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UNITED STATES PATENT OFFICE

2,588,982

DIRECT POSITIVE PHOTOGRAPHS USING HYDRAZINE IN THE EMULSION

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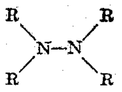
3 Claims. (Cl. 95—88)

This invention relates to photography and particularly to a method of making direct positive photographs.

In Fallesen U. S. Patent 2,497,875, a method is described for making direct positive photographs with an internal latent image type emulsion by developing the exposed emulsion in an aerial fogging developer with access of oxygen.

I have now found a method for developing direct positive images in an exposed internal latent image emulsion, which method is simpler and more convenient than that described in the Fallesen patent, and which uses a developer not containing formaldehyde; the developer therefore, has better keeping properties than developers hitherto used for this purpose. In addition, the method which I propose to use does not require the addition of oxidizing agents to the developer or any special aeration technique for production of the positive image.

According to my invention the internal latent image emulsion is exposed and then developed in a silver halide developing solution in the presence of a hydrazine compound of the general formula



in which at least two R's are hydrogen atoms and when less than four R's are hydrogen atoms, the remaining R's are aryl, aralkyl, acyl, or carboxylic acid amide groups. Preferably, the hydrazine compound does not contain more than one aralkyl, acyl, or carboxylic acid amide group, although it may contain either one or two aryl groups. The hydrazine compound may be present either in the developing solution itself or in the emulsion. Since hydrazines are reactive with aldehyde type compounds it is undesirable to use aldehyde, such as formaldehyde, for hardening purposes, in emulsions containing hydrazines.

The photographic emulsion used in the process of my invention is a gelatino-silver halide emulsion such as a silver bromide emulsion, a silver bromoiodide emulsion or a silver chloroiodide emulsion. It need not contain optical sensitizing dyes although certain sensitizing dyes may be added to it for the purpose of optical sensitizing or for promoting reversal. The emulsion should be undigested or if digested, the digestion should be carried out without the use of sulfur sensitizers. An emulsion of this type is that known as Burton's emulsion, described in Wall, "Photographic Emulsions," 1929, pages 52 and 53. Burton's emulsion is made as follows:

A

Silver nitrate____g__	100
Water ____cc__	500

Ammonia—to form clear solution.

B

Potassium bromide____g__	80
Potassium iodide____g__	50
Soft gelatin____g__	20
Water ____cc__	1000

C

Dry gelatine____g__	250

B is heated to 70° C. and A, cold, added to B with constant shaking, digested for 20 minutes at 50° C., and allowed to cool slowly. C is added after being allowed to swell for 20 minutes in water, drained and melted. The emulsion is then set and washed.

An internal latent image emulsion, that is, one which forms the latent image mostly inside the silver halide grains, as described on pages 296 and 297 of Mees' "The Theory of the Photographic Process," 1942, is especially useful for the process of my invention.

Most of the internal latent image emulsions are silver bromo-iodide emulsions of high iodide content, preferably containing at least 10%–20% of iodide. Burton's emulsion is an emulsion of this type, having a silver iodide content of approximately 40% of the content of silver halide. It is not absolutely essential, however, for the emulsion to contain silver iodide.

An internal latent image emulsion made as described in Davey and Knott U. S. application Serial No. 82,914, filed March 22, 1949, may also be used according to my invention. This emulsion is prepared by first forming in the absence of ammonia and 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 the grains to silver bromide or silver bromoiodide and if the silver iodide content of the emulsion is less than 6% calculated on the total silver halide, treating such grains with an iodine compound to bring the silver iodide up to at least 6%, 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 or bromide. An example of an emulsion made in this way is as follows:

Solution No. 1

Inert gelatine	20 grams	at 40° C.
KCl	20 grams	
Water	560 cc.	

Solution No. 2

KCl	100 grams	at 45° C.
Water	520 cc.	

Solution No. 3

$AgNO_3$	195 grams	at 45° C.
Water	520 cc.	

Solution No. 4

KBr	160 grams	at 45° C.
KI	40 grams	
Water	500 cc.	

Run Solutions Nos. 2 and 3 simultaneously into Solution No. 1 in a vessel, taking 90 seconds to do this. Then ripen for 1 minute at 45° C. Next add Solution No. 4, then ripen for 20 minutes at 45° C. Next add 235 grams of inert gelatine (dry). Then ripen at 45° C. for 15 minutes during which time the gelatine dissolves. Set and shred the emulsion and then wash until free from all soluble bromide and then add about 150 cc. of 10% solution of KCl (by weight), and then add water to make 3½ litres.

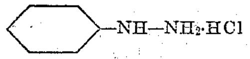
An internal latent image type of silver halide emulsion may be defined as one which, when a test portion is exposed to a light intensity scale for a fixed time between 1/100 and 1 second, and developed for 4 minutes at 20° C. in the ordinary, "surface" developer (Example I), exhibits a maximum density not greater than 1/5 the maximum density obtained when the same emulsion is equally exposed and developed for 3 minutes at 20° C. in an internal type developer (Example II). Preferably the maximum density obtained with the surface developer is not greater than 1/10 the maximum density obtained when the same emulsion is developed in the internal type developer. Stated conversely, an internal latent image emulsion, when developed in an internal type developer (Example II) exhibits a maximum density at least 5, and preferably at least 10, times the maximum density obtained when the same emulsion is exposed in the same way and developed in a surface developer (Example I).

My process is carried out by exposing the internal latent image emulsion layer to an object or image and then placing the exposed emulsion layer directly in a silver halide developing solution containing one or more of the hydrazine compounds, or if the hydrazine compound is incorporated in the emulsion, by placing the exposed layer in the developing solution without the hydrazine compound. Developing agents suitable for use in the process of my invention include the usual phenolic or aminophenol type developing agents, such as N-methyl-p-aminophenol sulfate, p-benzohydroquinone, catechol, 2-methyl hydroquinone, 2-chlorohydroquinone, p-aminophenol, and pyrogallol. If the hydrazine compound is in the developing solution, the developing solution should have a pH of from 10 to 13, depending upon the degree of activity of the particular hydrazine compound which it contains, although the preferred range with most hydrazine compounds is from pH 11 to pH 12.

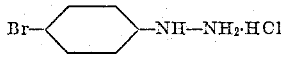
The following hydrazine compounds are suitable for use according to my invention:

$NH_2—NH_2·2HCl$

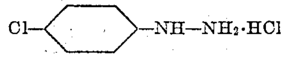
Hydrazine dihydrochloride



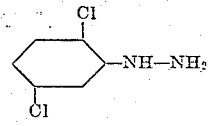
Phenylhydrazine hydrochloride



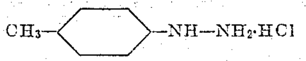
p-Bromphenylhydrazine hydrochloride



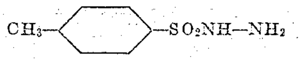
p-Chlorphenylhydrazine hydrochloride



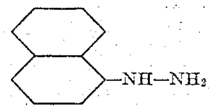
2,5-Dichlorophenyl hydrazine



p-Tolyl hydrazine hydrochloride

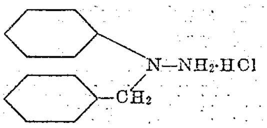


p-Toluene sulfonyl hydrazine

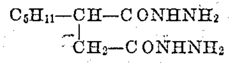


α-Naphthylhydrazine

p-Acetylphenylhydrazine

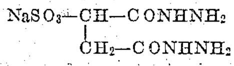


α-Benzyl-α-phenylhydrazine hydrochloride



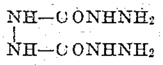
$$\begin{array}{l} C_5H_{11}—CH—CONHNH_2 \\ \qquad\quad | \\ \qquad\quad CH_2—CONHNH_2 \end{array}$$

n-Amyl succinyl dihydrazide



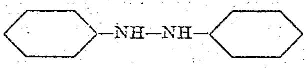
$$\begin{array}{l} NaSO_3—CH—CONHNH_2 \\ \qquad\quad | \\ \qquad\quad CH_2—CONHNH_2 \end{array}$$

Sodium sulfosuccinyl dihydrazide



$$\begin{array}{l} NH—CONHNH_2 \\ | \\ NH—CONHNH_2 \end{array}$$

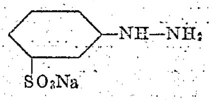
Hydrazine dicarbonic dihydrazide



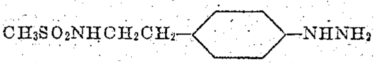
Hydrazobenzene

p-Hydrazinobenzoic acid

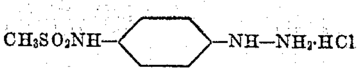
p-Hydrazinobenzene sulfonic acid (sodium salt)



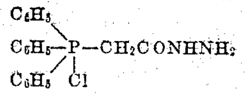
Phenylhydrazine-m-sulfonic acid (sodium salt)



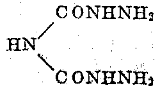
p-[p-(methylsulfonamido)ethyl] phenyl hydrazine



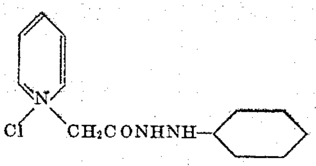
p-Methyl-sulfonamido-phenylhydrazine hydrochloride



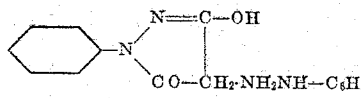
Triphenyl phosphonium chloride acetohydrazide



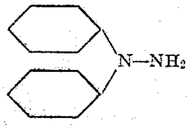
Diamino biuret



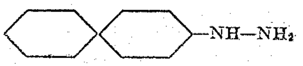
β-Phenyl acethydrazido pyridinium chloride



Addition product of phenyl hydrazine and 1-phenyl-3-hydroxy-5-pyrazolone of probable structure shown

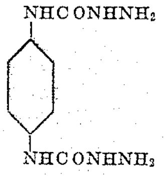


N,N-diphenyl hydrazine



p-Diphenyl hydrazine

p,p'-dihydrazino-diphenyl-dihydrochloride



4-p-Phenylene disemicarbazide

The hydrazines disclosed in Weissberger U. S. application Ser. No. 159,139 and Thirtle and Weissberger U. S. application Ser. No. 159,140 may also be used.

An ordinary, surface-type developer, that is, one which develops an image only on the surface of the grains of an internal latent image emulsion, is the following:

Example I

p-Hydroxyphenylglycine	g.	10
Sodium carbonate (crystals)	g.	100
Water to	liter	1

Development time, 4 min. at 20° C.

An internal type developer, that is, one which develops an image inside the grains of an internal latent image emulsion, is the following:

Example II

Hydroquinone	g.	15
Monomethyl-p-aminophenol sulfate	g.	15
Sodium sulfite (anhydrous)	g.	50
Potassium bromide	g.	10
Sodium hydroxide	g.	25
Sodium thiosulfate (crystals)	g.	20
Water to	liter	1

Development time, 3 min. at 20° C.

My invention will be further described by reference to the following specific example:

Example III

An emulsion made as described in the Davey and Knott application Serial No. 82,914 was coated on a support, dried and exposed on an intensity scale sensitometer to 3000° Kelvin tungsten illumination and developed for 3 minutes at 70° F. in a solution of the following composition:

N-methyl-p-aminophenol sulfate	g.	5
Hydroquinone	g.	10
Sodium sulfite (desiccated)	g.	75
Sodium metaborate	g.	30
Sodium hydroxide	g.	10
Phenyl hydrazine hydrochloride	g.	0.5
Water to	liter	1

With these developing conditions a direct positive image of satisfactory characteristics was obtained. A similar development using the same developing solution to which was added 0.2 g. per liter of 5-methyl benzotriazole also produced a satisfactory image although with no improvement in image development of unexposed areas.

In most cases, 5-methyl benzotriazole and similar compounds can be added to the developing solution without essentially modifying the resulting image. However, in one case, using p-toluene sulfonyl hydrazine, no reversal was obtained when the 5-methyl benzotriazole was added to the developer. In some cases the reversal was weakened by adding the benzotriazole. In other cases the maximum density was increased by adding 5-methyl benzotriazole to the developer, for example, with phenyl hydrazine or p-[β-(methylsulfonamido) ethyl]-phenyl hydrazine.

The incorporation of the hydrazine compound in the emulsion is illustrated by the following examples:

Example IV

To the amount of a chloro-bromoiodide emulsion made as described in the Davy & Knott application, Serial Number 82,914, containing 108 gms. of silver, there was added 2 gms. of p-methyl-sulfonamido - phenyl - hydrazine hydrochloride as a 1% solution in methyl alcohol at 40° C., and the mixture was coated on a documentary photographic paper support at the rate of 600 square feet per mole of silver. The paper was dried in the usual way and was exposed on an intensity scale sensitometer to 3000° Kelvin tungsten illumination and was developed for 90 seconds at 75° F. in a solution of the following composition.

N-methyl-p-amino-sulfate	gms.	5
Hydroquinone	gms.	10
Sodium sulfite (desiccated)	gms.	75
Sodium phosphate	gms.	75
Sodium hydroxide	gms.	12
Benzotriazole	gms.	0.2
Water to	liter	1

A direct positive image of satisfactory characteristics was obtained.

Example V

An emulsion was prepared and coated in the same way as described in Example IV except that 2 gms. of p-[β-(methyl-sulfonamido) ethyl] phenyl hydrazine was used instead of the hydrazine named in Example IV. This paper was dried as usual and exposed and developed as in

Example IV. A direct positive image of satisfactory characteristics was obtained.

Although the reversal effect obtained in my process does not require agitation of the developer or the presence of oxidizing agents, I believe that the fogging action obtained is related to aerial oxidation. The active agent, which is derived from the hydrazine compound appears to have a long life in the developing solutions and only brief exposures to atmospheric oxygen appear sufficient to produce fogging even in the absence of continued aeration. My process, therefore, has distinct advantages for deep tank photographic processing.

This application is a continuation-in-part of my application Serial No. 159,150, filed April 29, 1950, now Patent No. 2,563,785 of August 7, 1951.

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

I claim:

1. The method of obtaining a direct positive image in a silver halide emulsion layer, which comprises exposing to light rays to which the emulsion is sensitive, a silver halide emulsion layer a test portion of which upon exposure to a light intensity scale for a fixed time between $\frac{1}{100}$ and 1 second and development for 3 minutes at 20° C. in the following internal type developer (II):

	Grams
Hydroquinone	15
Monomethyl-p-aminophenol sulfate	15
Anhydrous sodium sulfite	50
Potassium bromide	10
Sodium hydroxide	25
Sodium thiosulfate	20
Water to 1 liter	

gives a maximum density at least 5 times the maximum density obtained when the equally exposed silver halide emulsion is developed for 4 minutes at 20° C. in the following surface developer (I):

	Grams
p-Hydroxyphenylglycine	10
Sodium carbonate	100
Water to 1 liter	

said emulsion containing a hydrazine compound of the general formula

$$H_2N—NHR$$

where R is a mononuclear aryl radical, and developing only the unexposed portion of said emulsion layer in a silver halide developer.

2. The method of obtaining a direct positive image in a silver halide emulsion layer, which comprises exposing to light rays to which the emulsion is sensitive, a silver halide emulsion layer a test portion of which upon exposure to a light intensity scale for a fixed time between $\frac{1}{100}$ and 1 second and development for 3 minutes

at 20° C. in the following internal type developer (II):

	Grams
Hydroquinone	15
Monomethyl-p-aminophenol sulfate	15
Anhydrous sodium sulfite	50
Potassium bromide	10
Sodium hydroxide	25
Sodium thiosulfate	20
Water to 1 liter	

gives a maximum density at least 5 times the maximum density obtained when the equally exposed silver halide emulsion is developed for 4 minutes at 20° C. in the following surface developer (I):

	Grams
p-Hydroxyphenylglycine	10
Sodium carbonate	100
Water to 1 liter	

said emulsion containing p-methyl-sulfonamidophenyl hydrazine hydrochloride, and developing only the unexposed portion of said emulsion layer in a silver halide developer.

3. The method of obtaining a direct positive image in a silver halid emulsion layer, which comprises exposing to light rays to which the emulsion is sensitive, a silver halide emulsion layer a test portion of which upon exposure to a light intensity scale for a fixed time between $\frac{1}{100}$ and 1 second and development for 3 minutes at 20° C. in the following internal type developer (II):

	Grams
Hydroquinone	15
Monomethyl-p-aminophenol sulfate	15
Anhydrous sodium sulfite	50
Potassium bromide	10
Sodium hydroxide	25
Sodium thiosulfate	20
Water to 1 liter	

gives a maximum density at least 5 times the maximum density obtained when the equally exposed silver halide emulsion is developed for 4 minutes at 20° C. in the following surface developer (I):

	Grams
p-Hydroxyphenylglycine	10
Sodium carbonate	100
Water to 1 liter	

said emulsion containing p-[p-(methylsulfonamido)ethyl] phenyl hydrazine, and developing only the unexposed portion of said emulsion layer in a silver halide developer.

CHARLES E. IVES.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
2,563,785	Ives	Aug. 7, 1951