

[54] **SILVER HALIDE EMULSION SENSITIZED WITH A POLYHEDRAL HALOBORANE**

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[58] Field of Search **96/107, 108**

[56] **References Cited**

UNITED STATES PATENTS

3,320,069	5/1967	Illingsworth	96/107
3,637,392	1/1972	Bigelow	96/108

3,367,778 2/1968 Berriman 96/108 X

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[57] **ABSTRACT**

Photographic silver halide, negative-working developing-out emulsions are prepared which have their sensitivity increased by the addition during the precipitation of the silver halides, of at least one polyhedral haloborane containing 10 or 12 boron atoms, or a derivative thereof, which may contain heteroskeletal atoms such as carbon, nitrogen and sulfur and in which at least some or all of the hydrogen atoms normally attached to the boron atoms have been replaced with halogen atoms, e.g., chlorine, bromine or iodine.

10 Claims, No Drawings

SILVER HALIDE EMULSION SENSITIZED WITH A POLYHEDRAL HALOBORANE

CROSS-REFERENCES TO RELATED APPLICATIONS

This application is related to U.S. application Ser. No. 134,086 (PDC-1,256) filed in the name of J. H. Bigelow and U.S. application Ser. No. 176308 (PDC-1275 filed in the name of J. H. Bigelow on Aug. 30, 1971.

BACKGROUND OF THE INVENTION

1. 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 the invention relates to sensitizing negative-working, silver halide emulsions by precipitating the silver halides in the presence of at least one polyhedral haloborane containing 10 or 12 boron atoms or a derivative thereof which may contain heteroskeletal atoms such as carbon, nitrogen and sulfur and in which at least some or all of the hydrogen atoms have been replaced with halogen atoms. Another aspect of this invention relates to negative-working elements comprising layers of emulsions, which have been sensitized with the above defined haloborane compounds according to the above process.

2. Description of the Prior Art

Chemical sensitizers are conventionally used in high speed modern emulsions to enhance the sensitivity of said emulsions. The most common and well-known 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 and palladium, reducing compounds, e.g., stannous chloride and hydrazine derivatives and other types of compounds for increasing the speed of the emulsion, e.g., quaternary ammonium compounds, polyethylene glycols and derivatives thereof and thioethers. Combinations of two or more of the above sensitizers have also been used. Such chemical sensitizers, especially the labile sulfur and noble metal compounds 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 a developing out emulsion.

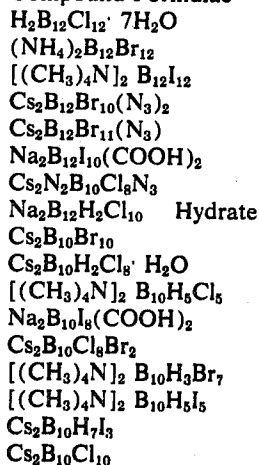
The process of chemical sensitization, however, using the prior art sensitizers has presented some serious problems. Despite its apparent simplicity, gold sensitization, for example, is quite difficult to carry out conveniently without increasing fog and instability. [See P. Glafkides, *Photographic Chemistry*, (translated by Keith M. Hornsby) Fountain Press (1958) page 319, Vol. 1]. The use of sulfur sensitization has a tendency to induce high intensity reciprocity failure. The prior art chemical sensitizers generally increase the residual fog, and moreover, reach a limit beyond which further addition or further ripening with the sensitizer present, merely increases the fog with no increase or, even a decrease in response to actinic radiation. In addition it has been found that the above chemical sensitizers may also have other deleterious effects such as substantially contributing to the instability of the emulsions during aging shelf-life especially under warm or tropical conditions.

SUMMARY OF THE INVENTION

The subject of this invention is a novel method of chemically sensitizing colloid silver halide, negative-working developing-out emulsions by incorporating either in the aqueous silver halide solution or the aqueous gelatin solution containing the water soluble halide salts, from 10^{-8} to 10^{-4} mole of a polyhedral haloborane per 1.5 moles of silver nitrate containing 10 or 12 boron atoms or a derivative thereof which may contain one or more skeletal atoms such as carbon, nitrogen and sulfur. Sensitized emulsions of this invention may contain additional materials, if desired, including other optical and non-optical sensitizing agents. The haloborane compounds defined herein can be used to sensitize a wide variety of negative-working, developing-out silver halide emulsions including radiographic emulsions, seismographic emulsions, variable contrast paper emulsions and panchromatic negative emulsions to name a few. As indicated above, the concentrations of the haloboranes may be varied over a wide range depending upon the intended purpose. Of course, certain of the compounds will be found to be more effective than others when used in equivalent quantities and the proper amount may be determined by a matter of simple testing, a procedure well-known and acknowledged by those skilled in the art.

Among the haloborane compounds as defined above, the following have been found to be particularly useful:

Compound Formulae



Methods of preparation of the compounds may be found in, *The Chemistry of Boron and Its Compounds*, E. L. Muetterties, John Wiley & Sons, N. Y., 1967; *Polyhedral Boranes*, E. L. Muetterties and W. H. Knoth, Marcel Dekker, Inc., N. Y., 1968 and in Miller and Muetterties, U. S. Pat. No. 3,551,120 patented Dec. 29, 1970.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The mechanism by which the haloboranes sensitize the silver halide emulsions when present at the stage of silver halide precipitation is not at all clear. It may be a process peculiar to the haloborane compounds themselves. It is emphasized that, to function as a sensitizer, the compounds must be present during the precipitation of the silver halides because many of the useful compounds of this invention will act as stabilizers and antifoggants when they are added at a later stage, e.g., during the digestion stage after the silver halide grains

have been formed. As indicated above the haloboranes may be incorporated either in the aqueous silver nitrate solution or the aqueous halide salt solution.

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 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 as thiazoles, triazoles, tetrazaindenes and the like, coating aids, hardeners, 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, silver iodobromide, and silver iodobromochloride.

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

EXAMPLE I

Emulsions were prepared in the following manner. An aqueous gelatin solution was made for each of four emulsions containing 1.56 moles of potassium bromide, 0.075 mole of strontium chloride, 0.025 mole of potassium iodide, and 50 grams of gelatin. To three of the gelatin solutions there were added the quantities of the haloborane; $(\text{NH}_4)_2\text{B}_{12}\text{Br}_{12}$ as indicated in Table I below. To each gelatin halide salt solution there was rapidly added an aqueous solution containing 1.5 moles of ammoniacal silver nitrate. The resulting emulsions were ripened for 15 minutes at 120°F., neutralized with

acetic acid and cooled at 85°F. They were then freed of excess salts by washing in the manner taught by Moe, U.S. Pat. No. 2,772,165 and redispersed at pH 6.0, the gelatin content was adjusted to 4.5 percent and the emulsions were digested for 30 minutes at 120°F. and cooled to coating temperature, a hardener and coating aids were added and the emulsions were coated on a photographic quality film support and dried in a conventional manner to give a coating weight as indicated in Table I.

Strips of the coated emulsions were exposed through a $\sqrt{2}$ step wedge at 10^{-6} seconds in an Edgerton, Germeshausen and Greer flash tube sensitometer Mark VII, and processed for 2 minutes at 80°F. in a commercial hydroquinone-formaldehyde developer, immersed in a short stop bath and fixed in a conventional fixing solution. The strips were washed and dried. Densities were read on a conventional densitometer and the results are shown in the table.

Considerably greater speeds are obtained with emulsions containing the haloborane compound as is shown by their greater density at lower step numbers.

EXAMPLE II

Example I was repeated except that the haloborane compounds $\text{H}_2\text{B}_{12}\text{Cl}_{12} \cdot 7\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{B}_{12}\text{Br}_{12}$ were added to the ammoniacal silver nitrate solution before precipitation as indicated in Table II. The emulsions were ripened for 10 minutes at 126°F. After washing the redispersed emulsions were digested for 60 minutes at 125°F. After adding 5.13×10^{-6} mole of the gold compound, HAuCl_4 plus sufficient potassium thiocyanate and sodium thiosulfate to provide 1.698×10^{-3} mole of CNS^- and 1.74×10^{-5} mole of $\text{S}_2\text{O}_3^{2-}$ per 1.5 moles of silver nitrate. The digested emulsions were coated, dried and tested as described in Example I to give the following results.

TABLE I.—EFFECT OF $(\text{NH}_4)_2\text{B}_{12}\text{Br}_{12}$ AT SILVER HALIDE PRECIPITATION IN HALIDE SALT—GELATIN SOLUTION

	Coating number			
	1	2	3	4
PHhB compound.....	None (control)	$(\text{NH}_4)_2\text{B}_{12}\text{Br}_{12}$		
Conc. moles/1.5 moles AgNO_3		8.87×10^{-6}	4.43×10^{-6}	1.77×10^{-6}
Ctg. wt. (mg. $\text{AgNO}_3/\text{ft.}^2$).....	878	763	739	817
D-Min.....	0.03	0.03	0.03	0.03
$\sqrt{2}$ Step number:				
6.....		.09		
7.....		.15	.05	
8.....		.28	.12	.05
9.....		.53	.25	.08
10.....	.05	.83	.44	.13
11.....	.09	1.19	.64	.21
12.....	.13	1.60	.87	.33
13.....	.23	2.05	1.14	.47
14.....	.37	2.53	1.31	.61
15.....	.55	2.81	1.62	.77
16.....	.73	3.05	1.71	1.01
17.....	.99	3.43	1.99	1.27
18.....	1.21	3.82	2.20	1.59
19.....	1.51	4.0+	2.41	1.75
20.....	2.11		2.75	1.97
21.....				

TABLE II.—POLYHEDRAL HALOBORANES ADDED IN THE AgNO_3 SOLUTION

	Coating number		
	1	2	3
Polyhedral haloborane compounds.....	None (control)	$\text{H}_2\text{B}_{12}\text{Cl}_{12} \cdot 7\text{H}_2\text{O}$	$(\text{NH}_4)_2\text{B}_{12}\text{Br}_{12}$
Conc. moles/1.5 moles AgNO_3		2.93×10^{-4}	1.5×10^{-5}
Ctg. wt. (mg. $\text{AgNO}_3/\text{ft.}^2$).....	870	704	660
D ₂ Min.....	0.03	0.04	0.03
$\sqrt{2}$ Step number:			
1.....		.05	.05
2.....		.07	.07
3.....		.07	.09
4.....	.04	.11	.17
5.....	.05	.15	.28
6.....	.09	.23	.51
7.....	.13	.39	.81
8.....	.21	.59	1.15
9.....	.36	.85	1.53
10.....	.57	1.17	2.09
11.....	.85	1.54	2.63
12.....	1.21	2.01	3.17
13.....	1.65	2.51	3.65
14.....	2.19	2.99	3.97
15.....	2.78	3.47	4.0+
16.....	3.27	3.83	
17.....	4.0+	4.0+	

The above results indicate that greater speeds are obtained in samples containing the haloborane compounds when added to the silver nitrate solution and when used in conjunction with conventional sulfur sensitizers added at digestion.

EXAMPLE III

Example I was repeated except that the polyhedral haloborane compound was incorporated in the aqueous gelatin solution contain the water soluble halides before precipitation of the silver iodobromide. The resulting emulsion was ripened for 10 minutes at 138°F.

Upon redispersion after washing the sulfur sensitizers of Example II were added and the optical sensitizing dye, 3,3'-diethyl-thiazoline carbocyanine iodide in an amount of 0.06 gram per 1.5 moles of silver halide, was added and the digestion pH was varied as indicated in Table III.

The emulsions were coated, dried, exposed and tested as described in Example I to give the following results.

EXAMPLE IV

A gelatino-silver chlorobromide emulsion was prepared by first making a gelatin-chloride salt solution containing 1.5 moles of ammonium chloride, 1.43×10^{-7} mole of $(\text{NH}_4)_3\text{RhCl}_6 \cdot \text{H}_2\text{O}$, 2 percent inert gelatin and 1.0×10^{-5} mole of the polyhedral haloborane, $\text{Cs}_2\text{B}_{10}\text{Cl}_{10}$. To this solution there was added in 1½ minutes an aqueous solution containing 1.5 moles of silver nitrate. The resulting emulsion was ripened for 2 minutes at 154°F. and then there was added 0.62 mole of ammonium bromide and after ripening for 10 minutes another quantity of 0.923 mole of ammonium bromide was added and ripening was continued for 5 minutes. The emulsion was cooled and washed as described in Example I. The emulsion was redispersed at pH 6.0 and added to a 3.75 percent gelatin solution at a temperature of 125°F. and held for 60 minutes after adding 5.13×10^{-6} mole of chloroauric acid and the sulfur sensitizers as set forth in Example II. The emulsions were coated, dried, exposed and tested as described in

TABLE III.— $\text{H}_2\text{B}_{12}\text{Cl}_{12} \cdot 7\text{H}_2\text{O}$ IN THE HALIDE SALT-GELATIN SOLUTION

	Coating number			
	1	2	3	4
Digestion pH.....	6.0	6.0	6.5	6.5
Polyhedral haloborane compounds.....	None (control)	$\text{H}_2\text{B}_{12}\text{Cl}_{12} \cdot 7\text{H}_2\text{O}$	None (control)	$\text{H}_2\text{B}_{12}\text{Cl}_{12} \cdot 7\text{H}_2\text{O}$
Conc. moles/1.5 moles AgNO_3		2.93×10^{-4}		2.93×10^{-4}
Ctg. wt. (mg. $\text{AgNO}_3/\text{ft.}^2$).....	597	520	1019	607
D ₂ Min.....	0.03	0.03	0.06	0.05
$\sqrt{2}$ Step number:				
1.....	.06	.05	.11	.07
2.....	.06	.07	.11	.11
3.....	.06	.11	.12	.17
4.....	.07	.21	.14	.60
5.....	.11	.45	.18	1.01
6.....	.16	.76	.27	1.38
7.....	.27	1.11	.43	1.81
8.....	.41	1.47	.64	2.19
9.....	.59	1.72	.89	2.59
10.....	.80	1.89	1.19	2.83
11.....	1.03	2.01	1.48	2.94
12.....	1.26	2.13	1.81	3.01
13.....	1.43	2.23	2.14	
14.....	1.58	2.24	2.53	
15.....	1.71	2.27	2.87	
16.....	1.93	2.31	3.29	
17.....	2.19		3.77	
18.....	2.45		4.0+	
19.....	2.55			
20.....	2.59			
21.....	2.63			

Example I to give the results in the following table.

TABLE IV
EFFECT OF $\text{Cs}_2\text{B}_{10}\text{Cl}_{10}$ IN SILVER
CHLOROBROMIDE EMULSION

Polyhedral haloborane compound Conc. moles/1.5 moles AgNO_3 D-Min 2 Step Number	Coating Number	
	1 None (Control)	2 $\text{Cs}_2\text{B}_{10}\text{Cl}_{10}$
	—	1.0×10^{-5}
	0.03	0.03
5		0.04
6	0.05	0.06
7	0.08	0.10
8	0.12	0.16
9	0.20	0.29
10	0.35	0.55
11	0.59	0.85
12	0.89	1.34
13	1.23	1.88
14	1.69	2.53
15	2.13	3.07
16	2.47	3.57
17	2.56	3.95
18	2.81	4.0+
19		

The above results indicate that polyhedral haloboranes containing 10 boron atoms in the structure are also effective agents for increasing the speed of silver halide emulsions when present during the precipitation of the silver halides.

EXAMPLE V

Example II was repeated except that the ripening temperature was 135°F. The polyhedral haloborane was added to the aqueous silver nitrate solution in the amounts indicated in Table V below. The film strips were processed as described in Example I except that the processing time was reduced to 1, 1/2 minutes. The results are shown in the following table.

TABLE V.—EFFECT OF $(\text{NH}_4)_2\text{B}_{12}\text{Br}_{12}$ IN AgNO_3 SOLUTION AT SILVER HALIDE PRECIPITATION

	Coating number			
	1	2	3	4
Polyhedral haloborane compound.....	None (control)	$(\text{NH}_4)_2\text{B}_{12}\text{Br}_{12}$		
Conc. (moles/1.5 moles AgNO_3).....		8.89×10^{-8}	8.89×10^{-6}	8.89×10^{-5}
Ctg. wt. (mg. $\text{AgNO}_3/\text{ft.}^2$).....	690	775	688	806
D-Min.....	0.03	0.03	0.03	0.03
2 Step number:				
6.....			.05	
7.....			.06	
8.....			.07	
9.....		.05	.07	.05
10.....	.05	.07	.09	.07
11.....	.06	.08	.15	.09
12.....	.07	.10	.39	.11
13.....	.09	.15	.93	.19
14.....	.19	.35	1.43	.55
15.....	.43	.87	1.95	1.17
16.....	.85	1.39	2.49	1.65
17.....	1.47	1.98	2.82	2.27
18.....	1.89	2.45	3.19	2.73
19.....	2.29	2.97	3.51	3.15
20.....	2.55	3.36	3.82	3.54
21.....	2.99	3.85	3.95	3.97

The above data show greater speed, i.e., greater density at a lower step number over a wide range of concentration of the haloborane compound.

The silver halide emulsions of this invention can be made with any of the macromolecular, water-permeable colloids known to be suitable for the pur-

pose of acting as a colloid carrier for silver halide grains. In addition to gelatin, there may be used polyvinyl alcohol and its derivatives, e.g., partially hydrolyzed polyvinyl acetates, ethers and acetals, hydrolyzed inter-polymers of vinyl acetate and unsaturated addition polymerizable compounds such as maleic anhydride, acrylic and methacrylic acid esters, poly-N-vinyl lactams, polysaccharides, e.g., dextran, dextrin, etc., the hydrophilic copolymers disclosed in Shacklett U.S. Pat. No. 2,833,650, hydrophilic cellulose ethers and esters, and acylamide 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. No. 3,142,568 issued July 28, 1964.

The emulsions of this invention may be coated on any suitable support including photographic quality paper and transparent film. For example, the cellulosic supports, e.g., cellulose acetate, cellulose triacetate, cellulose mixed esters, etc., may be used. Polymerized vinyl compounds, e.g., copolymerized vinyl acetate and vinyl chloride, polystyrene and polymerized acrylates may also be mentioned. The film formed from the polyesters made according to the teachings of Alles, U.S. Pat. No. 2,779,684 and the patents referred to in the specification of that patent. Other suitable supports are the polyethylene terephthalate/isophthalates of British Pat. No. 766,290 and Canadian Pat. 562,672 and those obtainable by condensing terephthalic acid and dimethyl terephthalate with propylene glycol, diethylene glycol, tetramethylene glycol or cyclohexane-1,4-dimethanol(hexahydro-p-ylene alcohol). The films of Bauer et al., U.S. Pat. No. 3,059,543 may also be used. The above polyester films are particularly suitable because of their dimensional stability. The emulsions are generally coated on the supports to give a coating weight equivalent to about 700 mg./ft.².

Many polyhedral haloborane compounds other than those referred to above can be used as chemical sensitizing agents for the silver halide photographic elements of this emulsion in accordance with this invention.

What is claimed is:

1. A photographic silver halide negative-working developing-out emulsion prepared by precipitating said silver halide in the presence of a sensitizing amount of at least one polyhedral haloborane containing 10 or 12 boron atoms and which may contain one or more heteroskeletal atoms selected from carbon, sulfur and nitrogen.

2. The silver halide emulsion of claim 1 wherein said polyhedral haloborane is supplied by incorporating it into the aqueous silver halide solution.

3. The silver halide emulsion of claim 1 wherein said polyhedral haloborane is supplied by incorporating it into the aqueous gelatin solution containing the water soluble halide salts.

4. The silver halide emulsion of claim 1 wherein said polyhedral haloborane is present in the amount of about 10^{-8} to about 10^{-4} moles per 1.5 moles of silver

halide.

5. The silver halide emulsion of claim 1 wherein said polyhedral haloborane contains at least one skeletal atom selected from the group consisting of carbon, nitrogen or sulfur.

6. The silver halide emulsion of claim 1 when said polyhedral haloborane is $H_2B_{12}Cl_{12} \cdot 7H_2O$.

7. The silver halide emulsion of claim 1 when said polyhedral haloborane is $(NH_4)_2B_{12}Br_{12}$.

8. The silver halide emulsion of claim 1 when said polyhedral haloborane is $Cs_2B_{10}Cl_{10}$.

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

10. The silver halide emulsion of claim 1 wherein said polyhedral haloborane is a homonuclear borane.

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