United States Patent Office

3,189,458
Patented June 15, 1965

3,189,458

SENSITIZING PHOTOGRAPHIC SILVER HALIDE EMULSIONS WITH ELEMENTAL SULFUR AND AN ORGANIC THIOL

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No Drawing. Filed Nov. 6, 1961, Ser. No. 151,413
22 Claims. (Cl. 96—108)

This application concerns photographic emulsions containing a novel sensitizer combination utilizing elemental sulfur and the process of sensitizing therewith.

It is well known that photographic silver halide emulsions can be chemically sensitized with a variety of materials to increase the speed of the emulsions as opposed to optical sensitizing in which the optical range of sensitivity is increased. My invention concerns photographic silver halide emulsions with increased speed.

Various sulfur containing compounds, such as thiourea or allylthiourea have been utilized as chemical sensitizers in photographic silver halide emulsions. Such sensitizing is commonly referred to as "sulfur-sensitizing" although elemental sulfur is not the incorporated emulsion addenda since it is known that elemental sulfur per se causes severe desensitization in many photographic silver halide emulsions. Moreover, in some photographic silver halide emulsions undesirable levels of fog result on storage when elemental sulfur per se is present. Hence, while certain sulfur containing compounds have been utilized as photographic emulsion sensitizers, elemental sulfur has generally been avoided.

It is known that various inorganic and organic compounds can react with sulfur to form thio-derivatives. Examples of such sulfur-acceptors are cyanide, arsenite, sulfite, sulfinates as well as tri-valent phosphorous and arsenic compounds. It has been found the combinations of these sulfur-acceptors with sulfur in photographic emulsions does not produce useful speed increases without concomitant increases in incubation fog, toxicity or stain produced by the undesired solvent action.

It is an object of this invention to provide photographic emulsions containing novel, synergistic sensitizing combinations.

It is also an object of this invention to provide photographic emulsions containing novel sensitizer combinations utilizing elemental sulfur.

It is likewise an object of this invention to sensitize photographic emulsions with new synergistic sensitizer combinations without accompanying undesirable increases in fog, toxicity or stain.

These and other objects of the invention are accomplished by associating in a photographic silver halide emulsion a sensitizing amount of a sensitizer combination comprising elemental sulfur and an organic thiol. In photographic silver halide emulsions the subject sulfur and thiol combinations are synergistic combinations in that the sensitizing effect of such combinations is substantially greater than the additive sensitizing effect of the components of such combinations. Sensitizer precursors can also be used.

Sensitizing amounts of the subject sensitizer combinations are utilized, such amounts being widely varied.

The amount of sensitizer utilized is varied depending on the effects desired, the degree of ripening, the silver content of the emulsion, the particular stage at which the sensitizer is added during the preparation of the emulsion and related variables familiar to those skilled in the art. Generally we utilize at least .0001 g. of elemental sulfur or precursor thereof and at least .001 g. of organic thiol or precursor thereof per mole of silver halide in the emulsion. About .0005 to .01 g. of elemental sulfur, about .01 to 1 g. of organic thiol, about .01 to 10 g. of sulfur precursor, and about .01 to 10 g. of organic thiol precursor, per mole of silver halide in the emulsion are preferably utilized. An excess, on a molar basis, of organic thiol or precursor thereof over elemental sulfur or precursor thereof is generally utilized, however, the relative proportions of these sensitizer components can be broadly varied.

In the sensitizing process of the invention the sulfur sensitizer combination component can be added to photographic silver halide emulsions as elemental sulfur per se or as a sulfur-containing precursor thereof which forms elemental sulfur in the emulsion. Illustrative sulfur precursors are certain sulfur-containing compounds such as disclosed by A. J. Parker and N. Kharash in Chem. Rev., 59, 583 (1959), and by O. Foss in Acta Scand., 4, 404 (1950). A useful sulfur precursor is dithiodimorpholine.

In the sensitizing process of the invention the organic thiol sensitizer combination component can be added to photographic silver halide emulsions as an organic thiol per se such as aryl or alkyl thiols or as a precursor thereof that forms an organic thiol in the emulsion. The thiol precursors or donors of the invention are normally non-sensitizing sulfur-containing compounds and include thioethers and disulfides.

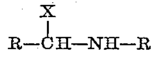
Typical thiols have the formulas Q—SH and

$$T(CH_2)_n\text{—}SH$$

wherein Q is an aryl radical and including carboxyl and alkyl radical substituents having 1 to 10 and preferably 1 to 4 carbon atoms, T is a hydrogen atom, a carboxyl, a hydroxyl, a sulfonate, a phenyl or an amino radical, and *n* is an integer of 1 to 10 and preferably 1 to 4.

Illustrative thiol precursors that can be utilized in the present sensitizing process are sulfur-containing derivatives having formulas

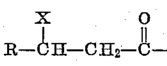
Formula A



$$R\text{—}\underset{}{\overset{X}{\overset{|}{C}}}H\text{—}NH\text{—}R$$

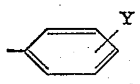
and

Formula B

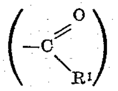


$$R\text{—}\overset{X}{\overset{|}{C}}H\text{—}CH_2\text{—}\overset{O}{\overset{\|}{C}}\text{—}R$$

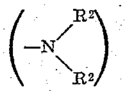
wherein R is an aryl radical, and wherein X is a thioether radical. The aryl radical for the substituent R is typically a phenyl radical or a substituted phenyl radical such as can be represented by the formula



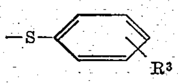
wherein Y is a hydrogen atom, a nitro radical, an alkoxy radical (—OR′), an acyl radical



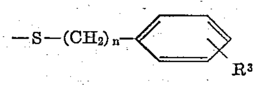
a tertiary amino radical



and others, with R^1 and R^2 being alkyl radicals having 1 to 20 and preferably 1 to 4 carbon atoms. The thioether radical for the substituent X can be represented by the formula —SZ wherein Z represents an organic radical such as an aryl radical, an aralkyl radical, a substituted alkyl radical, a heterocyclic radical or the like. Typical thioether radicals include such radicals as:



wherein R^3 is a carboxyl radical, an amino radical, or an alkyl radical generally having 1 to 20 and preferably 1 to 4 carbon atoms;

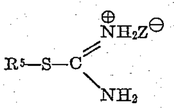


wherein *n* is an integer of 1 to 10 and preferably 1 to 4 and wherein R_3 is the same as described above;

$$—S—(R^4)—M$$

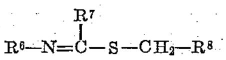
wherein R^4 is an alkylene radical having 1 to 20 and preferably 1 to 4 carbon atoms and M is an amido radical, a sulfonyl radical, a hydroxyl radical, an alkoxy radical, an amino radical, an ester radical, a corboxyl radical or a heterocyclic radical such as a morpholino radical; or a heterocyclic organic radical such as a phenyl tetrazine radical, a morpholino radical or the like. Illustrative alkyl radicals for the above substituents include methyl, ethyl, n-butyl, 2-ethylhexyl, n-decyl, n-dodecyl, stearyl, eicosyl etc. as well as analogous alkylene radicals for the alkylene substituents. The addenda having the structure of Formula A above are β-aminosulfides that can be readily prepared by reacting thiols and Schiff bases such as azamethines as described in Stacy et al., J.A.C.S., 77, 3869, 1955. The addenda having the structure of Formula B above are Michael adducts that can be readily prepared by reacting thiols and unsaturated compounds having an activating proton substituent as described in Tarbell and Harnish, Chem. Rev., 49, 23, 1951.

Other useful precursors for the subject thiol addenda are thiuronium compounds having the formula



wherein R^5 is an alkyl radical including substituted alkyl radicals and Z is a halogen atom, such as described by Knott et al. in U.S. Patent 2,461,987, issued February 15, 1949.

Suitable thiol precursors are formamidinothiomethyl compounds having the formula



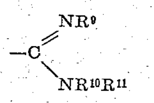
$$R^6—N=\overset{R^7}{\overset{|}{C}}—S—CH_2—R^8$$

wherein R^6 is a hydrogen atom, an alkyl radical (especially a lower alkyl radical having 1 to 4 carbon atoms), or an aryl group (especially monocyclic aryl radicals of the benzene series e.g. phenyl, tolyl etc.), R^7 is an amino radical (e.g. amino, monoalkyl and dialkylamino especially with lower alkyl moieties having 1 to 4 carbon atoms, monoaryl- and diarylamino, heterocyclylamino such as 2-thiazylamino and triazylamino), and R^8 is a carbalkoxyl radical (especially a carbalkoxyl radical containing 2 to 5 carbon atoms), an alkyl radical (especially an alkyl radical containing 1 to 4 carbon atoms), a heterocyclyl radical (e.g. tetrazaindenyl and pyridyl) or an amido radical such as amido, thiazylamido, phenylamido and aminocarbonyl, such as described by Spath in U.S. Patent 2,899,306, issued August 11, 1959.

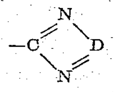
Knott et al. described in U.S. Patent 2,514,650, issued July 11, 1950, other useful thiol precursors that can be suitably utilized in the sensitizing process of the invention. Such compounds have the formula

$$B—S—A—S—B$$

wherein A is a divalent organic radical and B is a ureido radical, a substituted ureido radical or a nitrogen-containing heterocyclic radical having 5 or 6 atoms in the heterocyclic ring. For example, A can be a carbon chain such as alkylene generally having 1 to 10 and preferably 1 to 4 carbon atoms (e.g. methylene, ethylene, trimethylene etc.), substituted alkylene, methine, polymethine, or a radical comprising a carbocyclic component (e.g. ortho-, meta- or para-xylene). B can be a ureido radical having the formula

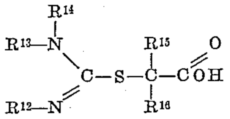


wherein R^9, R^{10} and R^{11} each can be hydrogen atoms, alkyl radicals, aralkyl radicals or a heterocyclic radical having the formula

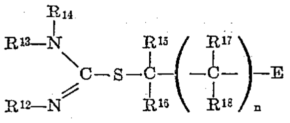


wherein D represents the non-metallic atoms necessary to complete a heterocyclic nucleus containing 5 or 6 atoms in the heterocyclic ring (e.g. iminazole, dihydroiminazole, benziminazole, pyrimidine, thiodiazine, thiodiazole etc.). I contemplate acid salts of such compounds as being included in my invention.

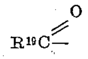
Particularly useful thiol precursors are isothiourea derivatives having the formulas



and

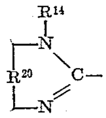


R^{12}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17} and R^{18} can be hydrogen atoms, hydrocarbon radicals such as aryl radicals as illustrated by phenyl radicals, alkyl-substituted phenyl and alkyl radicals and substituted alkyl radicals. R^{12} and R^{13} can also be acyl radicals having the formula

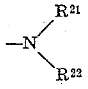


$R^{19}C(=O)-$

wherein R^{19} is an alkyl radical. R^{12} and R^{13} together can also be the necessary carbon and hydrogen atoms to form an alkylene radical linking both adjacent nitrogen atoms to form a cyclic nucleus as illustrated by the following moiety wherein R^{20} is an alkylene radical,

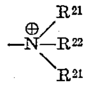


wherein R^{14} can be an acyl radical in addition to those substituents described above for R^{14}. The letter *n* can be an integer of at least 1, and generally 1 to 10, and preferably 1 to 3. The letter E can be a carboxyl radical, a sulfonate radical, a hydroxyl radical or an amino radical, including substituted amino radicals, of the formula



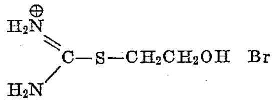
$-N(R^{21})R^{22}$

wherein R^{21} is a hydrogen atom or an alkyl radical, and wherein R^{22} is a hydrogen atom, an alkyl radical or an acyl radical, their salts having the formula

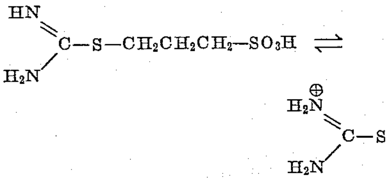


$-\overset{\oplus}{N}(R^{21})(R^{22})R^{21}$

or a morpholino radical, E being other than a carboxyl radical when *n* is 1 and R^{17} and R^{18} are hydrogen. Typical alkyl and alkylene radicals referred to above have 1 to 20 carbon atoms and more generally 1 to 4 carbon atoms. Illustrative alkyl radicals include methyl, ethyl, isopropyl, n-butyl, 2-ethylhexyl, n-decyl, stearyl, n-eicosyl and the like radicals. Alkylene radicals analogous to such alkyl radicals are suitable R^{20} substituents. Such isothiourea derivatives are bases but can be utilized as the salts of such acids as p-toluene sulfonic acid nitric acid, perchloric acid, hydrochloric acid, hydrobromic acid, etc., as illustrated by the salt,

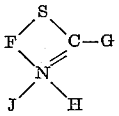


Such isothiourea derivatives of the invention also exist as inner salts as illustrated by the following equation,

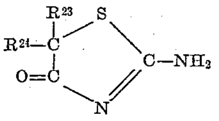


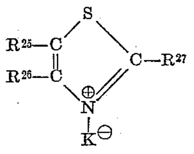
German Patent 1,031,303, published June 4, 1958, describes the preparation of typical isothiourea derivatives of the invention.

Brooker et al. in U.S. Patent 2,131,038, issued September 27, 1938, described thiazolines that can be suitably utilized as thiol precursors in the present process. Such thiazolines can be represented by the formula

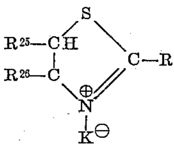


wherein F is an organic radical (e.g. vinylene, ethylene, phenylene and naphthylene), G is a hydrogen atom, an alkyl radical or a hydrocarbon radical of the benzene series, H is an acid radical and J is an alkyl radical. Typical suitable thiazoline derivatives have the formula

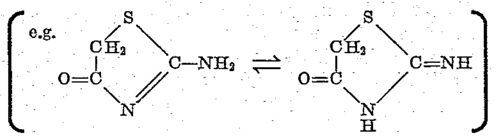




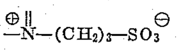
or



Certain of such derivatives have corresponding tautomeric forms, such tautomeric forms being included in our invention

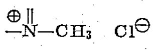


In the above formulas, R^{23}, R^{24}, R^{27} and R^{28} can be either hydrogen atoms or hydrocarbon radicals such as alkyl radicals or aryl radicals, typical suitable alkyl radicals having 1 to 20 carbon atoms and generally 1 to 8 carbon atoms such as methyl, n-propyl, 2-ethylhexyl, n-decyl, stearyl, n-eicosyl, etc., and typical suitable aryl radicals being phenyl and alkyl-substituted phenyl radical. In the above formulas, R^{25} and R^{26} can be hydrogen atoms, hydrocarbon radicals as described above for R^{23}, R^{24}, R^{27} and R^{28}, hydrocarbon radicals containing such substituents as hydroxyl radicals, or R^{25} and R^{26} together can be the necessary carbon and hydrogen atoms to form an aryl radical which includes the adjacent carbon atoms on the thiazoline nucleus. In the above formulas, K, in combination with the adjacent nitrogen atom on the thiazoline nucleus forms a covalent quaternary salt having no hydrogen atom attached to the nitrogen atom. The quaternary salt can include an electro-negative group such as sulfonate, carboxylic acid groups or the like to form an inner salt such as is illustrated by the quaternary salt group



$$\overset{\oplus\,\|}{-N}-(CH_2)_3-SO_3^{\ominus}$$

or alkyl quaternary salts including an anion or negatively charged ion such as a chloride ion, a perchlorate ion, a p-toluenesulfonate ion or the like such as illustrated by the quaternary salt group



$$\overset{\oplus\,\|}{-N}-CH_3\quad Cl^{\ominus}$$

Other useful thiol precursors useful in my process are disulfides such as 5-thioctic acid and di-o-formylalkylaminodiphenyldisulfides (e.g. di-o-formylethylaminodiphenyldisulfide).

The preparation of photographic silver halide emulsions such as are used with the addenda of the invention involves three separate operations: (1) emulsification and digestion of silver halide, (2) the freeing of the emulsion of excess water-soluble salts, suitably by washing with water, and (3) the second digestion or "after-ripening" to obtain increased emulsion speed or sensitivity. (Mees, "The Theory of the Photographic Process," 1954.) The addenda of the invention can added to the emulsion before the final digestion or after-ripening, or they can be added immediately prior to the coating.

The addenda of the invention can be added to photographic emulsions using any of the well-known techniques in emulsion making. For example, they can be dissolved in a suitable solvent and added to the silver halide emulsion, or they can be added to the emulsion in the form of a dispersion similar to the technique used to incorporate certain types of color-forming compounds (couplers) in a photographic emulsion. Techniques of this type are described in Jelley et al. U.S. Patent 2,322,027, issued June 15, 1943, and Fierke et al. U.S. Patent 2,801,171, issued July 30, 1957. The solvent should be selected so that it has no harmful effect upon the emulsion in accordance with usual practice, and generally solvents or diluents which are miscible with water are to be preferred. Water alone is a dispersing medium for some of the sensitizers of the invention. In other cases, the subject sensitizers can be dissolved in solvents, such as ethanol, acetone, pyridine, N,N-dimethylformamide, etc., and added to the emulsion in this form.

The emulsions of the invention can also contain chemical sensitizers other than those of the invention. The emulsions can be treated with salts of the noble metals such as ruthenium, rhodium, palladium, iridium and platinum. Representative compounds are ammonium chloropalladate, potassium chloroplatinate, and sodium chloropalladite, which are used for sensitizing in amonuts below that which produces any substantial for inhibition, as described in Smith and Trivelli U.S. Patent 2,448,060, issued August 31, 1948, and as antifoggants in higher amounts, as described in Trivelli and Smith U.S. Patents 2,566,245, issued August 28, 1951, and 2,566,263, issued August 28, 1951. The emulsions can also contain sensitizing amounts of gold salts as described in Waller et al. U.S. Patent 2,399,083, issued April 23, 1946, or stabilizing amounts of gold salts as described in Damschroder U.S. Patent 2,597,856, issued May 27, 1952, and Yutzy and Leermakers U.S. Patent 2,597,915, issued May 27, 1952. Suitable compounds are potassium chloroaurite, potassium aurithiocyanate, potassium chloroaurate, auric trichloride and 2-aurosulfobenzothiazole methochloride. The emulsions can be also contain sensitizing amounts of reducing agents such as stannous salts described in Carroll U.S. Patent 2,487,850, issued November 15, 1949, polyamines, such as diethylene triamine described in Lowe and Jones U.S. Patent 2,518,698, issued August 15, 1950, polyamines, such as spermine described Lowe and Allen U.S. Patent 2,521,925, issued September 12, 1950, or bis(β-aminoethyl)sulfide and its water-soluble salts described in Lowe and Jones U.S. Patent 2,521,926, issued September 12, 1950.

The emulsions can also be optically sensitized with cyanine and merocyanine dyes, such as those described in Brooker U.S. Patents 1,846,301, issued February 23, 1932; 1,846,302, issued February 23, 1932; and 1,942,854, issued January 9, 1934; White U.S. Patent 1,990,507, issued February 12, 1935; Brooker and White U.S. Patents 2,112,140, issued March 22, 1938; 2,165,338, issued July 11, 1939; 2,493,747, issued January 10, 1950; and 2,739,964, issued March 27, 1956; Brooker and Keyes U.S. Patent 2,493,748, issued January 10, 1950; Sprague U.S. Patents 2,503,776, issued April 11, 1950, and 2,519,001, issued August 15, 1950; Heseltine and Brooker U.S. Patent 2,666,761, issued January 19, 1954; Heseltine U.S. Patent 2,734,900, issued February 14, 1956; Van Lare U.S. Patent 2,739,149, issued March 20, 1956; and Kodak Limited British Patent 450,958, accepted July 15, 1936.

The emulsions of the invention can contain such stabilizing compounds as the mercury compounds of Allen, Byers, and Murray U.S. Patent 2,728,663, issued December 27, 1955; Carroll and Murray U.S. Patent 2,728,664, issued December 27, 1955; and Leubner and Murray U.S. Patent 2,728,665, issued December 27, 1955; the triazoles of Heimbach and Kelly U.S. Patent 2,444,608, issued July 6, 1948; the azaindenes of Heimbach and Kelly U.S. Patents 2,444,605 and 2,444,606, issued July 6, 1948; Heimbach U.S. Patents 2,444,607, issued July 6, 1948 and 2,450,397, issued September 28, 1948; Heimbach and Clark U.S. Patent 2,444,609, issued July 6, 1948; Allen and Reynolds U.S. Patents 2,713,541, issued July 19, 1955 and 2,743,181, issued April 24, 1956; Carroll and Beach U.S. Patent 2,716,062, issued August 23, 1955; Allen and Beilfuss U.S. Patent 2,735,769, issued February 21, 1956; Reynolds and Sagal U.S. Patent 2,756,147, issued July 24, 1956; Allen and Sagura U.S. Patent 2,772,164, issued November 27, 1956, and those disclosed by Birr in "Z. wiss. Phot.," vol. 47, 1952, pages 2–28; and the zinc and cadmium salts of Jones U.S. Patent 2,839,405, issued June 17, 1958.

The emulsions can contain a suitable gelatin plasticizer such as glycerin; a dihydroxy alkane such as 1,5-pentane diol as described in Milton and Murray U.S. Patent 2,960,-404, issued November 15, 1960; an ester of an ethylene bis-glycolic acid such as ethylene bis(methyl glycolate) as described in Milton U.S. Patent 2,904,434, issued September 15, 1959; bis(ethoxy diethylene glycol) succinate as described in Gray U.S. Patent 2,940,854, issued June 14, 1960, or a polymeric hydrosol as results from the emulsion polymerization of a mixture of an amide of an acid of the acrylic acid series, an acrylic acid ester and a styrene-type compound as described in Tong U.S. Patent 2,852,386, issued September 16, 1958. The plasticizer can be added to the emulsion before or after the addition of a sensitizing dye, if used.

The emulsion can be hardened with any suitable hardener for gelatin such as formaldehyde; a halogen-substituted aliphatic acid such as mucobromic acid as described in White U.S. Patent 2,080,019, issued May 11, 1937; a compound having a plurality of acid anhydride groups such as 7,8-diphenylbicyclo(2,2,2)-7-octene-2,3,5,6-tetracarboxylic dianhydride, or a dicarboxylic or a disulfonic acid chloride such as terephthaloyl chloride or naphthalene-1,5-disulfonyl chloride as described in Allen and Carroll U.S. Patents 2,725,294 and 2,725,295, both issued November 29, 1955; a cyclic 1,2-diketone such as cyclopentane-1,2-dione as described in Allen and Byers U.S. Patent 2,725,305, issued November 29, 1955; a bisester of methane-sulfonic acid such as 1,2-di-(methanesulfonoxy)ethane as described in Allen and Laakso U.S. Patent 2,726,162, issued December 6, 1955; 1,3-dihydroxymethylbenzimidazol-2-one as described in July, Knott and Pollak U.S. Patent 2,732,316, issued January 24, 1956; a dialdehyde or a sodium bisulfite derivative thereof, the aldehyde groups of which are separated by 2–3 carbon atoms, such as β-methylglutaraldehyde bis-sodium bisulfite; a bisaziridine carboxamide such as trimethylene bis (1-aziridine carboxamide) as described in Allen and Webster U.S. Patent 2,950,197, issued August 23, 1960; or 2,3-dihydroxy dioxane as described in Jeffreys U.S. Patent 2,870,013, issued January 20, 1959.

The emulsions can contain a coating aid such as saponin; a lauryl or oleoyl monoether of polyethylene glycol as described in Knox and Davis U.S. Patent 2,831,766, issued April 22, 1958; a salt of a sulfated and alkylated polyethylene glycol ether as described in Knox and Davis U.S. Patent 2,719,087, issued September 27, 1955; an acylated alkyl taurine such as the sodium salt of N-oleoyl-N-methyl taurine as described in Knox, Twardokus and Davis U.S. Patent 2,739,891, issued March 27, 1956; the reaction product of a dianhydride of tetracarboxybutane with an alcohol or an aliphatic amine containing from 8 to 18 carbon atoms which is treated with a base, for example, the sodium salt of the monoester of tetracarboxybutane as described in Knox, Stenberg and Wilson U.S. Patent 2,843,487, issued July 15, 1958; a water-soluble maleopimarate or a mixture of a water-soluble maleopimarate and a substituted glutamate salt as described in Knox and Fowler U.S. Patent 2,823,123, issued February 11, 1958; an alkali metal salt of a substituted amino acid such as disodium N-(carbo-p-tert.octylphenoxypentaethoxy)glutamate, or a sulfosuccinamate such as tetrasodium N-(1,2-dicarboxyethyl)-N-octadecyl sulfosuccinamate, or N-lauryl disodium sulfosuccinamate.

The addenda of the invention can be used in various kinds of photographic emulsions. In addition to being useful in orthochromatic, panchromatic, and infrared sensitive emulsions, they are also useful in X-ray and other non-optically sensitized emulsions. They can be added to the emulsion before or after any optical sensitizing dyes which may be used. Various silver salts can be used as the sensitive salt such as silver bromide, silver iodide, silver chloride, or mixed silver halides such as silver chlorobromide or silver bromoiodide. The subject addenda can be used in emulsions 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, emulsions of the mixed-packet type, such as described in Godowsky U.S. Patent 2,698,794, issued January 4, 1955, or emulsions of the mixed-grain type, such as described in Carroll and Hanson U.S. Patent 2,592,243, issued April 8, 1952. The subject addenda can also be used in emulsions which form latent images predominantly on the surface of the silver halide crystal or in emulsions which form latent images predominantly inside the silver halide crystal, such as those described in Davey and Knott U.S. Patent 2,592,250, issued April 8, 1952.

The subject addenda can also be used in emulsions intended for use in diffusion transfer processes which utilize the undeveloped silver halide in the non-image areas of the negative to form a positive 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. Patent 2,352,014, issued June 20, 1944, and Land U.S. Patents 2,584,029, issued January 29, 1952; 2,608,236, issued December 28, 1954, and 2,543,181, issued February 27, 1951. The addenda of the invention 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 processes of this type are described in Land U.S. Patents 2,559,643, issued July 10, 1951, and 2,698,798, issued January 4, 1955; Land and Rogers Belgian Patents 554,933 and 554,934, granted August 12, 1957; International Polaroid Belgian Patents 554,212, granted July 16, 1957, and 554,935, granted August 12, 1957; and Yutzy U.S. Patent 2,756,142, issued July 24, 1956.

In the preparation of the silver halide dispersions employed for preparing silver halide emulsions, there can be employed as the dispersing agent for the silver halide in its preparation, gelatin or some other colloidal material such as colloidal albumin, a cellulose derivative, or a synthetic resin, for instance, a polyvinyl compound, although gelatin is preferred. Some colloids which can be used as polyvinyl alcohol or a hydrolyzed polyvinyl acetate as described in Lowe U.S. Patent 2,286,215, issued June 16, 1942; a far hydrolyzed cellulose ester such as cellulose acetate hydrolyzed to an acetyl content of 19–26% as described in U.S. Patent 2,327,808 of Lowe and Clark, issued August 24, 1943; a water-soluble ethanolamine cellulose acetate as described in Yutzy U.S. Patent 2,322,085, issued June 15, 1943; a polyacrylamide having a combined acrylamide content of 30–60% and a specific viscosity of 0.25–1.5 on an imidized polyacrylamide of like acrylamide content and viscosity as described in Lowe, Minsk and Kenyon U.S. Patent 2,541,474, issued February 13, 1951; zein as described in Lowe U.S. Patent 2,563,791, issued August 7, 1951; a vinyl alcohol polymer containing urethane carboxylic acid groups of the type described in Unruh and Smith U.S. Patent 2,768,154, issued October 23, 1956; or containing cyano-acetyl groups such as the vinyl alcohol-vinyl cyanoacetate copolymer as described in Unruh, Smith and Priest U.S. Patent 2,808,331, issued October 1, 1957; or a polymeric material which results from polymerizing a protein or a saturated acylated protein with a monomer having a vinyl group as described in

Illingsworth, Dann and Gates U.S. Patent 2,852,382, issued September 19, 1958. If desired, compatible mixtures of two or more of these colloids can be employed for dispersing the silver halide in its preparation.

The above-described emulsions used in my process can be coated on a wide variety of supports in accordance with usual practice. Typical supports for photographic elements of the invention include cellulose nitrate film, cellulose acetate film, polyvinyl acetal film, polystyrene film, polyethyleneterephthalate film and related films of plastic or resinous materials, as well as glass, paper, wood, metals and others.

The invention is further illustrated by the following examples of preferred embodiments thereof.

EXAMPLE 1

The process of the invention was effected by incorporating synergistic combinations of the invention into a photographic gelatino-silver bromide emulsion, digesting the emulsion for 20 minutes at 52° C. immediately prior to coating, and then coating the emulsion on a cellulose acetate film support at a coverage of 355 mg. of silver and 840 mg. of gelatin per square foot. Elemental sulfur and the thiol precursor, N-methylbenzothiazolium methosulfate, was one synergistic combination, another being a combination of the sulfur precursor, dithiodimorpholine, and N-methylbenzothiazolium methosulfate. The elemental sulfur addenda was added to the emulsion in a solution of 50% acetone-50% ethanol. For purposes of comparison and to illustrate the synergism in the present instance, comparable coatings containing no sensitizing addenda and single components of the subject syergistic combinations were prepared. The prepared photographic elements were tested by exposing, both initially and after 4 weeks storage at 120° F. and 50% relative humidity, in the form of film strips in the usual manner in an Eastman Ib Sensitometer and thereafter by developing the exposed strips for 4 minutes at 68° F. in a photographic developer having the following formula:

	G.
N-methyl-p-aminophenol sulfate	2
Hydroquinone	8
Sodium sulfite (anhydrous)	90
Sodium carbonate monohydrate	52.5
Potassium bromide	5
Water to make 1 liter.	

The results of the sensitometric tests are summarized by the data set out in Table A below wherein the speed is relative speed and is expressed as a reciprocal relation of exposure at a density of 0.3 above fog. The concentrations of addenda in Table A are in terms of grams of addenda per mole of silver halide in the emulsion.

Table A

Addenda	Original test			4 weeks at 120° F., 50% R.H.		
	Rel. speed	Gamma	Fog	Rel. speed	Gamma	Fog
1) Control	20	.75	.06	135	.87	.06
2) 0.003 g. sulfur	16.2	1.2	.06	142	1.16	.14
3) 0.06 g. dithiodimorpholine	29	1.3	.05	235	1.28	.20
4) 0.15 g. N-methylbenzthiazolium methosulfate	35	1.09	.05	98	1.08	.04
5) 0.003 g. sulfur +0.15 g. N-methylbenzthiazolium methosulfate	142	1.3	.05	310	1.25	.12
6) 0.06 g. dithiodimorpholine +0.15 g. N-methylbenzthiazolium methosulfate	152	1.72	.06	282	1.29	.15

As can be observed from the data set out in Table A, when combinations of elemental sulfur or a sulfur precursor and a thiol precursor are added to photographic silver halide emulsions, a substantially increased speed is imparted to the emulsion.

EXAMPLE 2

A photographic gelatino-silver bromoiodide (6 mole percent iodide) emulsion containing various sensitizing addenda of the invention was prepared, coated and tested as described in Example 1. The resulting sensitometric data are summarized in Table B wherein the amount of addenda is set out in grams of addenda per mole of silver halide.

Table B

Addenda	Original test			4 weeks at 120° F., 50% R.H.		
	Rel. speed	Gamma	Fog	Rel. speed	Gamma	Fog
1) Control	~0.1	~.1	.04	1.1	.59	.05
2) 0.0015 g. sulfur	11	.73	.06	24	.67	.23
3) 0.06 g. dithiodimorpholine	13.8	.60	.10	22	.38	.05
4) 0.3 g. N-methylbenzothiazolium methosulfate	0.4	.29	.05	--------	.15	.05
5) 0.6 g. dithiodimorpholine +0.15 g. N-methylbenzothiazolium methosulfate	66	.56	.08	72	.48	.18
6) 0.0015 g. sulfur + 0.15 g. N-methylbenzothiazolium methosulfate	105	.53	.06	162	.51	.10

EXAMPLE 3

In accordance with the process of the invention, various sensitizer combinations of organic thiols or precursors thereof plus elemental sulfur were incorporated into a photographic gelatino-silver bromoiodide (6 mole percent iodide) emulsion, coated and exposed in an Eastman Ib Sensitometer and developed as described in Example 1. The resulting sensitometric data are summarized in Table C wherein the amount of addenda is set out in grams of addenda per mole of silver halide. The emulsions were digested for 20 minutes at 52° C. immediately prior to coating except the emulsions containing 5-thioctic acid and γ,γ'-dithiodibutyric acid which were digested for 30 minutes at 60° C.

Table C

Addenda	Relative speed	Gamma	Fog
1) Control	~1	------	------
2) 0.0015 g. sulfur	100	.51	.08
3) 0.0015 g. sulfur+0.09 g. N-methylthiosalicylamide	650	.57	.08
4) 0.0015 g. sulfur+0.09 g. sodium thioglycollate	158	.48	.08
5) 0.0015 g. sulfur+0.9 g. carboxymethyl isothiourea	283	.51	.08
6) 0.0015 g. sulfur+0.9 g. 1,2-ethane bis(isothiouronium bromide)	310	.50	.04
1) Control	~.5	------	------
2) 0.0015 g. sulfur	56	.65	.06
3) 0.0015 g. sulfur+0.09 g. bis(o-formylmethylaminophenyl) disulfide	270	6.7	.07
4) 0.0015g. sulfur+0.09g. bis(o-carboxyphenyl) disulfide	220	.56	.10
5) 0.0015 g. sulfur+0.09 g. bis(o-N-methylcarboxamidophenyl) disulfide	430	.51	.06
1) Control	~1.3	------	------
2) 0.0015 g. sulfur	135	.61	.36
3) 0.0015 g. sulfur+9 g. 5-thioctic acid	372	.58	.10
4) 0.0015 g. sulfur+9 g. γ,γ'-dithiodibutyric acid	540	.53	.08

Table C—Continued

When the various organic thiols or precursors thereof listed in Table C were incorporated in the emulsion in the absence of elemental sulfur, these compounds imparted none or negligible sensitizing or speed increasing properties to the emulsion.

EXAMPLE 4

Several additional organic thiols or their precursors were tested in a photographic gelatino-silver bromoiodide emulsion (6 mole percent iodide) as described in Example 1. The resulting sensitometric data are summarized in Tables D and E wherein the amount of addenda is expressed in terms of grams of addenda per mole of silver halide in the emulsion.

Table D

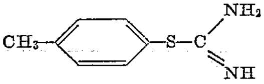
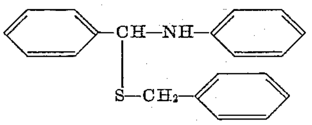
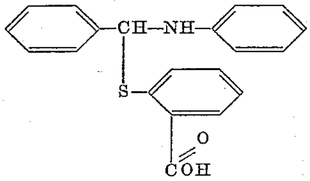
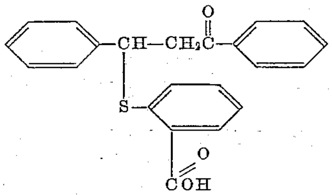
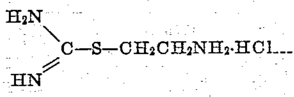
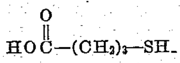
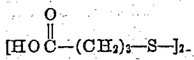
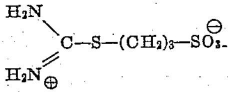
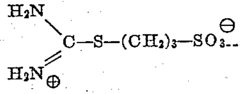
Addenda	Relative speed	Fog	
		Original	2 weeks at 120° F., 50% R.H.
1) Control	~1	------	------
2) 0.0015 g. sulfur	100	.14	.34
3) 0.0015 g. sulfur+0.03 g. p-tolylthiol	380	.14	.32
4) 0.0015 g. sulfur+0.09 g. p-tolylthiol	398	.07	.13
5) 0.0015 g. sulfur+0.9 g 	355	.10	.34
6) 0.0015 g. sulfur+0.09 g. benzylmercaptan	407	.08	.14
7) 0.0015 g. sulfur+9.0 g. benzylmercaptan	436	.06	.13
8) 0.0015 g. sulfur+0.15 g. 	436	.08	.16
9) 0.0015 g. sulfur+0.015 g. thiosalicylic acid	501	.10	.22
10) 0.0015 g. sulfur+0.09 g. 	302	.04	.08
11) 0.0015 g. sulfur+0.09 g. 	398	.04	.10
12) 0.0015 g. sulfur+0.09 g. 3-methylbenzothiazolium methosulfate	363	.18	.28
13) 0.0015 g. sulfur+0.3 g. 2,3-dimethlythiazolium perchlorate	795	.22	.36

Table E

Addenda	Relative speed	Fog	
		Original	2 weeks at 120° F., 50%R.H.
1) Control	~1	----------	----------
2) 0.0015 g. sulfur	100	.13	.33
3) 0.0015 g. sulfur+0.03 g. $HS-CH_2CH_2NH_2\cdot HCl$	589	.27	.40
4) 0.0015 g. sulfur+0.3 g. 	851	.12	.18
5) 0.0015 g. sulfur+0.09 g. $HS-CH_2CH_2OH$	436	.12	.14
6) 0.0015 g. sulfur+0.9 g. $(HO-CH_2CH_2-S-)_2$	355	.05	.10
7) 0.0015 g. sulfur+0.18 g.  $HO\overset{O}{\overset{\parallel}{C}}-(CH_2)_3-SH$	759	.12	.22
8) 0.0015 g. sulfur+3.0 g.  $[HO\overset{O}{\overset{\parallel}{C}}-(CH_2)_3-S-]_2$	447	.06	.13
9) 0.0015 g. sulfur+0.18 g. $HS-(CH_2)_3-SO_3^{\ominus}$ guanidine salt	646	.04	.06
10) 0.0015 g. sulfur+9.0 g. $[O_3\overset{\ominus}{S}-(CH_2)_3-S-]_2 2\overset{\oplus}{Na}$	537	.05	.17
11) 0.0015 g. sulfur +1.8 g. 	269	.08	.29
12) 0.0015 g. sulfur+5.4 g. 	562	.08	.24

When the various organic thiols or precursors thereof listed in Tables C and D were incorporated in the emulsion in the absence of elemental sulfur, these compounds imparted none or negligible sensitizing or speed increasing properties to the emulsion.

As can be observed from the data set out in the above tables, the preparation of photographic silver halide emulsions with the subject synergistic combinations of elemental sulfur and organic thiols or their precursors result in emulsions having substantially increased sensitivities. The data in the table also demonstrates that such increased sensitivities or speeds are not accompanied by undesirable fog levels that oftentimes accompany increased sensitization.

The invention has been described in considerable detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

I claim:

1. The process for sensitizing a photographic silver halide emulsion which comprises incorporating in said emulsion:

(A) At least .0001 gram per mole of silver halide in said emulsion of an addendum selected from the group consisting of
  (1) elemental sulfur, and
  (2) a sulfur-containing compound that forms elemental sulfur in said emulsion; and

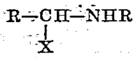
(B) At least .001 gram per mole of silver halide in said emulsion of a compound selected from the group consisting of
  (1) an organic thiol, and
  (2) a sulfur-containing compound that forms an organic thiol in said emulsion selected from the group consisting of
    (a) an organic thioether, and
    (b) an organic disulfide.

2. The process for sensitizing a photographic silver halide emulsion which comprises incorporating in said emulsion at least .0001 gram per mole of silver halide in said emulsion of elemental sulfur and at least .001 gram per mole of silver halide in said emulsion of an organic thiol having the formula R—SH wherein R is selected from the group consisting of an aryl radical and an alkyl radical.

3. The process for sensitizing a photographic silver halide emulsion which comprises incorporating into said emulsion at least .0001 gram per mole of silver halide in said emulsion of elemental sulfur and at least .001 gram per mole of silver halide in said emulsion of a sulfur-containing compound selected from the group consisting of an organic thioether and an organic disulfide, said sulfur-containing compound being capable of liberating an organic thiol in said emulsion.

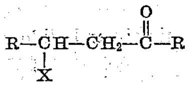
4. The process for sensitizing a photographic silver halide emulsion which comprises incorporating into said emulsion at least .0001 gram per mole of silver halide in said emulsion of elemental sulfur and at least .001 gram per mole of silver halide in said emulsion of a sulfur-con-

taining compound having a formula selected from the group consisting of



$R-\underset{\substack{| \\ X}}{CH}-NHR$

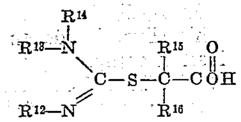
and



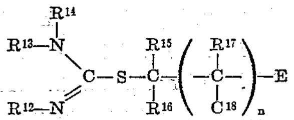
$R-\underset{\substack{| \\ X}}{CH}-CH_2-\overset{\substack{O \\ \|}}{C}-R$

wherein R is an aryl radical and X is a thioether radical.

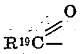
5. A process for sensitizing a photographic silver halide emulsion which comprises incorporating into said emulsion at least .0001 gram per mole of silver halide in said emulsion of elemental sulfur and at least .001 gram per mole of silver halide in said emulsion of a sulfur-containing compound having a formula selected from the group consisting of



and



wherein R^{14}, R^{15}, R^{16}, R^{17} and R^{18} are selected from the group consisting of a hydrogen atom and a hydrocarbon radical; R^{12} and R^{13} are selected from the group consisting of a hydrogen atom, a hydrocarbon radical, an acyl radical having the formula

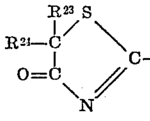


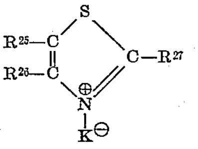
$R^{19}\overset{\substack{O \\ /\!/}}{C}-$

wherein R^{19} is an alkyl radical, and the necessary carbon and hydrogen atoms which together form an alkylene radical linking both adjacent nitrogen atoms to form a heterocyclic nucleus; *n* is an integer of at least 1; and E is a radical selected from the group consisting of an amino radical, a carboxyl radical, a sulfonyl radical and a hydroxyl radical; E being other than a carboxyl radical when *n* is 1 and R^{17} and R^{18} are hydrogen atoms.

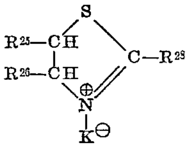
6. A process for sensitizing a photographic silver halide emulsion which comprises incorporating in said emulsion at least .0001 gram per mole of silver halide in said emulsion of elemental sulfur and at least .001 gram per mole of silver halide in said emulsion of a sulfur-containing compound capable of forming an organic thiol in said emulsion selected from the group consisting of a thiazole and a thiazoline.

7. A process for sensitizing a photographic silver halide emulsion which comprises incorporating in said emulsion at least .0001 gram per mole of silver halide in said emulsion of elemental sulfur and at least .001 gram per mole of silver halide in said emulsion of a sulfur-containing compound having a formula selected from the group consisting of





and



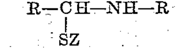
wherein R^{23}, R^{24}, R^{27} and R^{28} are selected from the group consisting of a hydrogen atom and a hydrocarbon radical; R^{25} and R^{26} are each selected from the group consisting of a hydrogen atom, a hydrocarbon radical, a hydrocarbon radical containing a hydroxyl group, and together the necessary carbon and hydrogen atoms to form an aryl radical; and K, in combination with the adjacent nitrogen atom, is a quaternary salt group.

8. A process for sensitizing a photographic silver halide emulsion which comprises incorporating into said emulsion at least .0001 gram per mole of silver halide in said emulsion of elemental sulfur and at least .001 gram per mole of silver halide in said emulsion of a sulfur-containing compound having the formula

$$B-S-A-S-B$$

wherein A is an alkylene radical and B is a ureido radical.

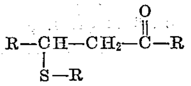
9. A process for sensitizing a photographic gelatino-silver halide emulsion which comprises incorporating in said emulsion at least .0001 gram per mole of silver halide in said emulsion of elemental sulfur and at least .001 gram per mole of silver halide in said emulsion of a sulfur-containing compound having the formula



$R-\underset{\substack{| \\ SZ}}{CH}-NH-R$

wherein R is an aryl radical and Z is selected from the group consisting of an aryl radical and an aralkyl radical.

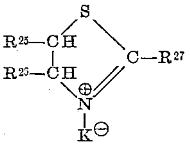
10. A process for sensitizing a photographic gelatino-silver halide emulsion which comprises incorporating into said emulsion at least .0001 gram per mole of silver halide in said emulsion of elemental sulfur and at least .001 gram per mole of silver halide in said emulsion of a sulfur-containing compound having the formula



$R-\underset{\substack{| \\ S-R}}{CH}-CH_2-\overset{\substack{O \\ \|}}{C}-R$

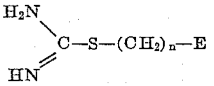
wherein R is an aryl radical.

11. A process for sensitizing a photographic gelatino-silver halide emulsion which comprises incorporating in said emulsion at least .0001 gram per mole of silver halide in said emulsion of elemental sulfur and at least .001 gram per mole of silver halide in said emulsion of a sulfur-containing compound having the formula



wherein R^{25} and R^{26} are selected from the group consisting of a hydrogen atom and together the necessary carbon and hydrogen atoms to form an aryl radical; R^{27} is an alkyl radical; and, K, in combination with the adjacent nitrogen atom, is a quaternary salt group.

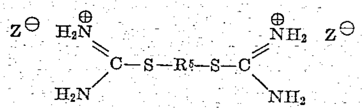
12. A process for sensitizing a gelatino-silver halide emulsion which comprises incorporating into said emulsion at least .0001 gram per mole of silver halide in said emulsion of elemental sulfur and at least .001 gram per mole of silver halide in said emulsion of a sulfur-containing compound having the formula



wherein *n* is an integer of 1 to 4 and E is selected from the group consisting of a carboxyl radical, a sulfonate radical and an amino radical, E being other than a carboxyl radical when *n* is 2.

13. A process for sensitizing a photographic gelatino-silver halide emulsion which comprises incorporating into said emulsion at least .0001 gram per mole of silver halide in said emulsion of elemental sulfur and at least .001

gram per mole of silver halide in said emulsion of a sulfur-containing compound having the formula



wherein R^5 is an alkylene radical having 1 to 4 carbon atoms and Z is a halogen atom.

14. The process for sensitizing a photographic gelatino-silver halide emulsion which comprises incorporating into said emulsion at least .0001 gram per mole of silver halide in said emulsion of elemental sulfur and at least .001 gram per mole of silver halide in said emulsion of N-methylbenzothiazolium methosulfate.

15. The process for sensitizing a photographic gelatino-silver halide emulsion which comprises incorporating into said emulsion at least .0001 gram per mole of silver halide in said emulsion of elemental sulfur and at least .001 gram per mole of silver halide in said emulsion of N-methylthiosalicylamide.

16. The process for sensitizing a photographic gelatino-silver halide emulsion which comprises incorporating into said emulsion at least .0001 gram per mole of silver halide in said emulsion of elemental sulfur and at least .001 gram per mole of silver halide in said emulsion of thiosalicylic acid.

17. The process for sensitizing a photographic gelatino-silver halide emulsion which comprises incorporating into said emulsion at least .0001 gram per mole of silver halide in said emulsion of elemental sulfur and at least .001 gram per mole of silver halide in said emulsion of 1,2-ethane bis(isothiouronium bromide).

18. The process for sensitizing a photographic gelatino-silver halide emulsion which comprises incorporating into said emulsion at least .0001 gram per mole of silver halide in said emulsion of elemental sulfur and at least .001 gram per mole of silver halide in said emulsion of benzylmercaptan.

19. The process for sensitizing photographic gelatino-silver halide emulsions which comprises incorporating into said emulsion at least .0001 gram per mole of silver halide in said emulsion of dithiodimorpholine and at least .001 gram per mole of silver halide in said emulsion of N-methylbenzothiazolium methosulfate.

20. A photographic silver halide emulsion containing a sensitizer combination comprising at least .0001 gram per mole of silver halide in said emulsion of elemental sulfur and at least .001 gram per mole of silver halide in said emulsion of an organic thiol.

21. A photographic silver halide emulsion containing a sensitizer combination comprising at least .0001 gram per mole of silver halide in said emulsion of elemental sulfur and at least .001 gram per mole of silver halide in said emulsion of an organic thiol having the formula R—SH wherein R is selected from the group consisting of an aryl radical and an alkyl radical.

22. A photographic silver halide emulsion containing a sensitizer combinaiton comprising at least .0001 gram per mole of silver halide in said emulsion of element sulfur and at least .001 gram per mole of silver halide in said emulsion of N-methylbenzothiazolium methosulfate.

References Cited by the Examiner

UNITED STATES PATENTS

1,898,512 2/33 Wendt ---------------- 96—108

OTHER REFERENCES

Steigmann: Journal Society Chemical Industry, vol. 64, pages 119–120 (1945).

Oba: Chemical Abstracts, vol. 46, page 2938 (1952).

NORMAN G. TORCHIN, *Primary Examiner.*

LOUISE P. QUAST, *Examiner.*

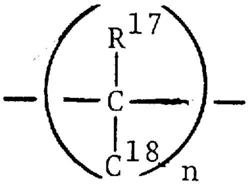
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,189,458 June 15, 1965

Arthur H. Herz

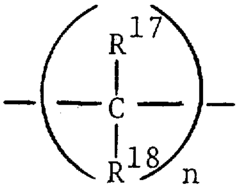
It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 17, lines 25 to 30, for that portion of the formula reading



$$-\left(-\overset{\overset{R^{17}}{|}}{\underset{\underset{C^{18}}{|}}{C}}-\right)_n-$$

read



$$-\left(-\overset{\overset{R^{17}}{|}}{\underset{\underset{R^{18}}{|}}{C}}-\right)_n-$$

column 20, line 22, for "combinaiton" read -- combination --; line 23, for "element" read -- elemental --.

Signed and sealed this 7th day of December 1965.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents