

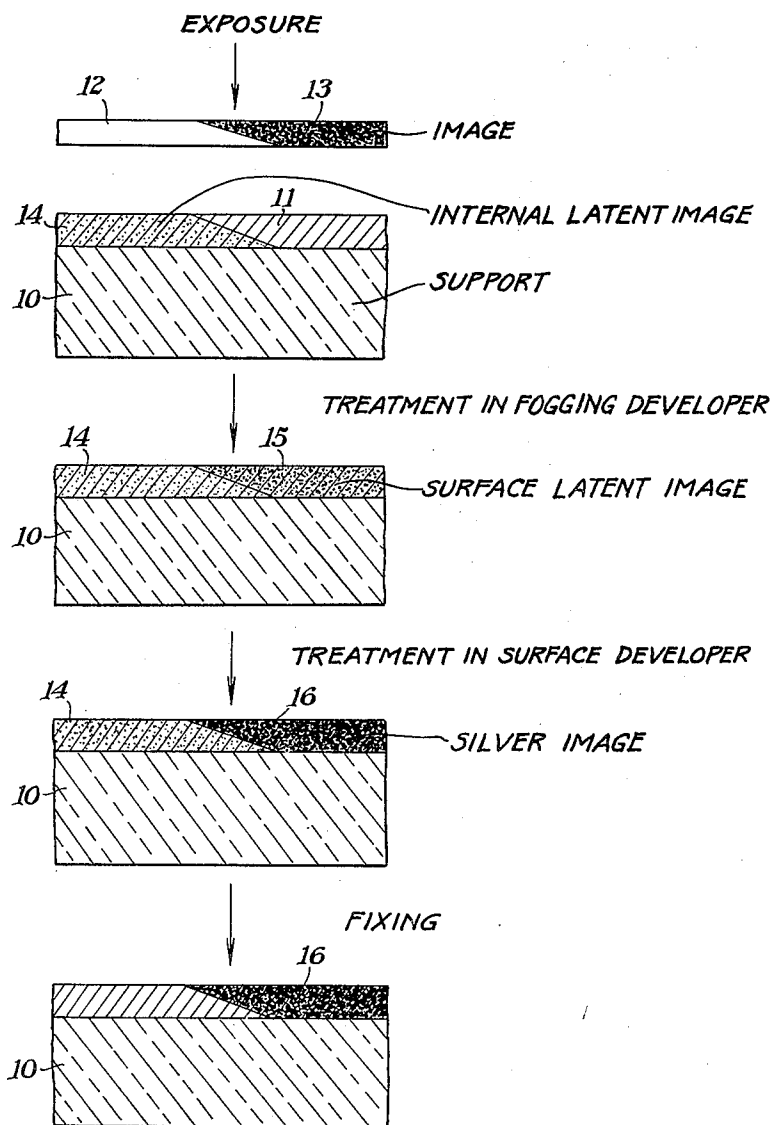
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TWO-BATH DIRECT POSITIVE PHOTOGRAPHIC PROCESS

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TWO-BATH DIRECT POSITIVE
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4 Claims. (Cl. 95—88)

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

In Fallesen U. S. application Serial No. 780,405 filed October 17, 1947, now Patent No. 2,497,875, February 21, 1950, a process of making direct positive photographs is described in which a special type of silver halide emulsion layer, capable of giving an internal latent image, is exposed and developed in a photographic developer which is capable of giving aerial fog. The first exposure of this emulsion produces an internal latent image and development of the exposed emulsion in a developer which gives aerial fog, develops a positive image in those regions of the emulsion layer which were not exposed. To produce a direct positive with this emulsion, it is necessary to use a special selectively fogging developer having low sulfite concentration and to use an agent in the developer or film which is effective to produce aerial fog in the emulsion. Such oxidizing of fogging agent may be oxygen of the air, or agents in the developer such as hydrogen peroxide, sodium perborate or certain dyes. The restriction in the choice of the developer entails certain inconveniences such as a limited rate of development of the emulsion.

It is therefore an object of the present invention to provide a novel method for obtaining direct positive photographs. A further object is to provide a method for obtaining direct positive photographs which does not require solarization or a second exposure and which permits rapid development of the exposed emulsion to a positive. A further object is to provide a method for obtaining direct positive photographs which does not require exposure of the emulsion to light after a first development step. Other objects will appear from the following description of my invention.

These objects are accomplished by exposing in the usual way a silver halide emulsion layer in which the emulsion is capable of producing an internal latent image, treating the exposed emulsion with a developer capable of producing aerial fog for only a relatively short time and then transferring the film to an active developer of the conventional type to produce a positive image in the emulsion.

In the accompanying drawing, sectional views of a photographic element at successive stages in my process are shown.

The photographic emulsion used in the process of my invention is a gelatino silver halide emulsion such as a silver bromide, silver bromiodide or silver chloriodide emulsion. It need not contain optical sensitizing dyes although certain

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sensitizing dyes may be added to it for the purpose of inducing aerial fog. 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. A further type of emulsion suitable for my process is an internal latent image emulsion described in Davey and Knott U. S. application Serial No. 790,232 filed December 6, 1947, now abandoned, of which application Serial No. 82,914, filed March 22, 1949, is a continuation-in-part.

Most of the "internal latent image" emulsions are silver bromiodide emulsions of high iodide content preferably containing at least 10 to 20% of the amount of silver halide as the iodide. Burton's emulsion in 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" 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 1), exhibits a maximum density not greater than $1/2$ 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 2). Preferably the maximum density obtained with the "surface" developer is not greater than $1/3$ 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 2) exhibits a maximum density at least 5 and preferably at least 10 times the maximum density obtained when the emulsion is exposed in the same way and developed in a "surface" developer (Example 1).

In the method of producing direct positive images described in Fallesen U. S. application Serial No. 780,405, now Patent 2,497,875 the exposed emulsion must be developed for from 5 to 6 minutes at 70° F. in the special selectively fogging developer. According to my method, this film after exposure is bathed in the selectively fogging developer for only about 30 to 40 seconds after which it is removed to a more active developer of the conventional type which as a result of the preliminary treatment is able to produce a direct positive picture. The film may be washed between these baths if it is desired to do so although no intermediate treatment is necessary

and no intermediate exposure is required. Only about a minute and a half in the active developer is required to produce about the same image quality as produced when the film is allowed to remain in the selectively fogging developer for 5 to 6 minutes. If, on the other hand, the conventional active developer in which the image is produced according to my process, were used without the preliminary bath in the selectively fogging developer, a negative image would result. The exposed film could be allowed to remain in the selectively fogging developer for about 6 minutes to produce a positive image or can be removed from the selectively fogging developer after about 30 seconds according to my process and placed in a conventional active developer to produce the positive image. Thus the process of my invention has the effect of reducing the time of treatment of the exposed emulsion from about 6 minutes to 2 minutes or less.

In the 30 to 40 second treatment in the selectively fogging developer used according to my invention no visible image appears in the emulsion. The treatment is mainly one of preparation and conditioning for subsequent development. Presumably the selectively fogging developer creates development centers on the surface of the silver halide grains and these are more susceptible to development in the ordinary surface type developer, than the development centers created inside the grains by the action of the earlier light exposure. When the emulsion is subjected to treatment in the selectively fogging developer, the grains affected by the light exposure are not susceptible to fogging and therefore do not develop when the emulsion is placed in the active developer.

The results of the various steps in my process will be readily understood by reference to the accompanying drawing which shows in sectional view a film at various stages in the process. As shown in the first stage of the drawing, a sensitive element comprising a support 10 having thereon a sensitive emulsion layer 11 of the internal latent image type is exposed to light under an image represented as having a transparent portion 12 and an opaque portion 13. This exposure produces an internal latent image at 14 in the emulsion layer 11.

Treatment of the exposed element in the selectively fogging developer produces a surface latent image at 15 in the portions of the layer which were not exposed, without affecting the internal latent image at 14 as shown in the second stage of the drawing.

A treatment of the element in an active conventional surface type developer reduces the surface latent image to a metallic silver image 16 as shown in the third stage of the drawing. The remaining silver halide is then removed by fixing to leave the silver image 16 in the portions of the layer which were unexposed by the original exposure as shown in the final stage of the drawing.

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

Example 1

	Grams
p-Hydroxyphenylglycine	10
Sodium carbonate (crystals)	100
Water to 1 liter.	
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 2

	Grams
Hydroquinone	15
Monomethyl-p-aminophenol sulfate	15
Sodium sulfite (anhydrous)	50
Potassium bromide	10
Sodium hydroxide	25
Sodium thiosulfate (crystals)	20
Water to 1 liter.	
Development time, 3 min. at 20° C.	

A developer which produces a direct positive image upon exposure and development of an internal latent image emulsion, as described in Stauffer U. S. application Ser. No. 780,569, filed October 17, 1947, now Patent No. 2,497,917, February 21, 1950, is the following:

Example 3

	Grams
Hydroquinone	10.0
Sodium sulfite (des.)	16.0
Paraformaldehyde	4.0
Sodium carbonate (des.)	25.0
Benzotriazole	0.4
Water to 1 liter.	

A conventional active surface developer which may be used to produce the positive image according to my invention after treatment of the exposed emulsion in a selectively fogging developer is the following:

Example 4

	Grams
Hydroquinone	45.0
Sodium sulfite (des.)	90.0
Sodium hydroxide	37.5
Potassium bromide	30.0
Water to 1.0 liter.	

In place of the developer of Example 4, other developers such as a monomethyl-p-aminophenol developer containing sulfite and carbonate, or even a ferrous oxalate developer, can be used.

My invention will now be described by reference to the following specific example.

An emulsion such as that described in Davey and Knott U. S. application Serial No. 790,232, filed December 6, 1947, was coated on a support, dried and exposed on an Eastman IIB Sensitometer (Journal Society Motion Picture Engineers), 17 (1931) page 536. The exposed emulsion was treated for 36 seconds by immersion in the developer, Example 3, at 70° F. The film was removed from this developer and no visible image was observed. The film was then immediately treated by immersing it in the developer, Example 4, for 1½ minutes at 70° F. after which time the film was removed from the developer, fixed in hypo, washed and dried. A direct positive image of satisfactory characteristics was produced.

In addition to the use of the selectively fogging developers of Fallesen U. S. application Serial No. 780,405, now U. S. Patent 2,497,875, and Stauffer U. S. application Serial No. 780,569, now U. S. Patent 2,497,917, as the pretreating baths of my invention, a developer of the following composition such as described in Glass and

Richey U. S. application Serial No. 780,574 filed October 17, 1947, now U. S. Patent 2,507,154 may be used in the process of my invention.

Example 5

	Grams
2-amino-5-diethylaminotoluene hydrochloride	3
Sodium sulfite (des.)	3
Sodium carbonate monohydrate	30
Sodium hydroxide	3
Acetoacet-2,5-dichloroanilide	3
Water to 1 liter.	

Using the selectively fogging developer of Example 5, I was able to produce a silver image of satisfactory quality with 30 seconds treatment of the exposed emulsion in the solution of Example 5 followed by 1½ minutes in the developer of Example 4.

It will be understood that the modifications and examples 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 ¼₁₀₀ and 1 second and development for 3 minutes at 20° C. in the following internal type developer:

	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 (crystals)	100
Water to 1 liter	

immersing the exposed emulsion layer in a developer selected from the class of (1) an aerial fogging developer with access of oxygen and (2) a primary aromatic amino developing agent solution containing an active methylene coupler compound capable of coupling with the oxidation product of said developing agent to produce a dye image, only long enough to render developable the unexposed silver halide grains but not long enough to develop a visible image, then developing a visible positive silver image in said layer in an active surface-type developer which develops the silver halide grains which are developable by developer (I) and which produces said positive image in a shorter time than if the first developer were used alone.

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

¼₁₀₀ and 1 second and development for 3 minutes at 20° C. in the following internal type developer:

	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 (crystals)	100
Water to 1 liter	

immersing the exposed emulsion layer in an aerial fogging developer with access of oxygen, only long enough to create development centers on the surface of the unexposed silver halide grains but not long enough to develop a visible image, then developing a visible image in said layer in an active surface-type developer which develops the silver halide grains which are developable by developer (I) and which produces said positive image in a shorter time than if the first developer were used alone.

3. 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 ¼₁₀₀ and 1 second and development for 3 minutes at 20° C. in the following internal type developer:

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

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 (crystals)	100
Water to 1 liter	

immersing the exposed emulsion layer in a developer selected from the class of (1) an aerial fogging developer with access of oxygen, (2) a primary aromatic amino developing agent solution containing an active methylene coupler compound capable of coupling with the oxidation product of said developing agent to produce a dye image, only long enough to render developable the unexposed silver halide grains but not long enough to develop a visible image, then developing said grains to a visible image in an active hydroxy benzene developer containing approximately 90 grams of sodium sulfite per liter of developing solution.

4. The method of obtaining a direct positive image in a silver halide emulsion layer, which

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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:

	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 (crystals)	100
Water to 1 liter	

immersing the exposed layer in an aerial fogging developer of the following composition for about 36 seconds at 70° F., while bubbling air through said developer in contact with said emulsion:

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	Grams
Hydroquinone	10
Sodium sulfite (des.)	10
Paraformaldehyde	4
Sodium carbonate (des.)	25
Benzotriazole	0.4
Water to 1 liter	

then immediately immersing said layer in the following surface developer for one and one-half minutes at 70° F.:

	Grams
Hydroquinone	45
Sodium sulfite (des.)	90
Sodium hydroxide	37.5
Potassium bromide	30
Water to 1 liter	

thereby forming a positive image in said layer, and fixing and drying said layer.

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REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
2,401,051	Crouse et al.	May 23, 1946

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