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(71) Applicant: **MINNESOTA MINING AND MANUFACTURING COMPANY**
3M Center,
P.O. Box 33427
St. Paul,
Minnesota 55133-3427 (US)

(72) Inventor: **Delprato, Ivano**
3M Italia Ricerche S.p.A.
I-17016 Ferrania (Savona) (IT)
Inventor: **Ghirardo, Stefania**
3M Italia Ricerche S.p.A.
I-17016 Ferrania (Savona) (IT)
Inventor: **Luzzi, Antonio**
3M Italia Ricerche S.p.A.
I-17016 Ferrania (Savona) (IT)

(74) Representative: **Checcacci, Giorgio**
PORTA, CHECCACCI & BOTTI s.r.l.
Viale Sabotino, 19/2
I-20135 Milano (IT)

(54) **Photographic silver halide elements comprising infrared sensitizing dyes.**

(57) A process for stabilizing solutions of infrared sensitizing dyes and in particular, a process wherein a stabilizing amount of an organic reducing agent and of an organic or inorganic alkaline buffering agent has been used to increase the stability of the solution of infrared sensitizing dyes. A silver halide photographic element comprising a support, at least one infrared sensitive silver halide emulsion photosensitive layer and at least one hydrophilic colloid non photosensitive layer, wherein at least one infrared sensitive layer contains an infrared sensitizing dye and a stabilizing amount of an organic reducing agent and of an organic or inorganic alkaline buffering agent.

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FIELD OF THE INVENTION

The present invention relates to a process for stabilizing a solution of infrared sensitizing dyes and to silver halide photographic elements comprising a layer containing such infrared sensitizing dyes.

BACKGROUND OF THE INVENTION

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 McMillan 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, 750 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 infared sensitive false colour-sensitized photographic elements as described in US Pat. No. 4,619,892.

There are numerous references to dye structures for infrared sensitizing dyes. Examples of patents disclosing such dyes are listed in US Pat. No. 4,011,083. The most common infrared sensitizing dyes are tricarbocyanine dyes. "Tricarbocyanine" is a term used in the art to include dyes having an amidinium-ion cromophoric system (see Mees and James above, page 201). Tricarbocyanine infrared sensitizing dyes are also described in US Patent Nos. 4,536,473, 4,959,294, 5,061,618, 4,619,892, 3,506,655, 3,552,974, 3,623,881 and 3,758,461.

The infrared sensitizing dyes can be directly dispersed in the emulsion, or, alternatively, they may be first dissolved in a suitable solvent to add them to the emulsion as a solution. Processes for adding the infrared sensitizing dye to the photographic emulsion are described in US Pat. Nos. 3,469,987, 3,676,147, 3,822,135, 4,199,360, 2,912,343, 3,342,605, 2996,287 and 3,429,835.

A problem with many known infrared sensitizing dye is the poor stability of their solutions during keeping which renders them of limited utility in making photographic elements. In fact, the solution of infrared sensitizing dyes must be added to silver halide emulsion within few hours after being made, otherwise the solution rapidly degrades and loses the sensitizing effect.

US Patent No. 5,147,756 describes a process for stabilizing an aqueous solution of aryl hydrazides. These solutions may be made by the addition of a stabilizing amount of ascorbic acid, tartaric acid, citric acid, glucose and the like. The aqueous solutions have longer shelf-life. The stabilized aryl hydrazide is useful in photographic silver halide emulsion to produce very high contrast images in graphic arts materials.

It is also known in the art that the ascorbic acid is useful to solve problems different from the problem of stabilizing solutions of infrared sensitizing dyes solved.

US Patent No. 5,037,734 describes a photographic silver halide emulsion spectrally sensitized in the infrared region of the electromagnetic spectrum, said emulsion being stabilized by the combination of an organic reducing agent having an oxidation potential from about +0.10 to about +0.70 volts vs SCE (Saturated Calomel Electrode), such as ascorbic acid or dihydroanhydropiperidino hexose reductone, and a nonionic surface active agent capable of deaggregating the infrared sensitizing dye. The problem of low oxidation potential and, as such, the tendence to oxidative decomposition of said infrared dyes has been by this way reduced, obtaining good photographic speed and fog levels. This patent solves the problem of stabilizing an emulsion spectrally sensitized in the infrared region, while a process for stabilizing a solution containing an infrared sensitizing dye to be added to the emulsion some hours later, during the coating phase, is not therein mentioned.

Ascorbic acid is also known in the art as supersentizer in light-sensitive materials having high sensitivity and excellent color reproduction. In fact, US Patent No. 4,917,997 describes a silver halide photographic emulsion combined with an ascorbic acid compound, a bisaminostilbene compound substituted by a pyrimidine derivative and one sensitizing dye, said photographic emulsion exhibiting an increased spectral sensitivity. US Patent No. 4,897,343 describes a spectrally sensitized silver halide photographic emulsion comprising at least one alkali metal sulfite compound and at least one ascorbic acid compound as supersensitizing agents for a spectrally sensitized dye.

Ascorbic acid is also known in the art as reduction sensitizing agent during the emulsion making process. European Patent Application No. 371,338 describes a monodisperse silver halide emulsion

reduction-sensitized during precipitation of silver halide grains in the presence of a thiosulphonic acid compound or by ascorbic acid in a process of manufacturing a silver halide emulsion. Process of manufacturing silver halide emulsions are roughly classified into, e.g., grain formation, desalting, chemical sensitization and coating steps. Grain formation is further classified into, e.g., nucleation, ripening and precipitation substeps. European Patent Application No. 378,841 describes a photographic material comprising an emulsion layer containing silver halide grains reduction-sensitized by ascorbic acid preferably performed before or simultaneously with sulfur sensitization, selenium sensitization or gold sensitization. European Patent Application No. 404,142 describes a process for treating a tabular silver halide emulsion comprising the steps of subjecting the emulsion to reduction sensitization by ascorbic acid and subjecting the tabular emulsion in the presence of a nitrogen-containing hetrocyclic compound which forms a complex with silver to sulfur sensitization, selenium sensitization or gold sensitization during the manufacture of the tabular emulsion.

It is an object of the present invention to provide a solution of infrared sensitizing dyes which maintains its stability during keeping, without losing the sensitizing effect after few hours it has been prepared. It is a further object of the present invention to provide a silver halide photographic material containing an infrared sensitizing dyes which contributes to obtain an image having a speed improvement. This problem is particularly relevant in medical imaging area, wherein there is a specific need to have images with high speed to facilitate the evaluation of the images by the final users.

SUMMARY OF THE INVENTION

The present invention refers to a process for stabilizing solutions of infrared sensitizing dyes. In particular, it refers to a process wherein a stabilizing amount of an organic reducing agent and of an organic or inorganic buffering agent has been used to increase the stability of the solution of infrared sensitizing dyes. Further, the present invention relates to a silver halide photographic element comprising a support, at least one infrared sensitive silver halide emulsion photosensitive layer and at least one hydrophilic colloid non photosensitive layer, wherein at least one infrared sensitive layer contains an infrared sensitizing dye and a stabilizing amount of an organic reducing agent and of an organic or inorganic buffering agent.

The process of the present invention allows to obtain solutions of infrared sensitizing dyes which maintain their stability during keeping, without loosing the sensitizing effect. This fact allows to add said solutions of infrared sensitizing dyes to the photographic material up to at least 2 days after the preparation, rather than very few hours as done in the past. An improvement in the photographic speed is also obtained by using stabilized solutions of infrared sensitizing dyes in silver halide photographic elements.

DETAILED DESCRIPTION OF THE INVENTION

Generally, the infrared sensitizing dyes to be used in the present invention 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 silver halide emulsion as a solution. The solution contains generally 0.02% to 1.0% by weight of the infrared sensitizing dye and must be added to the silver halide emulsion within 1-12 hours after being made. Otherwise, the solution degrades rapidly and its sensitizing effect decreases.

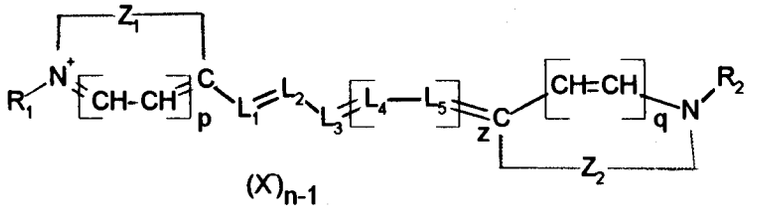
According to the present invention a stabilizing amount of an organic reducing agent and of an organic or inorganic alkaline buffering agent is used to stabilize said solutions of infrared sensitizing dyes. The solvent used to dissolve the infrared sensitizing dyes used in this invention is a mixture of water and alcohol (such as methyl alcohol, ethyl alcohol, phenyl cellosolve, and the like) or water alone. Said organic reducing agent is selected from the group consisting of ascorbic acid, an ascorbic acid isomer, glucose, cyclodextrin and a mixture thereof, while said organic and inorganic buffering agent is selected from the group consisting of alkali metal (e.g., sodium, potassium, lithium, and the like) acetate, citrate, phosphate, borate, tartarate and the like. Preferably the organic reducing agent is ascorbic acid or an ascorbic acid derivative (e.g., ascorbic acid, L-ascorbic acid, sodium L-ascorbate, sodium D-ascorbate, and the like). The amount of said organic reducing agent is in the range of from 5 to 500 mg, preferably in the range of from 10 to 300 mg, most preferably in the range of from 20 to 200 mg for 100 ml of solution containing 0.1% by weight of sensitizing dye. Preferably, the alkaline buffering agent is sodium acetate. The amount of said alkaline buffering agent is in the range of from 20 to 1000 mg, preferably in the range of from 100 to 500 mg per 100 ml of solution containing 0.1% by weight of sensitizing dye.

The preferred process of the present invention comprises dissolving the infrared sensitizing dye in phenylcellosolve solvent and heating at 50 °C to obtain a solution and, then, adding methyl alcohol and a

desired amount of sodium acetate and ascorbic acid. The resulting solution is made up to 100 ml with methanol at 20 °C. The solutions obtained with the reducing agent and the buffering agent are clear and retain their stability for a reasonable length of time e.g. at least 2 days versus only few hours without the reducing and buffering agents. In addition, the solutions with the reducing and buffering agents used in the present invention show no solids, while the solutions without reducing and buffering agents form solids after a short period of time, e.g., 1 to 12 hours.

Said stabilized solutions of infrared sensitizing dyes may be kept in storage conditions to be added later to the silver halide emulsion just before coating on a suitable support, without loosing the sensitizing effect even if they are not added to the silver halide emulsion immediately after their preparation.

Infrared sensitizing dyes, which can be used in the present invention include those which are represented by the following general formula (I):



(I)

wherein,

Z_1 and Z_2 each independently represents the atoms necessary to complete a substituted or unsubstituted 5- or 6-membered heterocyclic nucleus

R_1 and R_2 each independently represents a substituted or unsubstituted alkyl group,

L_1, L_2, L_3, L_4 and L_5 each independently represents a substituted or unsubstituted methine group,

X- represents an anion,

n represents an integer of 1 to 2, provided that n is 1 when the dye forms an intramolecular salt,

p and q each independently represents 0 or 1, and

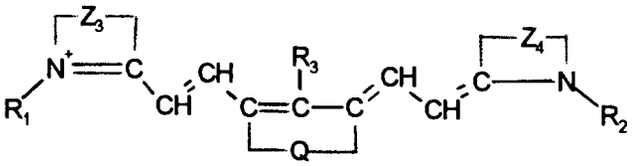
z represents 2.

According to the above formula (I), Z_1 and Z_2 each independently represents the atoms necessary to complete a substituted or unsubstituted 5- or 6-membered heterocyclic nucleus. These include a substituted or unsubstituted thiazole nucleus, quinoline nucleus, tellurazole nucleus, pyridine nucleus, thiazoline nucleus, oxazole nucleus, selenazole nucleus, and the like. These nuclei may be substituted by any of a number of groups known to be substituents for such nuclei. These includes sulfo, halogen (e.g. chloro, fluoro), alkyl of 1 to 12 carbon atoms (preferably of about 1 to 4 carbon atoms, e.g. methyl, ethyl, butyl, which may themselves be substituted with known elements such as hydroxy, halogen or sulfo), alkoxy of 1 to 12 carbon atoms (preferably of about 1 to 4 carbon atoms, e.g., methoxy, ethoxy, butoxy), carboxy, carboxylate of from 1 to 4 carbon atom (e.g., methyl ester, ethyl ester), sulfonamido or carbonamido.

R_1 and R_2 each independently represents a substituted or unsubstituted alkyl of 1 to 20 carbon atoms (preferably of from 1 to 6 carbon atoms). Examples of alkyl include methyl, ethyl, propyl, isopropyl, butyl, octyl, etc. and substituted alkyl groups (preferably a substituted lower alkyl of from 1 to 6 carbon atoms), such as a hydroxyalkyl group, e.g., β-hydroxyethyl, γ-hydroxypropyl, δ-hydroxybutyl, etc., a carboxyalkyl group, e.g., β-carboxyethyl, γ-carboxypropyl, etc., a sulfoalkyl group, e.g., β-sulfoethyl, δ-sulfopropyl, γ-sulfobutyl, δ-sulfobutyl, etc., a sulfatoalkyl group, e.g., β-sulfatoethyl, γ-sulfatopropyl, etc., or an acyloxyalkyl group, e.g., β-acetoxyethyl, γ-acetoxypropyl, γ-propoxypropyl, etc.

L_1-L_5 may be unsubstituted, i.e., -CH=, or substituted with known substituents such as alkyl of 1 to 12 carbon atoms (e.g., methyl, ethyl, butyl, etc.), aryl (e.g., phenyl), halogen (e.g., chloro, fluoro), heterocyclic groups, and the like. Additionally, substituents on the methine groups may form bridged linkages. For example, L_2, L_3 and L_4 methine groups may be bridged to form a 6-membered substituted or unsubstituted carbocyclic ring. Similarly, L_3, L_4 and L_5 methine groups may be bridged to form a 5- or 6-membered substituted or unsubstituted carbocyclic ring.

Preferred infrared sensitizing dyes which can be used in the present invention include those which are represented by the following general formula (II):



(II)

$(X)_{n-1}$

wherein,

Z_3 and Z_4 each independently represents the atoms necessary to complete a substituted or unsubstituted thiazole nucleus or a substituted or unsubstituted oxazole nucleus, or a substituted or unsubstituted selenazole nucleus,

Q represents the atoms necessary to complete a substituted or unsubstituted 5- or 6-membered carbocyclic ring,

R_1 and R_2 each independently represents a substituted or unsubstituted alkyl group,

R_3 represents hydrogen, alkyl of 1 to 4 carbon atoms, aryl, cyano, halogen or - NR_4R_5, wherein R_4 and R_5 each independently represents alkyl of 1 to 6 carbon atoms or aryl or together represent the non-metallic atoms necessary to form a substituted or unsubstituted 5- or 6-membered heterocyclic ring,

X^- represents an anion, and

n represents an integer of 1 to 2, provided that n is 1 when the dye forms an intramolecular salt.

In the formula of the preferred infrared sensitizing dyes of the present invention, Z_3 and Z_4 each independently represents the atoms necessary to complete a substituted or unsubstituted thiazole nucleus or oxazole nucleus or a substituted or unsubstituted selenazole nucleus. These nuclei may be substituted by any of a number of groups known to be substituents for such nuclei. These includes sulfo, halogen (e.g. chloro, fluoro), alkyl of 1 to 12 carbon atoms (preferably of about 1 to 4 carbon atoms, e.g. methyl, ethyl, butyl, which may themselves be substituted with known elements such as hydroxy, halogen or sulfo), alkoxy of 1 to 12 carbon atoms (preferably of about 1 to 4 carbon atoms, e.g. methoxy, ethoxy, butoxy), carboxy, carboxylate of from 1 to 4 carbon atom (e.g. methyl ester, ethyl ester), sulfonamido or carbonamido. Examples of useful nuclei for Z_3 and Z_4 include a thiazole nucleus, e.g. thiazole, 4-methylthiazole, 4-phenylthiazole, 5-methylthiazole, 5-phenylthiazole, 4,5-dimethylthiazole, 4,5-diphenylthiazole, 4-(2-thienyl)-thiazole, benzothiazole, 4-chlorobenzothiazole, 5-chlorobenzothiazole, 6-chlorobenzothiazole, 7-chlorobenzothiazole, 4-methylbenzothiazole, 5-methybenzothiazole, 6-methylbenzothiazole, 5-bromobenzothiazole, 6-bromobenzothiazole, 5-phenylbenzothiazole, 6-phenylbenzothiazole, 4-methoxybenzothiazole, 5-methoxybenzothiazole, 6-methoxybenzothiazole, 5-iodobenzothiazole, 6-iodobenzothiazole, 4-ethoxybenzothiazole, 5-ethoxybenzothiazole, tetrahydrobenzothiazole, 5,6-dimethoxybenzothiazole, 5,6-dioxymethylenebenzothiazole, 5-hydroxybenzothiazole, 6-hydroxybenzothiazole, naphtho[2,1-d]thiazole, naphtho[1,2-d]thiazole, 5-methoxynaphtho[2,3-d]thiazole, 5-ethoxynaphtho[2,3-d]thiazole, 8-methoxynaphtho-[2,3-d]thiazole, 7-methoxynaphtho[2,3d]thiazole, 4'-methoxythianaphtheno-7',6'-4,5-thiazole, etc., or an oxazole nucleus, e.g. 4-methyloxazole, 4-phenyloxazole, 5-methyloxazole, 4,5-diphenyloxazole, 4-ethyloxazole, 4,5-dimethyloxazole, 5-phenyloxazole, etc., a benzoxazole nucleus, e.g. benzoxazole, 5-chlorobenzoxazole, 5-methylbenzoxazole, 5-phenylbenzoxazole, 6-methyl-benzoxazole, 5,6-dimethyl-benzoxazole, 4,6-dimethyl-benzoxazole, 5-methoxybenzoxazole, 5-ethoxybenzoxazole, 5-chlorobenzoxazole, 6-methoxybenzoxazole, 5-hydroxybenzoxazole, 6-hydroxybenzoxazole, etc., a naphthoxazole nucleus, e.g. α-naphthoxazole, β-naphthoxazole, etc., or a selenazole nucleus, e.g. 4-methylselenazole, 4-phenylselenazole, 5-methylselenazole, 4,5-diphenyl-selenazole, 4-ethylselenazole, 4,5-dimethylselenazole, 5-phenylselenazole, etc., a benzoselenazole nucleus, e.g. benzoselenazole, 5-chlorobenzoselenazole, 5-methylbenzoselenazole, 5-phenylbenzoselenazole, 6-methylbenzoselenazole, 5,6-dimethyl-benzoselenazole, 4,6-dimethylbenzoselenazole, 5-methoxybenzoselenazole, 5-ethoxybenzoselenazole, 5-chlorobenzoselenazole, 6-methoxybenzo-selenazole, 5-hydroxybenzoselenazole, 6-hydroxybenzoselenazole, etc., a naphthoselenazole nucleus, e.g. α-naphthoselenazole, β-naphthoselenazole, etc.

R_1 and R_2 each represent a substituted or unsubstituted alkyl as defined for formula (I) above.

R_3 represents a hydrogen atom, an alkyl group of 1 to 4 carbon atoms (such as methyl, ethyl, propyl), an aryl group (such as phenyl), cyano, halogen (such as chloro, bromo, fluoro) or -NR_4R_5, wherein R_4 and R_5 each independently represents an alkyl group of 1 to 6 carbon atoms (such as methyl, ethyl, propyl), an aryl group (such as phenyl, p-methoxyphenyl) or together represent the non-metallic atoms necessary to form a substituted or unsubstituted 5- or 6-membered heterocyclic ring group. Preferably said heterocyclic

ring group is a heterocyclic aromatic ring including two conjugated double bonds in the ring. The aromatic character of said heterocyclic rings is well known in the chemical literature, as described for example in S.H. Pine, ***Organic Chemistry***, Fifth Edition, MacGraw-Hill Book Company, 1987, page 703. This ring may be substituted as known in the art. Examples of substituents include alkyl such as alkyl from 1 to 4 carbon atoms (e.g. methyl, ethyl, butyl), which may themselves be substituted with known elements such as hydroxy, halogen and the like (e.g., hydroxyethyl, chloroethyl), carboxylate of from 1 to 4 carbon atom (e.g. methyl ester, ethyl ester), amido, sulfonamido, halogen (e.g., chloro, fluoro) and others that would be known to one skilled in the art. Preferred examples of 5-membered N-containing aromatic ring include pyrazole, triazole, imidazole and pyrrole.

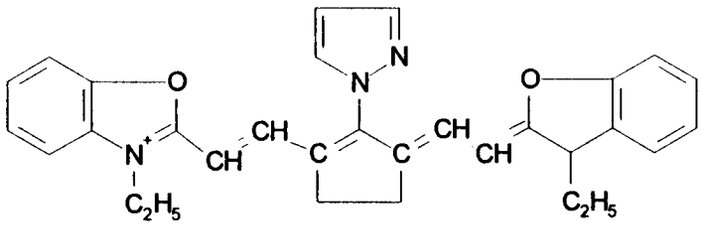
Q represents the atoms necessary to complete a substituted or unsubstituted 5- or 6- membered carbocyclic ring. This ring can be substituted, as known to one skilled in the art. Examples of substituents include substituted or unsubstituted alkyl of 1 to 12 carbon atoms (e.g., methyl, ethyl, propyl, chloroethyl, benzyl), substituted or unsubstituted aryl (e.g., phenyl, p-chlorophenyl), halogen (e.g., chloro, fluoro), hydroxy, alkoxy (e.g., methoxy, ethoxy) and other conventional dyes substituents that would be apparent to one skilled in the art.

The anion represented by X^-, although not particularly restricted, is for example, a halogen ion (e.g., chloride, bromide, iodide), p-toluene sulfonate (PTS^-), ethylsulfonate, perchlorate, or the like.

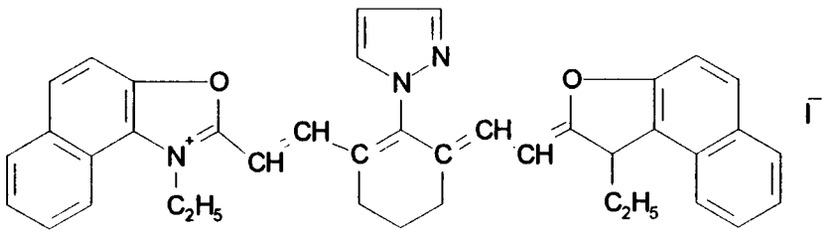
When the term "group" is used in this invention to describe a chemical compound or substituent, the described chemical material includes the basic group and that group with conventional substitution. Where the term "moiety" is used to describe a chemical compound or substituent, only an unsubstituted 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 substituents groups such as halogen, cyano, hydroxyl, nitro, amine, carboxylate, etc. On the other hand, "alkyl moiety" includes only methyl, ethyl, octyl, stearyl, cyclohexyl, etc.

Examples of infrared absorbing dyes according to this invention include the following; however the scope of this invention is not limited to them.

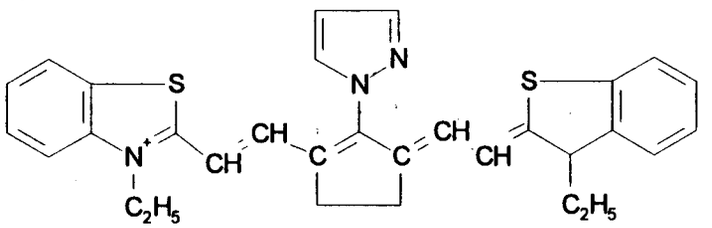
Dye 1



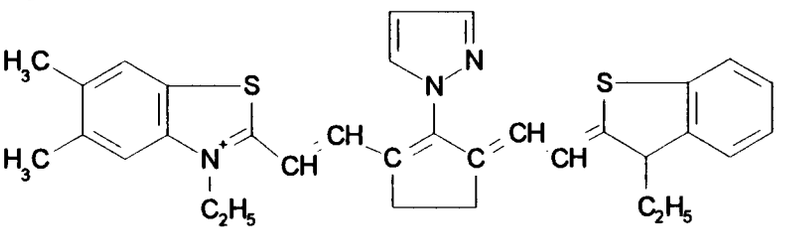
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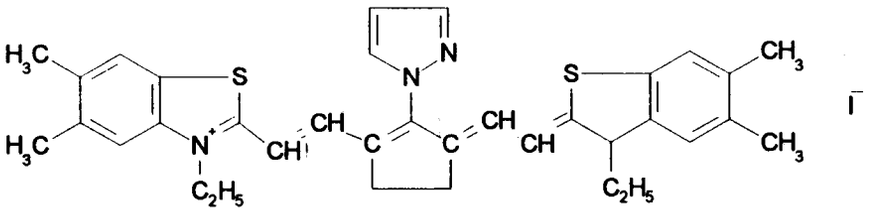
Dye 3



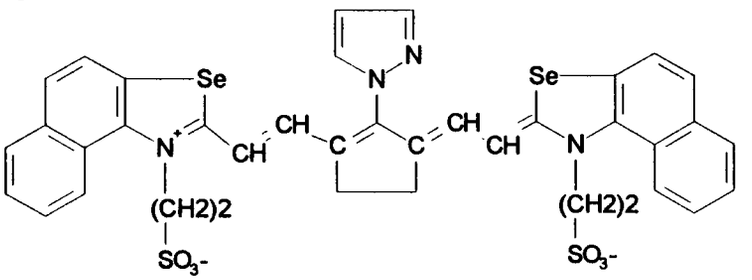
Dye 4



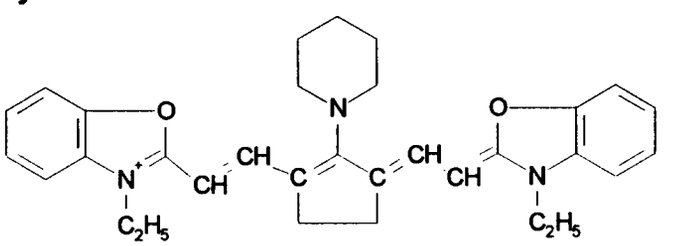
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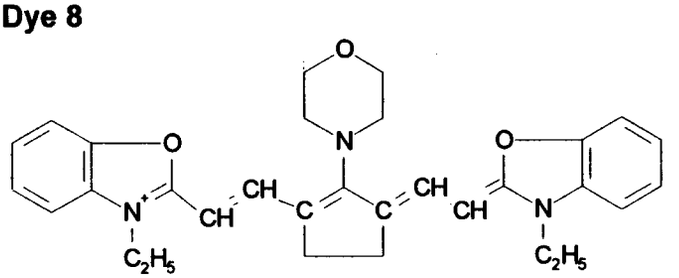
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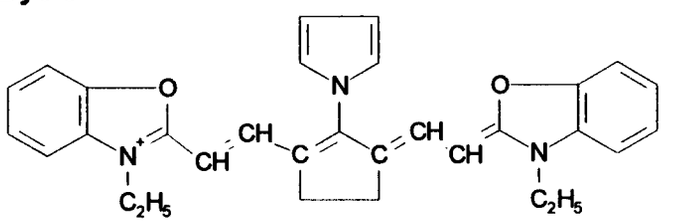
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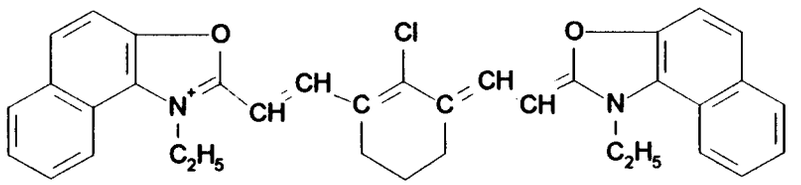
Dye 8



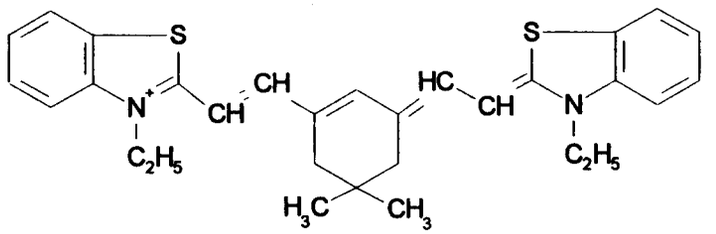
Dye 9



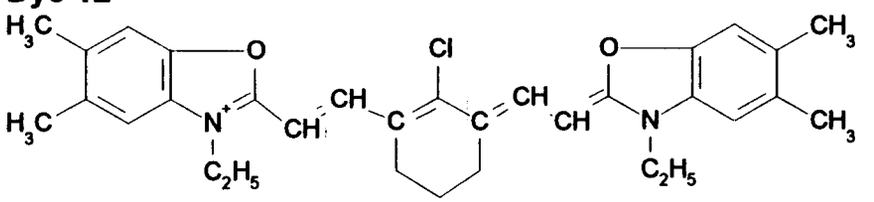
Dye 10



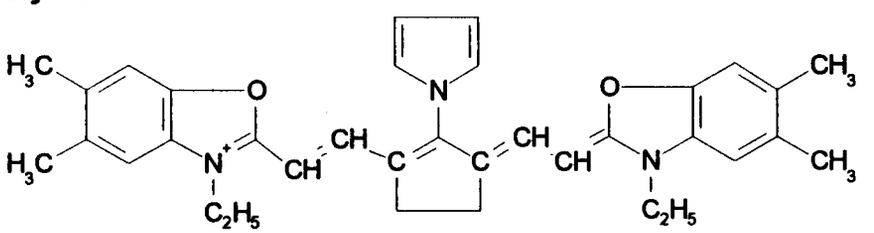
Dye 11



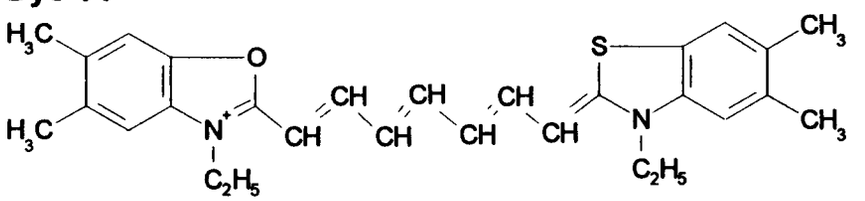
Dye 12



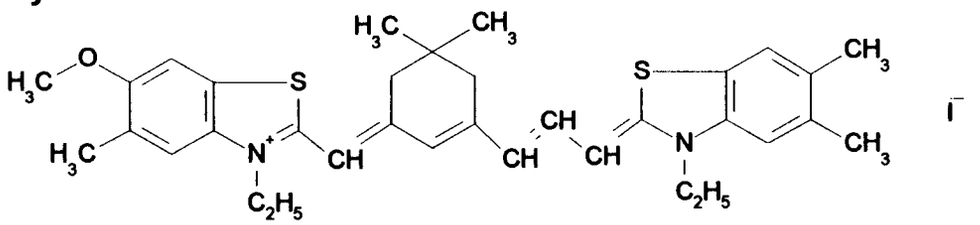
Dye 13



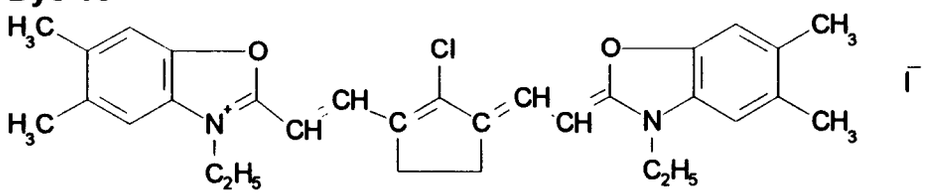
Dye 14



Dye 15



Dye 16



The infrared senziting 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 used in the present invention spectrally sensitize silver halide emulsions to radiation in the infrared from 700 nm upwards, especially from 750 to 850 nm, to provide photographic elements which are particularly suitable with a number of commercially available laser diodes. In addition to providing sensitization to the desired wave-length range, the sensitizing dyes used in this invention exhibit an increased stability of their solutions during keeping.

The infrared sensitizing dyes used in the present invention are incorporated in the silver halide photographic emulsion layer in a content of $5x10^{-7}$ mol to $5x10^{-3}$ mol, preferably $1x10^{-6}$ mol to $1x10^{-3}$ mol, more preferably $2x10^{-6}$ mol to $5x10^{-4}$ mol, per mol of silver within the particular layer which is being sensitized by that dye.

According to a further aspect of the present invention there is provided a silver halide photographic element comprising a support, at least one infrared sensitive silver halide emulsion layer and at least one hydrophilic colloid non photosensitive layer, wherein at least one infrared sensitive silver halide emulsion layer contains an infrared sensitizing dye and a stabilizing amount of an organic reducing agent and of an alkaline buffering agent.

Examples of silver halide photographic materials applicable to this invention include black-and-white and color photographic elements.

Infrared sensitive silver halide color photographic elements for use in the present invention are preferably those described in US Pat. No. 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 Pat. No. 4,619,892.

The dyes used in the present invention find particular utility when used for spectrally sensitizing to infrared radiation a silver halide emulsion layer in photographic elements that include at least one other infrared-sensitive silver halide layer. Preferred examples of said photographic elements are those comprising at least three silver halide emulsion layers on a substrate, each associated with different photographic colour image forming materials such as color couplers capable of forming dyes of different colors upon reaction with an oxidised color photographic developer, diffusing dyes, bleachable dyes or oxidizable leuco dyes, the three emulsion layers being sensitized to three different portions of the visible spectrum with at least one layer, preferably at least two layers, sensitized to radiation within the infrared region of the

spectrum.

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.

The silver halide grains in the photographic emulsion may be regular grains having a regular crystal structure such as cube, octahedron, and tetradecahedron, or the spherical or irregular crystal structure, or those having crystal defects such as twin plane, or those having a tabular form, or the combination thereof.

The photographic element comprising a layer including the dyes of this invention may be coated on any suitable support material used in photography such as cellulose acetate, cellulose nitrate, paper, polyesters, such as polyethylene terephthalate, etc.

As the binder or protective colloid for use in the photographic element, gelatin is advantageously used, but other hydrophilic colloid may be used alone or in combination with gelatin such as gelatin substitutes, collodion, gum arabic, cellulose ester derivatives such as alkyl esters of carboxylated cellulose, hydroxy ethyl cellulose, carboxy methyl cellulose, synthetic resins, such as the amphoteric copolymers described in US Pat. No. 2,949,442, polyvinyl alcohol, and others well known in the art.

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 Pat. No. 923,045 and US Pat. No. 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 Pat. No. 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 solvents, 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 Pat. No. 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 Pat. No. 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 Pat. No. 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 Pat. No. 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 Pat. No. 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.

Methods for making such elements, means for sensitizing them to infrared radiation, use of additives such as chemical sensitizers, antifoggant and stabilizers, desensitizers, brightening agents, couplers,

hardening agents, coating aids, plasticizers, lubricants, matting agents, high-boiling organic solvents, development accelerating compounds, antistatic agents, antistain agents, and the like are described for example, in Researh Disclosure Vol. 176, No. 17643, December 1979, Sections I to XIV.

The following examples illustrate the process for the stabilization of solutions of infrared sensitizing dyes and non-limiting examples of preferred embodiments of the present invention.

EXAMPLE 1

Sample 1 (reference)

0.1 g of spectral sensitizing Dye 4 were dissolved in 10 ml of 2-phenoxyethanol, the resulting solution was made up to 100 ml with methanol at 20 °C.

Sample 2 (reference)

As Sample 1, but the methanolic solution contained 250 mg of sodium acetate.

Sample 3 (reference)

As Sample 1, but the methanolic solution contained 100 mg of ascorbic acid.

Sample 4 (invention)

As Sample 1, but the methanolic solution contained 100 mg of ascorbic acid and 250 mg of sodium acetate.

Sample 5 (invention)

As Sample 1, but the methanolic solution contained 200 mg of ascorbic acid and 250 mg of sodium acetate.

Sample 6 (invention)

As Sample 1, but the methanolic solution contained 50 mg of ascorbic acid and 250 mg of sodium acetate.

Sample 7 (invention)

As Sample 1, but the methanolic solution contained 30 mg of ascorbic acid and 250 mg of sodium acetate.

Sample 8 (invention)

As Sample 1, but the methanolic solution contained 100 mg of ascorbic acid and 150 mg of sodium acetate.

Sample 9 (invention)

As Sample 1, but the methanolic solution contained 100 mg of ascorbic acid and 350 mg of sodium acetate.

The stability of the solutions of samples 1-9 was obtained by measuring the optical density at λmax after further dilution (1:500,000) with methanol on the fresh prepared solution and after 48 hours of shelf life. The following Table 1 reports the percentage of the optical density measured after 48 hours of shelf life with reference to the optical density measured on the fresh prepared solution.

Table 1

Sample	Percentage after 48 hours
1 (ref.)	78%
2 (ref.)	87%
3 (ref.)	precipitation
4 (inv.)	98.4%
5 (inv.)	94%
6 (inv.)	95%
7 (inv.)	95%
8 (inv.)	94%
9 (inv.)	95%

A solution can be considered stable if the value obtained is at least 90%, preferably at least 95% of the initial value, without any precipitation of the solution that renders it not useful for the incorporation in a silver halide photographic material. Table 1 shows that samples 4-9 are useful in the present invention.

EXAMPLE 2

Sample 10 (reference)

As sample 1 of Example 1, but the spectral sensitizing Dye 4 was replaced by the equimolar amount of Dye 16.

Sample 11 (invention)

As sample 4 of Example 1, but the spectral sensitizing Dye 4 was replaced by the equimolar amount of Dye 16.

Sample 12 (reference)

As sample 1 of Example 1, but the spectral sensitizing Dye 4 was replaced by the equimolar amount of Dye 15.

Sample 13 (invention)

As sample 4 of Example 1, but the spectral sensitizing Dye 4 was replaced by the equimolar amount of Dye 15.

Table 2 reports the stability data measured as in Example 1.

Table 2

Sample	Percentage after 48 hours
10 (ref.)	79%
11 (ref.)	96%
12 (ref.)	89%
13 (ref.)	99%

EXAMPLE 3

Film 1 (reference)

1000 gr of an AgBr emulsion (having 0.26 μm average grain size, 13% Ag coverage and silver/gelatin ratio of 1.25) were added to 466 ml of water, under stirring at 50 °C, comprising 6 ml of a solution 1N of

NaOH. A mixture of 7.5 ml of a 10% (w/w) aqueous solution of Hostapur™ SAS (an anionic surfactant of the alkane sulfonate sodium salt type manufactured by Hoechst AG) and 1.75 ml of a 50% (w/w) aqueous solution of glycerin was then added. Then, 117 ml of a 1% (w/w) aqueous solution of supersensitizer SS and 115 ml of a 0.025% (w/w) fresh prepared solution of spectral sensitizing Dye 16 were added. The composition was then maintained at 50 °C for 30 minutes under stirring. Then, 40 ml of a 20% (w/w) aqueous polyethylacrylate latex, a surfactant of the lauryl sulfate sodium salt type and 10 ml of a aqueous solution containing 3.7% of formaldehyde were added. The composition was coated onto a conventional photographic paper base at a silver coverage of 2.2 g/m^2. The photosensitive layer was overcoated with a protective layer comprising gelatin, a surfactant and a bis-vinylsulfonyl type hardener.

Film 2 (invention)

As Film 1, but the fresh prepared solution of spectral sensitizing Dye 16 contained also 0.1% of ascorbic acid and 0.25% of sodium acetate. The films were exposed to an EDG sensitometer with a neutral density filter and a Wratten^R 87 filter (manufactured by Eastman Kodak Co.) through a standard step-wedge and developed for 27 seconds at 35 °C in a 3M XAD/2 developer, fixed for 27 seconds at 30 °C, washed with tap water for 22 seconds at 35 °C and dried for 22 seconds at 35 °C in a Trimatic™ XP 515 roller transport processor. The sensitometric results in terms of Dmin and Speed are reported in Table 3. Speed values are expressed in Log E (where E represents exposure in meter-candle-seconds, measured at a density of 1.0 above Dmin).

Table 3

Film	Dmin	Speed
1 (ref.)	0.17	1.85
2 (inv.)	0.17	2.28

Table 3 shows that the film No. 2 of the present invention, containing a fresh prepared solution of spectral sensitizing dye stabilized by ascorbic acid and by sodium acetate presented a relevant speed improvement, still maintaining the same value of Dmin, compared to the reference sample, wherein the fresh prepared solution of spectral sensitizing dye has not been stabilized. Of course, the speed improvement of Film 2 is greater if the solution of spectral sensitizing dye is added to the silver halide emulsion after being kept on shelf life for at least 48 hours, compared with the speed of the reference film 1 using a non-stabilized solution of spectral sensitizing dye added to the silver halide emulsion after 48 hours storage.

EXAMPLE 4

Film 3 (reference)

To 29 gr of an AgCl emulsion (having 0.45 μm average grain size, 9.1% Ag and 5.47% gelatin) were added 120 g of an oil in water dispersion containing 7.2 g of coupler M and 6.72 g of gelatin. The composition was then diluted with 230 ml of water and added with 3% of gelatin. Then, 1.65 g of a 0.1% (w/w) fresh prepared solution of spectral sensitizing Dye 4 in a 9:1 (vol:vol) MeOH/phenylcellosolve solvent mixture, 0.515 g of stabilizer ST and 0.0145 g of supersensitizer SS were added to the composition. The composition was then maintained at 38 °C for 40 minutes. Then, 0.75 g of a 0.1% (w/w) aqueous solution of the antifogging agent AF were added. The composition was coated onto a conventional photographic paper base at a silver coverage of 0.28 g/m^2. The photosensitive layer was overcoated with a protective layer comprising gelatin, a surfactant and a bis-vinylsulfonyl type hardener.

Film 4 (invention)

As Film 3, but the fresh prepared solution of spectral sensitizing Dye 4 also contained 0.10% of ascorbic acid and 0.25% of sodium acetate.

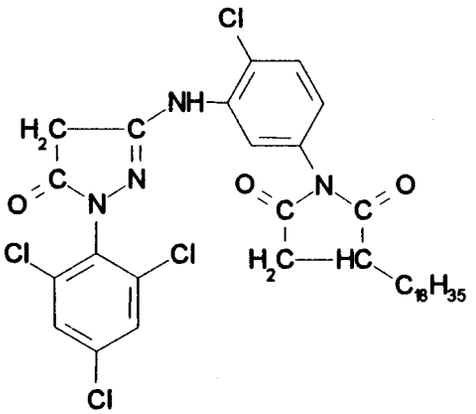
After conditioning for 72 hours at 33 °C, each film was exposed to a laser diode at 820 nm. The exposed coatings were developed in a Kodak RA-4 processing line. Table 4 shows the sensitometric results in terms of Dmin and Speed.

Table 4

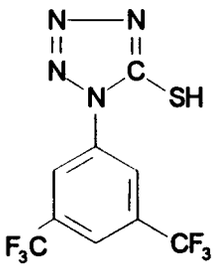
Film	Dmin	Speed
3 (ref.)	0.17	2.70
4 (inv.)	0.17	2.74

Table 4 shows that the film No. 4 of the present invention, containing a fresh prepared solution of spectral sensitizing dye stabilized by ascorbic acid and by sodium acetate presented a little speed improvement, still maintaining the same value of Dmin. As in Example 3, more relevant speed improvement can be obtained if the solutions of spectral sensitizing dyes are added after at least 48 hours from their preparation.

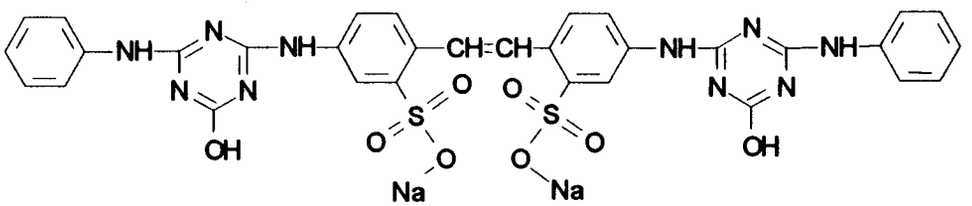
Coupler M



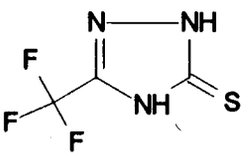
Stabilizer ST



Supersensitizer SS



Antifogging AF



Claims

1. Process for stabilizing solutions of infrared sensitizing dyes comprising adding to said solutions a stabilizing amount of a) an organic reducing agent selected from the group consisting of ascorbic acid, an ascorbic acid isomer, glucose, cyclodextrin and a mixture thereof and of b) an organic or inorganic buffering agent.

2. Process for stabilizing solutions of infrared sensitizing dyes according to claim 1, wherein the organic reducing agent is ascorbic acid.

3. Process for stabilizing solutions of infrared sensitizing dyes according to claim 1, wherein the organic reducing agent is added in an amount of from 5 to 1000 mg for 100 ml of solution containing 0.1% by weight of infrared sensitizing dye.

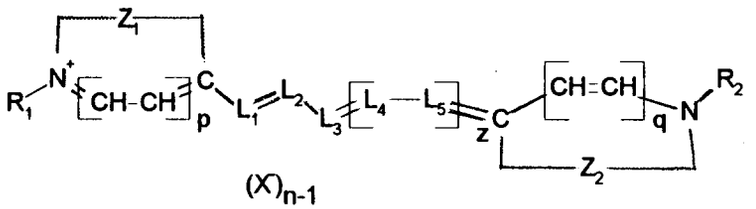
4. Process for stabilizing solutions of infrared sensitizing dyes according to claim 1, wherein the organic reducing agent is added in an amount of from 10 to 300 mg for 100 ml of solution containing 0.1% by weight of infrared sensitizing dye.

5. Process for stabilizing solutions of infrared sensitizing dyes according to claim 1, wherein the buffering agent is sodium acetate.

6. Process for stabilizing solutions of infrared sensitizing dyes according to claim 1, wherein the buffering agent is added in an amount of from 20 to 1000 mg for 100 ml of solution containing 0.1% by weight of infrared sensitizing dye.

7. Process for stabilizing solutions of infrared sensitizing dyes according to claim 1, wherein the buffering agent is added in an amount of from 100 to 500 mg for 100 ml of solution containing 0.1% by weight of infrared sensitizing dye.

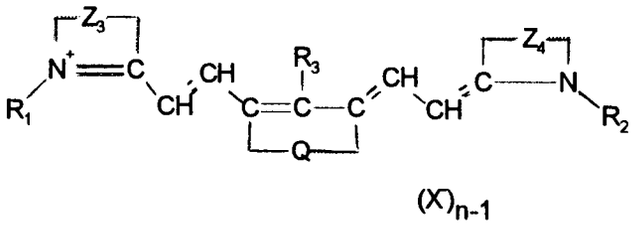
8. Process for stabilizing solutions of infrared sensitizing dyes according to claim 1, wherein said infrared sensitizing dyes are represented by the following formula:



(I)

wherein,
Z_1 and Z_2 each independently represents the atoms necessary to complete a 5- or 6-membered heterocyclic nucleus,
R_1 and R_2 each independently represents an alkyl group,
L_1, L_2, L_3, L_4 and L_5 each independently represents a methine group,
X^- represents an anion,
n represents an integer of 1 to 2, provided that n is 1 when the dye forms an intramolecular salt,
p and q each independently represents 0 or 1, and
z represents 2.

9. Process for stabilizing solutions of infrared sensitizing dyes according to claim 1, wherein said infrared sensitizing dyes are represented by the following formula:



(II)

$(X)_{n-1}$

wherein,

Z_3 and Z_4 each independently represents the atoms necessary to complete a thiazole nucleus, an oxazole nucleus or a selenazole nucleus,

Q represents the atoms necessary to complete a 5- or 6-membered carbocyclic ring,

R_1 and R_2 each independently represents an alkyl group,

R_3 represents hydrogen, alkyl, aryl, cyano, halogen or $-NR_4R_5$, wherein R_4 and R_5 each independently represents alkyl or aryl or together represent the non-metallic atoms necessary to form a 5- or 6-membered heterocyclic ring,

X^- represents an anion, and

n represents an integer of 1 to 2, provided that n is 1 when the dye forms an intramolecular salt.

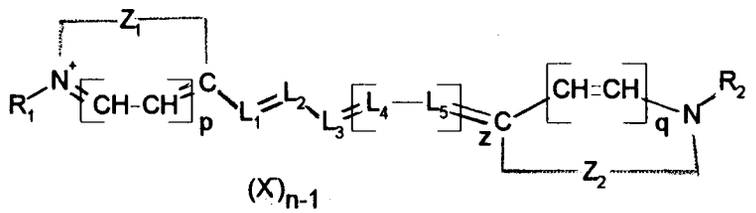
10. Process for stabilizing solutions of infrared sensitizing dyes according to claim 9, wherein R_3 represents the atoms necessary to complete a 5-membered N-containing aromatic ring selected in the group consisting of pyrazole, triazole, imidazole and pyrrole.

11. A silver halide photographic element comprising a support, at least one infrared sensitive silver halide emulsion photosensitive layer and at least one hydrophilic colloid non photosensitive layer wherein at least one infrared sensitive layer contains an infrared sensitizing dye, an organic reducing agent selected from the group consisting of ascorbic acid, an ascorbic acid isomer, glucose, cyclodextrin and a mixture thereof, and an organic or inorganic buffering agent.

12. A silver halide photographic element according to claim 11, wherein the organic reducing agent is ascorbic acid.

13. A silver halide photographic element according to claim 11, wherein the buffering agent is sodium acetate.

14. A silver halide photographic element according to claim 11, wherein said infrared sensitizing dye is represented by the following formula:



(I)

$(X)_{n-1}$

wherein,

Z_1 and Z_2 each independently represents the atoms necessary to complete a 5- or 6-membered heterocyclic nucleus,

R_1 and R_2 each independently represents an alkyl group,

L_1, L_2, L_3, L_4 and L_5 each independently represents a methine group,

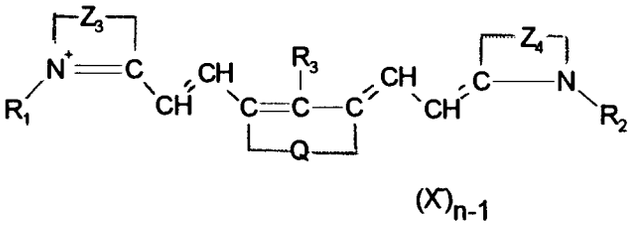
X^- represents an anion,

n represents an integer of 1 to 2, provided that n is 1 when the dye forms an intramolecular salt,

p and q each independently represents 0 or 1, and

z represents 2.

15. A silver halide photographic element according to claim 11, wherein said infrared sensitizing dye is represented by the following formula:



(II)

wherein,

Z_3 and Z_4 each independently represents the atoms necessary to complete a thiazole nucleus, an oxazole nucleus or a selenazole nucleus,

Q represents the atoms necessary to complete a 5- or 6-membered carbocyclic ring,

R_1 and R_2 each independently represents an alkyl group,

R_3 represents hydrogen, alkyl of 1 to 4 carbon atoms, aryl, cyano, halogen or $-NR_4R_5$, wherein R_4 and R_5 each independently represents alkyl of 1 to 6 carbon atoms or aryl or together represent the non-metallic atoms necessary to form a 5- or 6-membered heterocyclic ring,

X^- represents an anion, and

n represents an integer of 1 to 2, provided that n is 1 when the dye forms an intramolecular salt.

16. A silver halide photographic element according to claim 15, wherein R_3 represents the atoms necessary to complete a 5-membered N-containing aromatic ring selected in the group consisting of pyrazole, triazole, imidazole and pyrrole.

17. A silver halide photographic element according to claim 11, wherein the dye is in an amount of $5x10^{-7}$ $5x10^{-3}$ mole per mole of silver.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 10 1874

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)
X	DATABASE WPI Section PQ, Week 7633, Derwent Publications Ltd., London, GB; Class P83, AN 76-62327X & JP-A-51 075 432 (FUJI PHOTO FILM CO. LTD.) 1 July 1976 * abstract *	1-10	G03C1/005 G03C5/16 G03C1/20 G03C1/28
A	PATENT ABSTRACTS OF JAPAN vol. 12, no. 76 (P-675) (2923) 10 March 1988 & JP-A-62 215 261 (FUJI PHOTO FILM CO. LTD.) 21 September 1987 * abstract *	1-10	
A	PATENT ABSTRACTS OF JAPAN vol. 11, no. 156 (P-578) (2603) 21 May 1987 & JP-A-61 290 441 (KONISHIROKU PHOTO-INDUSTRY CO. LTD.) 20 December 1986 * abstract *	1-10	TECHNICAL FIELDS SEARCHED (Int.Cl.6) G03C
A	EP-A-0 568 850 (E.I.DU PONT DE NEMOURS AND CO.) * page 3, line 51 - page 4, line 1; examples 5-13,22 *	1-10	
X	US-A-4 897 343 (T IKEDA ET AL) * column 21, line 53 - line 62; claims 1-10 *	11-17	
X	US-A-3 695 888 (GARY L HILLER ET AL) * column 8, line 28 - column 9, line 53; claim 1; example 2; table II *	11-17	

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	12 July 1994	Bolger, W

CATEGORY OF CITED DOCUMENTS

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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)
D,A	US-A-4 917 997 (T IKEDA ET AL) * column 14, line 35 - line 48 * *compound II-12* *table 5,test nos. 1,2*	11-17	
A	US-A-3 753 721 (ALLAN G MILLIKAN) * column 6, line 63 - column 8, line 17 * * column 24, line 53 - column 26, line 10; table III *	11-17	
D,A	US-A-5 037 734 (JEROME R LENHARD ET AL) * claims 1,13; examples 1,2 *	11-17	
A	G HAIST 'MODERNOHOTOGRAPHIC PROCESSING VOLUME 1' 1979 , JOHN WILEY AND SONS , NEW YORK * page 246 *	1,11	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)

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