3,397,987
Patented Aug. 20, 1968

3,397,987

PHOTOGRAPHIC EMULSIONS CONTAINING MERCAPTO DEVELOPMENT ANTI-FOGGANTS

George W. Luckey and Bernard D. Illingsworth, Rochester, N.Y., assignors to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey

No Drawing. Filed May 24, 1965, Ser. No. 458,400
19 Claims. (Cl. 96—109)

ABSTRACT OF THE DISCLOSURE

Photographic silver halide emulsions comprising unfogged surface latent image grains and fogged internal image silver halide grains on which is adsorbed a heterocyclic nitrogen fog inhibiting compound and photographic elements comprising said emulsions are disclosed.

This invention relates to photographic materials and their preparation. In one of its aspects, this invention relates to photographic emulsions comprising fogged internal image silver halide grains and unfogged surface latent image grains, which emulsions exhibit good resistance to fog on development. In another of its aspects, this invention relates to a photographic element comprising an emulsion layer in which there are fogged internal latent image grains and unfogged surface latent image grains.

It is known that silver halide crystals of the type employed in photographic emulsions have both surface and internal sensitivity to light, and that these types of sensitivity may vary considerably among different emulsions. Silver halide grains having a high ratio of surface-to-internal sensitivity comprise the silver halide grains used in the majority of photographic emulsions.

Silver halide grains having a high ratio of internal-to-surface sensitivity are also well known but are less generally employed in practice. Emulsions containing such grains are described, for example, in Mees "The Theory of the Photographic Process," p. 221 (Revised edition), 1954; in "Journal of the Optical Society of America," 31 (1941), p. 382 and in Davey and Knott U.S. Patent 2,592,250, issued Apr. 8, 1952.

As described in U.S. Patents 2,996,382, issued Aug. 15, 1961 and 3,178,282, issued Apr. 13, 1965, the sensitivity and contrast characteristics of the combinations of various surface latent image emulsions with various internally fogged internal latent image emulsions are substantially greater than those obtainable from either type of emulsion used alone. However, such combination emulsions, particularly those sensitized to very high levels with onium salts and/or alkylene oxide polymers, tend to produce fog upon development. Attempts to reduce this fog have involved the use of antifogging agents which frequently have a mercapto function in their molecules. Many of these mercapto compounds are effective in reducing fog but they also result in diminished speed. It is evident, therefore, that it would be very desirable to reduce the fog exhibited by the aforementioned photographic silver halide emulsions by using mercapto compounds which do not significantly diminish photographic speed upon development.

Accordingly, it is an object of this invention to provide photographic materials which exhibit improved properties upon development.

Another object of this invention is to provide photographic silver halide emulsions which exhibit good sensitivity and contrast with very low fog.

Still another object of this invention is to provide photographic silver halide emulsions which are very highly sensitized with onium salts and/or alkylene oxide polymers, which emulsions still do not exhibit objectionable fog upon development.

Another object of this invention is to provide a means for reducing the fog exhibited by coatings of photographic silver halide emulsions comprising fogged internal latent image silver halide grains and unfogged surface latent image silver halide grains.

Still another object of this invention is to provide photographic elements embodying photographic emulsions of the type described.

Other objects of this invention will become apparent from an examination of the specification and claims that follow.

In accordance with this invention there is provided a method for inhibiting fog upon development of a photographic silver halide emulsion comprising fogged internal image silver halide grains and unfogged surface latent image silver halide grains using a heterocyclic nitrogen compound containing a mercapto function, as described herein.

A significant feature of this invention is that the heterocyclic compounds employed in the practice of this invention inhibit fog in the photographic silver halide emulsions upon development without substantially diminishing speed. In contrast, other mercepto compounds which do not contain a heterocyclic ring do not have the desired results with the photographic silver halide emulsions of U.S. Patents 2,996,382 and 3,178,282, as shown by Example 4, which follows. Furthermore, structurally closely related heterocyclic compounds which do not contain the required mercapto function cannot be used in the practice of this invention, as shown by Example 5.

Another feature of this invention is that the heterocyclic nitrogen compound employed in the practice of this invention is adsorbed to the fogged internal image silver halide grains. If the surface latent image silver halide grains are treated with the heterocyclic nitrogen compound there is a substantial loss in speed, as illustrated by Example 1 which follows.

The surface latent image emulsions used in the practice of this invention have a relatively high degree of surface sensitivity and relatively low internal sensitivity while the internal image emulsions used have a high degree of internal sensitivity but relatively low surface sensitivity. The surface latent image emulsions contain silver halide grains that have substantial surface sensitivity and form latent images when exposed to light on the surface thereof. Unlike the fogged silver halide internal latent image grains described herein, the surface latent image silver halide grains are substantially unfogged. Any of the photographic silver halides can be used in the preparation of the surface latent image emulsions and include, for example, silver bromide, silver bromoiodide, silver chloroiodide, silver chlorobromoiodide, silver chloride, silver chlorobromide and the like, the preferred halide being bromoiodide. For a description of suitable emulsions that form latent images on the surface of the silver halide grains, reference is made to Trivelli and Smith in "The Photographic Journal," volume LXXX, July 1940, (pages 285–288). Typically, such emulsions are those which, when measured according to normal photographic testing techniques by coating a test portion of the emulsion on a transparent support, exposing the test portion to a light intensity scale for a fixed time between 0.01 and 1 second and development for 6 minutes at 68° F. in Developer A as hereinafter defined, have a sensitivity, measured at a density of 0.1 above fog, greater than the sensitivity of an identical test portion of the same emulsions which has been exposed in the same way, bleached 5 minutes in aqueous 0.3% 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 and Developer B is an internal developer having high silver halide solvent activity.

The degree of internal sensitivity of the surface latent image emulsions is subject to wide variation. The surface latent image emulsions can have relatively little internal sensitivity or they can have a fair amount of internal sensitivity, but preferably not greater than the surface activity. The surface latent image emulsions can have high or low contrast since useful effects can be obtained with both types of emulsions. The surface latent image emulsions can also be characterized as having a $D_{max.}$ greater than about 0.50 when coated at a coverage of about 540 mg. silver per square foot, exposed to a step wedge and processed for 12 minutes in Developer C as hereinafter defined. Particularly good results are obtained with surface image silver iodo-halide surface latent image emulsions such as silver bromoiodide emulsions. Such emulsions can contain varying concentrations of iodide although especially useful results are obtained with such iodohalide surface latent image emulsions containing from about 0.5 to about 99 mole percent iodide.

The internal surface latent image photographic silver halide emulsions employed in the practice of this invention contain fogged internal latent image siliver grains. Any of the photographic silver halides can be used in the preparation of these internally fogged grains and include, for example, silver bromide, silver chlorobromoiodide, silver chlorobromide, silver chloride and the like. For a description of suitable emulsions that form latent images internal to the silver halide grains reference is made to Davey et al. U.S. Patent 2,592,250, issued Apr. 8, 1952, Luckey and Hoppe U.S. Patent 2,996,382, issued Aug. 15, 1961, and Luckey and Hoppe U.S. Patent 3,178,282, issued Apr. 13, 1965. Typically, such emulsions are those which, when measured according to normal photographic techniques in their unfogged state by coating a test portion of the emulsion on a transparent support, exposing to a light intensity scale having a fixed time between 0.1 and 1 second, bleaching 5 minutes in 0.3% potassium ferricyanide solution at 65° F. and developing for about 5 minutes at 65° F. in Developer B described hereinafter, have a sensitivity measured at a density of 0.1 above fog appreciably greater (for example, at least 1.4 log E greater) than the sensitivity of an identical test portion which has been exposed in the same way and developed for 6 minutes at 68° F. in Developer A described hereinafter. The internal image emulsions employed in the practice of this invention are fogged partly or completely before use. The fogging is generally sufficient to give a density of at least 0.05 when one mole (AgX) of the fogged emulsion is coated in a blend with 3 moles of surface image emulsion at a total coverage of about 540 mg. of silver per square foot and processed for 5 minutes in Developer B hereinafter described. The surface $D_{max.}$ of the unfogged internal image emulsions is generally less than about 0.30 when the emulsions are exposed to $D_{max.}$ and processed for 8 minutes in Developer C identified hereinafter.

The fogging of the internal image emulsions used in this invention can be effected using any method suitable for this purpose. For example, such fogging can be accomplished by exposing the emulsion to light. Other methods such as chemical fogging methods can also be used. The photographic silver halide emulsions having high internal fog but low surface sensitivity can also be prepared by fogging an emulsion having both internal and surface sensitivity and then bleaching the surface image with a solution of potassium ferricyanide. Another means of obtaining the fogged internal image emulsion is by exposure of non-fogged internal image emulsions to high energy radiation, such as X-rays.

The ratio of the surface latent image emulsion to the fogged internal image emulsion can be varied, depending upon the types of emulsions used, the contrast of the emulsions and other known variables. In general, quite useful results are obtained in those cases where the molar ratio of the surface image emulsion is at least equal to or greater than that of the fogged internal image emulsion. Useful results can be obtained even where the molar ratio, as explained above, is 42:1. Where the molar percent of the fogged internal image emulsion exceeds that of the surface image emulsion, such as a 1:3 ratio of surface to fogged internal image emulsion, there may be some loss of speed, although the contrast of the combination is considerably greater than that of the surface latent image emulsion. Accordingly, useful results can be obtained where the molar ratio of surface to fogged internal image emulsion varies from about 42:1 to 1:3.

The following developing solutions are referred to hereinabove.

A

	Grams
N-methyl-p-aminophenol sulfate	0.31
Sodium sulfite, desiccated	39.6
Hydroquinone	6
Sodium carbonate, desiccated	18.7
Potassium bromide	0.86
Citric acid	0.68
Potassium metabisulfite	1.5

Water to make 1 liter.

B

N-methyl-p-aminophenol sulfate	2.0
Sodium sulfite, desiccated	90
Hydroquinone	8.0
Sodium carbonate, monohydrate	52.5
Potassium bromide	5
Sodium thiosulfate	10

Water to make 1 liter.

C

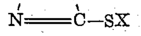
N-methyl-p-aminophenol sulfate	2.5
Sodium sulfite, desiccated	30
Hydroquinone	2.5
Sodium metaborate	10
Potassium bromide	0.5

Water to make 1 liter.

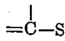
The photographic layers used in this invention can comprise blends or mixtures of surface image emulsions and fogged internal image emulsions, or these two types of emulsions can be coated in discrete layers which are in close proximity, i.e., in contiguous layers of the photographic element. In coating the two types of emulsions in separate layers, either emulsion can be coated on top, since the fogged internal image emulsions have sufficient transparency to enable the surface image emulsion to be placed closest to the support and still receive sufficient transmitted radiation through the fogged internal latent image emulsions for exposure. Exposure of the emulsion closest to the support can also be made through the support where this is transparent. However, for convenience of processing, the surface image emulsion is preferably coated over the fogged internal emulsion. Alternatively, the two types of emulsions can be mixed as a blend and coated over an emulsion layer comprising a fogged internal image emulsion, which may be identical to or different from the fogged internal image emulsion in the blend.

The development fog inhibitors employed in the practice of this invention are heterocyclic nitrogen compounds containing at least one mercapto function which is bonded to a carbon atom which is in the alpha position with respect to a nitrogen atom in a heterocyclic ring. The heterocyclic nucleus of such compounds contains one or more heterocyclic rings wherein the heterocyclic atoms (i.e., atoms other than carbon, including nitrogen, oxygen, sulfur, selenium and tellurium) are members of at least one heterocyclic ring. In the monoheterocyclic nitrogen compounds, the heterocyclic atoms are members of a single heterocyclic ring which can be fused or condensed to one or more rings which do not contain heterocyclic atoms. In contrast, diheterocyclic nitrogen compounds contain fused or condensed heterocyclic rings in which the heterocylic atoms are members of two heterocyclic rings. Suitable heterocyclic nitrogen compounds from which the heterocyclic nuclei can be derived include the azoles, oxazoles, selenazoles, triazoles (e.g., 1,2,4-triazoles, especially those containing an amino substituent in addition to the mercapto function), diazoles (e.g., imidazoles, benzimidazoles, imidazolines), pyrimidines, 1,2,4-triazines, s-triazines, monoazoles (e.g., benzoxazoles, benzothiazoles), azaindenes (e.g., tetrazaindenes) and the like.

Mercapto heterocyclic nitrogen compounds which can be employed in the practice of this invention can be represented by the formula:



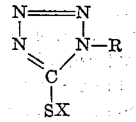
where Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus containing from 5 to 6, preferably 5, atoms in a heterocyclic ring and SX is a mercapto function. The mercapto function or group can be in the free (—SH) form or in the salt (—SX) form. X is a cation, for example, hydrogen, an alkali metal such as sodium or potassium, ammonium or an organic amine residue of such amines as triethyl amine, triethanol amine, morpholine and the like. In addition, many of the mercapto heterocyclic nitrogen compounds can be in the tautomeric form, for example, in the thione form, in which case the labile hydrogen atom in the mercapto function becomes bonded to the nitrogen atom and the



$$=\overset{|}{C}-SX$$

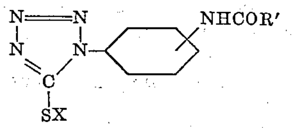
group becomes a thiocarbonyl ($>C=S$) group.

Any of the heterocyclic compounds which contain at least one nitrogen atom and a mercapto function, as described herein, will act as development fog inhibitors in the practice of this invention. However, particularly good results are obtained with the mercapto azoles, especially the 5-mercapto tetrazoles. 5-mercapto tetrazoles which can be employed in the practice of this invention include those having the formula:



where R is an aliphatic or aromatic radical containing up to 30 carbon atoms and SX is as defined hereinbefore. R can be hydrocarbon or non-hydrocarbon and includes alkyl or aryl radicals which can contain atoms or groups other than carbon and hydrogen. Suitable atoms or groups which can be present in R together with carbon and hydrogen include, for example, alkoxy, phenoxy, halogen, cyano, nitro, amino, substituted amino, sulfo, sulfamyl, substituted sulfamyl, sulfonylphenyl, sulfonylalkyl, fluosulfonyl, sulfonamidophenyl, sulfonamidoalkyl, carboxy, carboxylate, carbamyl, carbamylphenyl, carbamylalkyl, carbonylalkyl, carbonylphenyl and similar groups.

A very effective class of 5-mercapto tetrazoles which can be employed in the practice of this invention are the 1-phenyl-5-mercapto tetrazoles having the formula:



wherein R′ is a hydrocarbyl radical containing up to 22 carbon atoms and SX is as defined hereinbefore. Suitable R′ groups include, for example, alkyl, aryl, alkaryl, aralkyl or alkaralkyl radicals, the preferred R′ groups being alkyl radicals containing 1–8 carbon atoms. As shown in the formula, the —NHCOR′ group on the phenyl ring can be in the ortho, meta or para position. Such compounds can be prepared by the reaction of the 1-(aminophenyl)-5-mercaptotetrazole hydrochloride with an acid chloride having the formula R′COCl where R′ has the above indicated meaning. The 1-(aminophenyl)-5-mercaptotetrazole is prepared by reaction of an aminoacetanilide (ortho-, meta-, or para-), with thiophosgene to result in the formation of the corresponding acetamidophenyl isothiocyanate which is then reacted with an azide to form the mercaptotetrazole ring. This product is then hydrolyzed with concentrated hydrochloric acid to form the 1-(aminophenyl)-5-mercaptotetrazole hydrochloride. The formation of the mercaptotetrazole ring has been described by Stolle and Strittmatter in the Journal fuer Praktische Chemie, vol. 133, pages 60 to 64 and by Stolle and Fr. Henke-Stark in the same journal vol. 124, pages 261–300. An alternate method for the production of the 1-phenyl-5-mercaptotetrazole is to react an acetamidophenyl substituted thiosemicarbazide with nitrous acid as described by Freund and Hempel in Berichte der Deutschen Chemischen Gesellsdraft, vol. 28 at page 77.

Acid chlorides which can be employed in the reaction with the mercaptotetrazole hydrochloride include the chlorides of the following acids: acetic, aceto-acetic, difluoroacetic, propionic, valeric, iso-valeric, caproic, caprylic, undecanoic, stearic, benzoic, o-acetoxybenzoic, anthranilic, 3-amino-6-nitro-benzoic, p-tolyl acetic, 2,4-dinitrophenyl-acetic, methyl-sulfonic, o-toluene sulfonic, benzene sulfonic, p-bromobenzene sulfonic and o-formylbenzene sulfonic acid.

Some specific heterocyclic nitrogen compounds which can be employed in the practice of this invention are, for example,

2-mercapto-1-phenyl-tetrazole,
2-mercapto-5-phenyl-1,3,4-oxadiazole,
1-(3-caprimido)-phenyl-5-mercapto-tetrazole,
1-(3-pelargonamide)-phenyl-5-mercapto-tetrazole,
2,6-dimethyl-1,3,3a,7-tetrazaindene-4-thiol,
2-mercapto benzoxazole,
1-phenyl-5-mercapto-tetrazole,
5-ethyl-6-methyl-1,2,3a,7-tetrazaindene-4-thio,
2-mercapto imidazole,
4-methyl-1,2,3a,7-tetrazaindene-6-thio,
4-thiono-4a-azanaphthalene,
2-mercapto-β-naphthoxazole-2-thionothiazolidone,
4-mercapto-1-thia-3,5,7-triazaindene,
4-hydroxy-6-methyl-1,2,3a,7-tetrazaindene-3-thiol,
3-mercapto-1,2,4-triazole,
2-mercapto-5-(p-hydroxy-phenyl)-1,3,4-oxadiazole and
2-mercapto benzothiazole.

A number of such suitable mercapto heterocyclic nitrogen compounds are disclosed in Tregillus et al. U.S. Patent 3,017,270, issued Jan. 16, 1962.

As indicated hereinbefore, the antifoggants employed in the practice of this invention are adsorbed to the fogged internal latent image silver halide grains. This can be accomplished by adding the antifoggant to the internal latent image emulsion prior to coating the emulsion. The antifoggants can be added to the emulsion in aqueous solution or in any convenient solvent not injurious to the emulsion, such as lower aliphatic alcohols, acetone, and the like. The antifoggants are adsorbed to the fogged internal latent image silver halide grains and these grains can be blended with the surface latent image silver halide grains or coated in a separte layer. If, as preferred, the internal latent image emulsion and the surface latent image emulsions are coated in separate adjacent layers the antifoggants can simply be added to the internal image emulsion layer. The antifoggants cannot be added to blends of the internal image emulsions and surface image emulsions since this results in desensitization of the surface image emulsion. In general, the antifoggants are used in the fogged internal emulsion silver halide grains in concentrations of about 50 mg. to about 5 grams, preferably about 100 mg. to about 2 grams per mole of silver halide.

The surface image emulsions of our invention can be chemically sensitized by any of the accepted procedures. The emulsions can be digested with naturally active gelatin, or sulfur, selenium or tellurium compounds can be added such as those described in Sheppard U.S. Patent 1,574,944, issued Mar. 2, 1926, and Sheppard et al. U.S. Patent 1,623,499, issued Apr. 5, 1927 and Sheppard and Brigham U.S. Patent 2,410,689, issued Nov. 5, 1946.

The surface image emulsions can also 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 amounts below that which produces any substantial fog inhibition, as described in Smith and Trivelli U.S. Patent 2,448,060, issued Aug. 31, 1948, and as antifoggants in higher amounts, as described in Trivelli and Smith U.S. Patents 2,566,245, issued Aug. 28, 1951 and 2,566,263, issued Aug. 28, 1951.

The surface image emulsions can also be chemically sensitized with gold salts as described in Waller et al. U.S. Patent 2,399,083 issued Apr. 23, 1946, or stabilized with 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, aurite, potassium aurithiocyanate, potassium chloroaurate, auric trichloride and 2-aurosulfobenzo-thiazole methochloride.

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

As previously pointed out, the photographic silver halide emulsion employed in the practice of this invention can be very highly sensitized and still exhibit very low fog upon development. Thus, the surface latent image emulsion can also contain silver halide emulsion sensitizers other than those described above which will substantially increase the speed of the emulsion. Suitable examples of such sensitizers include the alkylene oxide polymer sensitizers. The alkylene oxides from which the polymers are derived contain from 2 to 4 carbon atoms, e.g., ethylene oxide, propylene oxide and butylene oxide. The preparation of polymers from these compounds is described in Ellis, The Chemistry of Synthetic Resins (1935), pages 990 to 994. These compounds are also referred to as polyalkylene glycols and their use as sensitizers for silver halide emulsions is described in U.S. Patents 2,423,549 and 2,441,389. Other alkylene oxide polymers which can be used to sensitize the photographic silver halide emulsions are prepared by condensing an organic compound containing an active hydrogen atom with an alkylene oxide polymer, or by condensing the active hydrogen compound with the alkylene oxide during the polymerization of the latter material.

Various other alkylene oxide polymers can be used to sensitize the emulsions, e.g., condensation products of alkylene oxide with organic compounds containing an active hydrogen atom. Examples of "active hydrogen organic compounds," i.e., compounds in which a hydrogen atom can be replaced by reaction of the compound with metallic sodium, methylmagnesium iodide, etc., include alcohols, amines, mercaptans, acids, amides, hydrocarbons such as acetylene, and compounds having the active hydrogen in a methylene group such as dibenzoylmethane. More specifically, we can employ condensation products of alkylene oxide with glycols such as those having from 8 to 18 carbon atoms as described in U.S. Patent 2,240,472 and British Patent 443,559 as well as condensation products of alkylene oxides with aliphatic alcohols, condensation products of alkylene oxides with aliphatic acids, e.g., lauric acid and glycine, condensation products of alkylene oxides with aliphatic amines or amides, e.g., glycine and lauryl amide, and condensation products of alkylene oxides with phenols, e.g., phenol. The preparation of these condensation products is described in U.S. Patent 1,970,578. Condensation products of alkylene oxides with hexitol ring dehydration products as described in U.S. Patent 2,400,532 can also be employed. Examples of other alkylene oxide polymers which can be used are described in U.S. Patents 2,674,619, 2,917,480, 2,886,437, 2,944,900 and British Patents 945,340, 947,790, 945,857, 949,643 and 949,644. In each case the polymeric sensitizer should have a molecular weight of at least 300, although the condensation products of ethylene oxide with long chain alcohols, acids, amines or amides generally have a molecular weight of about 700. In general, the very best results are obtained when the polymers are condensation products of ethylene oxide with long chain compounds having a chain length of 12 or more carbon atoms or ethylene oxide polymers and have a molecular weight of 1500 to 4000 or more. Such alkylene oxide polymer sensitizers are generally employed in concentrations in the range of about .05 to about 5 grams, preferably .1 to about 2 grams per mole of silver halide.

The surface latent image emulsions can also contain silver halide emulsion sensitizers containing at least one onium salt group. Such sensitizers generally contain one or more onium salt groups which are quaternary ammonium, quaternary phosphonium and/or ternary sulfonium salt groups. The polyonium salts contain an onium salt group, selected from the group consisting of quaternary ammonium, quaternary phosphonium and ternary sulfonium salt groups, linked through the onium atom by at least one bivalent organic radical to the onium group of another onium salt group selected from the group consisting of quaternary ammonium, quternary phosphonium and ternary sulfonium salt groups. Examples of suitable onium salts include sulfonium lauryl triethyl ammonium perchlorate, nonyl dimethyl sulfonium-p-toluene sulfonate, n-decyl triethyl phosphonium-p-toluene sulfonate, ethylene bis oxy methyl triethyl phosphonium chloride, ethylene bis oxy methyl-α-picolynium perchlorate, tetramethylene bis oxy methyl trimethyl phosphonium bromide, and the like. Suitable quaternary ammonium, quaternary phosphonium and ternary sulfonium salts are described in Carroll et al. U.S. Patents 2,271,622, 2,271,623, 2,275,727, 2,288,226, 2,944,900, British Patent 977,804 and Beavers et al. U.S. Patents 2,940,851, 2,940,855 and 2,944,898. These onium salt containing sensitizers are generally employed in the practice of this invention in concentrations in the range of about .1 to 5 grams per mole of silver halide.

The surface image emulsions can be spectrally sensitized, such as with cyanine or merocyanine dyes, if desired, and can contain antifoggants and stabilizers such as polyhydroxy benzenes, organic azoles, azaindenes, saccharides, metal salts such as cadmium, lead, mercury, gold or other noble metal salts.

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 example, a polyvinyl compound, although gelatin is preferred.

The photographic silver halide emulsion layers and other layers present in photographic elements made according to this invention can be hardened with any suitable hardener such as an aldehyde hardener, aziridine hardener, hardeners which are derivatives of dioxane, oxypolysaccharides such as oxystarch or oxy plant gums and other types of hardeners for gelatin and hydropholic colloids.

The photographic silver halide emulsions can contain the sensitizing dyes, antifoggants and other ingredients used in emulsions of this type, as described in Luckey and Hoppe U.S. Patents 2,996,382, issued Aug 15, 1961 and 3,178,282, issued Apr. 13, 1965, and can be used in the various color and black-and-white systems described in those U.S. Patents.

The photographic emulsions stabilized according to this invention can be coated on a wide variety of flexible supports. Typical supports include those generally employed for photographic elements, as exemplified by cellulose nitrate film, cellulose acetate film, polyvinyl acetal film, polystyrene film, polyethylene terephthalate film and related films of resinous materials as well as glass, paper, preferably paper coated with a polyolefin, e.g., polyethylene or ethylene butene copolymer.

Certain advantageous results are obtained when the developing compositions employed with the photographic silver halide layers contain certain additives. For example, use of a silver halide solvent in the development for the photographic silver halide emulsions of this invention generally results in a marked increase in speed, particularly in those cases where the silver iodide content of the surface image emulsion is low. Silver halide solvents which can be used in the developers comprise not only thiosulfate and sodium sulfite, but also water-soluble thiocyanates and water-soluble quaternary ammonium compounds, such as those illustrated in Welliver et al. U.S. Patent 2,648,604, issued Aug. 11, 1953. It has also been found that the addition of iodide ion to the developers can give unique effects. For example, potassium iodide can be added to developers of the type described herein to enhance their effects, particularly in processing surface image emulsions having a low iodide content.

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

The photographic silver halide emulsions of this invention, even when sensitized to very high levels, exhibit very low fog upon development. To illustrate, a fogged internal image gelatino silver chlorobromide emulsion, prepared as described in Example 4 of Luckey et al. U.S. Patent 2,996,382, issued Aug. 15, 1961, is mixed or blended with a high speed sulfur-gold sensitized gelatino bromoiodide emulsion having high surface sensitivity and low internal sensitivity. The sulfur and gold sensitized gelatino silver bromoiodide emulsion having high surface sensitivity and low internal sensitivity is of the type described in Example 1 of Luckey et al. U.S. Patent 2,996,382, issued Aug. 15, 1961.

The surface and internal sensitivities of these emulsions are essentially the same as those described in Example 1 of Luckey and Hoppe U.S. Patent 2,996,382, issued Aug. 15, 1961.

The surface image emulsion is coated on a conventional film support alone or in combination with the fogged internal image emulsion. An onium salt sensitizer and a mercapto azole are incorporated into certain of the coatings and omitted from others as shown in Table I which follows. The onium salt sensitizer employed is tetra-decamethylene-bis-(pyridinium perchlorate) and the mercapto azole is 1-(3-capramido)-phenyl-5-mercaptotetrazole, the latter being added to the fogged internal image emulsion in a methanol solution.

TABLE I

Coating No.:	
1	Surface sensitive silver bromoiodide emulsion (685 mg. Ag/ft.^{2}).
2	Surface sensitive silver bromoiodide emulsion (685 mg. Ag/ft.^{2}) coated over fogged internal image silver chlorobromide emulsion (175 mg. Ag/ft.^{2}).
3	Surface sensitive silver bromoiodide emulsion (685 mg. Ag/ft.^{2}) containing 1 g. of onium salt/mole silver.
4	Surface sensitive silver bromoiodide emulsion (685 mg. Ag/ft.^{2}) containing 4 g. onium salt/mole silver.
5	Surface sensitive silver bromoiodide emulsion (685 mg. Ag/ft.^{2}) containing 4 g. of onium salt/mole silver coated over fogged silver chlorobromide internal image emulsion (175 mg. Ag/ft.^{2}).
6	Surface sensitive silver bromoiodide emulsion (685 mg. Ag/ft.^{2}) containing 4 g. onium salt/mole silver coated over fogged silver chlorobromide internal image emulsion containing 0.5 g. of the mercapto azole/mole silver (175 mg. Ag/ft.^{2}).

The above coatings are exposed on an intensity scale sensitometer, developed at 20° C. in the following developer:

	Gram
1-phenyl-3-pyrazolidone	1
Hydroquinone	20
Sodium sulfite, desiccated	50
Sodium metaborate (8H_2O)	20
Potassium bromide	15
Sodium anthraquinone sulfonate	0.1

Water to 1 liter, pH=9.6.

After fixing, washing and drying, the following results are obtained:

TABLE II

Coating No.	Development Time, 20° C.	Net Fog	Relative Speed	Gamma
1	12′	0.12	180	1.2
	20′	0.16	220	1.2
2	9′	0.30	310	2.9
	15′	0.60	380	3.8
3	8′	0.16	225	1.1
	14′	0.32	230	1.1
4	6′	0.14	210	1.0
5	2′	0.32	112	0.5
6	5′	0.11	320	2.1
	6′	0.19	570	2.7

From the above table it can be seen that the heterocyclic compounds described herein are effective antifoggants for the photographic emulsions comprising fogged internal image silver halide grains and unfogged surface latent image silver halide grains.

Similar results are obtained when other heterocyclic nitrogen compounds containing a mercapto group are employed in the above procedure. For example, other compounds which give good results using the above procedure are 1-(3-pelargonamido)-phenyl-5-mercaptotetrazole, 2,6-dimethyl-1,3,3a,7-tetrazaindene-4-thiol, 2-mercapto benzoxazole, 1-phenyl-5-mercaptotetrazole, 2-mercaptoimidazole, 3-mercapto-1,2,4-triazole and 2-mercaptobenzothiazole.

The same advantageous results are also obtained when the tetra-decamethylene-bis-(pyridinium perchlorate) is replaced with other onium salts such as N,N′-ethylene di(oxymethyl pyridinium perchlorate), 1,10-decamethylene-bis-triethyl ammonium perchlorate, bis(lauryl methyl sulfonate-p-toluene sulfonate), N-decyl triethyl phosphonium-p-toluene, sulfonate, lauryl triethyl ammonium perchlorate, nonyl dimethyl sulfonium-p-toluene sulfonate and decyl pyridinium perchlorate.

As pointed out hereinbefore, the nitrogen compound is adsorbed to the fogged internal latent image silver halide grains and cannot be added to the surface latent image emulsion. To illustrate, the above procedure is repeated using a concentration of 4–16 mg. of the mercapto azole per mole of silver halide in the surface latent image emulsion. There is obtained a loss in sensitivity of up to 20%. Furthermore, when this procedure is repeated with a concentration of 0.5 gram of the mercapto azole/mole silver halide in the surface latent image emulsion there is a speed loss of 99%.

Example 2

A series of coatings is prepared as described in Example 1. The coatings are as follows:

TABLE III

Coating No:	
1	Surface sensitive gelatino-silver bromoiodide emulsion (685 mg. Ag/ft.^{2}) coated over a fogged internal image emulsion (75 mg. Ag/ft.^{2}).
2	Same as 1, except the fogged internal image emulsion contains 0.5 g. of 1-(3-capramido)-phenyl-5-mercaptotetrazole per mole of silver halide.
3	Same as 1, except the surface sensitive emulsion contains 1.0 g. of tetra-decamethylene-bis-(pyridinium perchlorate) per mole of silver halide.
4	Same as 1, except the surface sensitive emulsion contains 1.0 g. of tetra-decamethylene-bis(pyridinium perchlorate) per mole of silver halide and the fogged internal image emulsion contains 0.5 g. of 1-(3-capramido)-phenyl-5-mercaptotetrazole per mole of silver halide.

The coatings are exposed and processed as described in Example 1 to give the following results:

TABLE IV

Coating No.	Time of Development	Fog	Relative Speed	Gamma
1	6′	.12	153	1.82
	12′	.53	205	5.3
2	6′	.08	160	1.66
	12′	.21	460	2.30
3	6′	3.10	------	------
4	6′	.21	470	1.91

Example 3

As previously indicated, the photographic silver halide emulsions described herein can be sensitized with alkylene oxide polymers and still exhibit low fog upon development. To illustrate, the onium salt in Example 1 is replaced with the condensation product of oleyl alcohol with approximately 25 moles of ethylene oxide (polyethylene glycol oleyl ether). When processed as described in Example 1 the coatings containing the mercapto heterocyclic nitrogen compounds in combination with the alkylene oxide polymer sensitizer exhibit lower fog for a given speed than the corresponding coatings containing the alkylene oxide polymer sensitizers alone.

Similar improvements in fog are obtained using the above procedure when the mercapto heterocyclic nitrogen compounds are added to silver halide emulsions containing both the onium salt and an alkylene oxide polymer sensitizer. Furthermore, the onium salt and/or the alkylene oxide polymer sensitizer can be used in the developer rather than in the emulsion layer to give the desired results. In addition, the same advantageous results are obtained when other alkylene oxide polymer sensitizers are employed in the above procedure. Suitable alkylene oxide polymer sensitizers which can be used include the following polymers; the names of which are followed by a number indicating the average molecular weight of the polyethylene oxide chain:

Oleic ester polyethylene oxide 1000
Nonylphenol ether polyethylene oxide 1145
N-methylmyristylamino polyethylene oxide 1045
Oleyl ether polyethylene oxide 1500
N-methyl-n-dodecylamino polyethylene oxide 1145
Polyethylene oxide 1540
Polyethylene oxide 4000
Propylene oxide-ethylene oxide block copolymer 3000
Polyethoxyethyl-bis-sulfuric acid (M.W.=1500)
Polyethoxyethyl-bis-carboglutamic acid (Na salt) (M.W.=1600)

Alkylene oxide polymer sensitizers of this type are disclosed in Piper U.S. Patent 3,017,271, issued Jan. 16, 1962, Lundsted U.S. Patents 2,674,619, issued Apr. 6, 1954 and 3,022,335, issued Feb. 20, 1962.

Example 4

Mercapto compounds which do not contain at least one heterocyclic ring do not give the desired results when used with the photographic silver halide emulsions described herein. To illustrate, a series of coatings is prepared as described in Example 2 except that the following mercapto compounds are employed:

(1) Thio acetanilide
(2) Thio benzamide
(3) 2-mercapto adipic acid
(4) p-Mercapto benzoic acid
(5) 2(2-mercapto ethyl amino)ethanol

The coatings are exposed and processed as described in Example 1. In each case the coatings containing the mercapto compounds either show a loss in sensitivity of 25 to more than 100% or there is an increase in fog instead of a reduction as is the case when the mercapto heterocyclic nitrogen compounds are used.

Example 5

The heterocyclic nitrogen compounds used in this invention must contain at least one mercapto group. To illustrate, a series of coatings is prepared as described in Example 2 using the following heterocyclic compounds which do not contain a mercapto group:

(1) Benzotriazole
(2) 5-phenyl tetrazole
(3) 2-methyl benzothiazole
(4) 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene
(5) 5-amino-7-hydroxy-1,2,3,4,6-pentazaindene
(6) 2,5-dimethyl-7-hydroxy-1,4,7a-triazaindene

The coatings are exposed and processed as described in Example 1. The fog values obtained are 50 to over 200% greater at a given speed level than are the corresponding coatings containing the heterocyclic nitrogen compounds described herein.

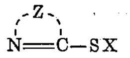
The emulsion blends or coatings described herein can be used in the same manner as those described in U.S. Patents 2,996,382 and 3,178,282 and they will exhibit improved resistance to fog upon development. Thus, these emulsion blends or coatings can be used for recording and measuring very small amounts or dosages of gamma rays, such as might be encountered in dealing with the development of synthetic radio-isotopes.

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.

We claim:

1. A photographic silver halide emulsion comprising fogged internal, latent image silver halide grains, un-

fogged surface latent image silver halide grains and, adsorbed to said fogged grains, a development fog inhibitor which is a heterocyclic nitrogen compound having the formula:



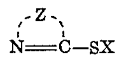
$$\overset{Z}{\overbrace{N{=}C}}{-}SX$$

where Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus containing from 5 to 6 atoms in a heterocyclic ring and SX is a mercapto function in which X is a cation.

2. The photographic silver halide emulsion of claim 1 in which the heterocyclic nitrogen compound is a mercapto azole.

3. A photographic silver halide emulsion comprising fogged internal latent image silver halide grains, unfogged surface latent image silver halide grains and, adsorbed to said fogged grains, a development fog inhibitor which is a 5-mercapto-tetrazole.

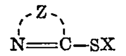
4. A photographic sulfur-sensitized silver halide emulsion comprising fogged internal latent image silver halide grains, unfogged surface latent image silver halide grains and, adsorbed to said fogged grains, a development fog inhibitor which is a heterocyclic nitrogen compound having the formula:



$$\overset{Z}{\overbrace{N{=}C}}{-}SX$$

wher Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus containing from 5 to 6 atoms in a heterocyclic ring and SX is a mercapto function in which X is a cation.

5. A photographic sulfur-sensitized silver halide emulsion additionally sensitized with a photographic silver halide emulsion sensitizer containing at least one onium salt group, said emulsion comprising fogged internal latent image silver halide grains, unfogged surface latent image silver halide grains and, adsorbed to said fogged grains, a development fog inhibitor which is a heterocyclic, nitrogen compound having the formula:

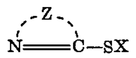


$$\overset{Z}{\overbrace{N{=}C}}{-}SX$$

where Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus containing from 5 to 6 atoms in a heterocyclic ring and SX is a mercapto function in which X is a cation.

6. A photographic sulfur-sensitized silver halide emulsion additionally sensitized with a photographic silver halide emulsion sensitizer containing at least one onium salt group, said emulsion comprising fogged internal latent image silver halide grains, unfogged surface latent image silver halide grains and, adsorbed to said fogged grains, a development fog inhibitor which is a 5-mercapto tetrazole.

7. A photographic sulfur-sensitized silver halide emulsion additionally sensitized with an alkylene oxide polymer sensitizer, said emulsion comprising fogged internal latent image silver halide grains, unfogged surface latent image silver halide grains and, adsorbed to said fogged grains, a development fog inhibitor which is a heterocyclic nitrogen compound having the formula:



$$\overset{Z}{\overbrace{N{=}C}}{-}SX$$

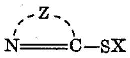
where Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus containing from 5 to 6 atoms in a heterocyclic ring and SX is a mercapto function in which X is a cation.

8. A photographic sulfur-sensitized silver halide emulsion additionally sensitized with an alkylene oxide polymer sensitizer, said emulsion comprising fogged internal latent image silver halide grains, unfogged surface latent image silver halide grains and, adsorbed to said fogged grains, a development fog inhibitor which is a 5-mercapto tetrazole.

9. A sulfur-sensitized photographic gelatino silver halide emulsion additionally sensitized with a photographic silver halide sensitizer containing at least one onium salt group, said emulsion comprising fogged internal latent image silver halide grains, unfogged surface latent image silver halide grains and, adsorbed to said fogged grains, a development fog inhibitor which is a 1-(3-capramido)-phenyl-5-mercapto-tetrazole.

10. A sulfur-sensitized photographic gelatino silver halide emulsion additionally sensitized with an alkylene oxide polymer sensitizer, said emulsion comprising fogged internal latent image silver halide grains, unfogged surface latent image silver halide grains and, adsorbed to said fogged grains, a development fog inhibitor which is a 1-(3-capramido)-phenyl-5-mercapto-tetrazole.

11. A photographic element comprising a support, fogged internal latent image silver halide grains, unfogged surface latent image silver halide grains and, adsorbed to said fogged grains, a development fog inhibitor which is a heterocyclic, nitrogen compound having the formula:

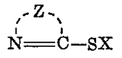


$$\overset{Z}{\overbrace{N{=}C}}{-}SX$$

where Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus containing from 5 to 6 atoms in a heterocyclic ring and SX is a mercapto function in which X is a cation.

12. A photographic element according to claim 11 in which the heterocyclic nitrogen compound is a mercapto azole.

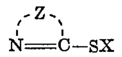
13. A photographic element comprising a support, a first discrete silver halide emulsion layer of fogged internal latent image silver halide grains and, in close proximity to said first discrete silver halide emulsion layer, a second discrete silver halide emulsion layer of unfogged surface latent image silver halide grains; adsorbed to said fogged grains, a development fog inhibitor which is a heterocyclic nitrogen compound having the formula:



$$\overset{Z}{\overbrace{N{=}C}}{-}SX$$

where Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus containing from 5 to 6 atoms in a heterocyclic ring and SX is a mercapto function in which X is a cation.

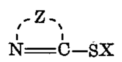
14. A photographic element comprising a support, a first discrete silver halide emulsion layer of fogged internal latent image silver halide grains and, in close proximity to said first discrete silver halide emulsion layer, a second discrete silver halide emulsion layer of unfogged surface latent image silver halide grains; adsorbed to said fogged grains, a development fog inhibitor which is a heterocyclic nitrogen compound having the formula:



$$\overset{Z}{\overbrace{N{=}C}}{-}SX$$

where Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus containing from 5 to 6 atoms in a heterocyclic ring and SX is a mercapto function in which X is a cation.

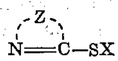
15. A photographic element comprising a support, a first discrete silver halide emulsion layer of fogged internal latent image silver halide grains and, in close proximity to said first discrete silver halide emulsion layer, a second discrete sulfur sensitized silver halide emulsion layer of unfogged surface latent image silver halide grains additionally sensitized with a photographic silver halide emulsion sensitizer containing at least one onium salt group; adsorbed to said fogged grains, a development fog inhibitor which is a heterocyclic nitrogen compound having the formula:



$$\overset{Z}{\overbrace{N{=}C}}{-}SX$$

where Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus containing from 5 to 6 atoms in a heterocyclic ring and SX is a mercapto function in which X is a cation.

16. A photographic element comprising a support, a first discrete silver halide emulsion layer of fogged internal latent image silver halide grains and, in close proximity to said first discrete silver halide emulsion layer, a second discrete sulfur-sensitized silver halide emulsion layer of unfogged surface latent image silver halide grains additionally sensitized with an alkylene oxide polymer sensitizer; adsorbed to said fogged grains, a development fog inhibitor which is a heterocyclic, nitrogen compound having the formula:



$$\overset{\overset{Z}{\frown}}{N{=\!=}C}-SX$$

where Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus containing from 5 to 6 atoms in a heterocyclic ring and SX is a mercapto function in which X is a cation.

17. A photographic element comprising a support, a sulfur-sensitized photographic silver halide emulsion additionally sensitized with a photographic silver halide emulsion sensitizer containing at least one onium salt group, said emulsion comprising fogged internal latent image silver halide grains, unfogged surface latent image silver halide grains and, adsorbed to said fogged grains, a development fog inhibitor which is a 5-mercapto tetrazole.

18. A photographic element comprising a support, a sulfur-sensitized photographic silver halide emulsion additionally sensitized with an alkylene oxide polymer sensitizer, said emulsion comprising fogged internal latent image silver halide grains, unfogged surface latent image silver halide grains and, adsorbed to said fogged grains, a development fog inhibitor which is a 5-mercapto tetrazole.

19. A photographic element comprising a support, a sulfur-sensitized photographic silver halide emulsion additionally sensitized with an alkylene oxide polymer sensitizer, said emulsion comprising fogged internal latent image silver halide grains, unfogged surface latent image silver halide grains and, adsorbed to said fogged grains, a development fog inhibitor which is a 1-phenyl-5-mercapto tetrazole.

No references cited.

NORMAN G. TORCHIN, *Primary Examiner.*

R. J. EVERETT, *Assistant Examiner.*