed to a high intensity light source and photodeveloped by exposure to a lower intensity light source.

Additionally, direct-print silver halide emulsions desirably contain silver halide grains grown or formed in the presence of an organic thioether silver halide solvent, typically in solution form. Aqueous solutions of suitable organic thioether silver halide solvents utilized during the grain growth or formation of the silver halide grains have a greater solubility for silver chloride than water. More specifically, such thioether silver halide solvents are those which, when utilized in aqueous solutions at 0.02 molar concentrations and at 60°C, are capable of dissolving more than twice the amount (by weight) of silver chloride than that which can be dissolved by water at 60°C.

The thioether silver halide solvent can be added to the silver halide emulsion at any stage of the preparation thereof before the silver halide grains have attained their ultimate size and shape, for example by being added to the colloidal material in which the silver halide is precipitated by being added in combination with one of the water-soluble salts utilized to form the silver halide, such as with the water-soluble silver salt (e.g., silver nitrate) or with a water-soluble halide such as an alkali metal halide, by being added to the silver halide prior to or during the ripening of the silver halide, or by being added during one or more of such emulsion preparation steps. The amount of thioether silver halide solvent utilized can be widely varied depending on the effect desired, the nature of the thioether utilized and related variables.

Typical organic thioether silver halide solvents that can be suitably utilized contain at least one moiety wherein oxygen and sulfur atoms are separated by an ethylene radical (e.g., $-O-CH_2CH_2-S-$). Generally, the silver halide solvents have one to three thioether atoms ($-S-$) although silver halide solvents having more than three thioether atoms can be utilized. Preferred thioether silverhalide solvents are described in detail in McBride, U.S. Pat. No. 3,271,157, especially from column 2, line 36, to column 3, line 26.

The concentrations of the subject hydrazonoalkyl substituted dyes employed as halogen acceptors in direct print elements are typically widely variable in accordance with usual practice. Generally, from about 0.1 to 100 mole percent, and preferably from about 1 to 50 mole percent, based on the silver halide in the emulsion, is used.

Photodevelopable photographic silver halide emulsions of the type described herein can contain other halogen acceptors as well as the addenda generally utilized in such products including spectral sensitizing dyes, hardeners, plasticizers, coating aids, and the like. Coating the composite emulsion onto a support such as those described herein is conveniently accomplished by usual methods such as those previously mentioned.

The formation of a light-developed image with a typical photographic element containing a direct-print emulsion as described herein can be accomplished by the following procedure.

The photographic element is initially exposed to a relatively short duration and high intensity source of electromagnetic radiation (e.g., at least about .1 foot-candle second at an intensity light source of the type used in oscillographs described in Heiland, U.S. Pat. No. 2,580,427, issued Jan. 1, 1952. The light source can emit various types of radiation, e.g., high intensity visible light, X-radiation and the like, to form a latent image in the emulsion of the photographic element. Typical suitable high-intensity light sources are mercury vapor lamps that have high blue and ultraviolet emission, xenon lamps that emit light of wavelengths similar to daylight, and tungsten lamps that have high red light emission. After a high intensity exposure, the resulting latent image is photo-developed by overall exposure of the emulsion to a radiation source (e.g., at least about 0.0001 foot-candle second) of lower intensity than the original exposure, such as to a conventional fluorescent light, light from incandescent lamps commonly used for general illumination, or even ordinary daylight. Generally, the latent image formed in the emulsion in the first instance is not visible and does not become visible until photodevelopment. Heat is desirably utilized during the photodevelopment step. Typically the emulsions are heated to a temperature of about 90°C. to 200°C. for about 1 to 30 seconds and photodeveloped after the initial high intensity exposure.

If desired, photographic elements containing the described direct-print emulsions can be developed and fixed in aqueous chemical developing-out and fixing solutions after the initial exposure forming the latent image, or after the abovedescribed photodevelopment, to make archival-quality records. Developing agents can be incorporated in the emulsions of the invention including such developing agents as hydroquinones, catechols, amino-phenols, 3-pyrazolidones and the like.

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

EXAMPLE 1

Four photographic elements (A-D) are prepared as follows: A polyethylene coated paper support material is coated with a light-sensitive layer containing an internal image silver halide emulsion as described in Exam-

ple 1 of U.S. Pat. No. 2,592,250 at a coverage of 30 mg. Ag. per ft²; gelatine at a coverage of 200 mg. per ft²; and a cyan dye-forming coupler, 1-hydroxy-2-[Δ-(2,4-di-tert-amylphenoxy)-n-butyl]naphthamide, to prepare Element A. Elements B, C and D are prepared in a similar fashion, except that, in the case of element B, a second layer containing a nucleating formyl-4-methylphenylhydrazine (19.4 mg/ft² coverage) agent, and gelating (150.0 mg/ft² coverage) is coated over and contiguous to the light-sensitive layer.

In each of Elements C and D, a composite spectral sensitizing dye, nucleating agent is added to the light-sensitive emulsion at a concentration sufficient to produce a coverage of 0.27 mg/ft². The dye-nucleating agents are as follows:

Element C - 3,3'-di(3-phenylhydrazonopropyl)thiacarbocyanine bromide.

Element D - 3-ethyl-9-methyl-3'-(3-phenylhydrazonopropyl)thiacarbocyanine bromide.

A portion of each of the elements A-D is then exposed on an Eastman Model 1-B sensitometer, the exposure being through a 3 Log E neutral density step wedge, and thereafter processed in a developer composition including

Benzyl alcohol	12 ml.
Sodium sulfite	1.5 g.
Potassium Bromide	1.0 g.
Potassium Carbonate	55.0 g.
5-Nitrobenzimidazole	0.005 g.
4-amino-3-methyl-N-ethyl-μ-β(methanesulfonamide)ethyl-aniline	7 g.
Water to make	1 liter

After development, the elements are treated for about 3 minutes and at a temperature of 20°C with a combination bleaching and fixing "bleach-fix" solution to remove developed silver and residual silver salts. The composition of the "bleach-fix" solution is

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

(Adjusted to pH of 5.0 with acetic acid.)

Subsequent to treatment in the "bleach-fix" solution, the elements are washed and dried, whereupon the processed elements exhibit a positive colored dye image. Alternatively separate bleaching and fixing baths of the conventional type can be used. Also, a wide variety of coupler compounds which can react with the oxidation product of p-phenylene diamine, dialkyl p-phenylene diamine or the like developers for color photography can be used interchangeably or together, such as in multi-layer photographic reversal elements.

DEVELOPER pH IS ADJUSTED TO 11.3 WITH SODIUM HYDROXIDE

A second portion of each of the elements A-D is exposed and developed in a similar fashion, except that the developer pH is adjusted to 10.1. Sensitometric results are summarized in the following table:

ELEMENT	Maximum Image Density	
	Developer pH	Developer pH
A	11.3	10.1
B	1.89	.82
C	1.96	1.27
D	2.23	1.90

A	.30	.31
B	1.89	.82
C	1.96	1.27
D	2.23	1.90

As indicated by the above material, the nucleating dyes useful herein are more effective nucleating agents at lower concentrations and at lower pH values than the well known hydrazine nucleating agent of Element A.

EXAMPLE 2

Additional elements are prepared, exposed and processed as elements C & D of Example 1, but containing the following nucleating dyes.

- 3-ethyl-5-[[3-(3-thiosemicarbazonopropyl)-2-benzothiazolinyldene]ethylidene]rhodanine,
- 3-ethyl-5-[[3-phenylhydrazonopropyl]benzothiazolinyldene]ethylidene]rhodanine,
- 2-p-dimethylaminostyryl-3-(3-thiosemicarbazonopropyl)benzothiazolium salt, and
- 2-p-dimethylaminostyryl-3-(3-phenylhydrazono)benzothiazolium salt.

Desirable reversal images are produced.

EXAMPLE 3

An element (A¹) like that of Element A (In Example 1) is prepared and exposed as in Example 1. Thereafter it is divided into two portions. Another Element (D¹) like that of Element D (in Example 1) is prepared in a similar fashion, but containing sufficient nucleating dye to produce a coverage of 0.040 mg/ft² in the layer. After exposure as in Example 1, this element is also divided into two portions. One portion of each element is then processed as in Example 1, at a developer pH of 11.3 and under conditions of low developer agitation. The remaining portion of each element is processed in a like fashion, but with high developer agitation. Sensitometric results are summarized in the following table:

MAXIMUM IMAGE DENSITY

ELEMENT	MAXIMUM IMAGE DENSITY	
	Low Developer Agitation	High Developer Agitation
A ¹	2.04	1.62
D ¹	2.08	2.02

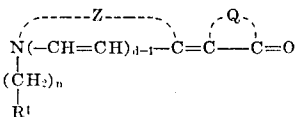
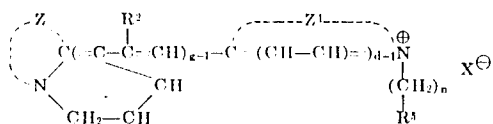
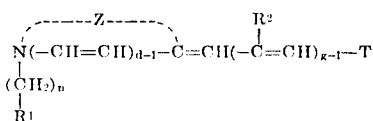
The above data indicates that the nucleating dyes useful in the present process exhibits a significantly lower agitation sensitivity than do known nucleating agents, i.e., hydrazine compounds.

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.

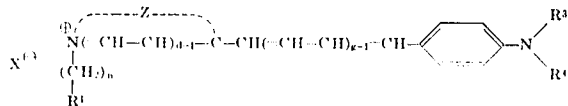
We claim;

- A photographic image-forming process for the preparation of direct positive images on an imagewise exposed photographic element comprising a support having coated thereon a light-sensitive photographic silver halide emulsion which forms latent images predominantly inside the silver halide grains, said emulsion comprising silver halide grains having a predomi-

nant amount of light sensitivity in the internal portion of said grains, and a composite nucleating agent-spectral sensitizing polymethine dye having a formula selected from the group consisting of



and

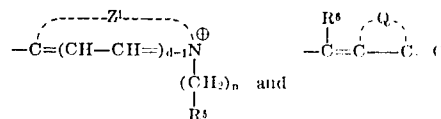


wherein:

- a. each of Z and Z¹ represents the non-metallic atoms necessary to complete a heterocyclic nucleus of the type used in cyanine dyes,
- b. d represents a positive integer having a value of from 1 to 2,
- c. n represents a positive integer having a value of from 2 to 6,
- d. g represents a positive integer having a value of from 1 to 3,
- e. T represents a member selected from the group consisting of:
 1. a heterocyclyl radical comprising a heterocyclic nucleus containing a nitrogen atom having substituted thereon a radical of the formula $\text{CH}_2 \rightarrow_n \text{R}^5$ wherein n is as defined above and R⁵ is as defined below, and having in said nucleus the additional non-metallic atoms to complete a heterocyclic nucleus of the type used in cyanine dyes, and
 2. a heterocyclidenemethyl radical having in the heterocyclic nucleus the non-metallic atoms, including the carbon atom of a keto group, necessary to complete a heterocyclic nucleus of the type used in merocyanine dyes,
- f. each of R¹ and R⁵ represents an organic substituent and at least one of R¹ and R⁵ represents a 1-hydrazonoalkyl radical,
- g. each of R², R³ and R⁴ represents a member selected from the group consisting of a hydrogen atom, an alkyl radical and an aryl radical, and
- h. X[⊖] represents an anion.
- i. Q represents the non-metallic atoms necessary to complete a heterocyclic nucleus containing from five to six atoms in the heterocyclic ring, three to four of said atoms being carbon, and two of said atoms being selected from the group consisting of

nitrogen, oxygen and sulfur, at least one of said two atoms being nitrogen, which process comprises contacting the imagewise exposed photographic element with a silver halide surface developer and thereby producing a visible photographic image in the unexposed areas of said element.

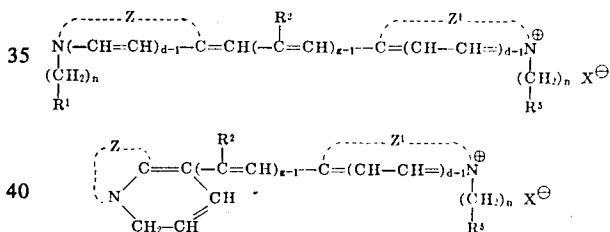
2. A photographic image-forming process as described in claim 1 wherein, in the composite nucleating agent-spectral sensitizing dye compound, the member represented by T has a formula selected from:



wherein:

- a. Z¹, d, R⁵ and X[⊖] are as previously defined,
- b. Q represents the non-metallic atoms necessary to complete a heterocyclic nucleus containing from five to six atoms in the heterocyclic ring, three to four of said atoms being carbon, and two of said atoms being selected from the group consisting of nitrogen, oxygen and sulfur, at least one of said two atoms being nitrogen, and
- c. R⁶ represents a member selected from the group consisting of a hydrogen atom, an alkyl radical.

3. A photographic image-forming process as described in claim 1 wherein said composite nucleating agent-spectral sensitizing dye compound has a formula selected from:



wherein:

- a. each of Z and Z¹ represents the non-metallic atoms necessary to complete a heterocyclic nucleus having in said nucleus at least one atom selected from the group consisting of nitrogen, oxygen, sulfur and selenium,
- b. n represents a positive integer having a value of from 2 to 6,
- c. d represents a positive integer having a value of from 1 to 2,
- d. g represents a positive integer having a value of from 1 to 3,
- e. X[⊖] represents an anion,
- f. each of R¹ and R⁵ represents a member selected from the group consisting of:
 1. a hydrogen atom,
 2. a hydroxyl radical,
 3. a carboxyl radical,
 4. a cyano radical,
 5. an acyl radical,
 6. an acyloxy radical,
 7. an alkoxy radical,
 8. a radical having the formula



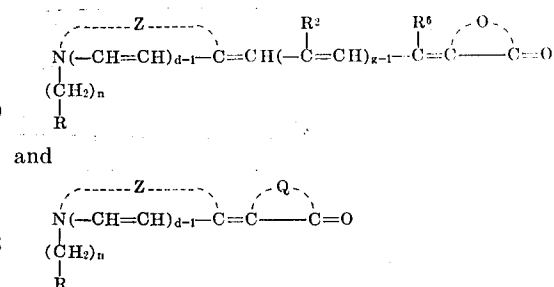
wherein T¹ and T², when taken alone, each represents a member selected from the group consisting of an alkoxy radical and an alkylthio radical, and T¹ and T², when taken together, represent the atoms necessary to complete a cyclic acetal selected from the group consisting of cyclic oxyacetals and cyclic thioacetals containing from five to six atoms in the heterocyclic acetal ring,

9. a sulfo radical,
10. a 1-hydroxy-1-sulfoalkyl radical,
11. an aryl radical, and
12. a 1-hydrazonoalkyl radical selected from the group consisting of
 - a 1-(thiosemicarbazono)alkyl radical,
 - a 1-(heterocyclylhydrazono)alkyl radical,
 - a 1-(phenylhydrazono)alkyl radical,
 - a 1-(N-arylcarbamoylethylhydrazono)alkyl radical,
 - a 1-(arylsulfonylhydrazono)alkyl radical, and at least one of R¹ and R⁵ represents a 1-hydrazonoalkyl radical.
4. A photographic image-forming process as described in claim 3 wherein, in said composite nucleating agent-spectral sensitizing dye compound:
 - a. each of Z and Z¹ represents the non-metallic atoms necessary to complete a heterocyclic nucleus selected from the group consisting of an indole nucleus, an imidazole nucleus, an oxazole nucleus, a thiazole nucleus, a selenazole nucleus and a quinoline nucleus
 - b. n has a value of 2, and
 - c. the 1-hydrazonoalkyl radical represented by R¹ or R⁵ is selected from the group consisting of
 1. a phenylhydrazonomethyl radical,
 2. a p-tolyldiazonomethyl radical,
 3. a p-sulfophenylhydrazonomethyl radical,
 4. a thiosemicarbazonomethyl radical,
 5. a 2-benzothiazolyldiazonomethyl radical,
 6. a p-carboxyphenylhydrazonomethyl radical,
 7. a p-tolylsulfonyldiazonomethyl radical,
 8. a p-chlorophenylhydrazonomethyl radical,
 9. a p-nitrophenylhydrazonomethyl radical,
 10. an N-phenylcarbamoylethylhydrazonomethyl radical,
 11. a 2,4-bis(methylsulfonyl)phenylhydrazonomethyl radical,
 12. a 2,4-dinitrophenylhydrazonomethyl radical,
 13. a 3-quinolyldiazonomethyl radical,
 14. a 1-(phenylhydrazono)ethyl radical,
 15. a 1-(phenylhydrazono)propyl radical,
 16. a 1-(p-tolyldiazono)ethyl radical,
 17. a 1-(2-benzothiazolyldiazono)propyl radical,
 18. a 1-(N-phenylcarbamoylethylhydrazono)butyl radical,
 19. a 1-(p-toluenesulfonyldiazono)ethyl radical, and
 20. a 1-(p-sulfophenylhydrazono)propyl radical.

5. A photographic image-forming process for the preparation of direct positive images on an imagewise exposed photographic element comprising a support having coated thereon a light-sensitive layer comprising a light-sensitive photographic silver halide emulsion which forms latent images predominantly inside the silver halide grains, said emulsion comprising silver halide grains having a predominant amount of light sen-

sitivity in the internal portion of said grains, and a composite nucleating agent-spectral sensitizing dye compound selected from the group consisting of

- 3,3'-bis(3-phenylhydrazonopropyl)thiacarbocyanine bromide,
- 3,3'-bis(3-phenylhydrazonopropyl)thiadicarbocyanine bromide,
- 3-ethyl-3'-(3-phenylhydrazonopropyl)oxathiadicarbocyanine iodide,
- 3-ethyl-9-methyl-3'-(3-phenylhydrazonopropyl)thiacarbocyanine bromide,
- 3-ethyl-3'-(3-thiosemicarbazonopropyl)thiacyanine bromide,
- 1'-ethyl-3-(3-thiosemicarbazonopropyl)thia-2'-cyanine bromide
- 3-ethyl-3'-(3-thiosemicarbazonopropyl)thiadicarbocyanine iodide,
- 3-ethyl-3'-(3-thiosemicarbazonopropyl)oxathiadicarbocyanine iodide,
- 3-ethyl-9-methyl-3'-(3-thiosemicarbazonopropyl)thiacarbocyanine bromide,
- a 3-ethyl-3'-(3-phenylhydrazonopropyl)oxathiadicarbocyanine iodide salt, and
- a 3-ethyl-9-methyl-3'-(3-phenylhydrazonopropyl)thiadicarbocyanine salt, which process comprises contacting the imagewise-exposed photographic element with a silver halide surface developer and thereby producing a visible photographic image in unexposed areas of said element.
6. A photographic image-forming process as described in claim 1 wherein said composite nucleating agent-spectral sensitizing dye compound has a formula selected from:



wherein:

- a. Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus having in said nucleus at least one atom selected from the group consisting of nitrogen, oxygen, sulfur and selenium,
- b. g represents a positive integer having a value of from 1 to 3,
- c. n represents a positive integer having a value of from 2 to 6,
- d. R represents a 1-hydrazonoalkyl radical, and
- e. each of R² and R⁶ represents a member selected from the group consisting of a hydrogen atom, an alkyl radical and an aryl radical, and
- f. Q represents the non-metallic atoms necessary to complete a heterocyclic nucleus containing from 5 to 6 atoms in the heterocyclic ring of said nucleus which is selected from the group consisting of a thiazolone nucleus, a 2-thio-2,4-thiazolidinedione nucleus, a 2-thio-2,5-thiazolidinedione nucleus, a

2-alkylmercapto-4(5)thiazolone nucleus, a thiazolidone nucleus, a 2-alkylphenylamino-4(5)thiazolone nucleus, a 2-diphenylamino-4(5)thiazolone nucleus, a 5(4) thiazolone nucleus, a 2-thio-2,4-oxazolidinedione nucleus, a pseudohydantoin nucleus, a 5(4) oxazolone nucleus, a 5(4)-isoxazolone nucleus, a hydantoin nucleus, a 2-thiohydantoin nucleus, a 2-alkylmercapto-5(4)-imidazolone nucleus, a thionaphthenone nucleus, a pyrazolone nucleus, an oxindole nucleus and a 2,4,6-triketohexahydropyrimidine nucleus.

7. A photographic image-forming process as described in claim 6 wherein, said composite nucleating agent-spectral sensitizing dye compound,

a. Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus selected from the group consisting of an indole nucleus, an imidazole nucleus, an oxazole nucleus, a thiazole nucleus, a selenazole nucleus and a quinoline nucleus,

b. n has a value of 2,

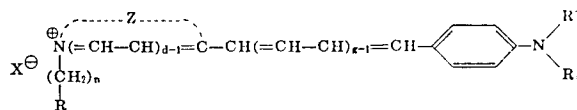
c. the 1-hydrazonoalkyl radical represented by R is selected from the group consisting of

1. a phenylhydrazonomethyl radical,
2. a p-tolylhydrazonomethyl radical,
3. a p-sulfophenylhydrazonomethyl radical,
4. a thiosemicarbazonomethyl radical,
5. a 2-benzothiazolyhydrazonomethyl radical,
6. a p-carboxyphenylhydrazonomethyl radical,
7. a p-tolylsulfhydrylhydrazonomethyl radical,
8. a p-chlorophenylhydrazonomethyl radical,
9. a p-nitrophenylhydrazonomethyl radical,
10. an N-phenylcarbamoylhydrazonomethyl radical,
11. a 2,4-bis(methylsulfonyl)phenylhydrazonomethyl radical,
12. a 2,4-dinitrophenylhydrazonomethyl radical,
13. a 3-quinolyldiazonomethyl radical,
14. a 1-(phenylhydrazono)ethyl radical,
15. a 1-(phenylhydrazono)propyl radical,
16. a 1-(p-tolylhydrazono)ethyl radical,
17. a 1-(2-benzothiazolyldiazono)propyl radical,
18. a 1-(N-phenylcarbamoyldiazono)butyl radical,
19. a 1-(p-toluenesulfonyldiazono)ethyl radical, and
20. a 1-(p-sulfophenylhydrazono)propyl radical.

8. A photographic image-forming process for the preparation of direct positive images on an imagewise exposed photographic element comprising a support having coated thereon a light-sensitive layer comprising a light-sensitive photographic silver halide emulsion which forms latent images predominantly inside the silver halide grains, said emulsion comprising silver halide grains having a predominant amount of light sensitivity in the internal portion of said grains, and a composite nucleating agent-spectral sensitizing dye compound selected from the group consisting of:

- 3-ethyl-5-[[3-(3-thiosemicarbazonomethyl)-2-benzothiazolylidene]ethylidene]-rhodanine, and
- 3-ethyl-5-[[3-(3-phenylhydrazonomethyl)benzothiazolylidene]ethylidene]rhodanine, which process comprises contacting the imagewise exposed photographic element with a silver halide surface developer and thereby producing a visible image in the exposed areas of said element.

9. A photographic image-forming process as described in claim 1 wherein said composite nucleating agent-spectral sensitizing dye compound has the formula:



wherein:

a. Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus at least one atom selected from the group consisting of nitrogen, oxygen, sulfur, and selenium,

b. n represents a positive integer having a value of from 2 to 6,

c. d represents a positive integer having a value of from 1 to 2,

d. g represents a positive integer having a value of from 1 to 3,

e. X[⊖] represents an anion,

f. R represents a 1-hydrazonoalkyl radical, and

g. each of R³ and R⁴ represents a member selected from the group consisting of a hydrogen atom, an alkyl radical and an aryl radical.

10. A photographic image-forming process as described in claim 9 wherein, said composite nucleating agent-spectral sensitizing dye compound,

a. Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus selected from the group consisting of an indole nucleus, an imidazole nucleus, an oxazole nucleus, a thiazole nucleus, a selenazole nucleus and a quinoline nucleus,

b. n has a value of 2, and

c. the 1-hydrazonoalkyl radical represented by R is selected from the group consisting of

1. a phenylhydrazonomethyl radical,
2. a p-tolylhydrazonomethyl radical,
3. a p-sulfophenylhydrazonomethyl radical,
4. a thiosemicarbazonomethyl radical,
5. a 2-benzothiazolyldiazonomethyl radical,
6. a p-carboxyphenylhydrazonomethyl radical,
7. a p-tolylsulfhydrylhydrazonomethyl radical,
8. a p-chlorophenylhydrazonomethyl radical,
9. a p-nitrophenylhydrazonomethyl radical,
10. an N-phenylcarbamoyldiazonomethyl radical,
11. a 2,4-bis(methylsulfonyl)phenylhydrazonomethyl radical,
12. a 2,4-dinitrophenylhydrazonomethyl radical,
13. a 3-quinolyldiazonomethyl radical,
14. a 1-(phenylhydrazono)ethyl radical,
15. a 1-(phenylhydrazono)propyl radical,
16. a 1-(p-tolylhydrazono)ethyl radical,
17. a 1-(2-benzothiazolyldiazono)propyl radical,
18. a 1-(N-phenylcarbamoyldiazono)butyl radical,
19. a 1-(p-toluenesulfonyldiazono)ethyl radical, and
20. a 1-(p-sulfophenylhydrazono)propyl radical.

11. A photographic image-forming process for the preparation of direct positive images on an imagewise exposed photographic element comprising a support having coated thereon a light-sensitive layer comprising a light-sensitive photographic silver halide emulsion which forms latent images predominantly inside the silver halide grains, said emulsion comprising silver halide grains having a predominant amount of light sensitivity in the internal portion of said grains, and a composite nucleating agent-spectral sensitizing dye com-

pound selected from the group consisting of:

- a 2-p-dimethylaminostyryl-3-(3-thiosemicarbazono-propyl)benzothiazolium salt, and
- a 2-p-dimethylaminostyryl-3-(3-phenylhydrazono)-benzothiazolium salt, which process comprises contacting the imagewise-exposed photographic element with a silver halide surface developer and thereby producing a visible photographic image in unexposed areas of said element.

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