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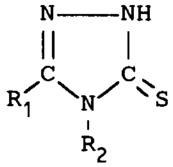
(54) Infrared sensitive silver halide phototographic elements.

(57) An infrared sensitive silver halide photographic element is disclosed comprising a support and at least one silver halide emulsion layer spectrally sensitized to the infrared portion of the electromagnetic spectrum. In particular, an infrared sensitive color photographic element, capable of providing full color images without exposure to corresponding visible radiation, is disclosed, said element comprising at least three silver halide emulsion layers on a substrate, each associated with different photographic color image forming materials, such as color couplers capable of forming dyes of different colors upon reaction with an oxidized color photographic developer, diffusing dyes, bleachable dyes, or oxidized leuco dyes. The three emulsion layers are sensitized to three different portions of the electromagnetic spectrum with at least two layers sensitized to different regions of the infrared region of the electromagnetic spectrum. The infrared sensitive element is characterized in that at least one infrared sensitized emulsion layer is associated with a 3-mercapto-1,2,4-triazole antifogging agent represented by the formula :



(I)

wherein R_1 and R_2 each independently represents hydrogen or an alkyl group, the sum of carbon atoms of R_1 and R_2 is 1 or 2, and at least one of R_1 and R_2 is a perfluoroalkyl group.

The infrared sensitive photographic element has high sensitivity to infrared radiation and undergoes less change in sensitivity during storage.

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(3.10/3.09/3.3.4)

FIELD OF THE INVENTION

This invention relates to silver halide photographic elements sensitive to infrared radiation. In particular, the present invention relates to color photographic elements having at least three silver halide emulsion layers associated with color image providing materials, each emulsion layer being sensitized to a different region of the electromagnetic spectrum and at least two emulsion layers being sensitized to radiation within the infrared region of the electromagnetic spectrum, wherein at least one infrared sensitized emulsion layer is associated with a mercaptotriazole antifogging agent.

BACKGROUND OF THE ART

It is well known that silver halide photographic elements can be spectrally sensitized to infrared radiation. See Mees and James, ***The Theory of Photographic Processes***, 3rd edition, The MacMillan Company, 1966, pages 198 and 199. Silver halides are intrinsically sensitive only to light in the blue region of the spectrum. Therefore, when silver halides are to be exposed to other wavelengths of radiation, such as green light, red light or infrared radiation, a spectral sensitizing dye is required to render silver halide sensitive to such radiation. As known in the art, silver halides having adsorbed on the grains spectral sensitizing dyes can be made sensitive to radiation of a wavelength other than the intrinsic blue sensitivity.

With the advent of lasers, and particularly solid state laser diodes emitting in the infrared region of the spectrum (e.g, 700 to 1500 nm), the interest in infrared sensitization has greatly increased. Many different processes and articles useful for exposure to laser diodes have been proposed. These include C.A.T. (Computer Assisted Tomography) scanners, graphic arts products and infrared sensitive false color-sensitized photographic elements as described in US 4,619,892. In this patent, photographic elements are described which are capable of providing full color images without exposure to corresponding visible radiation. This false address elements comprise at least three silver halide emulsions layers on a substrate, each associated with different photographic color image forming materials and sensitized to three different portions of the spectrum with at least two layers sensitized to different regions of the infrared region of the spectrum.

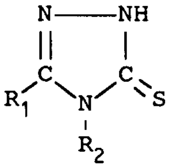
It is also known that the addition of specific organic compounds to a silver halide photographic material in addition to the spectrally sensitizing dyes can increase the spectrally sensitized speed of the emulsion by more than one order of magnitude. This is known as a supersensitizing effect. As organic compounds for supersensitization of infrared sensitive silver halide emulsions which are conventionally known, there are illustrated, for example, triazine derivatives disclosed in US Pat. Nos. 2,785,058 and 3,695,888, mercapto compounds described in US 3,457,078, thiourea compounds described in US Pat.No. 3,458,318, pyrimidine derivatives described in US 3,615,632, azaindene compounds described in US 4,011,083, triaryl compounds described in US 4,578,347, thiazolium and oxazolium salts described in US 4,596,767, combination of supersensitizers described in US 4,603,104, thiatriazoles described in US 4,780,404, arylmercaptotetrazole compounds described in EP 440,947, and the like.

However, the use of supersensitizing dyes generally produces an unwanted increase of fog. This is a particularly relevant problem for color light-sensitive materials, because a colored fog is more visible. US 4,910,129 describes an infrared light-sensitive material containing mercaptotetrazole supersensitizing agents in combination with 3-mercapto-1,2,4-triazole antifogging agents substituted in positions 4 and 5 with substituents having a total number of at least 3 carbon atoms.

The object of the present invention is to obtain an infrared light-sensitive material that inhibits fog formation without diminishing speed upon development.

SUMMARY OF THE INVENTION

An infrared sensitive photographic element is disclosed which comprises at least one silver halide emulsion layer spectrally sensitized to the infrared portion of the electromagnetic spectrum. In particular, the element comprises at least three silver halide emulsion layers on a substrate, each associated with different photographic color image forming materials, such as color couplers capable of forming dyes of different colors upon reaction with an oxidized color photographic developer, diffusing dyes, bleachable dyes, or oxidized leuco dyes. The three emulsion layers are sensitized to three different portions of the electromagnetic spectrum with at least two layers sensitized to different regions of the infrared region of the electromagnetic spectrum. The element is characterized in that at least one infrared sensitized emulsion layer is associated with a 3-mercapto-1,2,4-triazole antifogging agent represented by the formula (I):



(I)

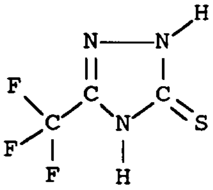
wherein R_1 and R_2 each independently represents hydrogen or alkyl group, the sum of carbon atoms of R_1 and R_2 is 1 or 2, and at least one of R_1 and R_2 is a perfluoroalkyl group.

The infrared sensitive photographic element has high sensitivity to infrared radiation and reduces the fog formation.

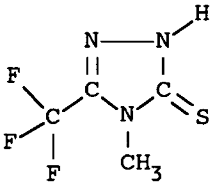
DETAILED DESCRIPTION OF THE INVENTION

An infrared sensitive photographic element is herein described which element comprises a support and one or more silver halide emulsion layers, at least one silver halide emulsion layer being spectrally sensitized to the infrared portion of the electromagnetic spectrum. In particular, an infrared sensitive color photographic element is herein described which element is capable of providing a full color image or three color images with exposure of at least two silver halide emulsion layers to radiation outside the visible region of the electromagnetic spectrum, which element comprises a substrate, and on one side of said substrate at least three silver halide emulsion layers, each of said silver halide emulsion layers being associated with means for forming a single color image of a color dye different from the color dyes of the other layers, said three emulsion layers being sensitized to three different portions of the electromagnetic spectrum with at least two layers sensitized to different regions of the infrared region of the electromagnetic spectrum. The element is characterized in that at least one infrared sensitized emulsion layer is associated with a 3-mercapto-1,2,4-triazole antifogging agent of formula (I). Examples of alkyl groups for R_1 and R_2 are methyl and ethyl, which may themselves be substituted with known elements such as hydroxy and halogen (e.g., hydroxyethyl, chloroethyl). Examples of perfluoroalkyl groups are pentafluoroethyl and trifluoromethyl.

Examples of antifogging agents according to this invention include the following. However, the scope of this invention is not limited to these compounds.



(I.1)



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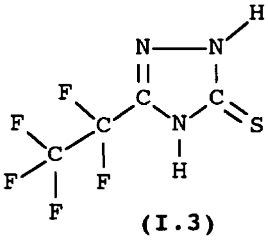

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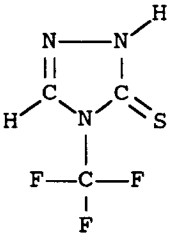

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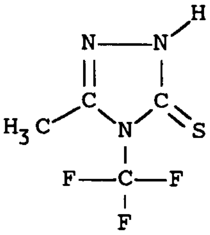


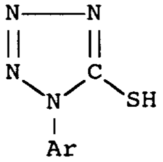
(I.5)

The 3-mercapto-1,2,4-triazole for use in the present invention may be synthetized by methods well known in the art. Synthesis of compound 1 is described, for example, in US 4,447,454.

The compounds represented by the general formula (I) may be added in any effective amount to the photographic emulsion. The concentration of said compounds can vary significantly in photographic emulsions. A generally useful range would be from 0.1 to 1.0 mmoles per mol of silver. A more preferred range would be from 0.3 to 0.8 mmoles per mol of silver.

The compounds can be directly dispersed in the photographic emulsion, or may be dissolved in a suitable solvent (e.g., water, methyl alcohol, ethyl alcohol, propanol, methyl cellosolve, acetone, etc.) or in a mixture of these solvents and added as a solution to the emulsion. In addition, said compounds can be added to the emulsion as a solution or as a colloid dispersion according to the processes for adding sensitizing dyes, as known to those skilled in the art.

The infrared sensitive color photographic element of the present invention contains at least a supersensitizing agent. Preferably, it is an 1-aryl-5-mercaptotetrazole compound substituted in the aryl group by at least one electron-attracting group as described in EP 440,947. More preferably, the supersensitizing agent is an 1-aryl-5-mercaptotetrazole represented by the structural formula (II):



(II)

wherein Ar is an aryl group bearing at least one electron-attracting group. More preferably, the aryl group is a phenyl group and the electron-attracting groups are selected from the group consisting of nitro, cyano, fluoroalkyl, halogen (preferably, chlorine or bromine), carbamoyl (preferably, a C_1 to C_4 straight or branched alkylaminocarbonyl or an un-substituted or substituted phenylaminocarbonyl group), sulfamoyl (preferably, a C_1 to C_4 straight or branched alkylaminosulfonyl or an un-substituted or substituted phenylaminosulfonyl group), acylamino (preferably, a C_1 to C_4 straight or branched alkylcarbonamido or an unsubstituted or substituted phenylcarbonamido group), sulfonamido (preferably, a C_1 to C_4 straight or branched alkylsulfonamido or an unsubstituted or substituted phenylsulfonamido group) and acyl (preferably, a C_1 to C_4 straight or branched alkylcarbonyl or an unsubstituted or substituted phenylcarbonyl group). Still more preferably, the compounds of the present invention are represented by the structural formula (II) wherein Ar is a phenyl group bearing one or more C_1 to C_4 straight or branched fluoroalkyl groups, wherein the alkyl group has at least one fluorine atom per carbon atom, preferably at least 1.5 fluorine atoms per carbon atom, more preferably all hydrogen atoms substituted with fluorine atoms.

When the term "group" is used in this invention to describe a chemical compound or substituent, the described chemical material includes the basic group and that group with conventional substitution. Where the term "moiety" is used to describe a chemical compound or substituent, only an unsubstituted chemical material is intended to be included. For example, "alkyl group" includes not only such alkyl moieties as methyl, ethyl, octyl, stearyl, etc., but also such moieties bearing substituent groups such as halogen, cyano, hydroxyl, nitro, amine, carboxylate, etc. On the other hand, "alkyl moiety" includes only methyl, ethyl, octyl, stearyl, cyclohexyl, etc.

Specific examples of aryl groups substituted with one or more electron-attracting groups are, for example, a 4-nitrophenyl group, 2-nitro-4-N,N-dimethylsulfamoylphenyl group, 2-N,N-dimethylsulfamoyl-4-nitrophenyl group, 2-cyano-4-methylsulfonylphenyl group, 2,4-dinitrophenyl group, 2,4,6-tricyanophenyl group, 2-nitro-4-N,N-dimethylcarbamoylphenyl group, 2,4-dimethanesulfonylphenyl group, 3,5-dinitrophenyl group, 2-chloro-4-nitro-5-methylphenyl group, 2-nitro-3,5-dimethyl-4-tetradecylsulfonylphenyl group, 2,4-dinitronaphthyl group, 2-ethylcarbamoyl-4-nitrophenyl group, 3,5-bistrifluoromethylphenyl group, 2,3,4,5,6-pentafluorophenyl group, 3-acetamidophenyl group, 2-acetyl-4-nitrophenyl group, 2,4-diacetylphenyl group, 2-nitro-4-trifluoromethyl phenyl group, 4-ethoxycarbonyl phenyl group.

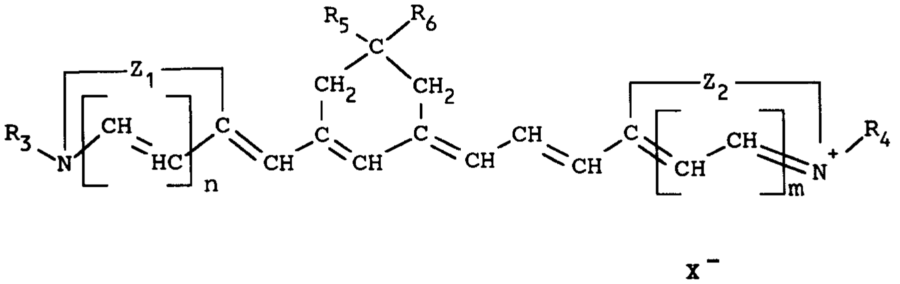
The compounds represented by the general formula (II) may be added in any effective stabilizing amount to the photographic emulsion. The concentration of said compounds can vary significantly in photographic emulsions. A generally useful range would be from 0.008 to 0.28 g per mol of silver. A more preferred range would be from 0.015 to 0.150 g per mol of silver.

The compounds can be directly dispersed in the photographic emulsion, or may be dissolved in a suitable solvent (e.g., water, methyl alcohol, ethyl alcohol, propanol, methyl cellosolve, acetone, etc.) or in a mixture of these solvents and added as a solution to the emulsion. In addition, said compounds can be added to the emulsion as a solution or as a colloid dispersion according to the processes for adding sensitizing dyes, as known to those skilled in the art.

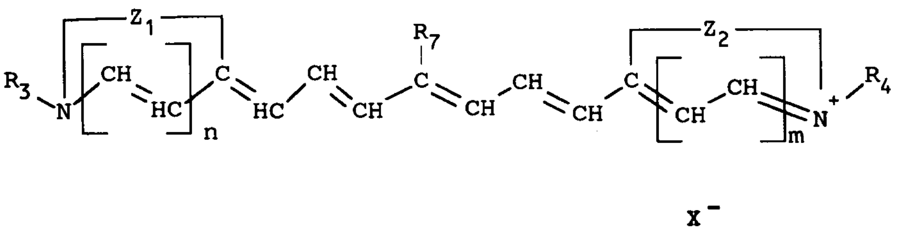
Any spectral sensitizing dye known to sensitize silver halide emulsions to infrared portion of the electromagnetic spectrum may be used in the practice of the present invention. The infrared portion of the electromagnetic spectrum is given various ranges, but is generally considered to be between 750 and 1500 nm which overlaps a small portion of the visible regions of the electromagnetic spectrum (e.g., about 750-

780 nm). Useful dyes for this purpose tend to be merocyanines, cyanines and especially tricarbocyanines. Such dye sensitizers for the infrared are described for example in US Pat. Nos. 3,457,078, 3,619,154, 3,682,630, 3,690,891, 3,695,888, 4,030,932 and 4,367,800. The preferred classes of dyes are the tricarbocyanines such as 3,3'-dialkylthiatricarbocyanines, thiatricarbocyanines (especially with rigidified chains), selenotricarbocyanines, and enamine tricarbocyanines.

Preferred classes of dyes are represented by the following general formula (III) or (IV):



(III)



(IV)

wherein:

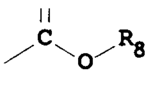
R_3 and R_4 can be a substituted alkyl group or a nonsubstituted alkyl group having from 1 to 8 carbon atoms such as , for example, methyl, ethyl, propyl, butyl, amyl, benzyl, octyl, carboxymethyl, carboxyethyl, sulfopropyl, carboxypropyl, carboxybutyl, sulfoethyl, sulfoisopropyl and sulfobutyl groups;

X^- is any acid anion such as, for example, chloride, bromide, iodide, tri-iodide, perchlorate, sulfamate, thiocyanate, p-toluenesulfonate and benzenesulfonate;

Z_1 and Z_2 are independently the non-metallic atoms necessary to complete an aromatic heterocyclic nucleus chosen within those of the thiazole series, benzothiazole series, (1,2-d)-naphthothiazole series, (2,1-d)-naphthothiazole series, oxazole series, benzoxazole series, selenazole series, benzoselenazole series, (1,2-d)-naphthoselenazole series, (2,1-d)-naphthoselenazole series, thiazoline series, 4-quinoline series, 2-pyridine series, 4-pyridine series, 3,3'-dialkyl-indolenine series (wherein alkyl has a meaning known to those skilled in the art including alkyl groups having 1 to 12 carbon atoms), imidazole series and benzimidazole series.

More particularly and preferably, the present invention refers to dyes of the type above indicated in which both heterocyclic nuclei are of the benzothiazole series.

R_5 and R_6 each represent a hydrogen atom, or an alkyl group having 1 to 5 carbon atoms such as a methyl group or an ethyl group; R_7 represents a hydrogen atom, a hydroxy group, a carboxy group, an alkyl group having 1 to 5 carbon atoms, an unsubstituted or substituted aryl group, an acyloxy group shown by



wherein R_8 represents an alkyl group having 1 to 5 carbon atoms, a phenyl group, or a substituted phenyl group.

The infrared sensitizing dyes used in the present invention are incorporated in the silver halide photographic emulsion in a content of 5×10^{-7} mol to 5×10^{-3} mol, preferably 1×10^{-6} mol to 1×10^{-3} mol, more preferably 2×10^{-6} mol to 5×10^{-4} mol, per mol of silver within the particular layer which is being sensitized by that dye.

The sensitizing dyes for use in the present invention can be prepared according to well-known procedures in the art, such those described in James, ***The Theory of Photographic Processes***, MacMillan, 4th Edition, 1977, in US Pat. Nos. 2,734,900, 3,148,187, 2,895,955 and 3,423,207, in CA 56 114571 and J.Org.Chem., Vol 42, 1977, page 885. Synthetic techniques are also described by Y.L.Slominskii et al, UKR. Khim. Zh., 40, pages 625-629, 1974 and Zh.Org.Khim., 15, page 400, 1979. Preparation processes of such dyes are illustrated in the examples herein below. Variations in the structures of the final dyes may be made by the appropriate selection of reagents and the use of these varied methods.

The infrared sensitizing dyes to be used in the present invention can be directly dispersed in the emulsion. Alternatively, they may be first dissolved in a suitable solvent such as methyl alcohol, ethyl alcohol, methyl cellosolve, acetone, water, pyridine, or a mixture thereof to add them to the emulsion as a solution. Processes for adding the infrared sensitizing dyes to the photographic emulsion are described, for example, in US Pat. Nos. 3,469,987, 3,676,147, 3,822,135, 4,199,360, and in US Pat. Nos. 2,912,343, 3,342,605, 2,996,287 and 3,429,835. The aforesaid infrared sensitizing dyes may be uniformly dispersed in the silver halide emulsion before coating on a suitable support. Of course, this dispersing procedure may be conducted in any suitable step of preparing the silver halide emulsion.

Infrared sensitive silver halide color photographic elements for use in the present invention are preferably those described in US 4,619,892, which is incorporated herein by reference. More preferably, the infrared sensitive silver halide color photographic elements for use in the present invention are those having all of the silver halide emulsion layers sensitized to different infrared regions of the electromagnetic spectrum. The order of these layers respect to the support, the difference in emulsion sensitivity among the layers and the sensitivity, contrast and D-max of each layer are preferably those described in said US 4,619,892.

Any of the various types of photographic silver halide emulsions may be used in the practice of the present invention. Silver chloride, silver bromide, silver iodobromide, silver chlorobromide, silver chloroiodobromide, and mixtures thereof may be used, for example, dispersed in a hydrophilic colloid or carrier. Any configuration of grains, cubic, orthorombic, hexagonal, epitaxial, or tabular (high aspect ratio) grains may be used. The colloid may be partially hardened or fully hardened by any of the variously known photographic hardeners. Such hardeners are free aldehydes, aldehyde releasing compounds, triazines and diazines, aziridines, vinylsulfones, carbodiimides, and the like may be used, as described, for example, in US Pat. Nos. 3,232,764, 2,870,013, 3,819,608, 3,325,287, 3,992,366, 3,271,175 and 3,490,911.

The silver halide photographic elements can be used to form dye images therein through the selective formation of dyes. The photographic elements described above for forming silver images can be used to form dye images by employing developers containing dye image formers, such as color couplers, as described, for example, in US Pat. Nos. 3,111,864, 3,002,836, 2,271,238, 2,236,598, 2,950,970, 2,592,243, 2,343,703, 2,376,380, 2,369,489, 2,899,306, 3,152,896, 2,115,394, 2,252,718, 2,108,602, and 3,547,650. In this form the developer contains a color developing agent (e.g., a primary aromatic amine which in its oxidized form is capable of reacting with the coupler to form the image dye). Also, instant self-developing diffusion transfer film can be used as well as photothermographic color film or paper using silver halide in catalytic proximity to reducable silver sources and leuco dyes.

The dye-forming couplers can be incorporated in the photographic elements, as illustrated by Schneider et al., ***Die Chemie***, Vol. 57, 1944, p.113, and in US Pat. Nos. 2,304,940, 2,269,158, 2,322,027, 2,376,679, 2,801,171, 2,748,141, 2,772,163, 2,835,579, 2,533,514, 2,353,754, 3,409,435 and Chen, Research Disclosure, Vol. 159, July 1977, Item 15930. The dye-forming couplers can be incorporated in different amounts to achieve differing photographic effects. For example, GB 923,045 and US 3,843,369 teach limiting the concentration of coupler in relation to the silver coverage to less than normally employed amounts in faster and intermediate speed emulsion layers.

The dye-forming couplers are commonly chosen to form subtractive primary (i.e., yellow, magenta and cyan) image dyes and are nondiffusible, colorless couplers, such as two and four equivalent couplers of the open chain ketomethylene, pyrazolone, pyrazolotriazole, pyrazolobenzimidazole, phenol and naphthol type hydrophobically ballasted for incorporation in high-boiling organic (coupler) solvents. Such couplers are illustrated in US Pat. Nos. 2,423,730, 2,772,162, 2,895,826, 2,710,803, 2,407,207, 3,737,316, 2,367,531, 2,772,161, 2,600,788, 3,006,759, 3,214,437, 3,253,924, 2,875,057, 2,908,573, 3,043,892, 2,474,293, 2,407,210, 3,062,653, 3,265,506, 3,384,657, 2,343,703, 3,127,269, 2,865,748, 2,933,391, 2,865,751, 3,725,067, 3,758,308, 3,779,763, 3,785,829, 3,762,921, 3,983,608, 3,311,467, 3,408,194, 3,458,315, 3,447,928, 3,476,563, 3,419,390, 3,419,391, 3,519,429, 3,222,176, 3,227,550, in GB Pat. Nos. 969,921, 1,241,069, 1,011,940, 975,928, 1,111,554, 1,248,924, and in CA 726,651. Dye-forming couplers of differing reaction rates in single or separate layers can be employed to achieve desired effects for specific photographic applications.

The dye-forming couplers upon coupling can release photo-graphically useful fragments, such as development inhibitors or accelerators, bleach accelerators, developing agents, silver halide sol-vents, toners, hardeners, fogging agents, antifoggants, competing couplers, chemical or spectral sensitizers and desensitizers. Development inhibitor-releasing (DIR) couplers are illustrated in US Pat. Nos. 3,148,062, 3,227,554, 3,733,201, 3,617,291, 3,703,375, 3,615,506, 3,265,506, 3,620,745, 3,632,345, 3,869,291, 3,642,485, 3,770,436, 3,808,945, and in GB Pat. Nos. 1,201,110 and 1,236,767. Dye-forming couplers and nondye-forming compounds which upon coupling release a variety of photographically useful groups are described in US 4,248,962. DIR compounds which do not form dye upon reaction with oxidized color developing agents can be employed, as illustrated in US Pat. Nos. 3,928,041, 3,958,993, 3,961,959, 4,049,455, 4,052,213 and in German OLS Nos. 2,529,350, 2,448,063 and 2,610,546.

DIR compounds which oxidatively cleave can be employed, as illustrated in US Pat. Nos. 3,379,529, 3,043,690, 3,364,022, 3,297,445 and 3,287,129. Silver halide emulsions which are relatively light insensitive, such as Lippmann emulsions, having been used as interlayers or overcoat layers to prevent or control the migration of development inhibitor fragments as described in US 3,892,572 can be employed.

The photographic elements can incorporate colored dye-forming couplers, such as those employed to form integral masks for negative color images, as illustrated in US Pat. Nos. 2,449,966, 2,521,908, 3,034,892, 3,476,563, 3,519,429, 2,543,691, 3,028,238, 3,061,432, and/or competing couplers, as illustrated in US Pat. Nos. 3,876,428, 3,580,722, 2,998,314, 2,808,329, 2,742,832 and 2,689,793.

As previously noted, the color provided in the image produced by exposure of each of the differently sensitized silver halide emulsion layers does not have to be produced by color coupler reaction with oxidized color developers. A number of other color image forming mechanisms well known in the art can also be used. Amongst the commercially available color image forming mechanisms are the diffusion transfer of dyes, dye-bleaching, and leuco dye oxidation. Each of these procedures is used in commercial products, is well understood by the ordinary skilled photographic artisan, and is used with silver halide emulsions. Multicolor elements using these different technologies are also commercially available. Converting the existing commercially available systems to the practice of the present invention could be done by routine redesign of the sensitometric parameters of the system and/or the addition of intermediate filter layers as described in US 4,619,892. For example, in a conventional instant color dye-diffusion transfer element, the sensitivity of the various layers and/or the arrangement of filter layers between the silver halide emulsion layers would be directed by the teachings of the above US patent, the element otherwise remaining the same. This would be true with either negative-acting or positive-acting silver halide emulsions in the element. The only major, and fairly apparent, consideration that must be given to such construction is to insure that the placement of any filter layers does not prevent transfer of the diffusion dye to a receptor layer within the element. Using a filter which is not a barrier layer between the receptor layer and the dye-containing layer is the simplest way to address that consideration. Such a layer should not prevent migration of the diffusion dye across the filter layer.

These types of imaging systems are well known in the art. Detailed discussions of various dye transfer, diffusion processes may be found for example in ***A Fundamentally New Imaging Technology for Instant Photography***, W.T. Harison, Jr., Photographic Science and Engineering, Vol. 20, No. 4, July/August 1976, and Neblette's ***Handbook of Photography and Reprography, Materials, Processes and Systems***, 7th Edition, John. M. Stunge, van Nostrand Reinhold Company, N.Y., 1977, pp. 324-330 and 126. Detailed discussion of dye-bleach color imaging systems are found for example in ***The Reproduction of Colour***, 3rd Ed., R.W.G. Hunt, Fountain Press, London, England, 1975, pp.325-330; and ***The Theory of the Photographic Process***, 4th Ed., Mees and James, Macmillan Publishing Co., Inc., N.Y., 1977, pp. 363-366. Pages 366-372 of Mees and James, supra, also discuss dye-transfer processes in great detail. Leuco dye oxidation in silver halide systems are disclosed in such literature as US Pat. Nos. 4,460,681, 4,374,821, and 4,021,240. Diffusion photothermographic color image forming systems such as those disclosed in GB Pat. Appln. No. 3,100,458 are also useful in the practice of the present invention.

The photographic elements can include image dye stabilizers. Such image dye stabilizers are illustrated in US Pat. Nos. 3,432,300, 3,698,909, 3,574,627, 3,573,050, 3,764,337, and 4,042,394 and in GB 1,326,889.

Filter dyes can be included in the photographic elements. Said dyes must be selected on the basis of their radiation filtering characteristics to insure that they filter the appropriate wavelengths. Filter dyes and their methods of incorporation into the photographic elements are well documented in the literature such as US Pat. Nos. 4,440,852, 3,671,648, 3,423,207, and 2,895,955, GB 485,624, and Research Disclosure, Vol. 176, December 1978, Item 17643. Filter dyes can be used in the practice of the present invention to provide room-light handleability to the elements. Dyes which will not allow transmission of radiation having wavelengths shorter than the shortest wavelength to which one of the emulsion layers has been sensitized can be used in a layer above one or more (preferably all) of the emulsion layers. The cut-off filter dye preferably does not transmit light more than approximately 50 nm less than the shortest wavelength to which any of the emulsion layers have been sensitized. Filter dyes should also be provided with non-fugitive (i.e., non-migratory) characteristics and should be decolorizable (by bleaching in developer or heat, for example) or leachable (e.g., removed by solvent action of any baths).

Other conventional photographic addenda such as coating aids, antistatic agents, acutance dyes, antihalation dyes and layers, antifoggants, latent image stabilizers, supersentizers, antikinking agents, high intensity reciprocity failure reducers, and the like may also be present.

The following examples illustrate preferred embodiments of the infrared sensitive photographic material of the present invention.

EXAMPLE

Sample 1

To 75 g of an AgCl emulsion (having 0.45 μm average grain size, 9.1% Ag and 5.47% gelatin) were added 291 g of an oil in water dispersion containing 65 g of coupler M, 0.295 g of compound A, 3.31 g. of compound B and 8.73 g. of gelatin. The composition was diluted with 227 ml of water and added with 3% of gelatin. Then, 0.2 mmole/mole Ag of spectral sensitizing dye SD, 0.96 mmole/mole Ag of stabilizer ST, and 0.75 mmole/mole Ag of supersensitizer SS were added in the order to the composition. The composition was then maintained at 38 °C for 40 minutes. The composition was coated onto a conventional photographic paper base at a coverage of 0.28 g/m^2. The photosensitive layer was overcoated with a protective layer comprising gelatin, a surfactant and a vinylsulfonyl hardener.

Sample 2

Sample 2 was prepared as Sample 1, but the stabilizer agent ST was added in an amount of 0.644 mmoles/mole Ag.

Sample 3

Sample 3 was prepared as Sample 1, but the antifogging agent C was added in an amount of 0.282 mmoles/mole Ag.

Sample 4

Sample 4 was prepared as Sample 2, but the antifogging agent C was added in an amount of 0.564 mmoles/mole Ag.

Sample 5

Sample 5 was prepared as Sample 1, but the antifogging agent (I.1) of the present invention was added in an amount of 0.295 mmoles/mole Ag.

Sample 6

Sample 6 was prepared as Sample 2, but the antifogging agent (I.1) of the present invention was added in an amount of 0.590 mmoles/mole Ag.

Sample 7

Sample 7 was prepared as Sample 1, but the antifogging agent (I.2) of the present invention was added in an amount of 0.337 mmoles/mole Ag.

Sample 8

Sample 8 was prepared as Sample 2, but the antifogging agent (I.2) of the present invention was added in an amount of 0.675 mmoles/mole Ag.

Sample 9

Sample 9 was prepared as Sample 1, but the antifogging agent D was added in an amount of 0.304 mmoles/mole Ag.

Sample 10

Sample 10 was prepared as Sample 2, but the antifogging agent D was added in an amount of 0.608 mmoles/mole Ag.

Sample 11

Sample 11 was prepared as Sample 1, but the antifogging agent E was added in an amount of 0.348 mmoles/mole Ag.

Sample 12

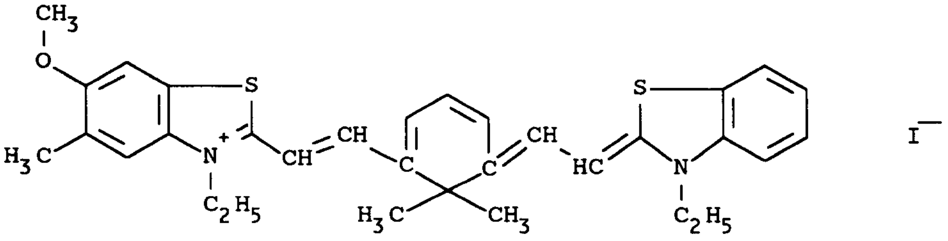
Sample 12 was prepared as Sample 2, but the antifogging agent E was added in an amount of 0.697 mmoles/mole Ag.

After conditioning for 72 hours at 33 °C, each sample was exposed to a laser diode at 820 nm. The exposed coatings were developed in a Kodak RA-4 processing line. The sensitometric results in terms of Dmin and speed are reported in Table 1. The amounts of the antifogging agents are expressed in mmoles/mole silver.

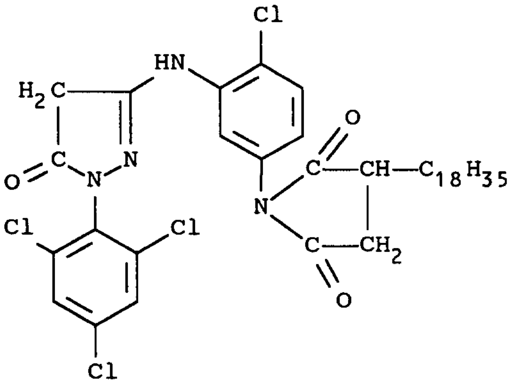
Table 1

	Antifog	**Amount**	**Dmin**	**Speed**
1.	--	--	0.22	235
2.	--	--	0.17	218
3. (ref.)	C	0.282	0.12	216
4. (ref.)	C	0.564	0.11	195
5. (inv.)	I.1	0.295	0.13	215
6. (inv.)	I.1	0.590	0.10	191
7. (inv.)	I.2	0.337	0.12	211
8. (inv.)	I.2	0.675	0.11	190
9.	D	0.304	0.18	221
10.	D	0.608	0.10	178
11.	E	0.348	0.23	195
12.	E	0.697	*	*
(*) Sample completely fogged				

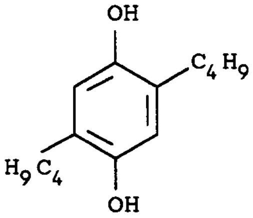
Table 1 shows that the sensitometric values obtained by samples 1 and 2, not containing any antifogging agents, present a high Dmin. Samples 5 to 8 of the present invention present results (low Dmin and high speed) comparable with those of reference samples 3 and 4, even if antifogging agents I.1 and I.2 have substituents with less than 3 carbon atoms. The values obtained by samples 9 to 12, containing antifogging agents not of the present invention, show a high Dmin and/or a low speed.



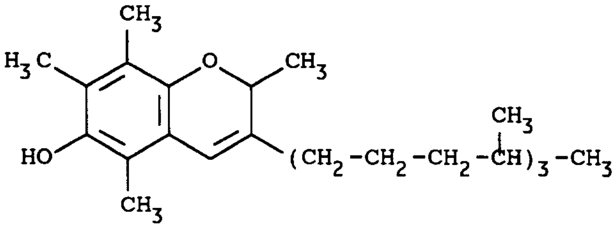
Sensitizing Dye SD



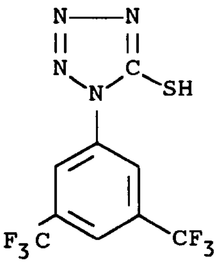
Coupler M



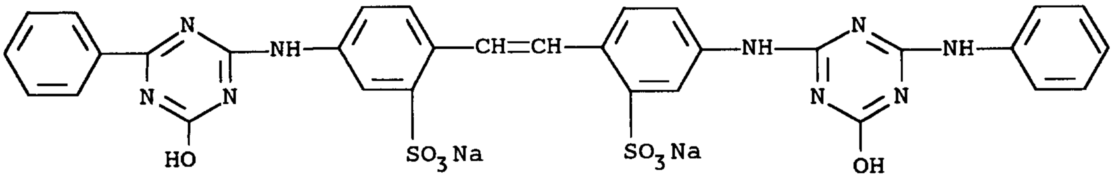
Compound A



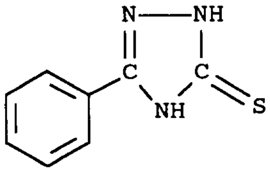
Compound B



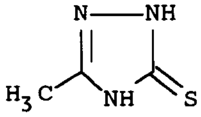
Stabilizer ST



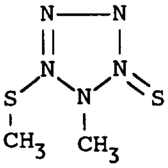
Supersensitizer SS



Antifogging Agent C



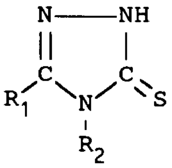
Antifogging Agent D



Antifogging Agent E

Claims

1. A silver halide photographic element comprising a support and at least one silver halide emulsion layer spectrally sensitized to the infrared portion of the electromagnetic spectrum, characterized in that said infrared sensitized emulsion layer is associated with a 3-mercapto-1,2,4-triazole antifogging agent represented by the formula :



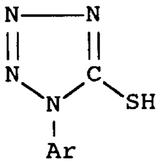
(I)

wherein R_1 and R_2 each independently represents hydrogen or an alkyl group, the sum of carbon atoms of R_1 and R_2 is 1 or 2, and at least one of R_1 and R_2 is a perfluoroalkyl group.

2. The silver halide photographic element of claim 1 comprising a support, and on one side of said support at least three silver halide emulsion layers, each of said silver halide emulsion being associated with a different color photographic coupler, each emulsion layer being sensitized to a different region of the electromagnetic spectrum and at least two emulsion layers being sensitized to radiation within the infrared region of the electromagnetic spectrum, characterized in that at least one of said infrared sensitized emulsion layer is associated with said 3-mercapto-1,2,4-triazole antifogging agent.

3. The silver halide photographic element of claim 1, wherein said infrared sensitized emulsion layer is associated with a 1-aryl-5-mercaptotetrazole compound substituted in the aryl group by at least one electron-attracting group.

4. The silver halide photographic element of claim 3, wherein said compound is represented by the structural formula:



(II)

wherein Ar is an aryl group bearing an electron- attracting group.

5. The photographic element of claim 3 wherein the aryl group is a phenyl group.

6. The photographic element of claim 3 wherein the electron-attracting group is selected from the group consisting of nitro, cyano, fluoroalkyl, halogen, carbamoyl, sulfamoyl, acylamino, sulfonamido and acyl.

7. The photographic element of claim 1 wherein the 3-mercapto-1,2,4-triazole is present in an amount from about 0.1 mmoles/mole silver to about 1.0 mmoles/mole silver halide.

8. The photographic element of claim 1 wherein said silver halide emulsion is sensitized by a dye selected form the class consisting of thia-, benzothia-, seleno-, benzoseleno-, imida-, benzoimida-, oxa-, benzoxa-, and enamine tricarbocyanines.

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 93 11 5143

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Y	EP-A-0 373 339 (AGFA-GEVAERT) * page 3, line 23 - line 54 * * page 6, line 19; examples A-10 * ---	1-8	G03C5/16 G03C1/28 G03C1/34
D,Y	US-A-4 910 129 (Y.TAKAHASHI ET AL.) * column 2, line 40 - column 4, line 45; claims * ---	1-8	
A	WO-A-92 02852 (MINNESOTA MINING AND MANUFACTURING COMPANY) * page 3, line 14 - page 6, line 3 * * page 11, line 1 - line 26 * -----		
			TECHNICAL FIELDS SEARCHED (Int.Cl.6) G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	18 February 1994	Philosoph, L

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document