

United States Patent

Overman

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[54] **DIRECT POSITIVE EMULSIONS
CONTAINING AMINE BORANES AND
BISMUTH SALTS**

[72] Inventor: **Joseph De Witt Overman**, Wilmington,
Del.

[73] Assignee: **E. I. du Pont de Nemours and Company**,
Wilmington, Del.

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[51] Int. Cl. **G03c 1/28, G03c 1/36**

[58] Field of Search. **96/108, 107, 101, 64, 66.3,
96/66.4, 94, 110**

[56]

References Cited

UNITED STATES PATENTS

3,361,564	1/1968	Bigelow	96/64
3,418,122	12/1968	Colt	96/107 X
3,445,235	5/1969	Burt	96/95
3,447,927	6/1969	Bacon	96/107 X
3,451,819	6/1969	Haugh	96/66.3 X
3,508,925	4/1970	Whitely	96/110 X

Primary Examiner—John T. Goolkasian

Assistant Examiner—M. E. McCamish

Attorney—Lynn Barratt Morris

[57]

ABSTRACT

Direct positive photographic silver halide emulsion layers containing about 0.00033 gram to 12.0 grams of an amine borane per mole of silver halide, and about 1.5×10^{-7} to 1.2×10^{-5} moles of a salt of bismuth per 1.5 moles of silver nitrate used to prepare the silver halide.

10 Claims, No Drawings

DIRECT POSITIVE EMULSIONS CONTAINING AMINE BORANES AND BISMUTH SALTS

BACKGROUND OF THE INVENTION

This invention relates to radiation-sensitive photographic materials, and more particularly to radiation-sensitive silver halide developing-out emulsions, and elements coated with such emulsions. Still more particularly, this invention relates to radiation-sensitive silver halide developing emulsions of the direct positive type. This invention, in addition, relates to processes for producing direct positive images utilizing the above emulsions.

Developing-out photographic emulsions are classified broadly into two types, namely (1) those which, when exposed and developed produce negative images of the originals and (2) those which when exposed and developed, produce positive images of the originals. This invention is concerned with this latter type.

Direct positive photographic elements have long been known and are highly useful in the copying and graphic arts fields for duplicating work.

Direct positive images may be produced in a variety of ways using silver halide emulsions. For example, a silver halide emulsion may be given a short, over-all exposure to high intensity radiation and then given a longer imagewise exposure to radiation of lower intensity. Upon development, a direct positive image will be obtained. Another method is to expose imagewise and develop and then flash expose and redevelop. A still further method is to chemically fog the silver halide grains with, for example, formaldehyde, hydrazine, sodium arsenite, silver ions and other nonsulfide fogging agents, instead of using a solarizing exposure. Upon imagewise exposure and development of such a chemically fogged element, a positive image is obtained. In direct positive photographic elements utilizing this latter method, there is usually incorporated a desensitizing compound, usually a colored desensitizing dye.

All of the above methods and elements leave something to be desired and suffer from such shortcomings as low reversal density, impractically long exposure times, undesirable stain from desensitizing dyes as well as undesirable contrast. Using more than one exposure or development step adds to the number of operations and to the complexity of the process. The use of formaldehyde as a chemical fogging agent is undesirable because it has a strong effect on the hardness of the gelatin colloid carrier.

In Assignee's Patent, Bigelow and Burt, U.S. Pat. No. 3,361,564, patented Jan. 2, 1968 there is disclosed and claimed a new and improved direct positive photographic element comprising a support having coated thereon a direct positive emulsion containing as a chemical fogging agent, an amine borane compound in an amount of from 0.00033 to 12 grams per mole of silver halide. The direct positive photographic elements made as described in the above application are extremely fast as compared to direct positive elements of the prior art and suffer from none of the disadvantages of long exposure times, undesirable stain due to desensitizing dyes, as well as undesirable contrast, and the multiplicity of exposure steps and processing operations. In a further improvement Assignee's Patent, Burt, U.S. Pat. No. 3,445,235 teaches the use of rhodium and iridium salts to prevent desensitization marks caused by kinking. The susceptibility toward kinking has never been troublesome in the prior art direct positive emulsion layers. This has probably been because of their very low sensitivity and slow speed. In the much more efficient system as set forth in the above application, kinking has become a problem and manifests itself by the fact that kinked areas bleach faster than nonkinked areas during exposure.

SUMMARY OF THE INVENTION

It has now been found that an improved high speed direct positive emulsion layer can be obtained by incorporating one or more amine borane compounds as fogging agents and a water-soluble salt of bismuth as a speed improver and anti-

kinking agent in the silver halide emulsion. The emulsion preferably is a gelatino-silver chlorobromide emulsion containing from about 80 to 90 percent by weight of silver bromide and optionally may contain, in addition to the two halides, from 0 to 6 percent by weight of silver iodide.

One, two, or more bismuth salts are used in amounts of from 1.5×10^{-7} to 1.7×10^{-4} mole per 1.5 moles of silver nitrate and preferably are added during the precipitation phase of making the emulsion. The optimum concentration of bismuth salt can be determined by observing the density changes in a kinked area when the element is given the customary bleaching light exposure as compared to unkinked areas and when the optimum speed is reached. High levels of the bismuth salts may cause an undesirable reduction in maximum densities. The method of kinking for test purposes involves merely bending a strip of film through an angle of about 90° over a small radius of curvature before exposure and determining the ratio of minimum net density in a kinked area to the net density in the nonkinked area.

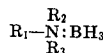
Suitable water-soluble bismuth salts include bismuth nitrate, bismuth trichloride, bismuth citrate, bismuth sulfate and bismuth tartrate.

The borane fogging agents may be added to the emulsions in amounts ranging from 0.00033 grams to 12.0 grams per mole of silver halide and preferably from 0.013 to 1.3 grams per mole of silver halide. They may be added either as a solid or dissolved in a suitable solvent. The effectiveness of the borane compounds in fogging a silver halide emulsion is influenced by the pH of the system, the higher the pH, the greater the fogging for a given amount of borane compound. Of course, certain of the borane compounds are more effective than others when used in equivalent quantities. The fogging effect produced by the borane compounds is bleachable by light exposure prior to development. A suitable developer may be any conventional alkaline, photographic developing solution which would be used for standard processing of the above direct positive emulsions in the absence of the amine borane compounds. Although the mechanism is not clearly understood, the light bleaching effect is believed due to solarization. Also, it is not clearly understood why soluble bismuth salts such as bismuth trichloride and bismuth nitrate prevent more rapid bleaching in kinked areas and still do not affect unkinked areas and tend to increase the speed and give lower minimum densities in direct positive emulsions. While the amine borane compounds will act to chemically fog all types of emulsion, the solarizing effect appears to be more efficient in silver chlorobromide emulsions.

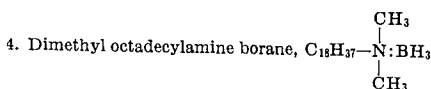
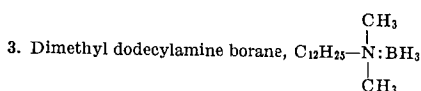
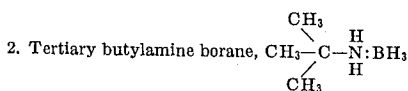
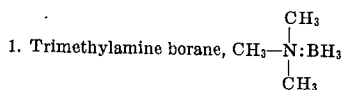
Among the amine borane compounds which have been found useful as chemical fogging compounds in this invention are the following:

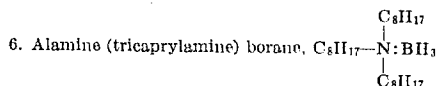
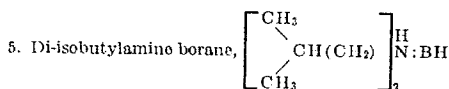
A. Alkylamine boranes

Typical of these amine boranes are those of the formula

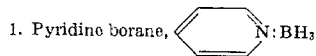


where R_1 is an alkyl radical of 1-20 carbon atoms, and R_2 and R_3 are H or alkyl of 1-20 carbon atoms. Examples of such boranes are



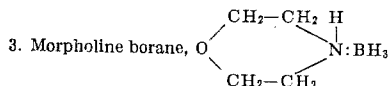
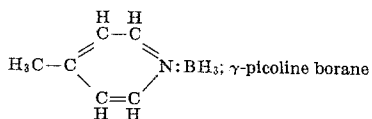
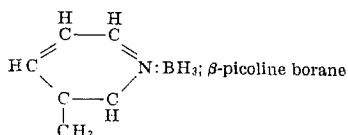
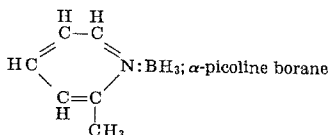


B. Heterocyclic amine boranes such as



2. α, β, γ -picoline borane.

α, β, γ -picoline borane is a mixture of α -picoline borane, β -picoline borane, and γ -picoline borane which have the following structural formulae:



DESCRIPTION OF THE PREFERRED EMBODIMENTS

For most efficient fogging action, it is preferred that the chemical fogging agents of this invention be added to the silver halide emulsion after it has been made, ripened, and washed to remove the excess soluble salts resulting from the precipitation of the silver halides. Conveniently, the borane compounds are added just prior to or during the digestion between pH 5 and 7 and maintained at this level during digestion. After digestion, the conventional coating aids are added. The emulsion is then coated and dried in the manner known to those skilled in photographic manufacturing methods.

In addition to bending test strips for kinking as described above, sensitometric characteristics of the direct positive emulsions may be determined by processing test strips of the coated layers in the following manner. A test strip in each of the following examples is fixed out in a conventional photographic fixer to provide a means of establishing the minimum density (D_{min}). Test strips are exposed in an intensity scale sensitometer (described on page 616, Mees, The Theory of the Photographic Process, Mac Millan Company, New York, 1942) using a 2 step wedge and log exposure 5.92. The exposed strip is developed for 1½ minutes at 68° F. in a developer having the composition:

Water	750 ml.
Methyl p-aminophenol hydrosulfate	1.5 gm
Sodium Sulfite (anhydrous)	19.5 gm
Hydroquinone	6.0 gm
Sodium Carbonate (anhydrous)	24.0 gm
Potassium Bromide	0.8 gm
Water to make	1.0 liter

The developed strip is then immersed in a conventional short stop for 5 to 10 seconds and then fixed for 3 minutes in a conventional fixer, and then washed and dried.

In evaluation of the processed strips, the minimum density (D_{min}) equals the lowest density above that of the fixed out strip mentioned above. The maximum density is the highest density above D_{min} . The speed of a typical commercial direct positive in terms of $100/E \times 10^{-5}$ is 10.3 and the conventional material has a D_{min} of 0.02 and a D_{max} of 3.5.

The invention will now be illustrated in and by the following examples.

EXAMPLE I

To acidified aqueous solutions containing 50 grams of gelatin and each containing 1.5 moles of potassium chloride and the quantities of bismuth trichloride, as set forth in the following table, there were rapidly added solutions containing 1.5 moles of silver nitrate. To each of the resulting mixtures there was added 0.6 mol of potassium bromide aqueous solution and the emulsions were then ripened by heating for 10 min. at 160° F. A second 0.9 mole of potassium bromide aqueous solution was added to each and the emulsions ripened for 10 min. at 160° F.

The resulting emulsions were then cooled, washed and redispersed in the manner disclosed in Moede, U.S. Pat. No. 2,772,165 issued Nov. 27, 1956. The temperature of the redispersed emulsion was raised to 130° F. and there was then added to each 87 grams of gelatin, and the pH was adjusted to 5.7. There was then added 2.8 milligrams of morpholine borane to each emulsion and the emulsions were digested at 130° F. for 40 minutes. The usual coating aids including a gelatin hardener were added and the emulsions were each coated on a photographic film support and dried in the conventional manner.

Sensitometric evaluation gave the following data:

Moles Bi+++ per 1.5 moles AgNO ₃	Kink sensitivity † (Ratio of min. density in kinked areas to density in nonkinked areas)	100/E × 10 ⁻⁵ speed	D _{max}	D _{min}
0	.35	1,800	5.12	.09
1.645 × 10 ⁻⁷	.46	2,000	5.02	.07
3.090 × 10 ⁻⁷	.56	2,400	4.53	.07
6.180 × 10 ⁻⁷	.75	3,090	4.87	.06
1.236 × 10 ⁻⁶	.90	3,770	4.79	.03
2.672 × 10 ⁻⁶	.87	4,550	4.65	.02
5.144 × 10 ⁻⁶	.85	4,290	4.50	.01
1.029 × 10 ⁻⁵	.88	4,290	4.51	.01

† Ideally the kink sensitivity should be equal to one.

EXAMPLE II

To acidified aqueous solutions of gelatin containing 1.5 moles of potassium chloride and the quantities of bismuth nitrate as set forth in the following table there was added a solution containing 1.5 moles of silver nitrate. To the resulting mixtures there was added 0.6 mole of potassium bromide in aqueous solution. The emulsions were then ripened by heating for 10 minutes at 160° F. A second 0.9 mole of potassium bromide in aqueous solution was added to the emulsions and they were ripened for 10 minutes at 160° F. The resulting emulsions were cooled, washed and redispersed in the manner disclosed in Example I. The temperature of the redispersed emulsions was raised to 130° F. and there was added 87 grams of gelatin to each and the pH was adjusted to 5.7. There was added 2.8 milligrams of morpholine borane per 1.5 moles of silver nitrate. The usual coating aids including a gelatin hardener were added and the emulsions were coated on film supports and dried in the conventional manner.

Sensitometric evaluation gave the following data:

Moles Bi+++ per 1.5 moles AgNO ₃	Kink sensitivity	100/E × 10 ⁻⁵ Speed	D _{max}	D _{min}
None	0.60	2490	4.68	0.07

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1.545×10^{-7}	0.80	3090	5.11	0.05
3.090×10^{-7}	0.90	3900	4.22	0.05
6.180×10^{-7}	1.00	4030	4.33	0.04
1.236×10^{-6}	1.00	5640	4.32	0.02
2.572×10^{-6}	1.00	6900	4.20	0.01
5.144×10^{-6}	1.00	5450	3.77	0.01
1.029×10^{-5}	1.00	5640	3.85	0.01

EXAMPLE III

Example II was repeated except that 2.8 milligrams of tertiary butylamine borane was used per 1.5 moles of silver nitrate. The sensitometric results are as follows:

Moles Bi***per 1.5 moles AgNO ₃	Kink sensitivity	100/E × 10 ⁻⁵ Speed	D _{max}	D _{min}
None	0.45	4870	3.95	0.08
1.545 × 10 ⁻⁷	0.45	8370	2.59	0.04
3.090 × 10 ⁻⁷	0.60	15000	2.57	0.02
6.180 × 10 ⁻⁷	0.73	16500	2.50	0.01
1.236 × 10 ⁻⁶	0.70	12300	3.97	0.01
2.572 × 10 ⁻⁶	0.90	25200	1.60	0.01
5.144 × 10 ⁻⁶	1.00	19400	2.59	0.01
1.029 × 10 ⁻⁵	1.00	20200	2.16	0.01

EXAMPLE IV

Example II was repeated except that there was added to each emulsion 160 milligrams of trimethylamine borane per 1.5 moles of silver nitrate. Sensitometric evaluation gave the following data:

Moles Bi ⁺⁺⁺ per 1.5 moles AgNO ₃	Kink sensitivity	100/E × 10 ⁻⁵ Speed	D _{max}	D _{min}
None	0.50	444	4.13	0.09
1.545 × 10 ⁻⁷	0.55	462	4.28	0.06
3.090 × 10 ⁻⁷	0.70	497	3.83	0.05
6.180 × 10 ⁻⁷	1.00	1190	3.85	0.02
1.236 × 10 ⁻⁶	1.00	652	4.13	0.02
2.572 × 10 ⁻⁶	1.00	1380	3.66	0.01
5.144 × 10 ⁻⁶	1.00	880	4.05	0.02
1.029 × 10 ⁻⁵	1.00	1530	3.98	0.02

EXAMPLE V

Example II was repeated except that there was added to each emulsion 8 milligrams of morpholine borane per 1.5 moles of silver nitrate. The sensitometric results were as follows:

Moles Bi ⁺⁺⁺ per 1.5 moles AgNO ₃	Kink sensitivity	100/E × 10 ⁻⁵ Speed	D _{max}	D _{min}
None	0.55	2400	4.04	0.05
2.58 × 10 ⁻⁶	1.00	6410	4.29	0.03
5.16 × 10 ⁻⁶	1.00	5450	4.39	0.02
1.032 × 10 ⁻⁵	1.00	5060	5.00	0.02
2.064 × 10 ⁻⁵	1.00	4160	5.02	0.01
4.128 × 10 ⁻⁵	1.00	4870	5.24	0.01
8.256 × 10 ⁻⁵	1.00	4030	5.31	0.01
1.651 × 10 ⁻⁴	1.00	4030	5.21	0.01

EXAMPLE VI

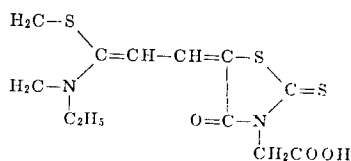
Example II was repeated except that 1.6 grams of potassium iodide and 8 milligrams of morpholine borane per 1.5 moles of silver nitrate was added to each emulsion. The amount of bismuth nitrate is shown in the following table along with the sensitometric data:

Moles Bi***per 1.5 moles AgNO ₃	Kink sensitivity	100/E × 10 ⁻³ Speed	D _{max}	D _{min}
None	0.42	2490	3.30	0.06
2.58 × 10 ⁻⁶	0.90	27900	3.20	0.02
5.16 × 10 ⁻⁶	0.87	25200	3.25	0.02
1.032 × 10 ⁻⁵	0.90	40200	2.50	0.020
2.064 × 10 ⁻⁵	1.00	38700	2.70	0.02
4.128 × 10 ⁻⁵	1.00	35100	2.90	0.02
8.256 × 10 ⁻⁵	1.00	43300	3.00	0.02
1.651 × 10 ⁻⁴	1.00	43300	2.90	0.02

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EXAMPLE VII

Example VI was repeated except that there was added 120 milligrams per 1.5 moles of silver nitrate of the dye, 3-carboxymethyl-5-(3'-ethyl-2'(3')-thiazolinyldiene) ethylidene rhodanine having the formula



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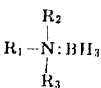
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The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

- 1. A direct positive photographic silver halide emulsion containing as a chemical fogging agent an amine borane compound, characterized in that said emulsion contains at least one water-soluble bismuth salt in an amount of 1.5×10^{-7} to 1.7×10^{-4} mole per 1.5 moles of silver nitrate used to prepare the silver halide in the emulsion.
- 2. An emulsion according to claim 1, wherein the emulsion is a gelatino-silver chlorobromide emulsion containing 80 to 90 percent by weight of silver bromide.
- 3. An emulsion according to claim 1, wherein said bismuth salt is bismuth trichloride.
- 4. An emulsion according to claim 1, wherein said bismuth salt is bismuth nitrate.
- 5. An emulsion according to claim 1, wherein said bismuth salt is bismuth citrate.
- 6. An emulsion according to claim 1, wherein the amine

borane compound is an alkylamine borane of the formula



where R_1 is an alkyl radical of one-20 carbon atoms, and R_2 and R_3 are H or alkyl of one-20 carbon atoms.

- 7. An emulsion according to claim 1, wherein the amine borane is morpholine borane.
- 8. An emulsion according to claim 1, wherein the amine borane is tertiary-butylamine borane.
- 9. An emulsion according to claim 1, containing an orthochromatic sensitizing dye.
- 10. A photographic element comprising a sheet support bearing a layer of an emulsion as defined in claim 1.

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