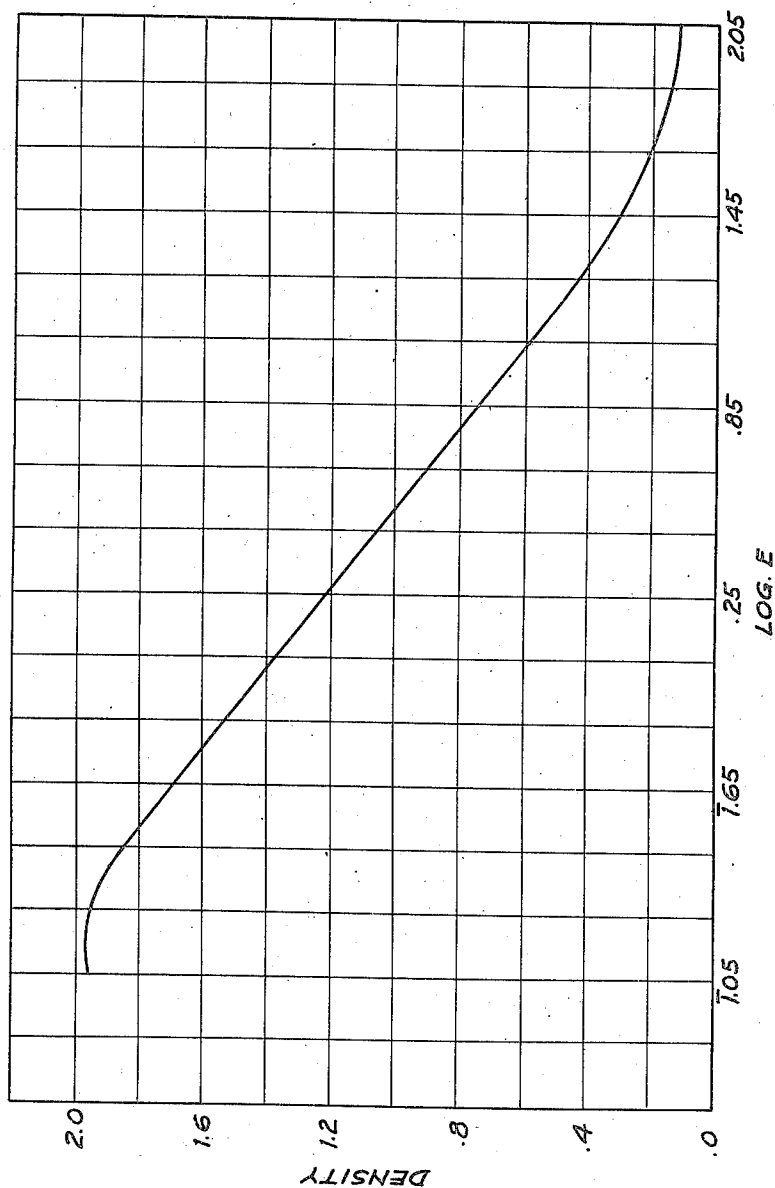


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DIRECT POSITIVE PHOTOGRAPHS USING
AERIAL FOGGING DEVELOPER
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DIRECT POSITIVE PHOTOGRAPHS USING
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This invention relates to photography and particularly to a method of making direct positive photographs.

Direct positive effects may be produced by solarizing the developable latent image by over-exposure, 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.

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, a second exposure or a redeveloping. A still further object is to provide a method for obtaining direct positive photographs which avoids the disadvantages of the prior art methods of obtaining such photographs. An additional object is to provide a method for obtaining direct positive photographs which does not require exposures of unusually high intensity nor secondary exposures. Other objects will appear from the following description of my invention.

These objects are accomplished by exposing in the usual way a suitable silver halide emulsion layer, preferably an internal latent image emulsion, and developing it in a photographic developer which is capable of giving aerial fog.

The accompanying drawing shows a sensitometric curve obtained according to my invention.

The photographic emulsion used in the process of my invention is a gelatino-silver halide emulsion such as a silver bromide emulsion, a silver bromiodide emulsion or a silver chloriodide 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 hereinafter. 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 | 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 gelatine | grams | 250 |

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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, now abandoned, 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 bromiodide 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 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 1), 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 2). 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 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 according to 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.

My new process is based on the production of fog in the unexposed areas of the emulsion and the inhibition of development in the exposed areas. With the emulsions heretofore described and with developers referred to in the preceding paragraph, this action occurs in the following way. The emulsion is exposed in the usual manner and is developed in such a way that aerial fog is produced. The unexposed silver halide grains are thoroughly and effectively fogged; at the same time, the development in the areas containing the latent image is so restrained that a very low density is obtained in the area of greatest exposure. The inhibition of fogging in the regions containing a latent image is proportional to the exposure, the least density being obtained in the region of greatest exposure. In this way, a reflection density of 0.02 has been measured on paper in the region of greatest exposure and a fog density of more than 1.5 has been measured in the regions of no exposure.

The "aerial fog" is produced according to my invention in various ways and may be accelerated or intensified by resorting to various expedients. The developer used should preferably have low sulfite content and should contain no silver halide solvent more powerful (as a silver halide solvent) than sulfite. As stated above, a hydroquinone developer having low sulfite concentration is especially adapted to the production of aerial fog. A developer of this type is illustrated in Example 3. 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.

In addition to the use of a developing solution which produces "aerial fog," the emulsion may

be made more susceptible to this fog by the addition to it of certain compounds. Certain sensitizing dyes such as 3,3'-diethyl-9-methyl-4,5,4',5'-dibenzthiocarbocyanine chloride (Brooker U. S. Patents 1,846,301 and 2,058,406) may be incorporated in the emulsion. Other compounds such as the quaternary salt, benzothiazole-methiodide, also increase the susceptibility of the emulsion to aerial fog, as do silver iodide and potassium iodide.

Fogging agents containing labile sulfur are generally unsuitable for use according to my invention. The fogging action should produce developable surface latent image in the unexposed silver halide grains.

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 1

p-Hydroxyphenylglycine	grams	10
Sodium carbonate (crystals)	do	100
Water to	liters	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	liters	1
Development time, 3 min. at 20° C.		

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

An emulsion such as the Davey and Knott emulsion described above was coated on a support, dried and exposed on an Eastman IIb Sensitometer (J. Soc. Mot. Pict. Eng., 17 (1931), page 536). The exposed emulsion was then developed for five minutes at 68° F. in the following developing solution.

Example 3

Hydroquinone	grams	22.5
Sodium sulfite	do	30
Paraformaldehyde	do	7.5
Potassium metabisulfite	do	2.6
Boric acid, crystals	do	7.5
Potassium bromide	do	1.6
Water to make	liters	1.0

The developer was agitated during the development by bubbling air through it so that the air came in contact with the emulsion. The emulsion was then fixed in hypo and washed. The resulting sensitometric curve was measured and plotted as in the accompanying drawing, in which increasing exposures are plotted as ordinates and density is plotted as the abscissa. It is apparent that a positive image having suitable characteristics was obtained as indicated by the slope and position of the curve.

It will be evident to those skilled in the art that my process affords a means for obtaining a direct positive photograph by a simple exposure and development technique and therefore avoids the necessity of high intensity exposures or a second exposure or redevelopment in order to obtain a direct positive image.

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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:

	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	100
Water to 1 liter	

and developing only the unexposed portion of said emulsion layer in an aerial fogging developer with access of oxygen.

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:

	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	

rendering only the unexposed silver halide grains of said layer developable in the following developing solution with access of oxygen:

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

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and developing said grains to metallic silver in the same solution in which they were rendered developable.

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 $\frac{1}{100}$ 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	100
Water to 1 liter	

and immediately immersing said layer in a developing solution of substantially the following composition with air bubbling through it in contact with said emulsion:

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

45 to develop metallic silver in the unexposed portions of said layer.

GEORGE EARLE FALLESEN.

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