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BORON HYDRIDES AS REDUCTION SENSITIZERS IN DEVELOPING-OUT SILVER HALIDE EMULSIONS

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ABSTRACT OF THE DISCLOSURE

Photographic silver halide, negative-working, developing-out emulsions are prepared which have their sensitivity increased by the addition of at least one boron hydride in which the skeletal framework forms a polyhedron or a fragment thereof, and contains from 6 to 12 boron atoms and may contain heteroskeletal atoms selected from the group, carbon, sulfur and nitrogen.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to chemically sensitized, photographic silver halide emulsions and to photographic material comprising a light-sensitive layer coated from such emulsions. One aspect of this invention relates to sensitizing negative-working, silver halide photographic emulsions with at least one boron hydride compound taken from the group consisting of polyhedral boranes, thiaboranes, azaboranes and carboranes containing from 6 to 12 boron atoms. Another aspect of this invention relates to negative-working photographic elements and silver halide emulsions which have been sensitized with the above borane compounds. The photographic emulsion sensitization according to this invention is generally applicable to negative-working silver halide developing-out emulsions which are well known in the art.

Description of the prior art

Chemical sensitizers are frequently used in photographic silver halide emulsions to enhance the sensitivity of said emulsions. The known chemical sensitizers are those containing a labile sulfur atom, e.g., sodium thiosulfate, thiuram disulfide, thiourea dioxide, etc., salts of noble metals, e.g., salts of gold, platinum or palladium and reducing compounds, e.g., stannous chloride and hydrazine derivatives. Combinations of two or more of the aforementioned sensitizers may have been used.

Such chemical sensitizers are believed to form, on the surface of the silver halide grains, minute amounts of silver sulfide or of silver or of gold or other noble metal and these so-called sensitivity specks are capable of greatly increasing the sensitivity of developing-out emulsion.

The process of chemical sensitization, however, using the prior art sensitizers has presented some serious problems. Despite its apparent simplicity, gold sensitization, for example, is very difficult to carry out conveniently without increasing fog and instability. [See P. Glafkides, Photographic Chemistry (translated by Keith M. Hornsby), Fountain Press (1958), p. 319, vol. 1.] The use of sulfur sensitization has a tendency to induce high intensity reciprocity failure. The prior art chemical sensitizers in general cause some increase in fog, and moreover, reach a limit of addition to the silver halide system beyond which further addition or further ripening with the sensitizer present, merely increases the fog with no increase or, even a decrease in sensitivity to actinic radiation. In addition, it has been found that the above chemical sensitizers also have other deleterious effects such as substantially contributing to the instability of the emulsions on tropical aging.

SUMMARY OF THE INVENTION

The subject of this invention is a novel photographic, silver halide, negative-working, developing-out emulsion containing a sensitizing amount of a boron hydride in which the skeletal framework forms a polyhedron or a fragment thereof. The boron hydride preferably contains from 6 to 12 boron atoms and may contain one or more heteroskeletal atoms such as carbon, sulfur and nitrogen. Sensitized emulsions of this invention may contain additional materials, if desired, including other optical and non-optical sensitizing agents.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The cage type boron hydride compounds set forth herein can be used to sensitize a wide variety of negative-working, developing-out silver halide emulsions including X-ray emulsions, seismographic emulsions, variable contrast paper emulsions and panchromatic negative paper emulsions to name a few. The concentrations of the borane compounds may be varied over a wide range depending on the intended purpose. Good sensitization is usually achieved when the boron hydrides are added in concentrations of from 10^{-11} to 10^{-6} moles per mole of silver halide with the added advantage of improving the stability of the emulsions, i.e., decreasing the tendency toward fog. Of course, certain of the compounds are more effective than others when used in equivalent quantities and the proper amount of boron hydride to be used will depend on the particular boron hydride, the type of emulsion and the amount of sensitization desired. Without intending to be limited in the scope of my invention it is suggested that the cage structure of the polyhedral boranes and derivatives tend to eliminate crystal size (or sensitivity) difference without actually changing the distribution of sensitization.

Among the boron hydrides and derivatives thereof as defined above, the following have been found to be particularly useful.

COMPOUND FORMULA
$(NH_4)_2B_{10}H_{10}$
$CsB_9H_{12}S$
$(CH_3)_3NNB_9H_{12}$
$(CH_3)_4N(CH_3)_2NNB_9H_{12}$
$[(C_6H_5)_3CH_3P]_2B_{11}H_{11}$
$B_{10}H_{12}CNH_3$
$(CH_3)_4N(CH_3)_3CNHCB_{10}H_{12}$
$(CH_3)_3NHB_{10}H_{12}CH$
$B_{10}H_{12}[S(CH_3)_2]_2$
$B_9H_{13}S(C_2H_5)_2$
$B_{10}H_{12}[S(C_2H_5)_2]_2$
$C_6H_5B_{11}H_{10}S$
$Na_2B_{12}H_{12}\cdot 2H_2O$

Methods of preparation of the compounds may be found in, The Chemistry of Boron and Its Compounds, E. L. Muetterties, John Wiley and Sons, New York, 1967, Polyhedral Boranes, E. L. Muetterties and W. H. Knoth, Marcel Dekker, Inc., New York, 1968, and numerous patents by the authors of the above publications.

The mechanism by which the above compounds sensitize the silver halide emulsions is not clear in all cases. In some cases, the process may be considered reduction sensitization; in others it may be a process peculiar to the borane compounds themselves.

The borane compounds may be added at any stage of emulsion manufacture including the precipitation stage, before ripening, at remelt, after washing to remove excess salts remaining after precipitation, before, during or at the end of the digestion period, or as an addendum just prior to coating. Preferably the compounds are added at silver halide precipitation during make or at the remelt

stage after washing. The borane compounds may be added to the emulsions as a solution with a suitable solvent, i.e., water. Generally, water or solvents which are miscible with water are preferred, e.g., ethyl alcohol, acetone, dioxane, etc. The useful boron hydrides in aqueous solution have considerable stability and may be made up in quantity in advance of use for manufacturing operations.

The novel sensitizers of this invention may be used as the sole sensitizer in the silver halide emulsion or they may be used in conjunction with other known sensitizers, i.e., labile sulfur compounds; precious metal compounds, e.g., gold salts; reducing agents, e.g., stannous salts; compounds which sensitize by development acceleration, e.g., polyalkylene oxides, etc. In addition, they can be sensitized with optical sensitizing dyes, e.g., cyanines, carbocyanines, merocyanines, etc.

Silver halide emulsions which can be sensitized according to this invention can also contain conventional additions such as plasticizers for the colloid carrier in which the silver halide crystals are dispersed, antifoggants such a thiazoles, triazoles, tetrazaindenes and the like, coating aids, hardeners such as aldehyde hardeners, e.g., mucochloric acid, glutaraldehyde, etc. Various silver salts may be used as the light-sensitive medium such as silver bromide, silver iodide, silver chloride or mixed silver halides such as silver chlorobromide or silver iodobromide, and silver iodochlorobromide.

The silver halide emulsions of this invention can be made with any of the macromolecular, water-permeable colloids known to be suitable for this purpose. Suitable materials include gelatin, polyvinyl alcohol and its derivatives, e.g., partially hydrolyzed polyvinyl acetates, ethers and acetals, hydrolyzed interpolymers of vinyl acetate and unsaturated addition polymerizable compounds such as maleic anhydride, acrylic and methacrylic acid esters, poly-N-vinyllactams, polysaccharides, e.g., dextran, dextrin, etc., the hydrophilic copolymers disclosed in Shacklett U.S. 2,833,650, hydrophilic cellulose ethers and esters, and acrylamide polymers. Mixtures of these binders can also be used as well as water permeable binding agents containing dispersed polymerized vinyl compounds such as those disclosed in Nottorf U.S. Pat. 3,142,-568 issued July 28, 1964.

The emulsions sensitized according to this invention can be coated on any suitable support, e.g., cellulose esters, cellulose mixed esters; superpolymers, e.g., polyvinyl chloride (CO) vinyl acetate, polyesters, e.g., polyethylene terephthalate, polyethylene terephthalate/isophthalate, polycarbonates, polyesters formed by condensing terephthalic acid and its derivatives, e.g., dimethyl terephthalate with propylene glycol, diethylene glycol, tetramethylene glycol, cyclohexane-1,4-dimethanol (hexahydro-p-xylene dialcohol); paper, metal, glass, etc.

The invention will now be illustrated in and by the following examples but they are not intended to limit it in any way except as set forth in the claims.

EXAMPLE I

A gelatino-silver iodobromide emulsion containing 1 mole percent silver iodide was made under proper safelight conditions. The emulsion, after precipitation of the silver halides but before ripening, was divided into 3 equal portions, (a) (b) and (c). No extra additions were made to portion (a). To portion (b) there was added 0.5 mole percent based on silver nitrate, of a polyhedral borane having the formula $(NH_4)_2B_{10}H_{10}$ in an aqueous solution. To portion (c) there was added 0.5 mole percent of the borane compound and 0.5 mole percent of silver nitrate also in an aqueous solution all based on the silver nitrate originally used at precipitation.

The emulsions were ripened by holding them for 40 minutes at 130° F. The emulsions were then cooled to 95° F., coagulated, washed and redispersed in the manner disclosed in Moede, U.S. Pat. 2,772,165, issued Nov. 27, 1956. The pH was adjusted to 7.0, bulking gelatin was added and the emulsion digested for 20 minutes at 110° F. during which 0.0125 mole of potassium iodide per 1.5 mole of silver nitrate was added. The emulsions were cooled to 95° F. and the conventional coating addenda, i.e., wetting agents, hardeners, etc., were added. The emulsions were then coated on a photographic quality papr support and dried in a manner well known to those skilled in the art.

The coated samples were exposed through a power of 2 step wedge in an Edgerton, Germeshausen and Greer Mark VII electronic flash sensitometer similar to that described by Wyckoff and Edgerton, Journal of the Society of Motion Picture and Television Engineers, 66, 474 (1957). This instrument uses a xenon discharge tube as the source of radiation and has available exposure times of .01 to .00001 sec. The exposure time used was 0.0001/sec.

The exposed strips were developed at 68° F. for 1½ minutes in a conventional hydroquinone developer containing a small amount of 1-phenyl-3-pyrazolidone.

The developed strips were fixed in a conventional acid fixer, washed and dried and the densities read. Speed equals $100/E$ at density of 0.1, where E is the time of exposure. $D_{max.}$ is the greatest density above fog and fog is the developed density in unexposed areas measured above the white paper base. The following results were obtained:

TABLE I

Sample	Speed	$D_{max.}$	Fog
(a) Control	12.0	.93	.01
(b) 0.5 mole percent $(NH_4)_2B_{10}H_{10}$	83.0	1.22	.09
(c) {0.5 mole percent $(NH_4)_2B_{10}H_{10}$ / 0.5 mole percent $AgNO_3$}	201.0	1.17	.15

It will be seen that the presence of the borane compound increases speed and $D_{max.}$ either alone or in with the addition of a small amount of silver nitrate.

EXAMPLE II

A gelatino-silver chlorobromide suitable for a variable contrast photographic element was prepared under proper safelight conditions wherein the emulsion was constituted of 75% silver bromide. After precipitation of the silver halides the emulsion was ripened for 26 minutes at 110° F. and then cooled and noodle-washed in a conventional manner to remove unwanted salts resulting from the silver halide formation.

The emulsion was then remelted and there was added to the molten emulsion, 6×10^{-5} mole of a conventional sulfur sensitizer per 1.5 moles of silver nitrate. The emulsion was then divided into portions as indicated in the following table. There were added the quantities indicated in molar quantities per 1.5 moles of silver nitrate of the borane compound, $B_{10}H_{12}CNH_3$. The emulsions were then digested for 60 minutes at 119° F. Ten minutes before the end of the digestion there was added to each emulsion per 1.5 moles of silver nitrate, .034 gram of the optical sensitizing dye, 5 - (3 - ethyl-2-thiazolinylidene-ethylidene) - 3 - ethyl - 2 - thio-2,4(3,5)-oxazoledione. As the emulsions were cooling after digestion, there were added to each emulsion per 1.5 moles of silver nitrate, .01665 gram of the antifoggan, 4 - hydroxy - 6 - methyl-1,3,3a,7 - tetrazaindene, 10.56 grams of saponin, about 2 grams of chrome alum and 0.52 gram of formaldehyde. The emulsion was coated on a photographic quality paper support and dried in a conventional manner.

The material was tested by exposing for 4 seconds in a conventional intensity scale sensitometer using as a light source, a sensitometer lamp, No. CPB sold by the Eastman Kodak Company which provides 39.5 candle power burning at 10 amperes and 4.6 volts which provides 117.5 meter-candle-seconds at the focal plane. The sensitometer was equipped with a Wratten No. 82C filter to give a color temperature of 3010° K. The material was exposed through a $\sqrt{2}$ neutral density step wedge and

through Du Pont Filters Nos. 0, 2 and 4, No. 0 filter giving the lowest contrast and No. 4 giving the highest contrast.

The exposed elements were developed for 1½ minutes at 68° F. in a conventional metol-hydroquinone developer.

The developed elements were rinsed in a short stop bath, fixed and dried in a conventional manner and the densities read on a densitometer. In the following table, $D_{max.}$ equals the highest density reading, speed equals $100/E$ at density of 0.10. Fog is indicated as 1X which is the density obtained after 1½ minutes in the above developer with no exposure and 3X which is the density obtained after 4½ minutes in the above developer. Total scale equals the number of steps between density 0.04 and 90% of $D_{max.}$ and is a measure of contrast. The samples were exposed fresh and after 7 days in an oven at 120° F. and 62% relative humidity which represents about 10 months of shelf aging. This indicated under "test age" in the following tables, "Fr." indicating fresh and "70T" indicating 7 days in the oven.

TABLE II

Emulsion additions	Filter	Speed	Total scale	$D_{max.}$	Fog, 1X/3X	Test age
Control (no borane compound)	0	28.5	12.1	1.60		Fr.
	2	30.4	8.0	1.57	.000/.000	Fr.
	4	21.5	7.4	1.60		Fr.
Do	0	40.9	13.3	1.60		70T
	2	52.4	8.4	1.64	.02/.04	70T
	4	33.7	7.9	1.56		70T
5.0 $\times 10^{-7}$ moles $B_{10}H_{12}CNH_3$ per 1.5 moles $AgNO_3$.	0	45.7	11.5	1.62		Fr.
	2	62.1	8.6	1.64	.02/.09	Fr.
	4	54.4	9.0	1.51		Fr.
Do	0	83.6	11.9	1.44		70T
	2	109.0	8.7	1.42	.07/.22	70T
	4	80.7	9.2	1.46		70T
5.0 $\times 10^{-9}$ moles $B_{10}H_{12}CNH_3$ per 1.5 moles $AgNO_3$.	0	29.4	11 3.	1.67		Fr.
	2	39.5	8.1	1.67	.000/.020	Fr.
	4	23.8	7.0	1.69		Fr.
Do	0	62.1	11.5	1.58		70T
	2	80.7	9.2	1.57	.010/.020	70T
	4	45.2	7.4	1.52		70T

It is seen that 5×10^{-7} mole of the borane compound produces too much fog but 5×10^{-9} gives greater speed and less fog than the control.

EXAMPLE III

Example II was repeated except there were added 5×10^{-7} mole and 5×10^{-9} mole per 1.5 moles of silver nitrate of the carborane compound,

$$(CH_3)_4N(CH_3)_3CNHCB_{10}H_{12}.$$

All other operations of making the emulsion, coating and testing were carried out as in Example II. The sensitometric results are shown in the table below.

TABLE III

Emulsion additions	Filter	Speed	Total scale	$D_{max.}$	Fog, 1X/3X	Test age
Control (no borane compound)	0	22.9	13.6	1.51		Fr.
	2	27.6	7.8	1.56	.000/.000	Fr.
	4	16.8	7.3	1.50		Fr.
Do	0	28.5	12.6	1.22		70T
	2	42.3	11.8	1.39	.000/.000	70T
	4	29.4	9.4	1.48		70T
5×10^{-7} moles $(CH_3)_4N(CH_3)_3CNHC$ $B_{10}H_{12}$ per 1.5 moles $AgNO_3$.	0	35.1	18.6	1.72		Fr.
	2	36.6	8.6	1.72	.01/.01	Fr.
	4	22.2	13.2	1.72		Fr.
Do	0	46.7	11.1	1.52		70T
	2	68.9	8.1	1.59	.005/.02	70T
	4	43.8	8.2	1.55		70T
5×10^{-9} moles $(CH_3)_4N(CH_3)_3CNHC$ $B_{10}H_{12}$ per 1.5 moles $AgNO_3$.	0	24.7	10.9	1.62		Fr.
	2	29.4	9.1	1.67	.005/.01	Fr.
	4	18.8	14.0	1.68		Fr.
Do	0	36.6	11.6	1.46		70T
	2	48.6	8.5	1.51	.000/.01	70T
	4	38	8.6	1.49		70T

Another sample of an emulsion made as described in Example II was prepared leaving out the sulfur sensitizer, but adding 5×10^{-7} mole of the borane compound. Test results are shown in the following table.

TABLE III-A

Emulsion additions	Filter	Speed	Total scale	$D_{max.}$	Fog, 1X/3X	Test age
Control	0	8.1	10.5	.40		Fr.
	2	10.9	6.3	.49	.005/.01	Fr.
	4	7.4	5.9	.48		Fr.
Do	0	24.7	12.4	1.02		70T
	2	33.7	8.5	1.90	.000/.000	70T
	4	22.2	8.1	1.02		70T
5 $\times 10^{-7}$ moles $(CH_3)_4N(CH_3)_3CNHC$- $B_{10}H_{12}$ per 1.5 moles $AgNO_3$.	0	17.5	11.7	.79		Fr.
	2	24.7	8.9	.82	.005/.01	Fr.
	4	15.6	7.1	.76		Fr.
Do	0	36.6	13.1	1.42		70T
	2	52.4	9.7	1.45	.000/.01	70T
	4	39.5	9.1	1.38		70T

It will be seen that speed is improved by the addition of the carborane compound whether the sulfur sensitizer is present or not.

EXAMPLE IV

A silver iodobromide developing-out emulsion suitable for seismographic work was prepared under proper safelight conditions by adding an aqueous solution containing 1.5 moles of silver nitrate to an aqueous gelatin solution containing 1.55 moles of ammonium bromide and 0.015 mole of potassium iodide. The gelatin solution also contained 0.131 mole of strontium chloride. After precipitation, the emulsion was ripened by heating at 120° F. for 40 minutes. The emulsion was then cooled, coagulated, washed and redispersed in the manner described in Moede, U.S. Pat. 2,772,165 issued Nov. 27, 1956.

The redispersed emulsion was divided into portions as indicated in the following table, the control having added thereto .004 mole or formaldehyde per 1.5 moles of silver nitrate as a sensitizer.

To the other portions, there were added the borane compounds indicated in the table below. The emulsions were digested at 125° F. for 30 minutes and cooled to 95° F. The emulsions were optically sensitized with the dye, 5 - (3 - methyl-2-thiazolinylidene-isopropylidene)-3-ethylrhodanine.

The usual coating addenda, e.g., antifoggant, surfactant, etc. were added and the emulsions were coated on a photograpic quality paper support and dried.

The emulsions were sensitometrically tested according to the following procedure.

Strips were exposed for 1/50 of a second in an intensity scale sensitometer to a $\sqrt{2}$ neutral density step wedge using as a light source, a General Electric No. DMX sensitometer lamp operating at 82 volts and 4 amperes to give a color temperature of 2877° K. This provided 19.2 meter-candle-seconds at the focal plane. The material was exposed through a Wratten K2 filter. The exposed strips were developed for 45 seconds at 68° F. in conventional metol-hydroquinone developer.

The developed strips were rinsed in a short stop bath, fixed and dried in a conventional manner and the densities read on a densitometer. In the following table, $D_{max.}$ equals the highest density reading, speed 1 ("Sp. 1") is equal to $100/E$ at density of 0.10 and speed 2 ("Sp 2") is equal to $100/E$ at density of 0.80. Total scale equals the number of steps between density 0.01 and $D_{max.}$—0.03 and is a measure of contrast. Fog is indicated as 1X which is the density obtained after 45 seconds in the above developer without any exposure and 3X is the density obtained after 2 minutes and 15 seconds in the above developer without exposure. The samples were exposed fresh and after 7 days in an oven at 120° F. and 62% relative humidity.

TABLE IV

Emulsion additions	Sp. 1	Sp. 2	Total scale	$D_{max.}$	Fog, 1X/3X	Test age
Control (no borane compound)	676	269	9	1.16	.08/.09	Fr.
Do	916	249	9.5	1.04	.10/.12	70T
$5X10^{-9}$ moles $[(C_6H_5)_3CH_3P]_2B_{11}H_{11}$ per 1.5 moles $AgNO_3$.	656	259	9.2	1.29	.02/.04	Fr.
Do	1.050	289	11	1.17	.03/.04	70T
Control (no borane compound)	766	289	9.4	1.22	.05/.05	Fr.
Do	886	249	9.8	1.08	.06/.08	70T
$5X10^{-9}$ moles $[C_6H_5)_3CH_3P]_2B_{11}H_{11}$ per 1.5 moles of $AgNO_3$.	518	198	7.4	1.32	.01/.02	Fr.
Do	916	279	9.5	1.16	.01/.02	70T

The borane compound, $[C_6H_5)_3CH_3P]_2B_{11}H_{11}$, is essentially as good a sensitizer as formaldehyde and fog is reduced substantially.

EXAMPLE V

Example IV was repeated using the quantities of azaborane compounds per 1.5 moles of silver nitrate as indicated in the table below.

TABLE V

Emulsion additions	Sp. 1	Sp. 2	Total scale	$D_{max.}$	Fog, 1X/3X	Test age
Control (no borane compound)	205	65.2	9.5	1.25	.02/.02	Fr.
Do	676	170	13.5	1.25	.03/.05	70T
$5X10^{-6}$ moles $(CH_3)_3NNB_9H_{12}$ per 1.5 moles $AgNO_3$.					$D_{max.}$	Fr.
Do					$D_{max.}$	70T
$5X10^{-7}$ moles $(CH_3)_3NNB_9H_{12}$ per 1.5 moles $AgNO_3$.	240	56	10.7	1.33	.000/.000	Fr.
Do	423	82	10	1.29	.01/.01	70T
$5X10^{-8}$ moles $(CH_3)_3NNB_9H_{12}$ per 1.5 moles $AgNO_3$.	299	88.6	8.8	1.27	.01/.01	Fr.
Do	636	155	10	1.27	.01/.01	70T
$5X10^{-9}$ moles $(CH_3)_3NNB_9H_{12}$ per 1.5 moles $AgNO_3$.	319	88.6	10	1.26	.01/.01	Fr.
Do	597	130	11.5	1.28	.01/.02	70T
$5X10^{-6}$ moles $(CH_3)_4N(CH_3)_2NNB_9H_{12}$ per 1.5 moles $AgNO_3$.	577	140	11	1.19	.05/.10	Fr.
Do	1.090	198	14	1.15	.13/.16	70T
$5X10^{-7}$ moles $(CH_3)_4N(CH_3)_2NNB_9H_{12}$ per 1.5 moles $AgNO_3$.	339	106	8.9	1.23	.02/.02	Fr.
Do	706	212	10.5	1.28	0.1/.02	70T
$5X10^{-8}$ moles $(CH_3)_4N(CH_3)_2NNB_9H_{12}$ per 1.5 moles $AgNO_3$.	309	102	8.9	1.23	.01/.01	Fr.
Do	736	177	12	1.30	.01/.02	70T
$5X10^{-9}$ moles $(CH_3)_4N(CH_3)_2NNB_9H_{12}$ per 1.5 moles.	319	102	8.5	1.23	.01/.02	Fr.
Do	706	184	9.0	1.27	.02/.03	70T
Control (no borane compound)	177	56.9	15	1.24	.00/.00	Fr.
Do	656	135	14	1.24	.04/.05	70T

These data show that the azaboranes, $(CH_3)_3NNB_9H_{12}$ and $(CH_3)_4N(CH_3)_2NNB_9H_{12}$ in proper concentrations,

are capable of producing greater speed, contrast and stability, and less fog than standard samples.

EXAMPLE VI

Example V was repeated using the thiaborane compound indicated in the following table. The oven tests were omitted in this example and the data are obtained from fresh exposures. The sensitometric results are shown below.

TABLE VI

Emulsion additions	Sp. 1	Sp. 2	Scale	$D_{max.}$	Fog, 1X/3X
Control (no borane compound)	145	60.3	5.9	1.27	.02/.03
$5X10^{-7}$ moles $CsB_9H_{12}S$ per 1.5 moles $AgNO_3$					(1)
$5X10^{-9}$ moles $CsB_9H_{12}S$ per 1.5 moles $AgNO_3$	395	145	8.1	1.28	.02/.03
$5X10^{-8}$ moles $CsB_9H_{12}S$ per 1.5 moles $AgNO_3$	367	156	7.0	1.31	.000/.00

[1] Very high.

Improvement in speed is given with $CsB_9H_{12}S$ in place of the formaldehyde sensitizing system.

EXAMPLE VII

Example V was repeated using the polyhedral borane, $(NH_4)_2B_{10}H_{10}$ in the quantities indicated in the following table. Speed was determined as $100/E$ at density of 0.10.

TABLE VII

	Type of sensitizer			
	$(NH_4)_2B_{10}H_{10}$		Formaldehyde control	
Concentration of sensitizer	Speed	Fog, 1X/3X	Speed	Fog, 1X/3X
$4X10^{-3}$ moles per 1.5 moles $AgNO_3$			200	.01/.015
$5X10^{-5}$ moles per 1.5 moles $AgNO_3$	338	.01/.01		
$5X10^{-6}$ moles per 1.5 moles $AgNO_3$	324	.005/.01		
$5X10^{-7}$ moles per 1.5 moles $AgNO_3$	353	.005/.01		
$5X10^{-8}$ moles per 1.5 moles $AgNO_3$	423	.005/.02		
$5X10^{-9}$ moles per 1.5 moles $AgNO_3$	329	.000/.00		

The above data show that the borane compound,

$$(NH_4)_2B_{10}H_{10},$$

gives about the same improvement over a wide range of concentration (10,000X) without the usual increase in fog or loss of stability.

EXAMPLE VIII

An emulsion containing 98.9 mole percent silver bromide and 1.2 mole percent silver iodide suitable for use for an X-ray film was prepared under proper safelight conditions. After ripening, the emulsion was coagulated, washed and redispersed in the manner described in Moede, U.S. Pat. 2,772,165 issued Nov. 27, 1956. To a portion of the emulsion which was used as a control there was added conventional gold and sulfur sensitizers. To other portions of the emulsion as indicated in the table below there were added quantities of two borane compounds as indicated in the table.

The emulsions were digested for 25 minutes at 129° F. Various addenda e.g., stabilizers, perservatives, coating aids, etc. were added and the emulsions were coated on a polyethylene terephthalate film base. The emulsions were overcoated with a conventional gelatin layer as is well known in the art of photographic manufacture.

The emulsion layers were exposed for 5 seconds in a sensitometer as described in Example II using a Wratten #39 filter and a 1.8 neutral density filter. The exposed material was developed for 40 seconds at 88° F. in a conventional X-ray developer containing a small amount of 1-phenyl-3-pyrazolidone and hydroquinone.

The developed layers were fixed, washed and dried and the densities read on a transmission densitometer. $D_{max.}$ equals the highest density reading, fog equals processed density where not exposed and speed equals $100/E$. Results were as follows:

TABLE VIII

Emulsion additions	$D_{max.}$	Fog	Speed [1]
Control (no borane compound)	.83	.032	74.16
$5X10^{-8}$ moles $CsB_9H_{12}S$ per 1.5 moles $AgNO_3$	.50	.038	229
$5X10^{-7}$ moles $[(C_6H_5)_3CH_3P]_2B_{11}H_{11}$ per 1.5 moles $AgNO_3$	.69	.036	272.5

[1] Speed point was read at density=0.03 (which was the 1st readable density).

A second set of the strips was tested and a duplicate set was aged 7 days in an oven at 120° F. at 62% relative humidity and tested. Sensitometric results are shown in the following table.

TABLE VIII-A

Emulsion additions	$D_{max.}$	Visible step No. at density=0.03	Test age
Control (No borane compound)	.67	13	Fresh.
Do	.23	18	70T
$5X10^{-7}$ moles $[(C_6H_5)_3CH_3P]_2B_{11}H_{11}$ per 1.5 moles $AgNO_3$.	.56	9.5	Fresh.
Do	.54	9.0	70T
$5X10^{-8}$ moles $CsB_9H_{12}S$ per 1.5 moles $AgNO_3$.	.40	10.5	Fresh
Do	.66	8.5	70T

The emulsions sensitized with thia- and polyhedral boranes show greater $D_{max.}$ and speed stability upon oven-aging compared with the control.

EXAMPLE IX

Emulsions were prepared in the following manner. An aqueous gelatin solution was made for each of six emulsions containing 1.56 moles of potassium bromide, 0.075 mole of strontium chloride, 0.025 mole of potassium iodide, 50 grams of gelatin. Sodium thiosulfate was added to 3 solutions as indicated. There was also added the borane compound, $CsB_9H_{12}S$. The emulsions, with and without sodium thiosulfate, were used as controls. Silver halide was rapidly precipitated by adding to each of the above gelatin solutions an aqueous solution containing 1.5 moles of ammoniacal silver nitrate. The emulsions were ripened for 15 minutes at 120° F. After ripening, the emulsions were neutralized and cooled to 85° F. The emulsions were coagulated, washed and redispersed in the manner taught by Moede, U.S. Pat. 2,772,165.

The aqueous gelatin content was adjusted to approximately 2.5%, and the emulsion was digested for 30 minutes at 120° F. Coating addenda were added and the emulsions were coated on a photographic film support at a coating weight of approximately 700 milligrams $AgNO_3$/sq. ft. and dried in a conventional manner.

Strips of the coated elements were exposed on the Edgerton, Germeshausen and Greek Mark VII sensitometer as described in Example I at 1.0 microsecond through a 21 step $\sqrt{2}$ wedge. The exposed strips were machine developed for 60, 120 and 180 seconds in a commercial hydroquinone-formaldehyde lithographic developer.

The developed strips were treated for 10 seconds in dilute acetic acid short stop and were fixed in a conventional fixing solution.

The strips were then washed and dried. Densities were read on a conventional densitometer for the various coatings at the three processing times. The results are shown in the following table.

TABLE IX-A

[60 sec. processing time—$CsB_9H_{12}S$]

	Sample numbers					
	1 (control)	2	3	4 (control)	5	6
Fog density	.04	.02	.03	.03	.03	.02
Step No./density (above fog) for step numbers:						
9		.01	.01			.01
10		.02	.02		.01	.02
11		.03	.04		.02	.04
12		.06	.08		.04	.10
13		.08	.14		.08	.16
14		.14	.24		.13	.32
15		.20	.40		.20	.54
16	.01	.31	.70	.01	.30	.85
17	.02	.51	1.00	.02	.50	1.23
18	.04	.84	1.36	.03	.82	1.52
19	.06	1.31	1.66	.04	1.10	1.87
20	.08	1.63	1.84	.07	1.34	2.20
21	.12	1.94	2.26	.10	1.70	2.52
Variations at AgHal precipitation:						
Moles $Na_2S_2O_3$ per 1.5 moles $AgNO_3$	8.72×10^{-6}	8.72×10^{-6}	8.72×10^{-6}	(1)	(1)	(1)
Moles $CsB_9H_{12}S$ per 1.5 moles AgN_3O	(1)	5×10^{-7}	10×10^{-7}	(1)	5×10^{-7}	10×10^{-7}

[1] None.

TABLE IX-B

[120 sec. processing time—$CsB_9H_{12}S$]

	Sample numbers					
	1 (control)	2	3	4 (control)	5	6
Fog density	.04	.04	.08	.03	.04	.06
Step No./density (above fog) for step numbers:						
4			.01			
5			.02			.02
6		.02	.04		.01	.04
7		.05	.10		.04	.08
8		.12	.22		.10	.22
9		.26	.44		.22	.44
10		.52	.74		.46	.77
11	.01	.81	1.14	.01	.72	1.18
12	.05	1.21	1.66	.03	1.06	1.73
13	.14	1.70	2.18	.08	1.44	2.26
14	.30	2.14	2.76	.20	1.82	2.92
15	.54	2.60	3.25	.36	2.13	3.48
16	.83	3.00	3.68	.60	2.40	3.80
17	1.26	3.40	3.88	.92	2.63	4.00+
18	1.75	3.70	4.00	1.34	2.78	4.00+
19	2.28	3.92	4.00+	1.80	2.90	4.00+
20	2.80	4.00	4.00+	2.30	3.00	4.00+
21	3.38	4.00+	4.00+	2.90	3.02	4.00+

TABLE IX-C

[180 sec. processing time—$CsB_9H_{12}S$]

	Sample numbers					
	1 (control)	2	3	4 (control)	5	6
Fog density	.03	.06	1.12	.03	.06	.10
Step No./density (above fog) for step numbers:						
2			.02			
3			.03			.01
4		.01	.04		.01	.02
5		.02	.06		.02	.04
6		.06	.10		.04	.07
7		.12	.20		.10	.15
8		.21	.36		.20	.32
9		.40	.60		.36	.56
10	.01	.67	.96	.01	.61	.92
11	.04	1.00	1.42	.04	.90	1.38
12	.12	1.42	1.96	.08	1.25	1.92
13	.24	1.86	2.56	.16	1.64	2.50
14	.44	2.34	3.20	.32	1.98	3.00
15	.68	2.76	3.70	.56	2.26	3.52
16	1.02	3.18	4.00+	.84	2.47	3.84
17	1.50	3.60	4.00+	1.24	2.71	4.00+
18	1.98	3.85	4.00+	1.70	2.83	4.00+
19	2.51	4.00+	4.00+	2.18	2.94	4.00+
20	2.97	4.00+	4.00+	2.70	3.02	4.00+
21	3.44	4.00+	4.00+	3.34	3.11	4.00+

The data above show that the presence of the borane compound, $CsB_9H_{12}S$ produces greater speed (greater density at lower step number) than the controls whether sodium thiosulfate is present or not. The speed advantage is 7 to 8 $\sqrt{2}$ steps, or 3½ to 4 doubles in speed.

EXAMPLE X

Example IX was repeated with the following exceptions:

(A) There was added to the aqueous gelatin solution of alkali metal halides before the addition of silver nitrate the various amounts of sodium thiosulfate and/or borane

compound, $Na_2B_{12}H_{12}\cdot 2H_2O$ as indicated in the tables below.

(B) Test strips were processed 60, 90 and 120 seconds instead of 60, 120, and 180 seconds as in Example IX. Results are as follows:

TABLE X-A

[60 sec. processing time—$Na_2B_{12}H_{12}\cdot 2H_2O$]

	Sample number					
	1 (control)	2	3	4	5	6
Fog density	.02	.02	.02	.02	.02	.16
Step number/density (above fog) for step numbers:						
10						.02
11					.02	.03
12					.04	.05
13					.05	.08
14				.01	.06	.17
15				.03	.10	.34
16		.01		.04	.14	.64
17		.02		.05	.22	1.02
18		.03	.10	.08	.34	1.50
19	.02	.04	.02	.09	.58	1.80
20	.03	.05	.03	.13	.84	2.03
21	.05	.06	.04	.16	1.28	2.20
Variations at AgHal precipitation:						
Moles $Na_2S_2O_3$ per 1.5 moles $AgNO_3$	8.72×10^{-6}	8.72×10^{-5}	None	None	None	None
Moles $Na_2B_{12}H_{12}\cdot 2H_2O$ per 1.5 moles $AgNO_3$	None	.0001	.0001	.001	.01	.05

TABLE X-B

[90 sec. processing time—$Na_2B_{12}H_{12}\cdot 2H_2O$]

	Sample number					
	1 (control)	2	3	4	5	6
Fog density	.03	.03	.03	.03	.03	2.41
Step No./density (above fog) for step numbers:						
7					.02	(1)
8					.04	(1)
9					.14	(1)
10					.34	(1)
11				.02	.68	(1)
12				.05	1.06	(1)
13		.01		.10	1.44	(1)
14		.02		.26	1.68	(1)
15	.02	.04	.02	.52	1.96	(1)
16	.04	.10	.04	.76	2.21	(1)
17	.08	.18	.11	1.07	2.44	(1)
18	.18	.38	.19	1.38	2.72	(1)
19	.48	.62	.38	1.61	2.94	(1)
20	.81	.90	.73	1.82	3.26	(1)
21	1.05	1.14	1.05	2.14	3.42	(1)

[1] Fog only.

TABLE X-C

[120 sec. processing time—$Na_2B_{12}H_{12}\cdot 2H_2O$]

	Sample number					
	1 (Control)	2	3	4	5	6
Fog density	.03	.03	.03	.03	.07	1.54
Step No./density (above fog) for step numbers:						
4					.00	(1)
5					.02	(1)
6					.10	(1)
7					.26	(1)
8					.52	(1)
9				.02	.82	(1)
10				.09	1.16	(1)
11		.02		.24	1.60	(1)
12		.06	.01	.48	1.99	(1)
13	.02	.14	.04	.72	2.29	(1)
14	.10	.28	.11	1.02	2.60	(1)
15	.26	.50	.24	1.38	2.84	(1)
16	.50	.72	.40	1.78	3.02	(1)
17	.80	1.04	.60	2.14	3.18	(1)
18	1.24	1.45	.90	2.58	3.30	(1)
19	1.75	1.87	1.26	2.96	3.40	(1)
20	2.30	2.34	1.72	3.32	3.50	(1)
21	2.73	2.71	2.14	3.58	3.60	(1)

[1] Fog only.

The tables show that the borane compound,

$$Na_2B_{12}H_{12}\cdot 2H_2O$$

produces greater speed (greater density at lower step number) at .001 to .05 mole per 1.5 moles of silver nitrate in the absence of sodium thiosulfate and at .0001 mole per 1.5 moles of silver nitrate with sodium thiosulfate. The greatest speed advantage is again about $8\sqrt{2}$ steps or 4 doubles in speed.

EXAMPLE XI

Example IX was repeated except that the borane compound, $Cs_2B_6H_6$ was added to the aqueous gelatin-salt solution before the addition of the aqueous silver nitrate solution. The emulsion was ripened for 10 minutes at 135° F. All other operations were carried out as in Example IX except that the digestion after washing and redispersion was carried out at 125° F. for 60 minutes. The emulsion was coated to give a coating weight of about 1100 mg. $AnNo_3/ft.^2$ and dried in a conventional manner.

Strips of the coated material were exposed in the sensitometer described in Example I for 1.0 microsecond through a 21 step $\sqrt{2}$ neutral density step wedge. The strips were developed for 90 and 120 seconds at 80° F. and fixed in a machine processor using the solution set forth in Example IX. Step desities and fog were read above base. Speed (1) is the step number at density equal to 0.2, and speed (2) is the number at density equal to 3.5. The lower the step number, the greater the speed. The sensitometric data are as follows:

TABLE XI

Moles $Cs_2B_6H_6$ per 1.5 moles Ag halide	Coating No.	Processing time, sec.	Speed (1)	Speed (2)	$D_{max.}$	Fog	Ctg. wt. (mg./ft.^{2})
None	1	90	11.2	------	2.00	.03	1.038
Do		120	8.4	19.0	3.82	.04	----------
5×10^{-7}	2	90	10.6	------	2.14	.03	1.093
5×10^{-7}		120	7.7	18.9	3.73	.04	----------
5×10^{-6}	3	90	4.6	18.9	3.62	.05	1.178
5×10^{-6}		120	2.0	12.5	4.81	.10	----------

It will be clear to those skilled in the art that the practice of the invention lends itself readily to a wide variety of applications. For example, the novel borane compounds may be used to greatly increase the speed of panchromatic negative papers useful in inverse transfer processes, and in high speed negative emulsions useful for phototypesetting systems, high speed microfilms, and for photographic elements generally.

I claim:

1. A silver halide, negative-working, developing out emulsion containing a sensitizing amount of a boron hydride having a polyhedral skeletal framework which has from 6 to 12 boron atoms and which may contain one or more heteroskeletal atoms selected from the group consisting of C, S and N, said silver halide being dispersed in a macromolecular, water-permeable colloid.

2. The emulsion of claim 1 wherein said boron hydride is $Na_2B_{12}H_{12}\cdot 2H_2O$.

3. The emulsion of claim 1 wherein said boron hydride is $(NH_4)_2B_{10}H_{10}$.

4. The emulsion of claim 1 wherein said boron hydride is $CsB_9H_{12}S$.

5. The emulsion of claim 1 wherein said boron hydride is $(CH_3)_3NNB_9H_{12}$.

6. The emulsion of claim 1 wherein said boron hydride is $(CH_3)_4N(CH_3)_2NNB_9H_{12}$.

7. The emulsion of claim 1 wherein said boron hydride is $[C_6H_5)_3CH_3P]_2B_{11}H_{11}$.

8. The emulsion of claim 1 wherein said boron hydride is $B_{10}H_{12}CNH_3$.

9. The emulsion of claim 1 wherein said boron hydride is $(CH_3)_4N(CH_3)_3CNHCB_{10}H_{12}$.

10. The emulsion of claim 1 wherein said boron hydride is $(CH_3)_3NHB_{10}H_{12}CH$.

11. The emulsion of claim 1 wherein said boron hydride is $B_{10}H_{12}[S(CH_3)_2]_2$.

12. The emulsion of claim 1 wherein said boron hydride is $B_9H_{13}S(C_2H_5)_2$.

13. The emulsion of claim 1 wherein said boron hydride is $B_{10}H_{12}[S(C_2H_5)_2]_2$.

14. The emulsion of claim 1 wherein said boron hydride is $C_6H_5B_{11}H_{10}S$.

15. The emulsion of claim 1 wherein said boron hydride is present in an amount of from about 10^{-11} to about 10^{-6} moles per mole of silver halide.

16. The emulsion of claim 1, said silver halide being selected from the group consisting of silver bromide, silver iodide, silver chloride, silver chlorobromide, silver iodobromide and silver iodochlorobromide.

17. A photographic element comprising a sheet support bearing a layer of a silver halide emulsion as defined in claim 1.

18. A photographic element comprising a sheet support bearing a layer of a silver halide emulsion as defined in claim 15.

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