

UNITED STATES PATENT OFFICE

2,419,974

SILVER HALIDE EMULSIONS CONTAINING
WATER-INSOLUBLE HYDRAZINE DERIVATIVES

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5 Claims. (Cl. 95—7)

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This invention relates to photographic emulsions and particularly to a method for incorporating hydrazine derivatives in an emulsion for increasing the speed or contrast, or both, 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 semicarbazides, in emulsions to effect an improvement in the sensitivity characteristics of the emulsion. When using the method of the Trivelli and Smith application, it is sometimes difficult to incorporate in the emulsion the hydrazine derivatives which are insoluble or substantially insoluble in water.

It is, therefore, an object of the present invention to provide a method for incorporating water-insoluble or substantially water-insoluble hydrazine derivatives in a gelatino-silver halide emulsion. A further object is to provide a method for increasing the speed or contrast of photographic emulsions by the use of water-insoluble or substantially water-insoluble hydrazine derivatives. Other advantages will be apparent from the following description of our invention.

These advantages are accomplished by dissolving the hydrazine derivatives in a substantially water-insoluble, water-permeable solvent for the hydrazine derivative and dispersing the mixture in the photographic emulsion.

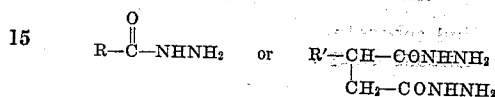
Our method possesses certain distinct advantages among which are the following: (1) The materials are readily incorporated in the emulsion before coating. (2) A certain buffering effect is established due to the distribution laws of a two phase system, which makes possible closer control of the photographic characteristics. (3) Because of its localization in a second phase, the hydrazine derivative may be more favorably placed as far as interfering reactions are concerned, notably hardening and keeping of the emulsion.

In general, our method consists in dissolving the hydrazine derivative of low solubility in water, in a substantially water-insoluble, water-permeable, high boiling solvent for the hydrazine derivative and this solution is then dispersed in water which may contain dispersing or wetting agents, gelatin, and other ingredients, or is dispersed in the gelatin itself. The water dispersion of the hydrazine-solvent phase is then added in the desired proportion to a suitable gelatino-

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silver halide emulsion and this is coated on plates or on film support and dried. These coatings, after exposure, are processed in suitable photographic developers to produce the improved sensitivity characteristics.

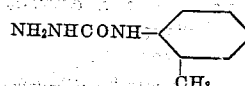
The water-insoluble hydrazine derivatives which may be employed according to our invention include any of the water-insoluble compounds disclosed in Trivelli and Smith application Serial No. 500,088. More specifically, we have found that water-insoluble hydrazine derivatives of the following composition are suitable for use according to our invention:



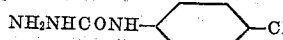
R=arylamine or aryl.

R'=alkyl or aryl.

The following compounds illustrate the water-insoluble hydrazine derivatives which may be employed according to our invention:

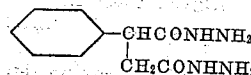


4-(o-tolyl)-semicarbazide



4-(p-chlorophenyl)-semicarbazide

The product formed by the reaction of hydrazine hydrate (85%) with o-benzoyl benzoic acid in methanol solution.



Phenyl succinic dihydrazide

(n) C₆H₁₁-CHCONHNH₂

CH₂CONHNH₂

n-Amyl succinic dihydrazide

The water-insoluble, water-permeable solvent for the hydrazine derivative may be any of the high boiling crystalloidal materials described in Jelley and Vittum U. S. Patent 2,322,027, granted June 15, 1943. These compounds are generally liquid at ordinary temperatures or low melting solids. They should have a high solvent action for the hydrazine derivative and should, of course, be inert toward the silver halide emulsion in which they are incorporated. They should be substantially colorless and stable to-

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ward light, heat and moisture in addition to being inert to the various processing baths which may be encountered, such as developers, silver removal baths, and fixing baths. They should be permeable to water and the photographic processing baths. They should be of low volatility and, in general, compounds which have boiling points above 175° C. at atmospheric pressure are suitable. They should have a sufficiently low refractive index so that the solutions of hydrazine derivatives in them have approximately the same refractive index as gelatin. They should be easily dispersible in emulsions and should be chemically inert toward the hydrazine derivatives.

The following water-insoluble, water-permeable solvents for the hydrazine derivatives have been found suitable for use in our invention, this list being illustrative only:

Phosphoric acid esters:

Tri-o-cresyl phosphate
Tri-m-cresyl phosphate

Phthalic acid esters:

Di-n-butyl phthalate
Methyl phthalate
Ethyl phthalate
 β -Methoxy ethyl phthalate
 β -n-Butoxy ethyl phthalate
n-Amyl phthalate

Other esters:

Guaicol acetate
Ethyl benzyl malonate
n-Hexyl benzoate
n-Butyl-o-methoxy benzoate
Ethyl sebacate

Miscellaneous compounds:

N-n-amy l phthalimide
Ethyl-N,N-di-n-butyl carbamate

It is sometimes desirable to employ a mixture of solvents in the same dispersion in order to obtain the desired combination of properties. For example, a solvent having exceptionally good solvent action might be used in combination with another solvent in the correct proportions to give the final dispersion the desired refractive index. Solvents should not be used which have adverse action on the emulsions such as desensitizing action. In certain cases a solvent which desensitizes when used alone may be employed in combination with another solvent to produce a mixture which does not have adverse desensitizing action on the emulsion.

In dispersing the mixture of hydrazine derivative and solvent in the aqueous solution, it is desirable to use an emulsifying agent such as Gardinol (a higher fatty alcohol sulfate), Arctic Syntax T (U. S. Patent 1,932,180), or Alkanol B. Gelatin may also be used as an emulsifying agent or the mixture of hydrazine derivative and solvent may be dispersed directly in the photographic emulsion.

The following example illustrates a suitable method for incorporating a substantially water-insoluble hydrazine derivative in an emulsion according to our invention:

5 grams of 4-(o-tolyl)-semicarbazide were dissolved at 40° C. in 100 grams of methyl phthalate. This solution was then dispersed in a solution composed of 125 cc. 10% gelatin, 21 cc. 10% Alkanol B, and 5 cc. of water were added to adjust the final gelatin concentration to 7.0%. To facilitate dispersion, the material was passed five times through a colloid mill with the rotor operating at 10,000 peripheral feet per minute and a

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rotor-stator clearance of 0.01 inch. The resultant dispersion was then incorporated into a chlorobromide photographic emulsion and coated on plates.

These plates were exposed and processed at 65° F. for 1½ minutes in a developer of the following composition which was diluted with 500 cc. of water for use:

	grams--	45
Hydroquinone	do	37.5
Sodium hydroxide	do	90
Sodium sulfite (desiccated)	do	30
Potassium bromide	do	1
Water to	liter--	

The plates were then rinsed in an acetic acid stop bath and fixed. When various amounts of dispersion of 4-(o-tolyl)-semicarbazide were added to the emulsion, the speed and contrast of the emulsion were increased as shown in the following table:

	10/i Speed	Gamma	Fog
Control	13.8	4.9	.05
25 200 cc. emulsion + 5 cc. semicarbazide dispersion	17.9	6.6	.05
200 cc. emulsion + 10 cc. semicarbazide dispersion	18.5	7.6	.05
200 cc. emulsion + 40 cc. semicarbazide dispersion	23.9	7.6	.06

The developing solution described above has a pH of 12.8. With developing solutions of lower pH, the improved speed or contrast characteristics may be obtained by the use of a lower sulfite concentration as described in the Trivelli and Smith application Serial No. 500,088.

An important criterion in the incorporation of the water-insoluble hydrazine in the emulsion is the distribution coefficient of the hydrazine between the water-insoluble solvent and water. Hydrazine derivatives of low solubility in water and high solubility in the organic solvent produce the best dispersions. Thus, high molecular weight water-insoluble hydrazine derivatives are the compounds which are most useful.

We believe that the chief advantages of our invention are obtained during preparation and storage of the photographic emulsion. While the improved speed and contrast characteristics are obtained upon development of the emulsion, the advantages of our method of incorporating the water-insoluble hydrazine derivatives in the emulsion are apparent mainly upon preparation and storage of the emulsion. We believe that, upon development of the emulsion, the hydrazine derivatives pass into the gelatin from the organic solvent, due to the action of the alkali in the developer. In the gelatin they exert an action on the silver halide grains during development which brings about an increase in speed or contrast characteristics. It is to be understood that this statement of theory is presented only to explain the apparent action of our compounds and not to limit the scope of our invention in any way.

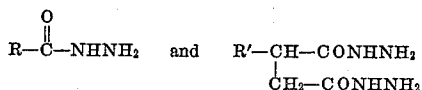
It will be understood that our invention is to be taken as limited only by the scope of the appended claims.

We claim:

1. 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

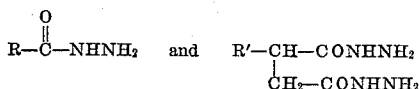
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therein a mixture of a substantially water-insoluble hydrazine derivative having a formula selected from the class consisting of



where R is selected from the class consisting of aryl and arylamine radicals and R' is selected from the class consisting of alkyl and aryl radicals, and a substantially water-insoluble organic solvent for said hydrazine derivative, said solvent having a boiling point above about 175° C. and being permeable to processing solutions.

2. 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 a mixture of a substantially water-insoluble hydrazine derivative having a formula selected from the class consisting of



where R is selected from the class consisting of aryl and arylamine radicals and R' is selected from the class consisting of alkyl and aryl radicals and a substantially water-insoluble phthalic acid ester solvent for said hydrazine derivative, said ester having a boiling point above about 175° C. and being permeable to photographic processing solutions.

3. 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 a mixture of a substantially water-insoluble 4-aryl semicarbazide and a substantially water-insoluble organic solvent for said semicarbazide, said solvent having a boiling point

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above about 175° C. and being permeable to photographic processing solutions.

4. 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 a mixture of 4-(o-tolyl)-semicarbazide in a substantially water-insoluble organic solvent for said semicarbazide, said solvent having a boiling point above about 175° C. and being permeable to photographic processing solutions.

5. 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 a mixture of 4-(o-tolyl)-semicarbazide and methyl phthalate.

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