Feb. 21, 1950 R. E. STAUFFER 2,497,917

METHOD OF PRODUCING DIRECT POSITIVE PHOTOGRAPHS HAVING INCREASED DENSITY

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FIG. 1.

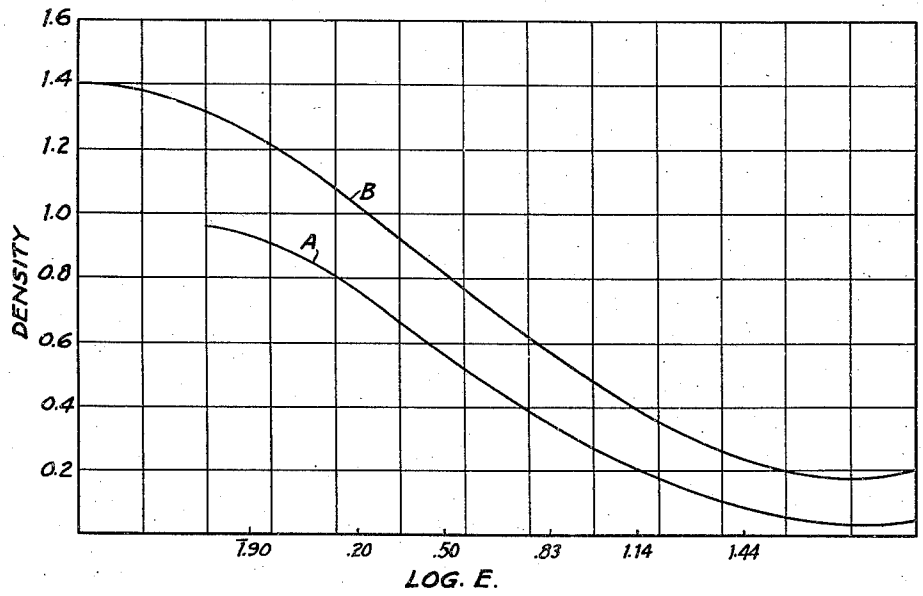
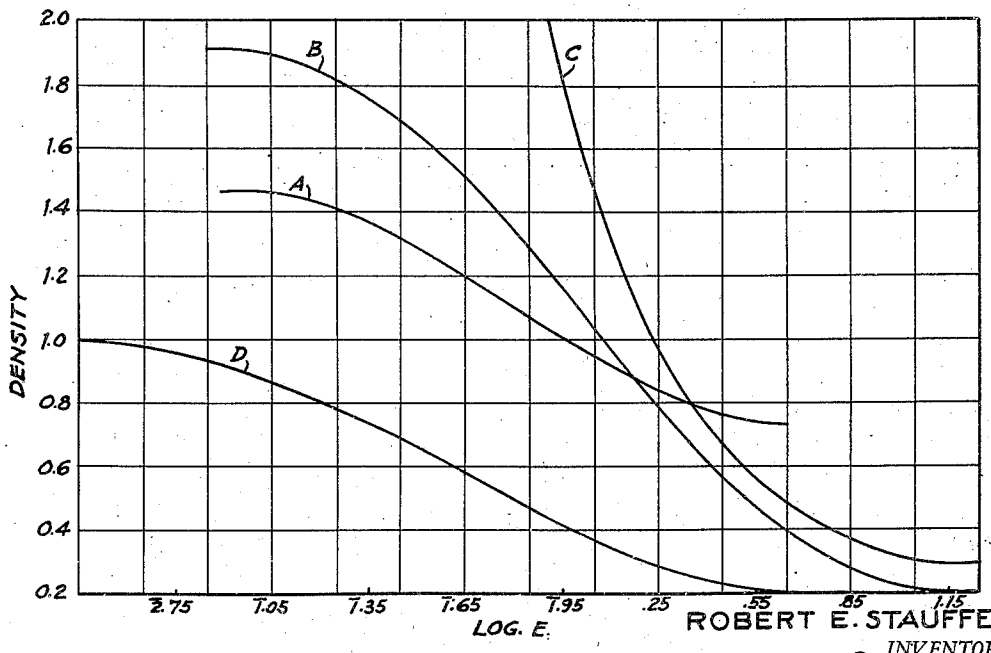


FIG. 2.



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METHOD OF PRODUCING DIRECT POSITIVE PHOTOGRAPHS HAVING INCREASED DENSITY

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Application October 17, 1947, Serial No. 780,569

4 Claims. (Cl. 95—88)

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

Direct positive effects may be produced by solarizing the developable latent image by overexposure, by using a second exposure to obtain the Sabattier or the Clayden effect or by redeveloping a developed negative image. Solarizable sensitized products require very intense exposures to obtain the desired direct positive photograph. The use of a second exposure has obvious disadvantages from the point of view of practical technique. Redevelopment adds at least two operations to the usual and normal developing procedure.

Fallesen U. S. patent application, Serial No. 780,405, filed concurrently herewith describes forming a direct positive image in a suitable silver halide emulsion by exposing the emulsion in the usual way and developing it in a developer which is capable of giving aerial fog. The emulsion is preferably of the internal latent image type such as described in Davey and Knott U. S. patent application, Serial No. 790,232, filed December 6, 1947, now abandoned.

I have discovered that certain compounds which have been used as photographic antifoggants or emulsion addenda may be added to the developers used in the process of Fallesen patent application, Serial No. 780,405, and that increased aerial fog, that is, higher maximum density of the reversal image, results from this use of the compound. The compounds which I propose to use are heterocyclic nitrogen-containing ring compounds having 5 or 6 atoms in the heterocyclic ring and so constituted as to increase the maximum density of the positive image obtained in developing solutions capable of producing aerial fog.

I have found that in the development of certain emulsions, such as the "internal latent image" emulsions, the use of certain anti-foggants or other compounds in the developing solutions increases the density in the unexposed areas by intensifying the aerial fog in the low exposure regions. At the same time, the ordinary anti-foggant property is exhibited in the toe portion of the reversal curves, that is, the areas of maximum exposure. I believe that this enhancement of aerial fog in unexposed areas is a new phenomenon which offers considerable value for direct positive photographic materials.

In the accompanying drawing, the two figures are characteristic curves of photographic emulsions illustrating results obtained according to my invention.

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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 chloro-iodide emulsion. It need not contain optical sensitizing dyes, although certain sensitizing dyes may be added to it for the purpose of inducing aerial fog, as explained more fully in Fallesen application, Serial No. 780,405. A suitable emulsion 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	grams	100
Water	cubic centimeters	500
Ammonia—to form clear solution		
B. Potassium bromide	grams	80
Potassium iodide	do	50
Soft gelatin	do	20
Water	cubic centimeters	1000
C. Dry gelatin	grams	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. 790,232, filed December 6, 1947, 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 cubic centimeters	
Solution No. 2:		
KCl	100 grams	at 45° C.
Water	520 cubic centimeters	
Solution No. 3:		
$AgNO_3$	195 grams	at 45° C.
Water	520 cubic centimeters	
Solution No. 4:		
KBr	160 grams	at 45° C.
KI	40 grams	
Water	500 cubic centimeters	

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 liters.

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 ⅕ 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 $\frac{1}{10}$ 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 2) 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 1).

The developer used in the method of my invention should be one which produces oxidation fog or aerial fog. Such developers have been described by Dundon and Crabtree in "American Photography," 1924, vol. 18, page 742. An example of such a developer is a hydroquinone developer containing little or no sulfite, and is illustrated in Example 3.

The "aerial fog" may be produced in the developer in various ways and may be accelerated or intensified by resorting to various expedients. The developer used should preferably have low sulfite ion content and should preferably contain no silver halide solvent more powerful (as a silver halide solvent) than sulfite. Aerial fog may also be increased by bubbling air vigorously through the developer in such manner that the air comes frequently into contact with the emulsion surface of the photograph during development. Certain chemical agents such as copper sulfate incorporated either in the developer or in the emulsion itself may be used to produce or encourage the production of aerial fog. Hydrogen

peroxide or certain dyes such as methylene blue increase aerial fog. Fogging agents containing labile sulfur are, however, unsuitable. The fogging action should produce developable surface latent image in the unexposed silver halide grains as explained in the Fallesen patent application Serial No. 780,405.

Compounds useful according to my invention for enhancing aerial fog and the preferred range of amounts of each are as follows:

Compound	Amount per liter of developer
	Grams
Benzotriazole	0.4
Methyl benzotriazole	0.05–0.2
Ethyl benzotriazole	0.05–0.1
1-Ethyl oxindole	0.10
5-Nitroindazole	.05–0.1
6-Nitrobenzimidazole	0.05–0.1
Histidine	0.10–0.2
Ethyl benzoxazole	0.10
N-ethyl pyrrole	0.1–0.2
2,5-Dimethylpyrrole	0.05–0.2
2,4-Dimethyl-5-carbethoxypyrrole	0.05–0.2
2,3-Dimethyl quinoxaline	0.05–0.40
2-Thio-2,4(3,5)-thiazoledione	0.05–0.20
2,4,6-Tri-isopropylamino-S-triazine	0.1–0.2
2,4-Dimethylamino-6-chloro-S-triazine	0.1–0.2
2,4-Di-(β-methoxyethylamino)-6-chloro-S-triazine	0.2
2,4,6-Tri-n-butylamino-S-triazine	0.2
1-Carboxymethyl-3-phenyl-2-thiohydantoin	0.1–0.5
1,4-diphenyl-3-anilino-5-phenylimino-1,2,4-triazoline	0.05 to 0.50

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

Example 1

p-Hydroxyphenylglycine	grams	10
Sodium carbonate (crystals)	do	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 2

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

Development time, 3 min. at 20° C.

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

Example 3

An emulsion such as the Davey and Knott emulsion described above 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 then developed for 12 minutes at 68° F. in the following developing solution:

Hydroquinone	grams	22.5
Sodium sulfite	do	30
p-Formaldehyde	do	7.5
Potassium metabisulfite	do	2.6
Boric acid crystals	do	7.5
Potassium bromide	do	1.6
Water to	liter	1

The developer was agitated during the development by forcing air through a sintered glass bub-

ble tube completely submerged in the developer tank. A similar emulsion exposed in the same way was developed for the same length of time in the same solution containing 0.4 g. of benzotriazole per liter of developing solution. Direct positive images were obtained in each case and were plotted as shown in Fig. 1 of the accompanying drawing. Curve A was obtained from the developer containing no benzotriazole and curve B was obtained from the developer containing benzotriazole. The curves show that a higher maximum density was obtained with the developer containing benzotriazole.

Example 4

The same emulsion as that used in Example 3 was exposed in the same way and portions were developed in a developer of the following composition:

	Grams
Hydroquinone	10
Sodium sulfite	16
Paraformaldehyde	4
Sodium carbonate	25
Water to 1 liter	

containing 0, 0.05, 0.1 and 0.4 g. of methylbenzotriazole per liter of developing solution. Sensitometric curves were obtained from these exposures as shown in Fig. 2 and these display the effect of a range of concentrations of anti-foggant. Curve A was obtained from the development containing no anti-foggant, curve B from the development containing 0.05 gm. per liter of methyl benzotriazole, curve C from the development containing 0.1 gm. per liter of methyl benzotriazole and curve D from the development containing 0.4 gm. per liter of methylbenzotriazole. These curves show that at concentrations of from 0.05 to 0.1 gm. of methyl benzotriazole per liter of developer, the maximum density and gamma are increased, but at higher concentrations, maximum density and gamma are decreased and at a concentration of 0.4 gm. per liter, they are lower than they were with the developer containing no methylbenzotriazole.

Example 5

Additional strips of the film used in Example 3 were exposed in the same way and developed in the developer of Example 4, with various concentrations of 6-nitro-benzimidazole nitrate added to the developer. The development then was 5 minutes and the developer was aerated as in Examples 3 and 4. The concentration of the order of 0.05 g. per liter of developer 6-nitrobenzimidazole nitrate was found to be effective in increasing maximum density and decreasing minimum density. At higher concentrations maximum density was decreased although at a concentration of 0.1 g. per liter of developer, the maximum density was higher and the minimum density lower than in the case of the developer containing no anti-foggant. The table indicates the maximum and minimum densities obtained from this treatment.

Table

Concentration of 6-nitrobenzimidazole nitrate	Maximum density	Minimum density
Control	0.56	0.48
0.05 gram per liter of developer	1.12	0.16
0.10 gram per liter of developer	0.90	0.16
0.20 gram per liter of developer	0.40	0.12
0.40 gram per liter of developer	0.12	0.12

The following examples illustrate developer formulas used to obtain an increase in maximum density over that obtained with the same developer containing no anti-foggant.

Example 6

	Grams
Hydroquinone	10
Sodium sulfite	16
p-Formaldehyde	4
Sodium carbonate	25
Benzotriazole	0.1
Water to 1 liter	

Example 7

	Grams
Hydroquinone	20
Sodium sulfite	32
p-Formaldehyde	8
Sodium carbonate	50
Benzotriazole	0.8
Water to 1 liter	

Example 8

	Grams
Hydroquinone	30
Sodium sulfite	48
p-Formaldehyde	12
Sodium carbonate	75
Benzotriazole	1.2
Water to 1 liter	

Example 9

	Grams
Hydroquinone	30
Sodium sulfite	48
p-Formaldehyde	12
Benzotriazole	2.4
Water to 1 liter	

Example 10

	Grams
Hydroquinone	30
Sodium sulfite	24
p-Formaldehyde	6
Benzotriazole	2.5
Water to 1 liter	

Example 11

	Grams
Hydroquinone	30
Monomethyl p-amino phenol sulfate	0.25
Sodium sulfite	50
p-Formaldehyde	12.5
Sodium hydroxide	6
Benzotriazole	2.5
Water to 1 liter	

When alkalis such as sodium hydroxide or sodium carbonate in large amounts are added to these developers in order to increase the pH for the purpose of decreasing development time, the developers exhibit a tendency to produce lower maximum density and higher minimum density. This tendency may be overcome by incorporating small amounts of agents such as p-phenylenediamine or N-methyl-p-amino phenol sulfate, hydroxy hydroquinone or hydroxy hydroquinone acetate, in the developers. Example 11 illustrates a developing solution of this type to which sodium hydroxide and N-methyl-p-amino phenol sulfate have been added. A disadvantage of the developers compounded with small amounts of diamino phenylenes or amino phenols is that the amino groups of these compounds apparently react slowly with the formaldehyde of the developer, yielding Schiff's bases; therefore these developers are most effective when used within a few hours after preparation.

The amounts of the diamino phenylenes and amino phenols which have proved most satisfactory for incorporation in the developers are of the order of 0.12 to 0.5 g. per liter of developing solution. In the case of hydroxy hydroquinone and hydroxy hydroquinone triacetate, amounts which have proved most efficacious are of the order of 0.12 to 0.4 g. per liter of developer.

Not all compounds which may exhibit anti-foggant properties are useful in increasing the maximum density of the reversal image obtained with internal latent image emulsions. For example, β-phenylindole, 1,3-dimethylindole, phenyl mercapto tetrazole, 2-methylbenzoxazole ethiodide, 2-methylbenzothiazole, metho-p-toluene sulfonate, thiobarbituric acid, 2,6-dimethylquinoline, 2,6-dimethyl quinolinium ethiodide and 5-sulfonamidobenzotriazole decreased the maximum density over that obtained with developers not containing these agents. Other compounds such as 3,5-dimethyl pyrazole, barbituric acid and 2-β-acetanilido vinyl benzoxazole ethiodide produced no effect on either the maximum or the minimum densities obtained.

From the foregoing examples and description, it will be seen that the novel and useful features of my invention consist in the discovery and application of certain anti-foggant or heterocyclic nitrogen compounds in developers for the production of direct positive photographic images of improved contrast and extended density scale (increased shoulder density) by development in low sulfite or formaldehyde bisulfite type developers. It is to be understood that the scope of my invention is not to be limited by the specific concentrations or formulations given in the above examples.

Observation of the developing solution containing benzotriazole before and after development revealed the fact that it was greatly discolored during development. It is thought that intermediate oxidation products of hydroquinone increased the production of aerial fog. In the developer containing benzotriazole, it appears from this observation that the rate of production of intermediate oxidation products from hydroquinone is increased and that this results in an increase in aerial fog production. This property of the compounds described herein would seem to be quite independent of their normal anti-foggant properties which may exist simultaneously with the accelerating action on the aerial fog as the toe characteristics of the above examples reveal.

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 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	100
Water to 1 liter	

and developing the unexposed portion of said emulsion layer in an aerial fogging developer with access of oxygen, and containing a heterocyclic, nitrogen-containing ring compound which increases the maximum density of the positive image obtained in said aerial fogging developer, said heterocyclic compound being selected from the group consisting of benzotriazole, methyl benzotriazole, ethyl benzotriazole, 1-ethyl oxindole, 5-nitroindazole, 6-nitrobenzimidazole, histidine, ethyl benzoxazole, N-ethyl pyrrole, 2,5-dimethylpyrrole, 2,4-dimethyl - 5 - carbethoxypyrrole, 2,3-dimethyl quinoxaline, 2-thio-2,4(3,5)-thiazoledione, 2,4,6-tri-isopropylamino - S - triazine, 2,4-dimethylamino-6-chloro - S - triazine, 2,4-di - (β - methoxyethylamino) - 6 - chloro - S-triazine, 2,4,6-tri-n-butylamino - S - triazine, 1-carboxymethyl-3-phenyl-2 - thiohydantoin, 1,4-diphenyl-3-anilino-5-phenylimino, and 1,2,4-triazoline.

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 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	100
Water to 1 liter	

and developing the unexposed portion of said emulsion layer in an aerial fogging developer with access of oxygen, and containing benzotriazole, which increases the maximum density of the positive image obtained in said aerial fogging developer.

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 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	100
Water to 1 liter	

and developing the unexposed portion of said emulsion layer in an aerial fogging developer with access of oxygen, and containing 5-nitroindazole, which increases the maximum density of the positive image obtained in said aerial fogging developer.

4. 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 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	100
Water to 1 liter	

and developing the unexposed portion of said emulsion layer in an aerial fogging developer with access of oxygen, and containing 6-nitrobenzimidazole, which increases the maximum density of the positive image obtained in said aerial fogging developer.

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