

UNITED STATES PATENT OFFICE

2,410,690

METHOD OF IMPROVING THE SENSITIVITY
CHARACTERISTICS OF EMULSIONS

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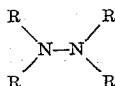
No Drawing. Application August 26, 1943,
Serial No. 500,087

9 Claims. (Cl. 95—6)

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This invention relates to photographic emulsions and particularly to a method for increasing the speed and contrast of such emulsions.

In Trivelli and Smith U. S. application Serial No. 500,088, filed concurrently herewith, a method is described for increasing the speed or contrast of gelatino-silver halide emulsions. This method involves the incorporation of hydrazine or its derivatives such as hydrazides or semi-carbazides in emulsions to effect an improvement in the sensitivity characteristics of the emulsion. The Trivelli and Smith application describes hydrazine derivatives of the general formula:



where at least two R's are hydrogen atoms and the remainder are carbon radicals. Compounds proposed in the Trivelli and Smith application were hydrazines such as hydrazine dihydrochloride, hydrazides such as malonic acid dihydrazide, semicarbazides such as semicarbazide hydrochloride and 4-(o-tolyl)-semicarbazide, biurets such as diaminobiuret, and hydrazones. These compounds were to be used in the emulsion or in the developer and the emulsion developed at a pH of at least 9.5 in the presence of the compounds.

We have found that certain compounds may be used in conjunction with the hydrazine compounds of the Trivelli and Smith application to yield marked increases in the effects obtained with the hydrazine compounds. These added compounds are cationic, onium compounds including cationic cyclammonium quaternary salts or sulfonium salts which do not act as desensitizers for the emulsion.

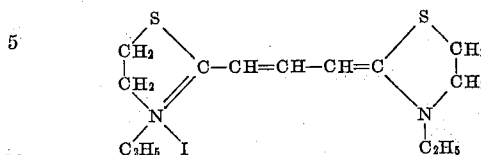
The cationic cyclammonium quaternary salts or sulfonium salts are used together with the hydrazine compound either in the emulsion or the developer. Both the hydrazine compound and the quaternary salt or sulfonium salt may be in the emulsion or both may be in the developer or one may be in the emulsion and the other in the developer.

The following compounds are representative of cationic cyclammonium quaternary salts or sulfonium salts which are suitable for use according to our invention:

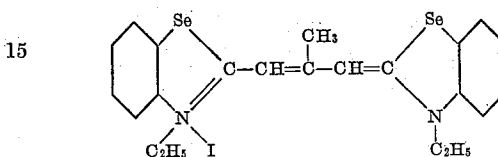
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BASIC OPTICAL SENSITIZING DYES

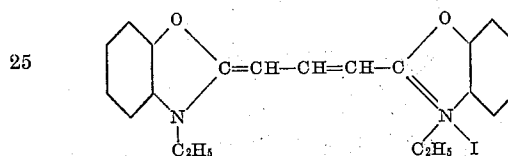
Cyanine dyes



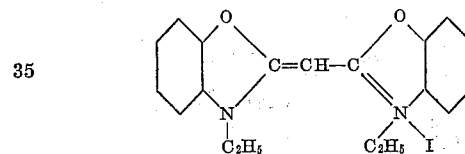
3,3'-diethylthiazolinocarbocyanine iodide (Brooker, U. S. Patent 1,950,876)



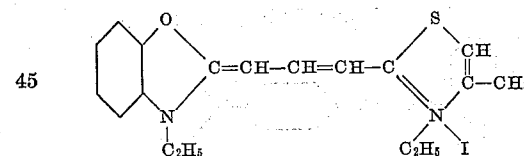
3,3'-diethyl-9-methylselenacarbocyanine iodide (White, U. S. Patent 1,990,681)



3,3'-diethyloxacarbocyanine iodide (Hamer, J. Chem. Soc., 1927, page 2796)

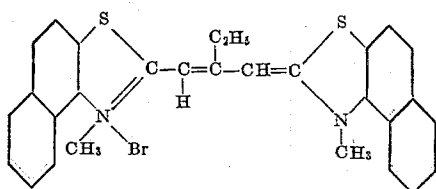


3,3'-diethyloxacyanine iodide (Fisher & Hamer, J. Chem. Soc., 1934, page 962)

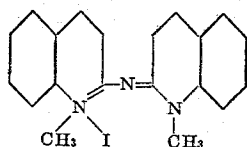


3,3'-diethyl-4'-methyloxathiazolocarbocyanine iodide (Mees, U. S. Patent 2,159,565)

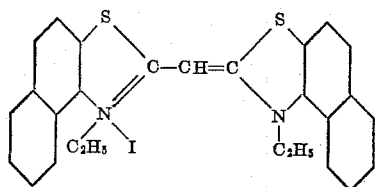
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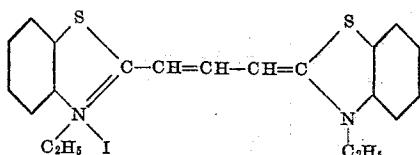
3,3'-dimethyl-9-ethyl-4,5,4',5'-dibenzothiacarbocyanine bromide
(Brooker, U. S. Patent 1,969,444)



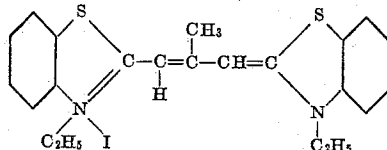
1,1'-dimethyl-9-aza-2,2'-cyanine iodide
(Mees, The Theory of the Photographic Process, 1942, page 1025)



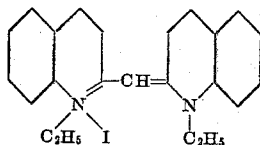
3,3'-diethyl-4,5,4',5'-dibenzothiacyanine iodide
(British Patent 504,821)



3,3'-diethylthiacarbocyanine iodide
(Hamer, J. Chem. Soc., 1927, page 2796)

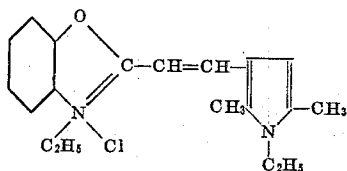


3,3'-diethyl-9-methylthiacarbocyanine iodide
(Hamer, J. Chem. Soc., 1928, page 3160)



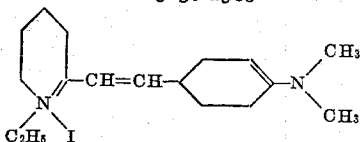
1,1'-diethyl-2,2'-cyanine iodide
(Mees, The Theory of the Photographic Process, 1942, page 1002)

Pyrrole dyes



(3-ethyl-2-benzoxazole)-(1-ethyl-2,5-dimethyl-3-pyrrole)-
dimethincyanine chloride

Styryl dyes

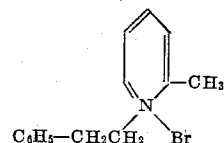


Pinaflavol

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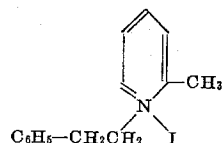
NON-SENSITIZING QUATERNARY SALTS

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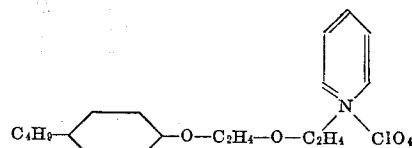
β -Phenylethyl- α -picolinium bromide

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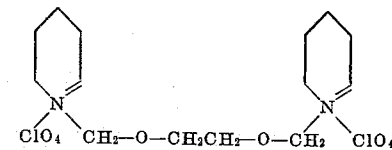
β -Phenylethyl- α -picolinium iodide

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p-Tert. butyl phenoxyethoxy-ethylpyridinium perchlorate

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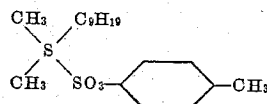


N,N'-ethylene-dioxymethyl pyridinium perchlorate

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SULFONIUM SALTS

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Nonyl dimethyl sulfonium p-toluene sulfonate

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The pyrrole dyes are described in Brooker and Sprague U. S. Patent 2,298,731. The non-sensitizing quaternary salts are referred to in Carroll U. S. Patent 2,271,623 and Carroll and Spence U. S. 2,334,864.

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It will be seen that the compounds suitable for use according to our invention include cyclammonium quaternary salts of the sensitizing and non-sensitizing types. All of these compounds are of the cationic type, that is, possess a complex cationic structure. In the case of the optical sensitizers, the effect which is produced according to our invention is separate and independent from optical sensitization as will be shown in the specific examples below.

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The mechanism of the action of the cationic quaternary salts appears to rest on the adsorption of the positive charges of the cationic agents to the negatively charged silver halide grain with resultant reduction of the induction period during development with negatively charged developer ions. Such induction effects are especially prominent with alkaline p-hydroquinone developers.

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Our invention will now be illustrated by reference to the following specific examples:

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EXAMPLE 1

A fine-grain gelatino-silver bromide emulsion was prepared and to portions of the emulsion were added hydrazine dihydrochloride and 3,3'-diethylthiazolinocarbocyanine iodide, separately and in combination. Coatings were made of these emulsions and, after drying, these coatings were exposed on a photographic sensitometer to the light transmitted from a 3200° K. tungsten source by a Wratten No. 35 filter. The first of

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these coatings was the plain emulsion without additions; the second coating contained 4 grams of hydrazine dihydrochloride per 4000 cc. of wet emulsion; the third coating consisted of the original emulsion with 100 mg. of 3,3'-diethylthiazolinocarbocyanine iodide and the fourth coating consisted of the original emulsion with 4 grams of hydrazine dihydrochloride and 100 mg. of 3,3'-diethylthiazolino carbocyanine iodide added per 4000 cc. of wet emulsion.

Since the carbocyanine dye added to the third and fourth coatings sensitizes to green light, all of the coatings were exposed through a Wratten No. 35 filter, which absorbs green light, in order to test the effect of the sensitizing dye on the emulsion independently of its optical sensitizing effect. The filter limited the exposure of all of the emulsions to the blue spectral region.

All of the coatings were processed after exposure for 1.5 minutes at 65° F. in a developer known as Kodak D-8 developer which has the following composition:

Hydroquinone	grams	45
Sodium hydroxide	do	27.5
Sodium sulfite (desiccated)	do	90
Potassium bromide	do	30
Water to	liters	1

The speed and contrast of each of the images was then determined and the following results were obtained.

	10/i speed	Contrast	Fog
Emulsion without additions	0.53	5.2	0.03
Emulsion+4 g. hydrazine dihydrochloride	.58	5.5	.03
Emulsion+100 mg. 3,3'-diethylthiazolinocarbocyanine iodide	1.31	5.6	.03
Emulsion+4 g. hydrazine dihydrochloride and 100 mg. 3,3'-diethylthiazolinocarbocyanine iodide	1.68	13.4	.04

EXAMPLE 2

A fine-grain gelatino-silver chlorobromide emulsion was prepared and to portions of its were added separately and in combination, 4-(o-tolyl) semicarbazide and 3,3'-diethylthiazolinocarbocyanine iodide. These portions were then coated and dried. The first coating consisted of the plain emulsion without additions; the second coating the emulsion to which had been added 100 mg. of 4-(o-tolyl)-semicarbazide per 200 cc. of wet emulsion; the third coating the original emulsion to which has been added 5 mg. of 3,3'-diethylthiazolinocarbocyanine iodide per 200 cc. of wet emulsion and the fourth coating the original emulsion to which had been added 100 mg. of 4-(o-tolyl)-semicarbazide and 5 mg. of 3,3'-diethylthiazolinocarbocyanine iodide per 200 cc. of wet emulsion. These emulsions were exposed through a Wratten No. 35 filter as in the case of Example 1 and were developed in the same manner. The following results were obtained:

	10/i speed	Contrast	Fog
Emulsion without additions	2.28	4.9	0.05
Emulsion+100 mg. 4-(o-tolyl)-semicarbazide	1.95	6.8	.05
Emulsion+5 mg. 3,3'-diethylthiazolinocarbocyanine iodide	2.22	4.2	.04
Emulsion+100 mg. 4-(o-tolyl)-semicarbazide and 5 mg. 3,3'-diethylthiazolinocarbocyanine iodide	2.82	23.0	.07

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EXAMPLE 3

A fine-grain gelatino-silver chlorobromide emulsion was prepared and to portions of it were added 4-(o-tolyl)-semicarbazide and a mixture of the semicarbazide and β -phenylethyl- α -picolinium bromide. The first portion consisted of the plain emulsion without additions, the second portion consisted of the original emulsion to which had been added 100 mg. of 4-(o-tolyl)-semicarbazide per 200 cc. of wet emulsion and the third portion consisted of the original emulsion to which had been added 100 mg. of 4-(o-tolyl)-semicarbazide and 200 mg. of β -phenylethyl- α -picolinium bromide per 200 cc. of wet emulsion. These three portions were separately coated and dried and exposed on a photographic sensitometer to light transmitted from a 3200° K. tungsten source. The Wratten filter was omitted because the quaternary salt used in this case was not an optical sensitizer. The emulsions were processed as in Example 1 and the following results were obtained:

	10/i speed	Contrast	Fog
Emulsion without additions	5.35	5.9	0.05
Emulsion+100 mg. 4-(o-tolyl)-semicarbazide	5.10	6.1	.05
Emulsion+100 mg. 4-(o-tolyl)-semicarbazide and 200 mg. β -phenylethyl- α -picolinium bromide	6.45	10.6	.09

EXAMPLE 4

A fine-grain gelatino-silver chlorobromide emulsion was prepared and to portions of it were added phenylmethyl-dimethylacethydrazido ammonium chloride and a mixture of the hydrazide and 3,3'-diethyl-9-methylthiacarbocyanine iodide. The first portion consisted of the plain emulsion without additions, the second portion consisted of the original emulsion to which had been added 200 milligrams of phenylmethyl-dimethylacethydrazido ammonium chloride per 200 cc. of wet emulsion and the third portion consisted of the original emulsion to which had been added 200 milligrams of the hydrazide and 5 milligrams of 3,3'-diethyl-9-methylthiacarbocyanine iodide per 200 cc. of wet emulsion. These three portions were separately coated and dried and exposed on a photographic sensitometer to light transmitted from a 3200° K. tungsten source through a Wratten No. 35 filter. These emulsions were developed as in the case of Example 1 and the following results were obtained:

	10/i speed	Contrast	Fog
Emulsion without additions	6.05	5.5	0.07
Emulsion+200 mg. phenyl-methyl-dimethylacethydrazido ammonium chloride	8.70	8.5	.06
Emulsion+200 mg. phenyl-methyl-dimethylacethydrazido ammonium chloride and 5 mg. 3,3'-diethyl-9-methylthiacarbocyanine iodide	9.00	13.3	.07

EXAMPLE 5

Three emulsion coatings were prepared as in Example 4, the first being the emulsion without additions, the second containing 200 milligrams of malonic acid dicarbohydrazido pyridinium bromide per 200 cc. of wet emulsion and the third containing 200 milligrams of the hydrazide and 5 milligrams of 3,3'-diethyl-9-methylthiacarbocyanine iodide per 200 cc. of wet

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emulsion. Upon exposure and development as in Example 4, the following results were obtained:

	10/i speed	Contrast	Fog
Emulsion without additions.....	6.05	5.5	0.07
Emulsion+200 mg. malonic acid dicarbohydrazido pyridinium bromide.....	7.60	10.2	.08
Emulsion+200 mg. malonic acid dicarbohydrazido pyridinium bromide and 5 mg. 3,3'-diethyl-9-methyl thiocarbocyanine iodide.....	9.55	9.6	.14

EXAMPLE 6

Three emulsion coatings were prepared as in Example 4, the first being the emulsion without additions, the second containing 20 milligrams of phenyl succinic dihydrazide per 200 cc. of wet emulsion and the third containing 20 milligrams of phenyl succinic dihydrazide and 8 milligrams of 3,3'-diethylthiazolino carbocyanine iodide per 200 cc. of wet emulsion. These coatings were exposed and developed as in Example 4 and the following results were obtained:

	10/i speed	Contrast	Fog
Emulsion without additions.....	1.62	4.4	0.06
Emulsion+20 mg. phenyl succinic dihydrazide.....	2.05	6.0	.07
Emulsion+20 mg. phenyl succinic dihydrazide and 8 milligrams 3,3'-diethylthiazolino-carbocyanine iodide.....	2.00	7.5	.06

EXAMPLE 7

The following example serves to illustrate the action of the cyclammonium quaternary salt in the developer with the hydrazine compound in the emulsion.

To a fine grain gelatino-silver chlorobromide emulsion there was added 1.5 grams per 4000 cc. of 4-(o-tolyl)-semicarbazide.

This emulsion was coated and dried and portions of the coating were exposed for one second to a 3000° K. light source on a photographic sensitometer. The separation portions of the coatings were then developed for two minutes at 65° F. in Kodak D-8 developer of the formula stated in Example 1, both without and with addition of varying amounts of 3,3'-diethylthiazolino-carbocyanine iodide. The amount of this quaternary salt was varied between 8.3 mg. and 33.3 mg. per liter of developer and the following sensitometric results were obtained:

Amount of quaternary salt	10/i speed	Contrast	Fog
0.....	13.0	6.0	0.05
8.3 mg. per liter.....	14.0	6.0	.05
16.7 mg. per liter.....	16.0	9.8	.05
33.3 mg. per liter.....	17.5	10.0	.05

EXAMPLE 8

The following example serves to illustrate the action of both the hydrazine and the cyclammonium quaternary salt in the developer.

A fine grain non-optically sensitized gelatino-silver chlorobromo emulsion was exposed for 10 seconds at 3000° K. on a photographic sensitometer and portions of the emulsion thus exposed were developed for two minutes at 65° F. in Kodak D-8 developer and in developer formulas to which the hydrazine and the cyclammonium quaternary salt had been added. The first developing formula thus tested contained 10 milli-

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grams of hydrazine dihydrochloride per liter of D-8 developer; the second developer contained 10 milligrams of hydrazine dihydrochloride and 16 milligrams of 3,3'-diethylthiazolinocarbocyanine iodide per liter of D-8 developer and the third developer contained 10 milligrams of hydrazine dihydrochloride and 33 milligrams of 3,3'-diethylthiazolinocarbocyanine iodide per liter of D-8 developer. The following sensitometric results were recorded with the various developers.

	10/i speed	Contrast	Fog
D-8.....	2.60	4.8	0.14
D-8+10 mg. hydrazine dihydrochloride per 1000 cc.....	3.60	9.0	.16
D-8+10 mg. hydrazine dihydrochloride+16 mg. 3,3'-diethylthiazolinocarbocyanine iodide/1000 cc.....	3.80	10.4	.16
D-8+10 mg. hydrazine dihydrochloride+33 mg. 3,3'-diethylthiazolinocarbocyanine iodide/1000 cc.....	9.10	15.5	.25

The acid optical sensitizing dyes such as erythrosine and the neutral optical sensitizers such as the merocyanines either cause losses in the effects produced by the hydrazine compounds or are inert sensitometrically from this standpoint. Accordingly, only the basic optical sensitizing dyes are suitable for use according to our invention.

The compounds which are used according to our invention should not desensitize the emulsion. Certain basic dyes are desensitizers and, therefore, are not satisfactory for use according to our invention. Phenosafranin, for example, is a basic dye which is a well known desensitizer. Although it might be classed as an optical sensitizing dye, it is better known for its desensitizing properties and is therefore, excluded from the scope of our invention. The structural distinction between those basic dyes which sensitize a photographic emulsion and those which desensitize an emulsion is described by Mees in "The Theory of the Photographic Process," 1942, pages 1040-1047.

The non-sensitizing quaternary salts such as β -phenyl-ethyl- α -picolinium bromide, which are listed above, have been used as supersensitizers in silver halide emulsions. However, our effect is not believed to be a supersensitization since not all supersensitizers enhance the effect produced by the hydrazine compounds. For example, 6-methoxyquinoline has been used as a supersensitizer but is inert with respect to improvement of the sensitometric characteristics in the manner contemplated by our invention.

The effect produced according to our invention is noticeable on various types of silver halide emulsions such as silver bromide, silver chlorobromide and silver bromiodide emulsions.

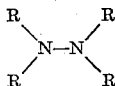
We have referred to the sensitivity characteristics of the emulsion. By "sensitivity characteristics" we mean the speed and contrast characteristics as indicated by the characteristic curve of the emulsion.

Where we refer to "actinic radiation" we intend to include visible light, as well as ultra-violet light, infra-red light, X-rays, and gamma rays, and also charged particles, such as α -rays, β -rays, and cosmic rays.

We claim:

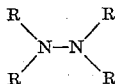
1. The method of producing an image in an undeveloped silver halide developing-out emulsion, which comprises exposing said emulsion and developing it with a hydroquinone developing agent at a pH of at least approximately 9.5 in

the presence of a compound selected from the group consisting of hydrazine compounds of the general formula:



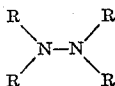
where at least two R's are hydrogen atoms and when less than 4 R's are hydrogen atoms the remainder are carbon radicals, and the salts of said compounds, and also in the presence of an onium compound selected from the group consisting of non-desensitizing cationic cyclammonium quaternary salts and sulfonium salts.

2. The method of improving the sensitivity characteristics with respect to actinic radiation of a silver halide photographic layer, which comprises exposing an undeveloped silver halide emulsion layer to actinic radiation and developing it with a hydroquinone developing agent at a pH of at least approximately 9.5 in the presence of a compound selected from the group consisting of hydrazine compounds of the general formula:



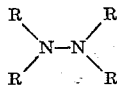
where at least two R's are hydrogen atoms and when less than 4 R's are hydrogen atoms the remainder are carbon radicals, and the salts of said compounds, and also in the presence of an onium compound selected from the group consisting of non-desensitizing cationic cyclammonium quaternary salts and sulfonium salts.

3. The method of improving the sensitivity characteristics with respect to actinic radiation of a silver halide photographic layer, which comprises exposing an undeveloped silver halide emulsion layer to actinic radiation and developing it with a hydroquinone developing agent at a pH of at least approximately 9.5 in the presence of a compound selected from the group consisting of hydrazine compounds of the general formula:



where at least two R's are hydrogen atoms and when less than 4 R's are hydrogen atoms the remainder are carbon radicals, and the salts of said compounds and also in the presence of a non-desensitizing cationic cyclammonium quaternary salt.

4. The method of improving the sensitivity characteristics with respect to actinic radiation of a silver halide photographic layer, which comprises exposing an undeveloped silver halide emulsion layer to actinic radiation and developing it with a hydroquinone developing agent at a pH of at least approximately 9.5 in the presence of a compound selected from the group consisting of hydrazine compounds of the general formula:



where at least two R's are hydrogen atoms and when less than 4 R's are hydrogen atoms the remainder are carbon radicals, and the salts of said compounds, and also in the presence of a

basic cationic cyclammonium quaternary salt optical sensitizing dye.

5. The method of improving the sensitivity characteristics with respect to actinic radiation of a silver halide photographic layer, which comprises exposing an undeveloped silver halide emulsion layer to actinic radiation and developing it with a hydroquinone developing agent at a pH of at least approximately 9.5 in the presence of a compound selected from the group consisting of hydrazine compounds of the general formula:

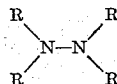


- 15 where R is selected from the class consisting of hydrogen and $-\text{CONHC}_6\text{H}_5$, and the salts of said compounds, and also in the presence of a non-desensitizing cationic cyclammonium quaternary salt.

- 20 6. The method of improving the sensitivity characteristics with respect to actinic radiation of a silver halide photographic layer, which comprises incorporating in a gelatino-silver halide emulsion a hydrazine and an onium compound selected from the group consisting of non-desensitizing cationic cyclammonium quaternary salts and sulfonium salts, coating the emulsion on a support, exposing the emulsion to actinic radiation, and developing it at a pH of at least approximately 9.5 in the presence of said hydrazine and onium compound.

7. The method of improving the sensitivity characteristics with respect to actinic radiation of a silver halide photographic layer, which comprises incorporating in a gelatino-silver halide emulsion a hydrazine and a non-desensitizing cationic cyclammonium quaternary salt, coating the emulsion on a support, exposing the emulsion to actinic radiation, and developing it at a pH of at least approximately 9.5 in the presence of said hydrazine and quaternary salt.

8. The method of improving the sensitivity characteristics with respect to actinic radiation of a silver halide photographic layer, which comprises exposing said layer to such radiation and developing it at a pH of at least approximately 9.5 in a solution containing a photographic developing agent, a hydrazine compound selected from a group consisting of compounds of the general formula:



- 50 where at least two R's are hydrogen atoms and when less than 4 R's are hydrogen atoms the remainder are carbon radicals, and the salts of said compounds, and an onium compound selected from the group consisting of non-desensitizing cationic cyclammonium quaternary salts and sulfonium salts.

9. The method of improving the sensitivity characteristics with respect to actinic radiation of a silver halide photographic layer, which comprises incorporating in a gelatino-silver halide emulsion a hydrazine compound, coating the emulsion on a support, exposing the emulsion to actinic radiation, and developing it at a pH of at least 9.5 in a developing solution containing a photographic developing agent and an onium compound selected from the group consisting of non-desensitizing cationic cyclammonium quaternary salts and sulfonium salts.

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