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3,537,858

REVERSAL SILVER HALIDE EMULSIONS

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18 Claims

ABSTRACT OF THE DISCLOSURE

Halogen accepting compounds, particularly merocyanine dyes are employed to improve the photographic speed of direct-positive silver halide emulsions. A still further increase in photographic speed is obtained when the halogen accepting compounds are used in combination with sulfonated organic compounds as described. The photographic silver halide grains present in the direct-positive emulsions comprise a central core of silver halide containing centers which promote the deposition of photolytic silver and an outer shell or covering for such core of a fogged silver halide.

This invention relates to photographic emulsions, their preparation and use. In one of its aspects, this invention relates to a novel direct-positive or reversal emulsion. In a specific aspect, this invention relates to a fogged direct-positive photographic silver halide emulsion containing a halogen accepting compound and to a photographic element comprising a layer of such emulsion.

It is known that photographic silver halide emulsions can be prepared from silver halide grains comprising a central core and one or more contiguous layers which can differ from one another in composition. Such grains can be prepared, e.g., as shown in Porter et al. U.S. Pat. 3,206,313 issued Sept. 14, 1965 and German Pat. 1,169,290 granted Apr. 30, 1964. Reversal or direct-positive emulsions can be prepared from fogged silver halide grains comprising a central core and one or more contiguous layers. Such reversal or direct-positive emulsions contain silver halide grains comprising a central core of silver halide containing centers which promote the deposition of photolytic silver and an outer shell or covering for such core of a fogged or spontaneously developable silver halide. The fogged shell of such grains develops to silver without exposure. Reversal or direct-positive emulsions of this type represent a distinct advance in the art, but they do not exhibit the high photographic speed which is necessary or at least desirable for many applications, including, for example, use in the duplicating or electron recording fields.

It is accordingly an object of this invention to provide a novel class of photographic reversal or direct-positive emulsions.

It is another object of this invention to provide direct-positive silver halide emulsions having high sensitivity or photographic speed.

It is another object of this invention to provide direct-positive photographic silver halide emulsions that combine high sensitivity or photographic speed with a low background or Dmin density which emulsions can be processed with conventional surface developing compositions.

It is still another object of this invention to provide direct-positive silver halide emulsions that have higher sensitivity than conventional direct-positive silver halide emulsions utilizing the Herschel effect.

Still another object of this invention is to provide fogged direct-positive photographic silver halide emulsions containing silver halide grains comprising a central core

2

and one or more contiguous layers and which have adsorbed to such grains a halogen accepting compound.

Still another object of this invention is to provide a means for effecting a substantial increase in the photographic speed or sensitivity of fogged direct-positive photographic silver halide emulsions.

These and other objects of this invention are accomplished with a uniformly fogged direct-positive photographic silver halide emulsion comprising (1) silver halide grains comprising a central core of silver halide containing centers which promote deposition of photolytic silver and an outer shell covering said core comprising a fogged silver halide that develops to silver without exposure and adsorbed to said fogged grains, (2) a halogen accepting compound having an anodic polarographic half-wave potential less than 0.85 and a cathodic polarographic halfwave potential which is more negative than -1.0.

It is a significant feature of this invention that the halogen accepting compounds adsorbed to the fogged silver halide grains have the polarographic halfwave potentials set forth hereinbefore. Thus, as shown by Example 2 which follows, fogged direct-positive silver halide emulsions containing halogen accepting compounds which do not have these polarographic halfwave potentials do not exhibit the excellent photographic speed or sensitivity characteristics of the emulsions of this invention.

Another significant feature of this invention is that certain high molecular weight organic compounds, particularly sulfonated compounds as described hereinafter, can be used in combination with halogen accepting compounds to effect an even greater increase in photographic speed or sensitivity. This feature of the invention is illustrated by Example 6 which follows.

The silver halide grains employed in the practice of this invention comprise a central core of a silver halide containing centers which promote the deposition of photolytic silver and an outer shell or covering for such core of a fogged or spontaneously developable silver halide. Silver halide grains containing such fogged shells develop to silver without exposure.

Before shell formation, the core forming photographic silver halide is chemically or physically treated by methods previously described in the prior art to produce centers to promote the deposition of photolytic silver, i.e., latent image nucleating centers. Such centers can be obtained by various techniques as described herein. Chemical sensitization techniques of the type described by Antoine Hautot and Henri Saubnier in Science et Industries Photographiques, vol. XXVIII, January 1957, pages 57 to 65, are particularly useful. Such chemical sensitization includes three major classes, namely, gold or noble metal sensitization, sulfur sensitization, such as by a labile sulfur compound, and reduction sensitization, i.e., treatment of the silver halide with a strong reducing agent which introduces small specks of metallic silver into the silver salt crystal or grain.

When the core forming emulsion is chemically sensitized, it is preferably sensitized so that when examined according to normal photographic testing techniques by coating a test portion of the emulsion on a transparent support, exposing to a light intensity scale for a fixed time between 0.01 and 1 second and developed for 6 minutes at 68° F. in Developer A, as hereinafter defined, it has a sensitivity greater than the sensitivity of an identical test portion of the same emulsion (measured at a density of 0.1 above fog), which has been exposed in the same way, bleached 5 minutes in an aqueous 0.3 percent potassium ferricyanide solution at 65° F. and developed for 5 minutes at 65° F. in Developer B, as hereinafter defined. Developer A is the usual type of surface image developer

3

and Developer B is an internal developer having high silver halide solvent activity.

DEVELOPER A

	Grams
N-methyl-p-aminophenol sulfate -----	2.5
Ascorbic acid -----	10.0
Potassium metaborate -----	35.0
Potassium bromide -----	1.0
Water to 1.0 liter.	
pH of 9.6.	

DEVELOPER B

N-methyl-p-aminophenol sulfate -----	2.0
Sodium sulfite, desiccated -----	90.0
Hydroquinone -----	8.0
Sodium carbonate, monohydrate -----	52.5
Potassium bromide -----	5.0
Sodium thiosulfate -----	10.0
Water to 1.0 liter.	

The core forming emulsions can be chemically sensitized by any method suitable for this purpose. For example, the core forming emulsions can be digested with naturally active gelatin, or sulfur compounds can be added, such as those described in Sheppard U.S. Pat. 1,574,944, issued Mar. 2, 1926; Sheppard et al. U.S. Pat. 1,623,499, issued Apr. 5, 1927; and Sheppard et al. U.S. Pat. 2,410,689, issued Nov. 5, 1946.

The core forming emulsions can also be chemically sensitized with gold salts as described in Waller et al. U.S. Pat. 2,399,083, issued Apr. 23, 1946, and Damschroder et al. U.S. Pat. 2,642,361, issued June 16, 1953. Suitable compounds are potassium chloroaurate, potassium aurithiocyanate, potassium chloroaurate, auric trichloride and 2-aurosulfobenzothiazole methochloride.

The core forming emulsions can also be chemically sensitized with reducing agents, such as stannous salts (Carroll U.S. Pat. 2,487,850, issued Nov. 15, 1949), polyamines, such as diethylene triamine (Lowe and Jones U.S. Pat. 2,518,698, issued Aug. 15, 1950), polyamines, such as spermine (Lowe and Allen U.S. Pat. 2,521,925, issued Sept. 12, 1950), or bis(β -aminoethyl)sulfide and its water-soluble salts (Lowe and Jones U.S. Pat. 2,521,926, issued Sept. 12, 1950).

The core forming emulsions can also be treated during or after the formation of the silver halide with salts of polyvalent metals such as bismuth, the noble metals and/or the metals of Group VIII of the Periodic Table, such as ruthenium, rhodium, palladium, iridium, osmium, platinum and the like. Representative compounds are ammonium chloropalladate, potassium chloroplatinate, sodium chloropalladate and the like.

The core forming emulsions can also be subjected to fogging by exposure to light either to low or high intensity light, to produce centers which promote the deposition of photolytic silver prior to forming the shell thereon.

The shell of the aforementioned silver halide grains can be prepared by precipitating over the core grain a light sensitive silver halide that can be fogged and which fog is removable by bleaching. The shell is of sufficient thickness to prevent access of the developer used in processing the silver halides to the core. The silver halide shell is surface fogged to make it developable to metallic silver with conventional surface image developing compositions. Substantially all of the silver halide grains in an emulsion are fogged prior to exposure and/or processing, i.e., such emulsions are uniformly fogged. Such fogging can be effected by chemically sensitizing to fog with the sensitizing agents described for chemically sensitizing the core forming emulsion, high intensity light and like fogging means well known to those skilled in the art. While the core need not be sensitized to fog, the shell is fogged, for example, reduction fogged with a reducing agent such as stannous chloride. Fogging by means of a reduction sensitizer, a noble metal salt such as a gold salt plus a reduc-

4

tion sensitizer, high pH and low pAg silver halide precipitating conditions, and the like can be suitably utilized.

In one embodiment of the invention, the core of the aforementioned grains is a coarse grained silver halide and a silver halide from a finer grained silver halide is deposited thereon by Ostwald ripening to form the shell. Also, coarse grained silver halides can be used to form a shell over a finer grained core when the shell-forming silver halide is more water-soluble than the core silver halide. In another embodiment of the invention the silver halide shell is formed immediately after formation of the core without interrupting the precipitation.

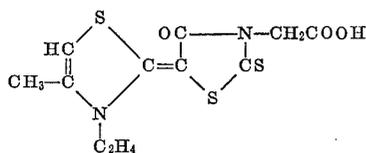
Generally, about 2 to 8 molar equivalents of shell silver halide per molar equivalent of core silver halides are used in the grains comprising the emulsion layers employed in this invention. These silver halides can be termed "covered grains" and emulsions containing them "covered grain emulsions." The population of grains in such emulsions is substantially uniform in grain-size distribution, as contrasted with emulsion blends which contain at least two types of grains, which are separate and distinct in their physical, and frequently, photographic properties. The grain size of these covered grain emulsions widely varies, typical emulsions having an average grain size of about 0.05 to 10 microns in diameter. Such grains are generally coated at silver coverages in the range of about 10 to about 400 mg. silver per square foot, preferably about 20 to about 100 mg. silver per square foot, and when exposed to an image and thereafter developed in a conventional surface image developer having low silver salt solvent action, form a reversal or direct-positive silver image. The unexposed grains develop without substantial reduction of the imagewise exposed grains.

The silver halide grains employed in the practice of this invention are fogged sufficiently to give a density of at least 0.5 when developed without exposure for five minutes in Developer A, described hereinbefore, when a direct-positive emulsion layer containing such grains is coated at a coverage of about 50 to about 500 mg. of silver per square foot of support.

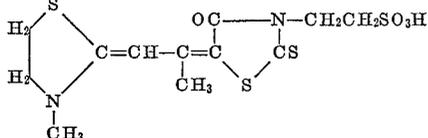
The halogen accepting compounds employed in practicing this invention are adsorbed to the fogged silver halide grains. The halogen acceptors which give particularly good results in the practice of this invention can be characterized in terms of their polarographic halfwave potentials, i.e., their oxidation reduction potentials determined by polarography. Cathodic measurements can be made with a 1×10^{-4} molar solution of the halogen acceptor in a solvent, for example, methanol which is 0.05 molar in lithium chloride using a dropping mercury electrode with the polarographic halfwave potential of the most positive cathodic wave being designated $E_{(c)}$. Anodic measurements can be made with 1×10^{-4} molar aqueous solvent solution, for example methanolic solutions of the halogen acceptor which are 0.05 molar in sodium acetate and 0.005 molar in acetic acid using a carbon paste or pyrolytic graphite electrode, with the voltmetric half peak potential for the most negative anodic response being designated $E_{(a)}$. In each measurement, the reference electrode can be an aqueous silver-silver chloride (saturated potassium chloride) electrode at 20° C. Electrochemical measurements of this type are known in the art and are described in New Instrumental Methods in Electrochemistry, by Delahay, Interscience Publishers, New York, N.Y., 1954; Polarography, by Kolthoff and Lingane, 2nd edition, Interscience Publishers, New York, N.Y., 1952; Analytical Chemistry, 36, 2426 (1964) by Elving; and Analytical Chemistry, 30, 1576 (1958) by Adams.

Compounds which can be employed as halogen acceptors in the practice of this invention include organic or inorganic compounds having an anodic polarographic halfwave potential $E_{(a)}$ less than 0.85 and a cathodic polarographic potential $E_{(c)}$ which is more negative than -1.0. A preferred class of halogen accepting compounds is characterized by an anodic halfwave potential which is

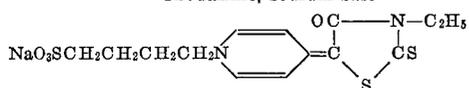
- (VII) 3-carboxymethyl-5-(3-ethyl-4-methyl-4-thiazolin-2-ylidene)rhodanine



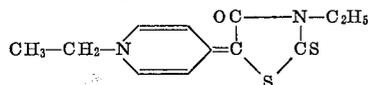
- (VIII) 5-[(3-methyl-2-thiazolidinylidene)-1-methylethylidene]-3-(2-sulfoethyl)rhodanine



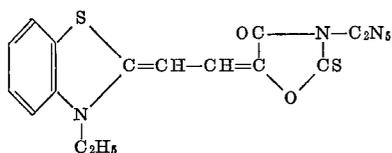
- (IX) 3-ethyl-5-[1-(4-sulfoethyl)-4(1H)-pyridylidene]rhodanine, sodium salt



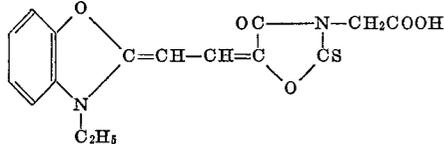
- (X) 3-ethyl-5-(1-ethyl-4-(1H)-pyridylidene)rhodanine



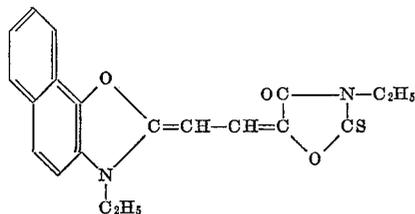
- (XI) 3-ethyl-5-[(3-ethyl-2-benzothiazolinylidene)ethylidene]-2-thio-2,4-oxazolidinedione



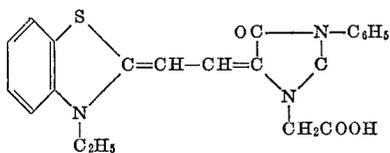
- (XII) 3-carboxymethyl-5-[(3-ethyl-2-benzoxazolinyldene)ethylidene]-2-thio-2,4-oxazolidinedione



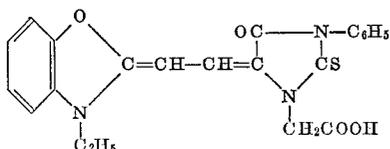
- (XIII) 3-ethyl-5-[(3-ethylnaphth[2,1-d]oxazolin-2-ylidene)ethylidene]-2-thio-2,4-oxazolidinedione



- (XIV) 1-carboxymethyl-5-[(3-ethyl-2-benzothiazolinylidene)ethylidene]-3-phenyl-3-thiohydantoin

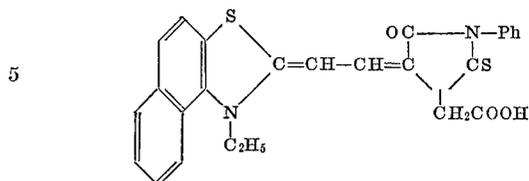


- (XV) 1-carboxymethyl-5-[(3-ethyl-2-benzoxazolinyldene)ethylidene]-3-phenyl-2-thiohydantoin

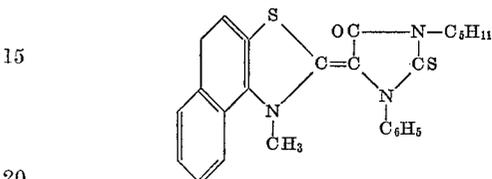


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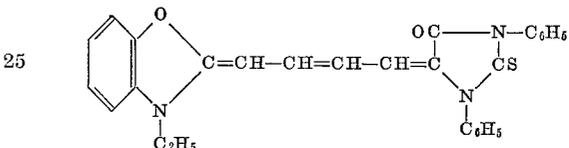
- (XVI) 1-carboxymethyl-5-[(1-ethylnaphtho[1,2-d]thiazolin-2-ylidene)ethylidene]-3-phenyl-2-thiohydantoin



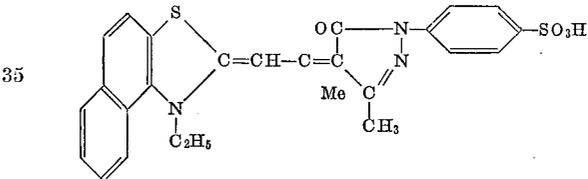
- XVII 3-heptyl-5-(1-methylnaphtho[1,2-d]thiazolin-2-ylidene)-1-phenyl-2-thiohydantoin



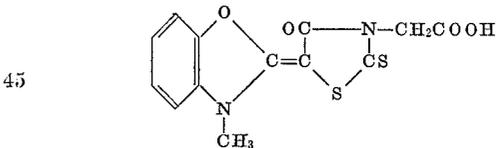
- XVIII 5-[4-(3-ethyl-2-benzoxazolinyldene)-2-butenylidene]-1,3-diphenyl-2-thiohydantoin



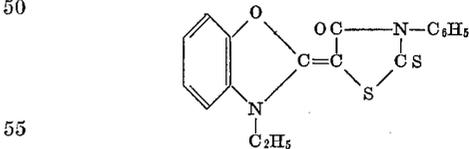
- XIX 4-[(1-ethylnaphtho[1,2-d]thiazolin-2-ylidene)-1-methylethylidene]-3-methyl-1-(4-sulfoethyl)-2-pyrazolin-5-one



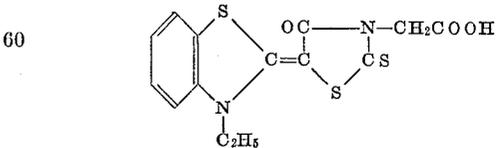
- XX 3-carboxymethyl-5-(3-methyl-2-benzoxazolinyldene)-rhodanine



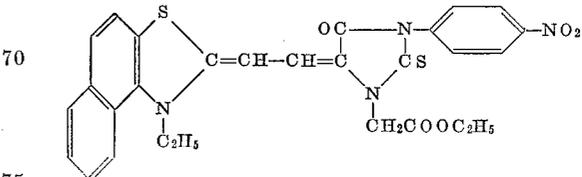
- XXI 5-(3-ethyl-2-benzoxazolinyldene)-3-phenyl-rhodanine



- XXII 3-carboxymethyl-5-(3-ethyl-2-benzothiazolinylidene)-rhodanine

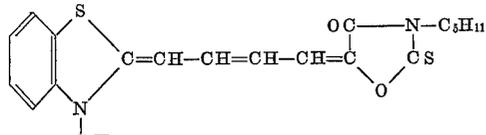


- XXIII 1-ethoxycarbonylmethyl-5-[(1-ethylnaphtho[1,2-d]thiazolin-2-ylidene)ethylidene]-3-(4-nitrophenyl)-2-thiohydantoin

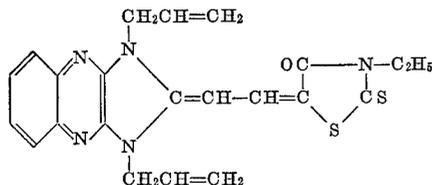


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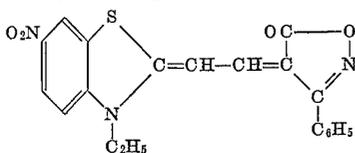
XXIV 5-[4-(3-ethyl-2-benzothiazolinyldiene)-2-butenylidene]-3-heptyl-2-thio-2,4-oxazolidinedione



XXV 5-[(1,3-diallylimidazo[4,5-b]quinoxalin-2(3H)-ylidene)ethylidene]-3-ethylrhodanine



XXVI 4-[(3-ethyl-6-nitro-2-benzothiazolinyldiene)-ethylidene]-3-phenyl-2-isoxazol-5-one

Dye
Number

- XXVII 3-ethyl-5-(3-methyl-2-thiazolidinyldiene)-ethylidene]-2-thio-2,4-oxazolidinedione
 XXIX 5-[(3-(2-carboxyethyl)-2-thiazolidinyldiene)-ethylidene]-3-ethylrhodanine
 XXX 5-[(3-methyl-2-thiazolidinyldiene)-1-methylethylidene]-3-(2-morpholinoethyl)rhodanine
 XXXI 5-[(3-(2-carboxyethyl)-2-thiazolidinyldiene)-1-methylethylidene]-3-carboxymethylrhodanine
 XXXII 5-[(3-(2-carboxyethyl)-2-thiazolidinyldiene)-1-methylethylidene]-3-(2-methoxyethyl)rhodanine
 XXXIII 3-(3-dimethylaminopropyl)-5-[(3-methyl-2-thiazolidinyldiene)ethylidene]rhodanine

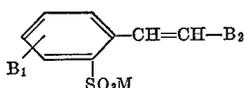
The halogen accepting compounds employed in the practice of this invention can be used in widely varying concentrations. However, the halogen accepting compounds are generally employed at concentrations in the range of about 100 mg. to about 1.0 g., preferably about 150 to about 600 milligrams per mole of silver halide.

As already indicated, the halogen accepting merocyanine dyes described herein can be employed in combination with certain types of high molecular weight organic compounds to achieve an even greater increase in the photographic speed of direct-positive emulsions. These compounds are sulfonated and comprise polynuclear aromatic compounds containing at least one sulfo group. The term "polynuclear aromatic" as used herein is intended to mean 2 or more benzene rings fused together (for example, as in naphthalene, pyrene, etc.), or at least 2 benzene rings or aromatic rings directly joined together (for example, as in diphenyl, terphenyl, quaterphenyl, etc.), or through an aliphatic linkage. Such sulfonated derivatives can conveniently be represented by the following general formula:



wherein R^1 represents a polynuclear aromatic group as defined above and M represents a cation such as a hydrogen atom or a water-soluble cation salt group (e.g., sodium, potassium, ammonium, triethylammonium, triethanolammonium, pyridinium, etc.). Among the most useful of the sulfonated derivatives embraced by Formula I above are the compounds represented by the following general formula:

II



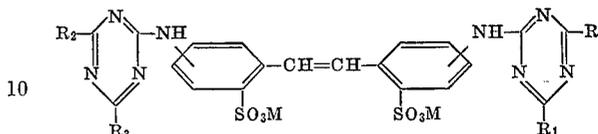
wherein B_1 represents a 2-benzotriazolyl group or a 1,3,5-triazin-6-ylamino group, B_2 represents an aromatic group (i.e., benzene or substituted benzene) and M has the value given above.

10

Typical of sulfonated derivatives of Formula II above, wherein B_1 represents a 1,3,5-triazin-6-ylamino group (i.e., a 1,3,5-triazin-2-ylamino group) are the compounds selected from those represented by the following general formula:

5

IIa

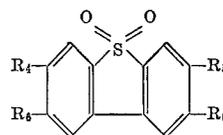


wherein M has the value given above and R, R_1 , R_2 , R_3 , each represents a hydrogen atom or a substituent group, such as hydroxyl, aryloxy (e.g., phenoxy, o-toloxyl, p-sulfophenoxy, etc.), alkoxyl (e.g., methoxyl, ethoxyl, etc.), a halogen atom (e.g., chlorine, bromine, etc.), a heterocyclic radical (e.g., morpholinyl, piperidyl, etc.), an alkylthio group (e.g., methylthio, ethylthio, etc.), an arylthio group (e.g., phenylthio, tolylthio, etc.), a heterocyclithio group (e.g., benzothiazylthio, etc.), an amino group, an alkylamino group (e.g., methylamino, ethylamino, propylamino, dimethylamino, diethylamino, dodecylamino, cyclohexylamino, β -hydroxyethylamino, di- β -hydroxyethyl amino, β -sulfoethylamino, etc.), an arylamino group (e.g., anilino, o-, m-, and p-sulfoanilino, o-, m-, and p-chloroanilino, o-, m-, and p-anisylamino, o-, m-, and p-toluidino, o-, m-, and p-carboxyanilino, hydroxyanilino, sulfonaphthylamino, o-, m-, and p-aminoanilino, o-acetamidoanilino, etc.), and the like.

Compounds of Formula IIa wherein R, R_1 , R_2 and/or R_3 each represents a heterocyclamino group (e.g., 2-benzothiazolylamino, 2-pyridylamino, etc.), can also be used in practicing my invention.

Another group of sulfonated derivatives which are useful in practicing my invention are dibenzothiophene dioxides such as those represented by the following general formula:

40



wherein R_4 is an acylamido group (e.g., acetamido, sulfo-benzamido, 4-methoxy-3-sulfobenzamido, 2-ethoxybenz-amido, 2,4-diethoxybenz-amido, p-tolylamido, 4-methyl-2-methoxybenz-amido, 1-naphthoylamino, 2-naphthoylamino, 2,4-dimethoxybenz-amido, 2-phenylbenz-amido, 2-thienylbenz-amido) or a sulfo group, R_5 represents an acylamido group (e.g., as defined by R_4 above) or a sulfoaryl group (e.g., sulfophenyl, p-sulfodiphenyl, etc.), and R_6 represents a hydrogen atom or a sulfo group, said compound containing at least one sulfo group.

Still other useful sulfonated derivatives of Formula I above include compounds containing diphenyl, terphenyl, quaterphenyl, phenanthrene, pyrene, chrysene, etc., nuclei. Many of the sulfonated compounds described herein are shown in McFall et al. U.S. Pat. 2,933,290, issued Apr. 19, 1960 and Jones U.S. Pat. 2,961,318, issued Nov. 22, 1960.

Included among the sulfonated derivatives of Formula I are the following typical examples.

- | Compound: | Name |
|-----------|---|
| A ----- | Calcofluor White-MR. This is the trade name for a bis(s-triazine-2-ylamino) stilbene-2,2'-disulfonic acid, sodium salt. |
| B ----- | Leucophor B. This is the trade name for a bis(s-triazine-2-ylamino) stilbene-2,2'-disulfonic acid, sodium salt. |
| C ----- | Sodium 6-(4-methoxy-3-sulfo-w-phenylacryloyl)-pyrene. |

Compound:	Name
D -----	3,4-bis(4-methoxy - 3 - sulfobenzamido)-dibenzothiophene dioxide, sodium salt.
E -----	4',4''-bis(2,4-dimethoxy - 5 - sulfobenzamido)-p-terphenyl, disodium salt.
F -----	Chrysene-6-sulfonic acid, sodium salt.
G -----	4,4'-bis[2-phenoxy - 4 - (2 - hydroxyethylamino)-1,3,5-triazine - 6 - yl-amino]stilbene - 2,2'-disulfonic acid, disodium salt.

These sulfonated derivatives are generally used in the same manner and in approximately the same concentrations disclosed in U.S. Pat. 2,937,089, i.e., in concentrations in the range of about 0.02 to about 10 g. per mole of silver halide.

The silver halides employed in the practice of this invention include any of the photographic silver halides as exemplified by silver bromide, silver iodide, silver chloride, silver chlorobromide, silver bromiodide and the like. A preferred class of silver halides is the silver halides in which at least 50 mole percent of the halide is chloride.

Various colloids can be used as vehicles or binding agents for the silver halide grains in the direct-positive materials of this invention. Satisfactory colloids which can be used for this purpose include any of the hydrophilic colloids generally employed in the photographic field, including, for example, gelatin, colloidal albumin, polysaccharides, cellulose derivatives, synthetic resins such as polyvinyl compounds, including polyvinyl alcohol derivatives, acrylamide polymers, and the like. In addition to the hydrophilic colloids, the vehicle or binding agent can contain dispersed polymerized vinyl compounds, particularly those which increase the dimensional stability of photographic materials. Suitable compounds of this type include water-insoluble polymers of alkyl acrylates or methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates, and the like.

The light sensitive compositions described herein can be coated on a wide variety of supports in practicing this invention. The photographic silver halide grains can be coated on one or both sides of the support which is preferably transparent and/or flexible. Typical continuous supporting sheets include, for example, cellulose nitrate film, cellulose acetate film, polyvinyl acetal film, polystyrene film, polyethylene terephthalate film and other polyester film as well as glass, paper, metal, wood and the like. Supports such as paper which are coated with α -olefin polymers, particularly polymers of α -olefins containing two or more carbon atoms, as exemplified by polyethylene, polypropylene, ethylenebutene copolymers, and the like, give good results.

The silver halide layers and any other hydrophilic colloid containing layers present in the elements of this invention can be hardened with any suitable hardener, including aldehyde hardeners such as formaldehyde and mucochloric acid, aziridine hardeners, hardeners which are derivatives of dioxane, oxypolysaccharides, such as oxy starch or oxy plant gums, and the like. The silver halide layers can also contain additional additives, particularly those known to be beneficial in photographic emulsions, including, for example, lubricating materials, stabilizers, speed increasing materials, plasticizers, and the like. The fogged silver halide layers described herein can also contain spectral sensitizing dyes which are not halogen acceptors, as defined herein. Suitable spectral sensitizers of this type include the cyanines, merocyanines, complex(trinuclear)cyanines, complex(trinuclear)merocyanines, styryls and hemicyanines. The silver halide layers can also be developed using incorporated developers such as polyhydroxybenzenes, aminophenols, 3-pyrazolidones, and the like.

It is sometimes advantageous to employ surface active agents or compatible mixtures of such agents in the preparation of the photographic materials described herein.

Suitable agents of this type include non-ionic, ionic and amphoteric types, as exemplified by polyoxyalkylene derivatives, amphoteric amino acid dispersing agents, including sulfobetaines, and the like. Such surface active agents are described in U.S. Pat. 2,600,831 issued June 17, 1952; U.S. Pat. 2,271,622, issued Feb. 3, 1942; U.S. Pat. 2,271,623, issued Feb. 3, 1942; U.S. Pat. 2,275,727, issued Mar. 10, 1942; U.S. Pat. 2,787,604, issued Apr. 2, 1957; U.S. Pat. 2,816,920, issued Dec. 17, 1957; U.S. Pat. 2,739,891, issued Mar. 27, 1956 and Belgian Pat. 652,862.

The halogen accepting dyes employed in the following working examples are identified by the number used in listing such dyes hereinbefore.

This invention can be further illustrated by the following examples of preferred embodiments thereof although it will be understood that these examples are included merely for purposes of illustration and are not intended to limit the scope of the invention unless otherwise specifically indicated.

EXAMPLE 1

A significant increase in photographic speed is obtained when halogen accepting compounds, as described herein, are incorporated into light sensitive photographic direct-positive emulsions containing silver halide grains comprising a central core of silver halide containing centers which promote deposition of photolytic silver and an outer shell covering said core comprising a fogged silver halide that develops to silver without exposure. To illustrate, a silver bromide photographic emulsion having the desired reversal characteristics is prepared by simultaneously adding, over a period of about 20 minutes, a solution containing 340 g. of silver nitrate and 520 ml. of distilled water and a solution containing 240 g. of potassium bromide and 500 ml. of distilled water, to a well-stirred aqueous solution of 500 ml. of 0.004 molar potassium bromide at 70° C., containing 20 g. of gelatin. A portion of the resulting silver halide core emulsion is cooled to a temperature of 40° C., and 100 mg. of potassium chloro-iridate (dissolved in 100 ml. of water) is added and the emulsion is heated to 70° C. This emulsion constitutes the silver bromide core containing discontinuities which trap electrons over which is formed a shell of silver bromide.

The shell of silver bromide is formed by adding to the core emulsion simultaneously, over a period of about 20 minutes, a solution containing 340 g. of silver nitrate and 520 ml. of distilled water and a solution containing 240 g. of potassium bromide and 500 ml. of distilled water, at a temperature of 70° C. 160 g. of gelatin previously soaked in 340 ml. of water is stirred and the emulsion cooled. An aqueous solution of potassium iodide is added equivalent to 2 mole percent of the silver present in the emulsion. 3.5 mg. of thiourea dioxide per mole are added to the emulsion at 40° C. The pH of the emulsion is adjusted to 9.5 and the emulsion is fogged by heating it to a temperature of 70° C. and holding for 5 minutes at this temperature. It is cooled immediately to 40° C. and the pH adjusted to 6.0.

The unsensitized portion of emulsion and a portion sensitized with 200 mg. of Dye VI per silver mole are coated in a conventional manner. A sample of each coating is exposed in an intensity scale sensitometer to tungsten light and developed for 30 seconds in Kodak D-72 Developer at 68° F., fixed, washed and dried. The results are as follows:

Coating:	Relative speed	D _{max.}
Control-----	100	0.90
Dye VI-----	2,140	1.00

EXAMPLE 2

As already indicated, the halogen accepting compounds employed in the practice of this invention require an anodic polarographic halfwave potential less than 0.85 and a cathodic halfwave potential which is more negative than

—1.0. To illustrate this feature of the invention, the halogen accepting compounds listed in the following table are added to separate portions of the control emulsion described in Example 1.

Dye	G. of dye/mole AgX	Anodic potential, E_a^1	Cathodic potential, E_c^1	Rel. at 365 μ	Rel. speed white light	$D_{max.}$	Gamma	$D_{min.}$
None (control)	0	-----	-----	100	<1.2	1.8	2.65	.09
VI	.24	.49	-1.47	795	316.0	1.36	4.00	.05
VI	.50	.49	-1.47	832	240.0	1.20	1.95	.05
VI	1.00	.49	-1.47	1,000	398.0	1.30	2.66	.05
XIII	.24	.53	-1.45	1,050	479.0	1.54	5.30	.06
V	.24	.56	-1.45	813	331.0	1.38	4.50	.05
I	.24	.46	-1.36	603	126.0	1.46	5.10	.07
IV	.24	.60	-1.37	725	263.0	1.51	4.50	.05
XI	.24	.60	-1.31	1,260	289.0	1.40	3.60	.05
XII	.24	.63	-1.48	447	83.0	1.34	1.22	.09
II	.24	.57	-1.27	200	22.0	1.64	1.95	.43
IX	.24	.53	-1.70	525	166.0	1.53	4.20	.08
X	.24	.57	-1.68	692	282.0	1.60	5.20	.10
VII	.24	.72(.68)	-1.81	302	73.0	1.37	5.10	.05
XXV	.24	.80	-1.10	200	7.8	1.28	2.58	.11
XXIV	.24	.31	-1.15	-----	-----	1.39	-----	1.26
XXIV	.50	.31	-1.15	132	13.8	1.02	1.04	.10
XIV	.24	.37	-1.48	955	589.0	.98	1.87	.05
XVI	.24	.28	-1.46	1,200	912.0	.78	1.25	.06
XVIII	.24	.22	-1.28	603	95.0	.90	.73	.10
None (control)	0	-----	-----	100	<1.2	1.8	2.65	.09
XX	.24	.85	-1.76	69	12.3	1.35	5.40	.06
XX	1.00	.85	-1.76	91	13.2	1.34	2.52	.07
XXI	.24	.89	-1.72	33	3.0	1.55	4.20	.23
XXI	1.00	.89	-1.72	35	2.0	1.51	1.44	1.00
XXII	.24	.86	<-1.70	80	32.0	1.28	6.60	.04
XXII	1.00	.86	<-1.70	83	20.0	1.48	2.38	.07
XXVI	1.00	>1.0	-0.61	28	-----	1.76	-----	-----

¹ E_a is determined on a polarograph using a methanol solution of the dye and a pyrolytic graphite electrode vs. a Ag/AgCl electrode in saturated KCl.

² E_c is determined on a polarograph using a methanol solution of the dye and a dropping mercury electrode vs. a Ag/AgCl electrode in saturated KCl.

It can be seen from the above table, that a significant increase in photographic speed is obtained when the halogen accepting dyes have an anodic halfwave potential (E_a) less than 0.85 and a cathodic halfwave potential (E_c) more negative than -1.0 are employed in the practice of this invention. It is also to be noted that a significant increase in blue speed (365 μ) is obtained with the direct-positive emulsions of this invention. Such an increase is completely unexpected, particularly in view of the fact that the halogen acceptors do not impart this blue speed increase to negative type silver halide emulsions.

EXAMPLE 3

A gelatin silver chloride photographic emulsion is prepared by simultaneously adding, over a period of about 20 minutes, 1000 ml. of a 4 molar silver nitrate aqueous solution and 1000 ml. of a 4 molar sodium chloride aqueous solution, to a well-stirred aqueous solution of 1000 ml. of 0.01 molar sodium chloride at 70° C. containing 40 grams of gelatin; 5000 ml. of water containing 280 grams of gelatin is added and the emulsion is cooled. One-eighth of the resulting gelatin silver chloride emulsion (containing 0.5 mole percent silver chloride) is melted at 40° C. 100 mg. of potassium chloroiridite (dissolved in water) is added, and the emulsion is heated to 70° C. This prepared emulsion constitutes the silver chloride core containing discontinuities which trap electrons over which is formed a shell of silver chloride.

The shell of silver chloride is formed by adding to the core emulsion 500 ml. of 4 molar silver nitrate aqueous solution and 500 ml. of 4 molar silver chloride aqueous solution simultaneously over a period of 20 minutes. 160 g. of gelatin, previously soaked in 340 ml. of water, is stirred in and the emulsion cooled. During both additions of the silver nitrate and sodium chloride (i.e., to form both the core and the shell), the two solutions are added at approximately constant rates. Sufficient silver chloride is formed in the shell to give a ratio of 4 moles of shell silver chloride to 1 mole of core silver chloride.

The emulsion is cooled to 40° C. and fogged by adding 25 ml. 1.0 N silver nitrate and 4 ml. of 2.5 N sodium hydroxide per mole of silver. The emulsion is heated to 55° C. held for 30 minutes, and cooled. The emulsion is acid-

ified, and gelatin added to bring the total to 160 g. of gelatin per silver mole. Part of the emulsion is coated on a paper support at 1000 square foot per silver mole. Another part of the emulsion is spectrally sensitized by add-

ing to it 300 mg. of Dye XV per silver mole and coated as above. Portions of the coatings are exposed in a sensitometer to tungsten light and developed for 30 seconds in Kodak D-72 Developer (1:1) at 68° F., fixed, washed and dried. The results are as follows:

Coating	Relative speed	$D_{max.}$	$D_{min.}$
Control	100	1.2	0.1
300 mg. Dye XV/Ag mole	20,000	1.2	0.1

In the above procedure, the core forming emulsion is treated with potassium chloroiridite to form centers which promote deposition of photolytic silver. However, similar results are achieved when other Group VIII metal compounds or polyvalent metal compounds such as bismuth nitrate are used for this purpose.

EXAMPLE 4

A silver chloride emulsion is prepared as in Example 3 except that 2 mg. thiourea dioxide per silver mole is used to fog the surface of the emulsion grains instead of silver nitrate. Part of this emulsion is sensitized with 150 mg. of Dye VI per silver mole. Non-sensitized and sensitized parts are coated and processed as in Example 3. The results are as follows:

Coating	Relative speed	$D_{max.}$	$D_{min.}$
Control	100	1.30	0.07
150 mg. Dye VI/Ag mole	87,000	1.26	0.02

EXAMPLE 5

A silver chloride emulsion is prepared as in Example 4. An unsensitized portion and a portion sensitized with 200 mg. of Dye XXVII per silver mole are coated as in Example 3; development is for 10 seconds as in Example 1. The results are as follows:

Coating	Relative speed	$D_{max.}$	$D_{min.}$
Control	100	1.03	0.14
200 mg. Dye XXVII/Ag mole	9,550	0.99	0.06

15
EXAMPLE 6

As pointed out previously, certain high molecular weight sulfonated compounds can be used in combination with the halogen accepting merocyanine dyes employed in the practice of this invention to obtain even greater increases in speed.

To illustrate, the compounds listed in the following table are added to separate portions of the emulsion prepared as described in Example 4. Each portion is coated on a paper support, exposed and processed as described in Example 3. The following results are obtained.

Coating	Mg./Ag mole	Relative speed	D _{max.}	D _{min.}
Control.....	(1)	100	1.32	0.08
Dye VI.....	150	87,000	1.20	0.08
Dye VI plus organic sulfonic acid ²	150 860	105,000	1.20	0.06
Dye XXIX plus organic sulfonic acid ²	150 860	159,000	1.18	0.07
Dye XXXI plus organic sulfonic acid ²	150 860	251,000	1.28	0.03
Dye XXXII plus organic sulfonic acid ²	150 860	398,000	1.12	0.03
Dye XXXIII plus organic sulfonic acid ²	150 860	316,000	1.15	0.03

¹ No dye.

² Sodium salt of bis(s-triazin-2-ylamino)stilbene-2,2'-disulfonic acid.

EXAMPLE 7

The photographic emulsions of this invention must be uniformly fogged in order to achieve the desired increase in speed. To illustrate, an internal image silver halide emulsion is prepared by the procedure described in Example 1 of Davey and Knott U.S. Pat. 2,592,250. The emulsion is divided into two portions. One portion is fogged by heating with 10 mg./silver mole of thiourea dioxide and heating for 5 minutes at 70° C. at a pH of 9.0. After fogging, the emulsion pH is adjusted to 5.5. The fogged and unfogged portions are coated with various amounts of Dye VI. Each portion is coated on a paper support at a laydown of 242 mg. of silver and 534 mg. of gelatin per square foot. Samples of each coating are exposed on an intensity scale sensitometer to blue light at a wavelength of 365 mμ. Samples of each coating are processed in a hydroquinone-aminophenol developer such as Kodak D-72, fixed, washed and dried with the following results.

Coating No.:	Dye VI (mg./Ag mole)	Relative speed	D _{max.}
1, unfogged.....	0	(1)	(1)
2, unfogged.....	150	(1)	(1)
3, unfogged.....	300	(1)	(1)
4, fogged.....	0	100	1.18
5, fogged.....	150	159	1.20
6, fogged.....	300	251	1.16

¹ No image.

It can be seen from the above results that the dye gives a speed increase in the emulsion only when the emulsion has been fogged prior to image exposure.

EXAMPLE 8

Run I

A silver chlorobromide (50/50 mole percent) emulsion is prepared by adding a salt solution (containing 234 g. of NaCl and 476 g. of KBr in 1400 cc. water) and a silver solution (containing 1360 g. of AgNO₃ in 2030 cc. water) simultaneously to a gelatin solution (containing 80 g. of gelatin, 1.16 g. of NaCl and 2000 cc. of water) at 70° C. The emulsion is cooled to 40° C. and a solution containing 560 g. of gelatin and 600 cc. of water is added. The emulsion is surface fogged with 2 mg. of thiourea dioxide and 1.2 g. of KI per mole of silver halide for 50 minutes at 65° C. and cooled to 40° C. The fogged emulsion is split into two portions and coated with and without Dye VI on a paper support at 125 mg. Ag/square

16

foot and 185 mg. gelatin per square foot. The coatings prepared from these two emulsion portions are exposed for 10 seconds in an intensity scale sensitometer to light of 3000° K. with and without a Wratten #47 filter, developed for 2 minutes in Kodak D-72 Developer at 68° F., fixed, washed and dried. As shown in the following table, the white light and blue sensitivity of the coating containing Dye VI are considerably higher than the coating containing no dye.

Run II

To one mole of the unfogged emulsion (as core or nuclei) obtained as in Run I (the salt solution and silver

solution (in the same halide ratio and precipitation conditions as in Run I) are added to build up the grain size approximately two times larger than the original emulsion. This emulsion is surface fogged with 2 mg. of thiourea dioxide, 1.2 g. of KI per mole of silver halide for 30 minutes. Two portions are coated with and without Dye VI on a paper support at 125 mg. of Ag per square foot and 185 mg. of gelatin per square foot.

Run III

The procedure of Run II is repeated except the core emulsion is precipitated in the presence of 1.63 mole percent KI.

The coatings prepared from the emulsions of Runs II and III are exposed for 1 second in a sensitometer to white light of 3000° K. and to blue light, developed for 10 seconds in Kodak D-72 Developer at 68° F., fixed, washed and dried with the results given in the following table.

Coating No.	Dye	Relative speed ¹	
		White light exposure	Blue light exposure
Run I:			
1.....	None.....	100	100
2.....	VI.....	1,260	1,590
Run II:			
1.....	None.....	100	100
2.....	VI.....	3,160	708
Run III:			
1.....	None.....	100	100
2.....	VI.....	1,447	1,260

¹ Relative speeds determined at a density of 0.4.

Silver halide emulsion made according to this invention can be used in photographic coatings intended for color photography; for example, emulsions containing color-forming couplers or emulsions to be developed by solutions containing couplers or other color generating materials. In addition, photographic emulsions made according to this invention can be used in diffusion transfer processes which utilize the non-developed silver halide in the exposed areas to form an image by dissolving the undeveloped silver halide and precipitating it on a receiving layer in close proximity to the original silver halide emulsion layer. Such processes are described in Rott U.S. Pat. 2,352,014, Land U.S. Pat. 2,543,181 and Yackel et al. U.S. Pat. 3,020,155. The silver halide emulsions described herein can also be used in color transfer processes which utilize the diffusion transfer of an imagewise distribution of developer, coupler or dye from a light-sensitive layer to

a second layer while the two layers are in close proximity to one another. Color transfer processes of this type are described in Yutzy U.S. Pat. 2,856,142, Land et al. U.S. Pat. 2,983,606, Whitmore et al. British Pats. 904,364 and 840,731 and Whitmore et al. U.S. Pat. 3,227,552. The silver halide emulsions of this invention can be processed in monobath processes such as described in Haist et al. U.S. Pat. 2,287,048 or in stabilization type processes.

Although the invention has been described in considerable detail with reference to certain preferred embodiments thereof, it will be understood that variations and modifications can be effected without departing from the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

I claim:

1. In a uniformly fogged direct-positive photographic silver halide emulsion which comprises silver halide grains comprising a central core of silver halide containing centers which promote deposition of photolytic silver and an outer shell covering said core comprising a fogged silver halide that develops the silver without light exposure, the improvement comprising adsorbed to said fogged grains a halogen-accepting merocyanine compound having an anodic polarographic halfwave potential less than 0.85 and a cathodic polarographic halfwave potential which is more negative than -1.0 .

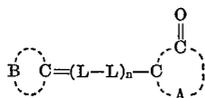
2. The photographic emulsion of claim 1 in which the halide in said silver halide grains comprises at least 50 mole percent chloride.

3. The photographic emulsion of claim 1 in which said fogged silver halide grains comprise a central core of silver halide having centers attributable to Group VIII metal ions, which centers promote deposition of photolytic silver.

4. The photographic emulsion of claim 1 in which said Group VIII metal ions are iridium ions.

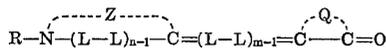
5. The photographic emulsion of claim 1 in which said adsorbed merocyanine dye is present in a concentration of about 100 mg. to about 1 g. per mole of silver.

6. The photographic emulsion of claim 1 in which said merocyanine compound has the formula:



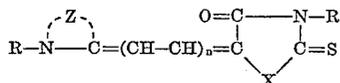
where A represents the atoms necessary to complete an acidic heterocyclic nucleus, B represents the atoms necessary to complete a basic nitrogen-containing heterocyclic nucleus, each L represents a methine linkage and n is an integer of from 0 to 2.

7. The photographic emulsion of claim 1 in which said merocyanine compound has the formula:



where R is an alkyl or aryl group, each L is a methine linkage, n is an integer of from 1 to 2, m is an integer of from 1 to 3, 2 represents the non-metallic atoms necessary to complete a heterocyclic nucleus containing from 5 to 6 atoms in the heterocyclic ring and Q represents the non-metallic atoms necessary to complete a heterocyclic nucleus containing 5 atoms in the heterocyclic ring.

8. The photographic emulsion of claim 1 in which said merocyanine dye has the formula:



where each R is an alkyl or aryl group, n is an integer of from 1 to 2, Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus containing from 5 to 6 atoms in the heterocyclic ring and X is an oxygen atom,

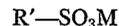
a sulfur atom, a selenium atom or a group of the formula ---NR_1 where R_1 is an alkyl or aryl group.

9. The photographic emulsion of claim 7 in which Q represents the atoms necessary to complete a rhodanine nucleus.

10. The photographic emulsion of claim 7 in which Q represents the atoms necessary to complete a 2-thiohydantoin nucleus.

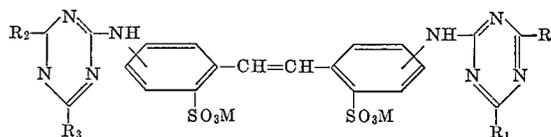
11. The photographic emulsion of claim 1 in which said outer shell of silver halide is chemically fogged.

12. The photographic emulsion of claim 1 comprising, in combination with said halogen-accepting merocyanine compound, a sulfonated compound having the formula:



where R' represents a polynuclear group and M represents a cation.

13. The photographic emulsion of claim 1 comprising, in combination with said halogen-accepting merocyanine compound, a sulfonated compound having the formula:



where M represents a cation, and each of R, R_1 , R_2 and R_3 represents a hydrogen atom, a hydroxyl group, an aryl-oxy group, an alkoxy group, a halogen atom, a heterocyclic radical, an alkylthio group, an arylthio group, a heterocyclithio group, an amino group, an alkylamino group or an acylamino group.

14. The photographic emulsion of claim 1 in which said halogen-accepting merocyanine compound is 3-carboxymethyl - 5 - [(3 - methyl - 2-thiazolidinylidene)-1-methylethylidene]rhodanine.

15. The photographic emulsion of claim 1 in which said halogen-accepting merocyanine compound is 1-carboxymethyl - 5 - [(3-ethyl-2-benzoxazolinyldene)-ethylidene]-3-phenyl-2-thiohydantoin.

16. A photographic element comprising a support and a layer of said uniformly fogged direct-positive photographic silver halide emulsion of claim 1.

17. In a uniformly fogged direct-positive photographic silver halide emulsion which comprises silver halide grains comprising a central core of silver halide containing centers which promote deposition of photolytic silver and an outer shell covering said core comprising a fogged silver halide that develops the silver without light exposure, the improvement comprising adsorbed to said fogged grains a halogen-accepting merocyanine compound which increases the blue-light sensitivity of said emulsion and has an anodic polarographic halfwave potential less than 0.85 and a cathodic polarographic halfwave potential which is more negative than -1.0 .

18. A photographic element comprising a support and a layer of said uniformly fogged direct-positive photographic silver halide emulsion of claim 17.

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U.S. Cl. X.R.

96—102

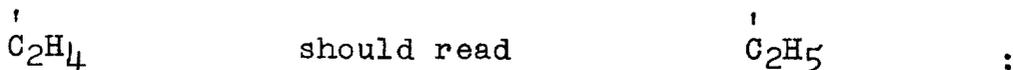
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,537,858 Dated November 3, 1970

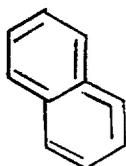
Inventor(s) Albert W. Wise

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

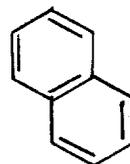
Column 2, line 27, "characteristics" should read ---charac-
teristic---. Column 6, line 8, "prefereably" should read ---
preferably---; line 43, that part of formula reading "-(3-ethyl-
benzothiazolinyldene)-" should read --- -(3-ethyl-2-benzothi-
azolinyldene)- ---; line 46, that part of formula reading
"-(CH₃)" should read --- -(CH₃)₂ ---; line 68, that part of for-
mula reading "-thiazolidinyldene)-" should read --- thiazoli-
dinyldene)- ---. Column 7, line 8, that part of formula read-
ing



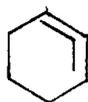
line 24, that part of formula reading "-4-(1H)-" should read ---
-4(1H)- ---; line 32, that part of formula reading "-C₂N₅"
should read --- -C₂H₅ ---; lines 49-55, that part of formula
reading



should read



Column 8, lines 14-17, that part of formula reading



should read



line 31, that part of formula reading "-sulfophenyl-2-" should
read --- -sulfophenyl)-2- ---; line 67, that part of formula
reading "1,2-di" should read --- 1,2-d ---. Column 9, line

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,537,858

Dated November 3, 1970

Inventor(s) Albert W. Wise

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

72, "of" should read ---or---. Column 10, line 16, "aryloxy" should read ---aryloxyl---; line 40, before the formula should be inserted ---III---; line 67, that part of formula reading "-triazine-" should read --- -triazin- ---; line 71, that part of formula reading "-triazine-" should read --- -triazin- ---. Column 11, line 9, that part of formula reading "-triazine-" should read --- -triazin- ---. Column 13, line 8, in the table heading, "365 μ " should read ---365 μ ---; under table heading Dmin., next to last line, ".07" should read ---.06---. Column 15, line 31, "illustarte" should read ---illustrate---. Column 16, line 7, after "blue" should be inserted ---light---; line 12, "Run I (the" should read ---Run I, the---. Column 17, line 8, "2,287,048" should read ---2,875,048---.

SIGNED AND

FILED

FEB 23 1971

SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

WILLIAM E. SCHUMER, JR.
Commissioner of Patents