

[54] SILVER HALIDE EMULSION STABILIZED WITH ISOSELENOUREAS OR KETOSELENOZOLIDINES

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[73] Assignee: Eastman Kodak Company, Rochester, N.Y.

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[52] U.S. Cl. 96/100, 96/109

[51] Int. Cl. G03c 1/34

[58] Field of Search 96/109, 100, 110

[56] **References Cited**
UNITED STATES PATENTS

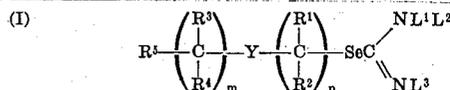
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|-----------|---------|--------------------|----------|
| 3,226,232 | 12/1965 | Dersch et al. | 96/109 X |
| 3,189,453 | 6/1965 | Herz et al. | 96/109 X |
| 3,220,839 | 11/1965 | Herz et al. | 96/109 X |
| 3,728,126 | 4/1973 | Pollet et al. | 96/109 |

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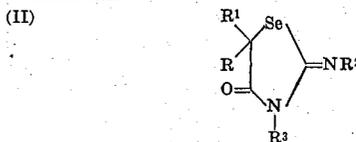
[57] **ABSTRACT**

Photographic silver halide emulsions and elements comprising said emulsions are stabilized against fog by selenium-containing organic compounds having the

formulae:



where each of R¹, R², R³, R⁴ and R⁵ is hydrogen or a hydrocarbon residue or an acid residue, or combined are not more than one selenourea derivative or its salts, a bisiselenourea compound and L¹, L² and L³ can be hydrogen or hydrocarbon groups which can be linked together to form a completed heterocyclic ring and m is an integer of from about 0 to about 4 and n is an integer of from about 0 to about 4 such that their combined total is a positive integer of not more than about 8; and —Y— is a divalent group; or



as a free base or its salts in which the groups R, R¹, R² and R³ are each hydrogen or hydrocarbon residues.

6 Claims, No Drawings

SILVER HALIDE EMULSION STABILIZED WITH ISOSELENOUREAS OR KETOSELENOZOLIDINES

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to the stabilization of photographic elements and compositions. More particularly it relates in one aspect to the stabilization of silver halide containing compositions against spontaneous fog. In another aspect, the invention relates to certain new and known organic selenium derivatives which are useful in stabilizing light sensitive silver halide emulsions and layers of photographic elements.

2. Description of the Prior Art

It is well known in the art that photosensitive silver halide emulsion and layers tend to lose their sensitivity and spontaneously develop without exposure to light. The detectable amount of silver salt reduced during development of those unexposed areas is commonly referred to as "fog" and more specifically, chemical fog.

While the degree of fog depends in part on the particular emulsion and conditions of development, fog usually increases with increases in time, temperature and relative humidity of storage conditions.

Various addenda have been employed in the past to increase the stability of the photosensitive silver halide-containing elements and compositions. Some such addenda reduce the tendency to fog but likewise exhibit the disadvantage of decreasing the sensitivity and/or the contrast of the silver halide-containing element and composition. This is especially true in those photographic preparations which are optically sensitized to the various spectral regions, such as those preparations adapted for use in color photography.

While it is known that certain organic sulfur and selenium derivatives might exhibit similar antifoggant and stabilizing properties, such selenium analogs of sulfur do not appear to be better than their corresponding sulfur compounds.

For example, while in U.S. Pat. No. 2,195,150 issued Mar. 26, 1940 to Kendall, there are described various selenamercapto-4-hydroxy pyrimidines as fog-stabilizers, the use of both mercapto-containing compounds and pyrimidines has been reported thereafter, such as in U.S. Pat. No. 2,819,965 and 2,935,404 issued Jan. 14, 1958 and May 3, 1960 respectively.

However, because of the peculiar nature of the antifogging and stabilizing compounds and their total effect on the silver halide-containing element, it is not believed that even those persons skilled in the art can predict the effectiveness of various compounds with any certainty or justification. Consequently, it is not surprising to learn from various references such as U.S. Pat. No. 3,284,206 issued Nov. 8, 1966 to Blake that certain silver salts of organic selenols are useful in greater than fog-inhibiting amounts as photosolubilizers due to their lower solubility in water than silver chloride.

British Patent 1,115,038 issued May 22, 1968 to McVeigh discloses the use of organic selenium compounds as a sensitizer for silver halide emulsions. Similarly in British 1,098,466 issued to Dunn Jan. 10, 1968, small amounts of organic selenium derivatives are used in conjunction with noble metal sensitizers in order to produce unexpected increases in sensitivity.

In Polaroid British Patent 1,080,228 issued Aug. 23, 1967, the prior art discussion refers to U.S. Pat. No. 2,131,038 of Brooker issued Sept. 27, 1938, wherein N-alkyl substituted azoles containing an oxygen, sulfur or selenium atom as a component of the azole ring are disclosed as photographic antifogging agents which, unfortunately, appear to desensitize the emulsions in which they are placed. The modification of the prior art compounds of U.S. Pat. No. 2,131,038 to their N-carboxyalkyl or N-sulfoalkyl analogs provided the unexpected properties of good emulsion stabilization against fog without desensitization. This reference further emphasizes the unpredictability of acceptable emulsion stabilization and antifogging properties of seemingly related compounds and particularly those containing the selenium atom.

While isothioureia derivatives have been disclosed as antifoggants in U.S. Pat. Nos. 3,189,453 issued June 15, 1965 to Herz et al. and 3,220,839 issued Nov. 30, 1965 to Herz et al. for the above reasons and as shown in the examples which follow, it is unobvious to expect corresponding selenium compounds to act in a similar manner.

Since many prior art antifoggants and emulsion stabilizers also provide unwanted desensitizing activity, the need still exists for such addenda which exhibit substantially only those fog restraining properties.

SUMMARY OF THE INVENTION

This invention relates to new photographic compositions and elements comprising light sensitive silver halide which is fog stabilized by an effective concentration of a selenium-containing organic compound. These compounds are generically described as, isoselenoureas and ketoselenozolidines.

It is an object of this invention to provide photographic silver halide-containing compositions and elements which are stabilized against fog. It is another object of this invention to stabilize emulsions and layers of silver halide without adversely affecting to any substantial degree, the photographic sensitivity of said silver halide.

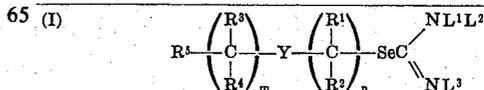
It is still another object of the present invention to provide new compounds which are useful in accomplishing these and other objects.

A further object of the invention is to provide stabilized silver halide containing compositions and elements comprising development modifiers by employing certain selenium containing organic compounds.

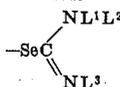
Still other objects will become apparent from an examination and reading of the specification and claims which follow.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with our invention, it has been found that certain selenium-containing organic compounds act as effective fog stabilizers and antifoggants for silver halide emulsions and layers, without causing significant reduction in their photographic sensitivity. These selenium-containing compounds have the general formula:

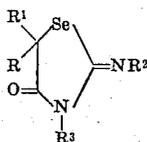


wherein m and n are each about 0 to 4 and together represent a positive integer generally less than about 8. Since these pseudoselenourea compounds are bases, their HX salts can be used where X is an organic anion, like p-toluene sulfonate or an inorganic anion like bromide and the like. Y is a divalent organic moiety such as ether (—O—), thioether (—S—), keto and the like and each R¹ to R⁵ group is hydrogen or a hydrocarbon like phenyl or lower alkyl, i.e., having one to six carbon atoms, or is an acid residue like carboxylic, sulfuric, sulfonic and the like or their corresponding anionic derivatives like sulfonates, or a selenourea group like



in order to complete a bisiselenourea compound, L¹, L² and L³ having the same meaning as below or its salts such as bromides and the like, and L¹, L² and L³ are each hydrogen or organic residue which can be linked together to complete a heterocyclic ring or

(II)



as a free base or its salts in which the R, R¹, R² and R³ groups are each hydrogen or organic residues such as hydrocarbon residues like alkyl groups and preferably lower alkyl such as having from one to six carbon atoms like methyl, ethyl, propyl, butyl and the like; and, since these selenazolidine-4-ones are bases, their HX salts can be used where X is an organic anion like para-toluenesulfonate and the like or an inorganic anion such as a chloride, bromide and the like.

Organic residues can be hydrocarbon and functionally substituted hydrocarbon groups like alkyl or substituted alkyl groups such as lower alkyl like those having one to six carbons including methyl, ethyl, butyl, isopropyl and the like while substituted groups are exemplified by haloalkyl, hydroxyalkyl and various aromatic alkyl groups. These include hydroxyethyl, chloroethyl and the like and phenylethyl, chloronaphthyl and substituted pyridyl and the like. Monocyclic or polycyclic nuclei are well known and include respectively phenyl, naphthyl and the like groups.

Typical of compounds which are defined by the formula (I) include for example: 3-(amidoseleno)-1-pro-

panesulfonic acid; 4-(amidoseleno)butyric acid; 2-(2-hydroxyethyl-2-selenopseudourea hydrochloride; 2-(1-methyl-3-sulfopropyl-2-selenopseudourea; 2-(amidoseleno)butyric acid hydrobromide; 2,2'-ethylene bis (2-selenopseudourea)dihydrobromide; 6-(amidoseleno)butyric acid hydrobromide; 6-(amidoseleno)hexanoic acid hydrobromide; 4-(N,N-dimethylamidoseleno)-1-butanefulfonic acid; 4-(N,N'-dimethylamidoseleno)-1-butanefulfonic acid; 4-(amidoseleno)-1-butanefulfonic acid; 2-(amidoseleno)valeric acid; 3-(2-imidazoline-2-ylseleno)-1-propanesulfonic acid; 2,2'-pentamethylene bis (2-selenopseudourea)dihydrobromide and 2,2'-ethylenedi(oryethyl)bis(2-selenopseudourea) dihydrobromide and the like.

Likewise representative examples of compounds included within the definition of structural formula (II) include: 2-iminoselenazolidine-4-one; 2-imino-5-methylselenazolidine-4-one and the like.

The stabilizing compounds defined by these structural formulae can be utilized in a variety of ways such as being incorporated directly into silver halide containing elements, such as in the silver halide layer, silver halide emulsions or in various layers contiguous thereto such as overcoat, intermediate and the like layers. In this manner it can be said that these selenium containing antifoggant compounds are incorporated into photographic elements and compositions in a concentration and manner sufficient to insure a fog-inhibiting effect. This relationship is likewise insured by use of said compounds in various solutions or sprays in which the finished or processed photographic material is so stabilized or in using various wrapping or storage materials or environments juxtaposed to the layers, emulsions or elements.

In another preferred embodiment the compounds within the scope defined by the above formulae are effective antifoggants and emulsion stabilizers when employed either in or contiguous to a photographic silver halide gelatin-containing emulsion layer. A preferred concentration of said compounds of Formula I is from about 0.005 to about 1.0 gram per mole of silver halide and that of Formula II is from about 0.01 to about 1.0 gram per mole of silver halide while for purposes of incorporating an alkali and/or heat releasable silver halide solvent for transfer or clearing use, the desired molar concentration of compounds of Formula I and II can be similar to that of the silver halide.

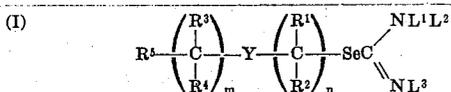
As shown in in the copending application Ser. No. 139,941, filed May 3, 1971 now U.S. Pat. No. 3,732,103, issued May 8, 1973 various sulfoalkyl selenols can serve as fixing agents or silver solvents in diffusion transfer processes. Their precursors, such as the selenopseudoureas of Formula I or 2-imino-selenozolidine-4-ones of Formula II do not prevent development of exposed areas of the emulsion but protect the unexposed areas of the emulsion against print out after development of the emulsion. Thus, with emulsions containing these compounds of this invention, silver images can be formed and stabilized without using the conventional fixing process. The subject addenda are generally stable and do not act as fixing agents in acidic or neutral media such as coated photographic emulsions but may hydrolyze to the corresponding selenol in alkaline processing solutions.

If, however, the developing solution is not sufficiently alkaline to activate the selenium containing derivatives

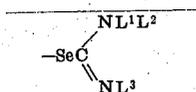
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of this invention, the photographic element having the developed emulsion coated thereon can subsequently be immersed in a stronger alkaline bath for fixing. Under such conditions a stable and generally soluble complex is formed with the silver halide in the unexposed and undeveloped areas of the emulsion. When the subject addenda are used as fixing agents in photographic silver halide emulsions, approximately one mole of addenda is utilized for each mole of silver halide in the emulsion.

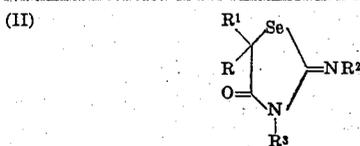
Still another preferred embodiment resides in photographic silver halide emulsions which further comprise color-coupler forming compounds such as those which are phenolic, pyrazolone and open-chain reactive methylene compounds which are capable of forming a dye with the oxidation product of an aromatic primary amine silver halide color developing agent. In yet another embodiment of the invention there is provided a photographic element comprising a support bearing a fog stabilized light sensitive silver halide-containing layer and comprising a silver halide solvent concentration of a selenium-containing organic compound having the structural formula:



where m and n are each about 0 to about 4 and together are a positive integer generally less than about 8; since these pseudoselenourea compounds are bases, their HX salts can be used where X is an organic anion like p-toluene sulfonate or an inorganic anion like bromide and the like. Y is a divalent organic moiety such as ether (—O—), thioether (—S—), keto and the like and each R¹ to R⁵ group is hydrogen or a hydrocarbon like phenyl or lower alkyl, i.e., having one to six carbon atoms, or is an acid residue like carboxylic, sulfuric, sulfonic and the like or their corresponding anionic derivatives like sulfonates, or a selenourea group like



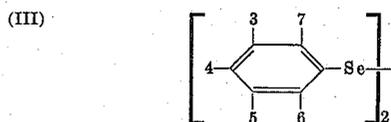
in order to complete a bisoselenourea compound, L¹, L² and L³ having the same meaning as below or its salts such as bromides and the like, and L¹, L² and L³ are each hydrogen or organic residue which can be linked together to complete a heterocyclic ring or



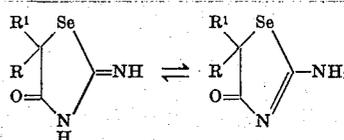
as a free base or its salts in which the R, R¹, R² and R³ groups are each hydrogen or organic residues such as alkyl groups, preferably lower alkyl such as having from one to six carbon atoms like methyl, ethyl, propyl,

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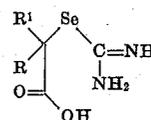
butyl and the like; and since the selenazolidine-4-ones are bases, their HX salts can be used where X is an organic anion like p-toluene sulfonate or an inorganic anion such as a halide like chloride, bromide and the like; or in which the phenyl group can be part of a condensed polycyclic or hetero aromatic nucleus, for example, naphthalene, quinoline; and the like or it can be substituted with other functional groups, for example, amine, amide, acylamino, carboxylate groups and the like.



Yet another embodiment comprising the compounds of Formula II which possess the unexpected antifoggant and emulsion stabilization properties described herein, can tautomerize as shown:



which upon hydrolysis become β -carboxyethyl isoselenourea of Formula I



Method of Preparation of Compounds Formulae I and II

The compound can be prepared by the following general procedures.

Compounds of formula (I) can be generally prepared as described in Knott et al U.S. Pat. No. 2,514,650 issued July 11, 1950, by using the corresponding selenourea derivatives. These compounds, especially those compounds containing a ureido group, are preferably employed as their salts, e.g., hydrohalide which are usually more stable than the bases and are water-soluble.

Compounds of formula (II) can be prepared in a manner analogous to that used to obtain the sulfur compounds in Herz et. al. U.S. Pat. No. 3,189,453 issued June 15, 1965.

Various novel processes are employed in the preparation of some of these aforescribed compounds. For example, 3-(amidinoseleno)-1-propanesulfonic acid is prepared from 39 g (0.25 mole) of 1-bromo-3-chloropropane and 25 g (0.20 mole) of sodium sulfite which are stirred and refluxed for 2 hours in 300 ml of a 1:1 mixture of ethyl alcohol and water. This mixture is concentrated to about 100 ml and 20 g (0.17 mole) of

selenourea is added. This mixture is stirred and refluxed for one-half hour, concentrated to 75 ml., then chilled. From a mushy, off-white cream, the final product is recrystallized from about 50 ml of water in a 16 g yield which has a melting point of 225° to 227°C.

The process for preparing the 6-(amidoseleno)hexanoic acid hydrobromide is also novel. In this method, 20 g (0.1 mole) of 6-bromohexanoic acid and 12 g (0.1 mole) of selenourea are dissolved in 125 ml of isopropyl alcohol, placed on a heating mantle and stirred and refluxed for about 4 hours, then filtered hot. The solvent is removed in vacuo and the remaining solid of 27 g crude weight is then recrystallized from 150 ml of acetic acid. The resulting white crystals are washed with acetone and dried to yield 19.8 g having a melting point of 170° to 171°C.

The silver halide emulsions used in the practice of this invention can be additionally protected against the production of fog and can be stabilized against loss of sensitivity during keeping. Suitable other antifoggants and stabilizers each used alone or in combination include thiazolium salts described in Brooker et al U.S. Pat. No. 2,131,038 issued Sept. 27, 1938, and Allen et al U.S. Pat. No. 2,694,716 issued Nov. 16, 1954; the azaindenes described in Piper U.S. Pat. No. 2,886,437 issued May 12, 1959; and Heimbach et al. U.S. Pat. No. 2,444,605 issued July 6, 1958; the mercury salts as described in Allen et al. U.S. Pat. No. 2,728,663 issued Dec. 27, 1955; the urazoles described in Anderson et al. U.S. Pat. No. 3,287,135 issued Nov. 22, 1966; the sulfocatechols described in Kennard et al. U.S. Pat. No. 3,236,652 issued Feb. 22, 1966; the oximes described in Carrol et al. British Patent 623,448 issued May 18, 1949; nitron; nitroindazoles; the mercaptotetrazaoles described in Kendall et al. U.S. Pat. No. 2,403,927 issued July 16, 1946; Kennard et al. U.S. Pat. No. 3,266,897 issued Aug. 16, 1966, and Luckey et al. U.S. Pat. No. 3,397,987 issued Aug. 20, 1968; the polyvalent metal salts described in Jones U.S. Pat. No. 2,839,405 issued June 17, 1958; the thiuronium salts described in Herz et al. U.S. Pat. No. 3,220,839 issued Nov. 30, 1965; the palladium, platinum and gold salts described in Trivelli et al. U.S. Pat. No. 2,566,263 issued Aug. 28, 1951, and Yutzy et al., U.S. Pat. No. 2,597,915 issued May 27, 1952.

In addition to the above unexpected uses of the various selenium containing organic compounds, we have found that the isoselenourea derivatives are alkali or heat releasable agents able to convert silver halides to the various alkyl, aryl or heteroaromatic residues (such as phenyl, benzothiazolyl and the like) of silver selenide.

In addition to the above-identified compounds, still other selenium-containing compounds are unexpectedly effective as emulsion stabilizers and antifoggants.

These compounds can be represented by the general structural formula:



in which R is ethyl, phenyl, naphthyl; R₁ is hydrogen, alkali metal or a substituted alkyl group ending in an acid radical. Typical compounds are:

- 2-carboxybenzoselenazole, potassium salt;
- 2-(3'-trichloro-2'-hydroxypropyl)benzoselenazole;
- 1-phenyl-5-selenyltetrazole potassium salt;

- 4,6-diamino-2-selenopyrimidine;
- 2-selenylbenzothiazole potassium salt;
- 7-selenyl-1,3,4,6-tetraazaindene;
- 4-selenyl-6-methyl-1,3,3a,7-tetraazaindene;
- 1-ethylnaphtho-[1,2-d]selenazoline-2-thione and the like.

In combination with the various selenium-containing silver halide antifoggants and stabilizers, various polyazaindenes can be used with good results. For example, tri- and tetraazaindenes such as 1,3,4 and 1,3,5-tri and 1,2,3,4- and 1,2,3,5-tetraazaindenes are effective antifoggants when incorporated in the silver halide layer, a layer adjacent thereto and in various solutions, such as processing solutions and the like, used to contact the silver halide and other layers. These polyazaindenes are conveniently prepared from their corresponding diaminopyridines by conventional methods. An effective concentration range is from about 0.95 g to about 4.0 g/mole of silver and preferably from about 0.75 g/mole to about 3.0 g/mole.

Based upon their incorporation into various processing solutions such as a hydroquinone type developer these polyazaindenes are effective in concentrations of from about 0.15 to about 0.75 grams/liter and preferably 0.25 to about 0.50 grams/liter of solution.

The silver halide emulsions used with this invention can comprise silver chloride, silver bromide, silver bromiodide, silver chlorobromiodide or mixtures thereof. The emulsions can be coarse or fine grain and can be prepared by any of the well-known procedures, e.g., single jet emulsions, double jet emulsions, such as Lippmann emulsions, ammoniacal emulsions, thiocyanate or thioether ripened emulsions such as those described in Nietz et al. U.S. Pat. No. 2,222,264 issued Nov. 19, 1940; Illingsworth U.S. Pat. No. 3,320,069 issued May 16, 1967; and McBride U.S. Pat. No. 3,271,157 issued Sept. 6, 1966. Surface image emulsions can be used or internal image emulsions such as those described in Davey et al U.S. Pat. No. 2,592,250 issued May 8, 1952; Porter et al. U.S. Pat. No. 3,206,313 issued Sept. 14, 1965; Berriman U.S. Pat. No. 3,367,778 issued Feb. 6, 1968; and Bacon et al. U.S. Pat. No. 3,447,927 issued June 3, 1969. If desired, mixtures of surface and internal image emulsions can be used as described in Luckey et al U.S. Pat. No. 2,996,382 issued Aug. 15, 1961. Negative type emulsions can be used or direct positive emulsions such as those described in Leermakers U.S. Pat. No. 2,184,013 issued Dec. 19, 1939; Kendall et al., U.S. Pat. No. 2,541,472 issued Feb. 13, 1951; Berriman U.S. Pat. No. 3,367,778 issued Feb. 6, 1968; Schouwenaars British Patent 723,019 issued Feb. 2, 1955; Illingsworth et al. French Patent 1,520,821 issued Mar. 4, 1968; Ives U.S. Pat. No. 2,563,785 issued Aug. 7, 1951; Knott et al., U.S. Pat. No. 2,456,953 issued Dec. 21, 1948, and Land U.S. Pat. No. 2,861,885 issued Nov. 25, 1958. The emulsions can be regular grain emulsions such as the type described in Klein and Moisar, *J. Phot. Sci.*, Vol. 12, No. 5, Sept./Oct., 1964, pp 242-251.

The emulsions used this invention can be sensitized with chemical sensitizers, such as with reducing agents; sulfur, selenium or tellurium compounds; gold, platinum or palladium compounds; or combinations of these. Suitable procedures are described in Sheppard et al. U.S. Pat. No. 1,623,499 issued Apr. 5, 1927; Waller et al. U.S. Pat. No. 2,399,083 issued Apr. 23, 1946; McVeigh U.S. Pat. No. 3,297,447 issued Jan. 10, 1967;

and Dunn U.S. Pat. No. 3,297,446 issued Jan. 10, 1967.

The photographic and other hardenable layers used in the practice of this invention can be hardened by various organic or inorganic hardeners, alone or in combination, such as the aldehydes, and blocked aldehydes, ketones, carboxylic and carbonic acid derivatives, sulfonate esters sulfonyl halides and vinyl sulfonyl ethers, active halogen compounds, epoxy compounds, aziridines, active olefins, isocyanates, carbodiimides, mixed function hardeners and polymeric hardeners such as oxidized polysaccharides like dialdehyde starch and oxyguar gum and the like.

The photographic emulsions and elements described in the practice of this invention can contain various colloids alone or in combination as vehicles, binding agents and various layers. Suitable hydrophilic materials include both naturally occurring substances such as proteins, for example, gelatine, gelatine derivatives, cellulose derivatives, polysaccharides such as dextran, gum arabic and the like; and synthetic polymeric substances such as water soluble polyvinyl compounds like poly(vinylpyrrolidone), acrylamide polymers and the like.

The described photographic emulsion layers and other layers of a photographic element employed in the practice of this invention can also contain alone or in combination with hydrophilic, water permeable colloids, other synthetic polymeric compounds such as dispersed vinyl compounds such as in latex form and particularly those which increase the dimensional stability of the photographic materials. Suitable synthetic polymers include those described, for example, in Nottorf U.S. Pat. No. 3,142,568 issued July 28, 1964; White U.S. Pat. No. 3,193,386 issued July 6, 1965; Houck et al. U.S. Pat. No. 3,062,674 issued Nov. 6, 1962; Houck et al U.S. Pat. No. 3,220,844 issued Nov. 30, 1965; Ream et al. U.S. Pat. No. 3,287,289 issued Nov. 22, 1966; and Dykstra U.S. Pat. No. 3,411,911 issued Nov. 19, 1968; particularly effective are those water-insoluble polymers of alkyl acrylates and methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates, those which have crosslinking sites which facilitate hardening or curing, those having recurring sulfobetaine units as described in Dykstra Canadian Patent 774,054.

The photographic layers and other layers of a photographic element employed and described herein can be coated on a wide variety of supports. Typical supports include cellulose nitrate film, cellulose ester film, poly(vinyl acetal) film, polystyrene film, poly(ethylene terephthalate) film, polycarbonate film and related

olefin polymer, particularly a polymer of an alpha-olefin containing two to 10 carbon atoms such as polyethylene, polypropylene, ethylenebutene copolymers and the like.

The photographic layers employed in the practice of this invention can contain plasticizers and lubricants such as polyalcohols, e.g., glycerin and diols of the type described in Milton et al, U.S. Pat. No. 2,960,404 issued Nov. 1, 1966; fatty acids or esters such as those described in Robijns U.S. Pat. No. 2,588,765 issued Apr. 11, 1952, and Duane U.S. Pat. No. 3,121,060 issued Feb. 11, 1964; and silicone resins such as those described in DuPont British Patent 955,061 issued Apr. 15, 1964.

The emulsions containing a compound obtained in accordance with this invention can be used in diffusion transfer processes which utilize the undeveloped silver halide in non-image areas of the negative to form a positive by dissolving the undeveloped silver halide and precipitating it on a silver layer in close proximity to the original silver halide emulsion layer. The emulsions can also be used in 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.

The following examples are intended for a further understanding and description of our invention.

EXAMPLE I

In order to demonstrate the unexpected fog reduction and emulsion stabilization imparted by various organic selenium compounds, a gold and sulfur sensitized silver bromiodide gelatin emulsion containing a carbocyanine spectral sensitizer, is adjusted to approximately pBr 3 and a pH of 6.6. This emulsion is then coated on a film support at 459 mg silver/ft² and 840 mg gelatin/ft². After the emulsion is dried down and exposed, the film is developed for 5 minutes in hydroquinone-methylated p-aminophenol. Speed is expressed relatively as a reciprocal of exposure on an Eastman 1B sensitometer and is measured at 0.3 density units above fog.

In order to demonstrate the effectiveness of the isoselenouronium derivatives of formula I as antifogants in accordance with the practice of the present invention, various such derivatives are added to portions of the same control emulsion described above and coated and processed in the same manner as described.

TABLE I

The same emulsion, coating and processing system disclosed above are employed in this example.

TABLE I

| Compound in g/mole Ag | Original Speed | 2 Wk. Storage 50% RH, 48°C | |
|--|----------------|-------------------------------|------|
| | | Fog | Fog |
| Control | 100 | .11 | 1.09 |
| 3-(amidinoseleno)-1-propanesulfonic acid | 3.0 g | 100 | .08 |
| 3-(amidinothio)-1-propanesulfonic acid | 3.0 g | 100 | .08 |

films or resinous materials, as well as glass, paper, metal and the like. Typically, a flexible support is employed, especially a paper support, which can be partially acetylated or coated with baryta and/or an alpha-

Table II

The same emulsion and coating are employed as in Example I and the processing system is as described herein.

TABLE II

| Compound in g/mole Ag | 12' Elon*-Hq at 20°C | |
|---|----------------------|---------|
| | Speed | Fog |
| Control | | 100 .19 |
| 5-(amidinothio) valeric acid | 0.15 g | 97 .18 |
| 5-(amidinothio) valeric acid | 0.45 g | 91 .16 |
| 4-(amidinoseleno) butyric acid | 0.18 g | 107 .15 |
| 4-(amidinoseleno)butyric Acid | 0.54 g | 102 .15 |
| Control plus polythioether development accelerator | | 129 .44 |
| 5-(amidinothio) valeric acid | 0.15 g | 129 .41 |
| 4-(amidinoseleno) butyric acid | 0.54 g | 129 .35 |

*Elon is a trademark of the Eastman Kodak Company for its methylated-para-aminophenol.

The same emulsion, coating and processing system as in Example I. Some coatings are also processed in a methylated-p-aminophenol hydroquinone developer for 12 minutes at 20°C.

It can be seen from the preceding table that the compounds of the invention (2-iminoselenazolidine-4-one and imino-5-methylselenazolidine-4-one) lower fog and stabilize photographic speed.

TABLE III

| Compound in g/mole Ag | Original | | 2 Wk. Storage 50% RH, 48°C | |
|--------------------------------------|----------|---------|-------------------------------|-----|
| | Speed | Fog | Speed | Fog |
| *Control | | 100 .10 | 58 .34 | |
| 6-(amidinoseleno)hexanoic acid HBr | 0.39 g | 110 .08 | 87 .18 | |
| *Control | | 100 .14 | 33 .85 | |
| 2-imino-5-methylselenazolidine-4-one | 0.03 g | 95 .12 | 39 .24 | |

*Two different comparative control coatings and the above addenda are employed in separate emulsion and developer batches to produce the above results.

EXAMPLE II

The following example illustrates the antifoggant properties of the compounds described by formula II.

An emulsion is prepared, coated and processed as described in Example I. To various samples of the emul-

Example III

In addition to employing the same emulsion coating and processing system as described in Example I, the following results are obtained by also processing in a hydroquinone-containing developer for 12 minutes at 20°C.

TABLE V

| Compound in g/mole Ag | Original | | 1 Wk. Storage 50% RH, 120°F | | 12' Elon-Hq | |
|---------------------------------|--------------------|-------------------|--------------------------------|-----|-------------------|-----|
| | Speed | Fog | Speed | Fog | Speed | Fog |
| Control | | 100 .15 | 59 .53 | | 100 .21 | |
| Control plus Benzene selenol | 0.003 g 0.015 g | 107 .13 97 .10 | 97 .29 100 .18 | | 107 .20 97 .16 | |

prior to coating are added the various compounds described in the following table.

EXAMPLE IV

The same emulsion coating and processing system as

TABLE IV

| Compound (g/Ag mole) | Fresh | | 2 Wk. | |
|------------------------------------|------------|---------|------------|-----|
| | Rel. Speed | Fog | Rel. Speed | Fog |
| * Control | | 100 .10 | 58 .34 | |
| 2-iminoselenazolidine-4-one | (0.39) | 110 .08 | 87 .18 | |
| * Control | | 100 .14 | 33 .85 | |
| Imino-5-methylselenazolidine-4-one | (0.03) | 95 .12 | 89 .24 | |

*Two different comparative control coatings and the above addenda are employed in separate emulsion and developer batches to produce the above results.

in Example I to obtain the following results wherein the 4,6-diamino-2-seleno-pyrimidine exhibits substantial antifogging activity on incubation of the emulsion.

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TABLE VI

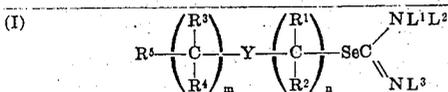
| Compound in g/mole Ag | | Original | | Storage at 50% RH, 48°C | | | |
|---|--------|----------|-----|-------------------------|-----|---------|-----|
| | | Speed | Fog | 1 Wk. | | 2 Weeks | |
| | | | | Speed | Fog | Speed | Fog |
| Control | | 100 | .14 | 78 | .27 | 33 | .85 |
| Control plus 4,6-diamino-2-seleno-pyrimidine | 0.06 g | 80 | .12 | 100 | .14 | 76 | .35 |

As will be understood from the foregoing, the isoselenouronium compounds, described by formula I include those compounds where the divalent linking organic radical can be alkylene, such as an alkylene chain having from one to 10 carbon atoms such as methylene, ethylene, trimethylene and the like and including in that chain, atoms such as ether oxygen atoms thioether, keto- and the like interrupting groups or a xylylene ring. The use of up to three oxygen atoms is preferred but more or less and even no oxygen atoms can be employed. The xylylene rings include those attached at ortho, meta or para positions and the rings can be substituted, e.g., by alkyl groups like lower alkyl of one to four carbons such as methyl xylylene groups and the like. These compounds can be also prepared by the methods used to prepare sulfur analogs described in Knott U.S. Pat. No. 254,650 issued July 11, 1950. The L¹, L² and L³ of formula I when linked together, form heterocyclic groups including diazo, 5- or 6-membered rings where they comprise non-metallic atoms needed to complete the heterocyclic nucleus.

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

There is claimed:

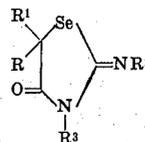
1. A photographic element comprising a support bearing a light sensitive silver halide-containing layer and, in a fog-stabilizing concentration from about 0.005 to about 1.0 g/mole silver halide, an organic compound having the structural formula:



where each R¹, R², R³, R⁴ and R⁵ is hydrogen, hydrocarbon or an acid residue selected from the group consisting of carboxylic, sulfuric and sulfonic residues and their corresponding anionic derivatives or a selenourea group or its salts and L¹, L² and L³ are each hydrogen or organic residue groups which can be linked together to form a completed heterocyclic ring and m is an integer of from about 0 to about 4 and n is an integer from about 0 to about 4 such that their combined total represent a positive integer of not more than about 8; and

—Y— is a divalent organic moiety selected from the group consisting of ether moieties, thioether moieties and keto moieties or

(II)



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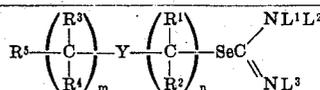
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as a free base or its salts in which each R, R¹, R² and R³ are each hydrogen or a hydrocarbon or functionally substituted hydrocarbon group.

2. The element of claim 1 in which said compound in fog-stabilizing concentration is present in the silver halide-containing layer.

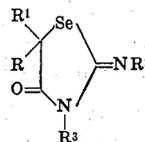
3. The element of claim 1 comprising the compound of formula I in which said formula corresponds to 3-(amidinoseleno-1-propanesulfonic acid or 4-(N,N-dimethyl-amidinoseleno)-1-butan-sulfonic acid.

4. A silver halide gelatin-containing photographic emulsion, stabilized against fog by the presence in a concentration range of from about 0.005 to about 1.0 g/mole of silver halide, of a compound having the formula:



where each of R¹, R², R³, R⁴ and R⁵ is hydrogen, a hydrocarbon or an acid residue selected from the group consisting of carboxylic, sulfuric and sulfonic residues and their corresponding derivatives or a selenourea group or its salts and L¹, L² and L³ can be hydrogen or organic residue groups which can be linked together to form a completed heterocyclic ring; m is an integer of about 0 to about 4; n is an integer of from about 0 to about 4 and the combined total of m and n is a positive integer of not more than about 8; and —Y— is a divalent organic moiety selected from the group consisting of ether moieties, thioether moieties and keto moieties or

(II)



as a free base or its salts in which R, R¹, R² and R³ are each hydrogen or a hydrocarbon or functionally substituted hydrocarbon group.

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5. The emulsion of claim 4 further comprising a coupler compound of a phenolic-, a pyrazolone- or open chain reactive methylene compound capable of forming a dye with the oxidation product of an aromatic pri-

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mary amine silver halide color-developing agent.

6. The emulsion of claim 4 further comprising development modifiers.

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