

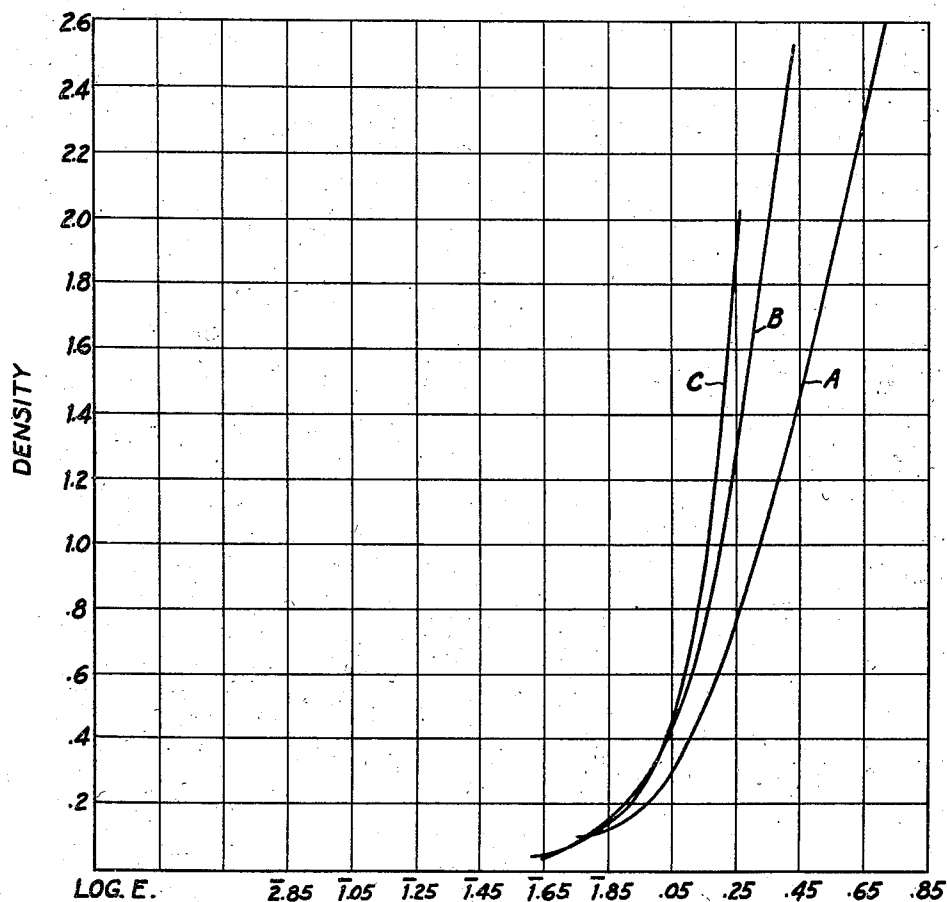
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A. P. H. TRIVELLI ET AL

2,419,975

INCREASING SPEED AND CONTRAST OF PHOTOGRAPHIC EMULSIONS

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INCREASING SPEED AND CONTRAST OF
PHOTOGRAPHIC EMULSIONS

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

The invention relates to the use of hydrazine and related compounds in a photographic process.

Hydrazine and hydrazine derivatives have been used in photographic emulsions or developers for many purposes. One well known use of hydrazine compounds in photographic emulsions is that of a halogen acceptor or halogen absorber. During the exposure of a sensitive silver halide emulsion, the silver halide is thought to release halogen such as bromine or chlorine and the sensitivity of the material is improved if the halogen thus released is immediately combined with a compound which prevents it from recombining with silver. The use of hydrazines for this purpose is described in Caldwell U. S. Patent 956,567. This effect of absorbing or accepting halogen is manifested only during exposure of the sensitive material. The hydrazine or other compound used in this way is intended to be used up during the exposure of the sensitive material and it is customary to remove the unused compound prior to development.

Hydrazine derivatives have also been used as anti-foggants in sensitive emulsions. This use is described in Sheppard and Wightman U. S. Patent 1,763,990. When used for this purpose, the hydrazines prevent the formation of emulsion fog at the time of exposure of the sensitive material or shortly before or thereafter. They have no function in the development of the exposed material.

Hydrazines have also been used in photographic emulsions to increase the infra-red speed and contrast of the material as described in Trivelli and Carroll U. S. Patent 2,245,236. When used in this way the hydrazines act in the infra-red region of optically sensitized material. It was not known that an increase in speed and contrast in the visible and ultra-violet regions of the spectrum could be obtained by the use of these materials.

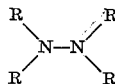
Hydrazines have also been used in photographic developers for two purposes. They have been used as the developing agent and have also been used in fogging second developers to render reversal exposure of the material unnecessary. When used in this way they do not affect the speed or contrast of the material. Since the effective speed and contrast are determined by the original development, the hydrazines in the second developer do not affect these characteristics of the

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material but are used only to fog all of the unexposed silver halide.

It is an object of the present invention to provide an improved method for sensitizing photographic silver halide emulsions. A further object is to provide a new method for increasing the speed of photographic silver halide emulsions. A still further object is to provide a new method for increasing the contrast of photographic silver halide emulsions. A further object is to provide a new method for processing photographic silver halide emulsions to effect improved properties in the resulting image. Other objects will appear from the following description of our invention.

These objects are accomplished by developing an undeveloped silver halide photographic emulsion, after exposure, at a pH of about 9.5 or higher in the presence of a hydrazine, hydrazine salt, or hydrazine derivative of the general formula:



where at least two R's are hydrogen atoms and the remainder are carbon radicals, more specifically an aliphatic radical, a heterocyclic radical, or a carbonyl group directly connected to an aliphatic carbon atom of a carbon radical, a heterocyclic carbon atom of a carbon radical, an oxygen atom of a carbon radical or a nitrogen atom of a carbon radical.

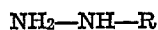
The drawing illustrates typical sensitometric curves showing the improvement obtained by our invention.

We secure an improvement in the sensitivity characteristics, that is, the speed or contrast, or both, of photographic material by developing the exposed material in the presence of a hydrazine or a compound related to hydrazine. It is important that these compounds be present at the time of photographic development since the effect which we obtain is a development effect. Our compounds may, accordingly, be added to the emulsion or to the developer as long as they are present during development of the exposed material. Prior users of hydrazines in the photographic emulsion have sought to obtain benefits from their use, during exposure of the material and not during development. The only exception is the Trivelli and Carroll U. S. Patent 2,245,236, referred to above, and in this case the effect is limited to the red and infra-red region of the spectrum. When the hydrazines employed in the prior art have been incorporated in the developing solution, they have been used either

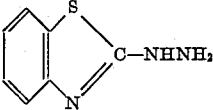
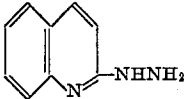
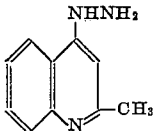
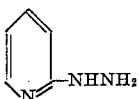
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as the developing agent or as the fogging agent in a reversal developer and would not effect an improvement in sensitometric properties of the photographic material.

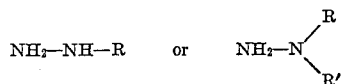
The following classes of compounds have been found suitable for use according to our invention: Hydrazines of the general formula:



in which R is hydrogen, an acid ester group or a heterocyclic group. The following compounds illustrate this class.

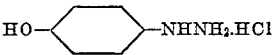
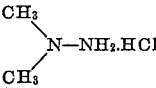
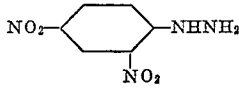
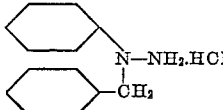
1. $\text{NH}_2\text{NH}_2 \cdot 2\text{HCl}$
Hydrazine hydrochloride
2. $\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$
Hydrazine hydrate
3. $\text{NH}_2\text{NHCOC}_2\text{H}_5$
Ethyl hydrazine carbonate
4. 
2-benzothiazolyldiazine
5. 
2-quinolylhydrazine
6. 
4-hydrazinoquinoline
7. 
2-pyridylhydrazine

Alkyl or aryl hydrazines of the general formula:

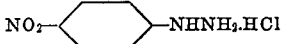
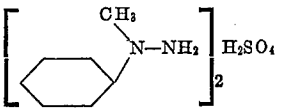


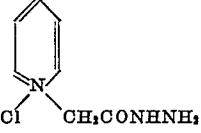
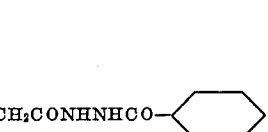
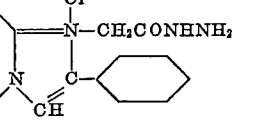
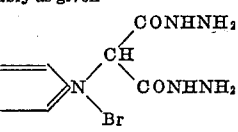
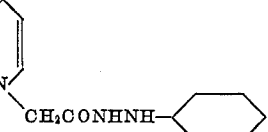
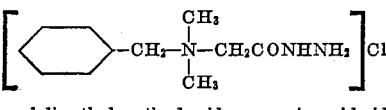
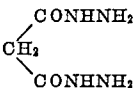
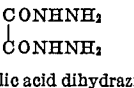
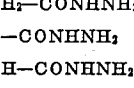
where R and R' are alkyl or aryl groups.

The following compounds illustrate this group:

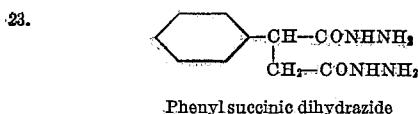
8. 
p-Hydroxyphenylhydrazine HCl
9. 
as Dimethylhydrazine hydrochloride
10. 
2,4-dinitrophenylhydrazine
11. 
 α -Benzyl- α -phenylhydrazine hydrochloride

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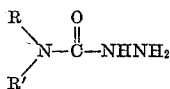
12. 
p-Nitrophenylhydrazine hydrochloride
13. 
 α -Methyl- α -phenylhydrazine sulfate
10. Hydrazides (acyl hydrazines) having the general formula:
$$\text{R}-\text{C}(=\text{O})-\text{NHNH}_2 \quad \text{or} \quad \text{R}-\text{C}(=\text{O})-\text{NH}-\text{NH}-\text{C}(=\text{O})-\text{R}'$$

where R is an alkyl radical or a chemical bond to a similar radical and R' is an aryl radical.
14. 
 α -Acethydrazide pyridinium chloride
20. 
 β -Benzoylacethydrazidopyridinium chloride
25. 
The product made by adding ethyl chloroacetate to 2-phenyl pyrimidazole, followed by treatment with hydrazine. The structure is presumably as given
30. 
Malonyl dihydrazide pyridinium bromide
35. 
 β -Phenylacethydrazidopyridinium chloride
40. 
Benzyl-dimethyl-acethydrazido-ammonium chloride
45. 
Malonic acid dihydrazide
50. 
Oxalic acid dihydrazide
55. 
Aconitic acid trihydrazide
59. 
Aconitic acid trihydrazide

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Semicarbazides, carbohydrazides and amino biurets having the formula:



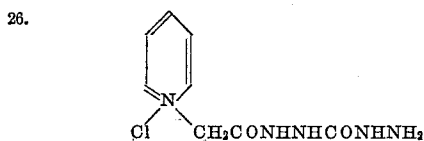
where R is hydrogen and R' is hydrogen, NH_2 which may or may not be substituted, an aryl radical, or a carboxylic acid amide radical.



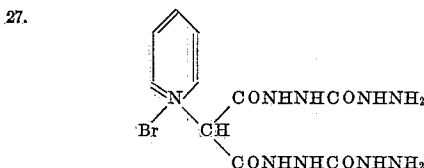
Semicarbazide hydrochloride



Carbohydrazide hydrochloride



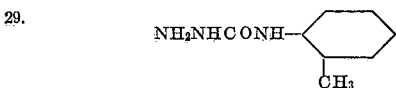
Acetcarbohydrazide pyridinium chloride



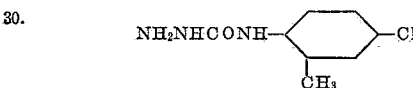
Malonyl dicarbohydrazide pyridinium bromide



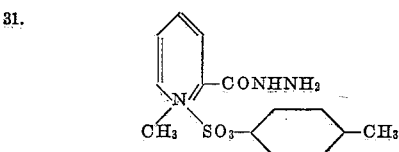
4-(p-chlorophenyl)-semicarbazide



4-(o-tolyl)-semicarbazide



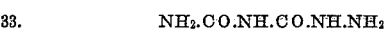
4-(4'-chloro-2'-methyl-phenyl)-semicarbazide



N-methyl-2-carbohydrazyl pyridinium p-toluenesulfonate



Diamino biuret



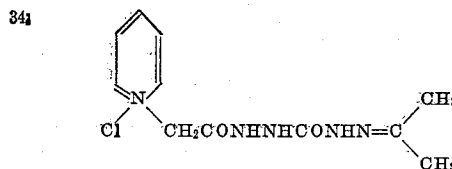
Amino biuret

Hydrazones. These compounds contain the grouping:

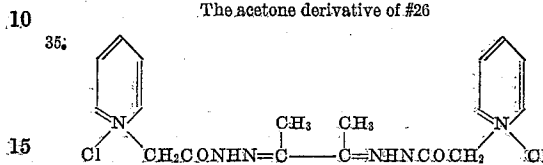


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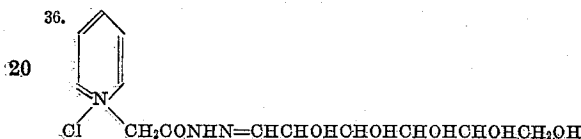
Typical compounds are as follows:



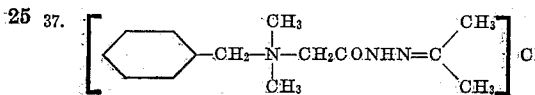
The acetone derivative of #26



The diacetyl derivative of #14



The glucose derivative of #14



Acetone derivative of #19

30 The increase in sensitivity or contrast which we obtain by the introduction of hydrazines to the emulsion or developer, whether as water-soluble or as water-insoluble compounds increases considerably with increase in pH of the developer. The pH of the developer used with our materials should be about 9.5 or higher. With a developer having a pH of 12.8, the use of hydrazine in a silver chlorobromide emulsion produces a strong effect by which the gamma can be increased from 3 to a gamma of 10 or higher. With some emulsions a gamma as high as 24 has been obtained. Speed increase without gamma increase, speed increase with gamma increase and gamma increase without speed increase have been observed.

35 In addition to pH, the pAg or silver ion concentration, of the emulsions to which an active compound is added, is an important factor in controlling the effect which we obtain. Higher silver ion concentrations tend in general to increase the effect as do high pH's. It is also important not to add carbonyl hardening agents to the emulsion. If present in equimolar concentrations such hardeners usually destroy the effect probably due to hydrazone formation. The explanation of this apparent inconsistency is that the hydrazones listed above are believed to decompose to release hydrazine or hydrazine derivatives. The hydrazones formed by reaction of the carbonyl hardening agents with gelatin are not readily decomposed and therefore do not improve the sensitometric characteristics of the emulsion. Chrome alum may, however, be used as a hardening agent. The pAg of the emulsions which we use lies in the range of 6.0 to 9.5. Emulsions of various types such as chloride, bromide, bromiodide, and chlorobromide may be employed. The effect has been found to be especially noticeable in the case of high contrast emulsions.

70 The increase in sensitivity or contrast which we produce is obtained with any type of developing agent such as the phenolic type, such as monomethyl-p-aminophenolsulfate, catechol, p-hydroquinone and pyrogallol. A developer of the

following composition such as Kodak Formula D-8 which has a pH of 12.8 is suitable.

Sodium sulfite (desiccated)-----	grams--	90
Hydroquinone-----	do-----	45
Sodium hydroxide-----	do-----	37
Potassium bromide-----	do-----	30
Water to-----	liters--	1

A developer of the following composition, such as Kodak Formula D-19, which has a pH of 10.2, is also suitable:

Monomethyl-p-aminophenol sulfate-----	grams--	2.2
Hydroquinone-----	do-----	9
Sodium sulfite (desiccated)-----	do-----	96
Sodium carbonate (desiccated)-----	do-----	48
Potassium bromide-----	do-----	5
Water to-----	liters--	1

It has been found that the novel effect produced by hydrazine or its derivatives may be extended to developers of normal pH, by regulating the concentration of sulfite in the developer. In developers of pH 10 or higher, such as Kodak Formula D-19, the concentration of sulfite may be high. With developers of lower pH the concentration of sulfite must be decreased in order to achieve the advantages of the use of hydrazine or its derivatives. For example, a developer of the following composition, which has a pH of 9.7, and contains hydrazine dihydrochloride is suitable for increasing the speed of silver halide emulsions.

Monomethyl-para-aminophenolsulfate	grams--	2.2
p-Hydroquinone-----	do-----	8.8
Sodium sulfite (desiccated)-----	do-----	16.0
Potassium bromide-----	do-----	5.0
Sodium carbonate-----	do-----	48.0
Hydrazine dihydrochloride-----	do-----	0.2
6-Nitrobenzimidazole nitrate-----	do-----	0.05
Water to-----	liters--	1

The improved effect obtained by controlling the sulfite concentration of the developer is not limited to the particular formula stated above. The formula which may be employed depends upon the type of emulsion and the sensitometric characteristics sought. The anti-foggant employed in this developer is not essential although its use is desirable for controlling fog and development time. The hydrazine compound may also be incorporated in the emulsion and the improved effect obtained by development in a developing solution of low sulfite content.

The amount of hydrazine or hydrazine derivative added to the developer differ depending upon the composition of the hydrazine and of the developer employed. Amounts in the range of 0.01 gram to 5 grams per liter of developer in general are satisfactory.

When the compounds are added to the emulsion, they may be added before, during or after second ripening. A necessary requirement is that they be present during the development of the exposed material. It is also essential to our invention that the hydrazine compounds should not function as anti-foggants in the emulsion. The amounts used in the emulsion will vary with the composition of the hydrazine compound and of the emulsion but the amount used should not be sufficient to cause fog. In general, amounts ranging from 0 to 2 grams per pound of wet emulsion are satisfactory.

The following table shows the improvement in speed and gamma obtained upon addition of hy-

drazine dihydrochloride in an amount of 0.06 gram to 1 liter of D-8 developer having the composition stated above. A normal speed gelatino-silver bromide emulsion was exposed and developed for 1½ minutes in the developer, a comparison being made with the developing solution without the hydrazine. The speed contrast and fog recorded in the two cases were as follows, the speed being measured as ten times the reciprocal of the inertia.

	Speed 10/i	Gamma	Fog
Check-----	9.55	2.3	.07
+Hydrazine dihydrochloride (0.06 g. per l. D-8 developer)-----	25.0	9.4	.06

The following tables show the change in speed and contrast obtained when various compounds according to our invention were added to a normal speed chlorobromide emulsion:

Compound	Concentration, Gms. per 10 lb. Emulsion	10/i	Gamma	Fog
Semicarbazide HCl-----	0	14	4.40	.06
	10	11	8.70	.06
	0	18	4.15	.10
Do-----	1.0	18	4.40	.08
	2.0	14	6.15	.10
	3.0	17	7.30	.09
	0	21.5	3.81	.08
	4.0	19.0	7.4	.09
	6.0	18.0	11.3	.07
Do-----	8.0	22.0	11.0	.07
	10.0	18.0	14.0	.06
	12.0	17.0	9.0	.07
	14.0	22.0	18.6	.07
	16.0	22.5	17.0	.06
Hydrazine dihydrochloride-----	0.5	15.5	9.5	.07
	1.0	22.5	18.2	.10
	0	16	4.5	.06
	1.0	18.5	6.6	.06
Ethyl hydrazine carbonate-----	1.5	20.5	6.8	.06
	2.0	22.5	7.0	.06
	4.0	23.0	12.6	.06
	0	15.0	6.8	.06
4-(p-chlorophenyl)-semicarbazide	3.0	16.5	5.1	.08
	5.0	23.5	7.9	.07
	10.0	15.0	9.6	.04
4-(o-tolyl)-semicarbazide-----	0	18.0	4.5	.08
	3.0	18.0	6.0	.07
	5.0	19.5	9.4	.07
	7.0	24.5	13.2	.05
	10.0	23.5	9.0	.06
N-chloro-N-pyridinoacetic acid carbohydrazide-----	0	16.0	4.5	.06
	4.0	23.5	6.4	.16
1-(N-chloro-N-pyridine acetic acid)-4-carbohydrazone-----	0	16.0	4.5	.06
	4.0	22.5	6.1	.14
2-pyridyl hydrazine-----	0	20.5	2.4	-----
	3.2	21.5	3.2	-----
as-Dimethyl hydrazine HCl-----	0	12.3	5.1	.13
	9.66	16.5	5.7	.20
2,4-Dinitrophenyl hydrazine-----	0	12.3	5.1	.13
	4.2	16.5	5.1	.13
α-Benzyl-α-phenyl hydrazine HCl-----	0	13.5	5.0	.26
	.042	18.0	4.5	.21
p-Nitrophenyl hydrazine HCl-----	0	13.5	5.0	.26
	.21	20.5	5.3	.27

The emulsions developed according to our invention may be exposed by any kind of actinic radiation, but in certain cases we prefer to employ light of wave-length shorter than infra-red, that is, visible light, ultra-violet light, X-rays or gamma rays. Charged particles such as α-rays, β-rays and cosmic rays may also be used for the exposure.

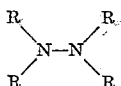
The improvement secured by our invention will be more readily apparent by reference to the accompanying drawing which shows typical sensitometric curves of exposed and developed photographic material. These curves were made by plotting density against the logarithm of the exposure in the well known manner. Curve A shows the result of exposing and developing a normal speed chlorobromide emulsion for 1½

minutes in D-8 developer at 65° F. Curve B was obtained from a similar emulsion exposed and developed under the same conditions as the emulsion resulting in curve A, but with an addition of 0.625 gram per liter of emulsion of orthotolyl semicarbazide. Curve C was obtained with an emulsion similar to that of Curve A, but with the addition of 0.9375 gram per liter of emulsion of orthotolyl semicarbazide. It will be noted that in curves B and C the speed of the emulsion has been increased and the contrast has also been increased. No increase in fog is evident in these curves. The untreated emulsion showed a 10% speed of 8.9; a contrast of 3.9; and a fog density of .04. The emulsion from which curve B was obtained showed a speed of 9.4 and a gamma of 6.3. The emulsion from which curve C was obtained showed a speed of 9.6 and a gamma of 8.3. The fog density in all three emulsions was the same.

It will be understood that the examples and modifications included herein are illustrative only and that our invention is to be taken as limited only by the scope of the appended claims.

We claim:

1. The method of improving the sensitivity characteristics of a silver halide photographic layer with respect to radiation consisting of light of wave length shorter than red, which comprises exposing an undeveloped silver halide emulsion layer to said radiation and developing it with a phenolic developing agent at a pH of at least approximately 9.5 in a developing solution selected from the class of developing solutions containing an appreciable amount of sulfite up to 16 grams per liter when the pH is between 9.5 and 9.7, and containing more than 16 grams per liter of sulfite when the pH is higher than 9.7, 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 selected from the class consisting of aliphatic radicals, heterocyclic radicals, and a carbonyl group directly connected to a member of the class consisting of an aliphatic carbon atom of a carbon radical, a heterocyclic carbon atom of a carbon radical, an oxygen atom of a carbon radical, and a nitrogen atom of a carbon radical, and the salts of said compounds, said compound having no fog inhibiting action on said emulsion.

2. The method of increasing the speed 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 phenolic developing agent at a pH of at least approximately 9.5 in a developing solution selected from the class of developing solutions containing an appreciable amount of sulfite up to 16 grams per liter when the pH is between 9.5 and 9.7, and containing more than 16 grams per liter of sulfite when the pH is higher than 9.7 in the presence of an aliphatic acyl hydrazine.

3. The method of increasing the speed of a silver halide photographic layer with respect to radiation consisting of light of wave length shorter than red, which comprises exposing an

undeveloped silver halide emulsion layer to said radiation and developing it with a phenolic developing agent at a pH of at least approximately 9.5 in a developing solution selected from the class of developing solutions containing an appreciable amount of sulfite up to 16 grams per liter when the pH is between 9.5 and 9.7, and containing more than 16 grams per liter of sulfite when the pH is higher than 9.7 in the presence of a semicarbazide.

4. The method of increasing the speed of a silver halide photographic layer with respect to radiation consisting of light of wave length shorter than red, which comprises exposing an undeveloped silver halide emulsion layer to said radiation and developing it with a phenolic developing agent at a pH of at least approximately 9.5 in a developing solution selected from the class of developing solutions containing an appreciable amount of sulfite up to 16 grams per liter when the pH is between 9.5 and 9.7, and containing more than 16 grams per liter of sulfite when the pH is higher than 9.7 in the presence of hydrazine dihydrochloride.

5. The method of increasing the speed of a silver halide photographic layer, with respect to radiation consisting of light of wave length shorter than red, which comprises exposing an undeveloped silver halide emulsion layer to said radiation and developing it with a phenolic developing agent at a pH of at least approximately 9.5 in a developing solution selected from the class of developing solutions containing an appreciable amount of sulfite up to 16 grams per liter when the pH is between 9.5 and 9.7, and containing more than 16 grams per liter of sulfite when the pH is higher than 9.7 in the presence of semicarbazide hydrochloride.

6. The method of increasing the speed to actinic radiation of a silver halide photographic layer, which comprises incorporating an aliphatic acyl hydrazine in a gelatino-silver halide emulsion, coating the emulsion on a support, exposing the undeveloped layer to actinic radiation and developing it with a phenolic developing agent at a pH of at least approximately 9.5 in a developing solution selected from the class of developing solutions containing an appreciable amount of sulfite up to 16 grams per liter when the pH is between 9.5 and 9.7, and containing more than 16 grams per liter of sulfite when the pH is higher than 9.7 in the presence of said hydrazine.

7. The method of increasing the speed of a silver halide photographic layer with respect to radiation consisting of light of wave length shorter than red, which comprises incorporating a semi-carbazide in a gelatino-silver emulsion, coating the emulsion on a support, exposing the undeveloped layer to said radiation and developing it with a phenolic developing agent at a pH of at least approximately 9.5 in a developing solution containing an appreciable amount of sulfite up to 16 grams per liter when the pH is between 9.5 and 9.7, and containing more than 16 grams per liter of sulfite when the pH is higher than 9.7 in the presence of said semi-carbazide.

8. The method of increasing the speed of a silver halide photographic layer with respect to radiation consisting of light of wave length shorter than red, which comprises incorporating hydrazine dihydrochloride in a gelatino-silver halide emulsion, coating the emulsion on a support, exposing the undeveloped layer to actinic radiation and developing it with a phenolic developing agent at a pH of at least approximately

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9.5 in a developing solution selected from the class of developing solutions containing an appreciable amount of sulfite up to 16 grams per liter when the pH is between 9.5 and 9.7, and containing more than 16 grams per liter of sulfite when the pH is higher than 9.7 in the presence of said hydrazine dihydrochloride.

9. The method of increasing the speed of a silver halide photographic layer with respect to radiation consisting of light of wave length shorter than red, which comprises incorporating semicarbazide hydrochloride in a gelatino-silver halide emulsion, coating the emulsion on a support, exposing the undeveloped layer to said radiation and developing it with a phenolic developing agent at a pH of at least approximately 9.5 in a developing solution selected from the class of developing solutions containing an appreciable amount of sulfite up to 16 grams per liter when the pH is between 9.5 and 9.7, and containing more than 16 grams per liter of sulfite when the pH is higher than 9.7 in the presence of said semicarbazide hydrochloride.

10. The method of increasing the speed 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 phenolic developing agent in a developing solution having a pH of at least approximately 9.5 and containing an aliphatic acyl hydrazine and being selected from the class of developing solutions containing an appreciable amount of sulfite up to 16 grams per liter when the pH is between 9.5 and 9.7, and containing more than 16 grams per liter of sulfite when the pH is higher than 9.7.

11. The method of increasing the speed to actinic radiation of silver halide photographic layer which comprises exposing an undeveloped silver halide emulsion layer to actinic radiation and developing it with a phenolic developing agent in a developing solution having a pH of at least approximately 9.5 and containing a semicarbazide and being selected from the class of developing solutions containing an appreciable amount of sulfite up to 16 grams per liter when the pH is between 9.5 and 9.7, and containing more than 16 grams per liter of sulfite when the pH is higher than 9.7.

12. The method of increasing the speed 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 phenolic developing agent in a developing solution containing hydrazine dihydrochloride at a pH of at least 9.5, said developing solution being selected from the class of developing solutions containing an appreciable amount of sulfite up to 16 grams per liter when the pH is between 9.5 and 9.7, and containing more than 16 grams per liter of sulfite when the pH is higher than 9.7.

13. The method of increasing the speed to actinic radiation of silver halide photographic layer which comprises exposing an undeveloped

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silver halide emulsion layer to actinic radiation and developing it with a phenolic developing agent in a developing solution having a pH of at least approximately 9.5 and containing a semicarbazide hydrochloride and being selected from the class of developing solutions containing an appreciable amount of sulfite up to 16 grams per liter when the pH is between 9.5 and 9.7, and containing more than 16 grams per liter of sulfite when the pH is higher than 9.7.

14. A gelatino-silver halide emulsion capable of exhibiting improved speed and contrast characteristics when exposed and developed in a developing solution having a pH of at least approximately 9.5, comprising a gelatino-silver halide emulsion having therein an appreciable amount, not greater than 2 grams per pound of wet emulsion, or a semi-carbazide.

15. A gelatino-silver halide emulsion capable of exhibiting improved speed and contrast characteristics when exposed and developed in a developing solution having a pH of at least approximately 9.5, comprising a gelatino-silver halide emulsion having therein an appreciable amount, not greater than 2 grams per pound of wet emulsion, of an aliphatic acyl hydrazine.

16. A gelatino-silver halide emulsion capable of exhibiting improved speed and contrast characteristics when exposed and developed in a developing solution having a pH of at least approximately 9.5, comprising a gelatino-silver halide emulsion layer having uniformly dispersed therein an appreciable amount, not greater than 2 grams per pound of wet emulsion, of an aryl semicarbazide.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
956,567	Caldwell	May 3, 1910
1,082,622	Caldwell	Dec. 30, 1913
1,560,240	Jelley	Nov. 3, 1925
1,763,990	Sheppard et al.	June 17, 1930
2,127,573	Sheppard et al.	Aug. 23, 1938
2,220,929	Kirby	Nov. 12, 1940
2,245,236	Trivelli et al.	June 10, 1941
2,311,098	Swan et al.	Feb. 16, 1943
2,196,734	Marriage	Apr. 9, 1940
2,266,442	Schinzel	Dec. 16, 1941
2,286,662	Weyde et al.	June 16, 1942
2,309,492	Albers et al.	Jan. 26, 1943
2,339,213	Woodward et al.	Oct. 16, 1939

OTHER REFERENCES

Carroll, "Sensitization of Photographic Emulsions by Colloidal Materials," "Bureau of Standards Journal of Research," vol. I, October, 1928, pp. 565-588, p. 584 cited. (Photostat Copy in Division 7.)