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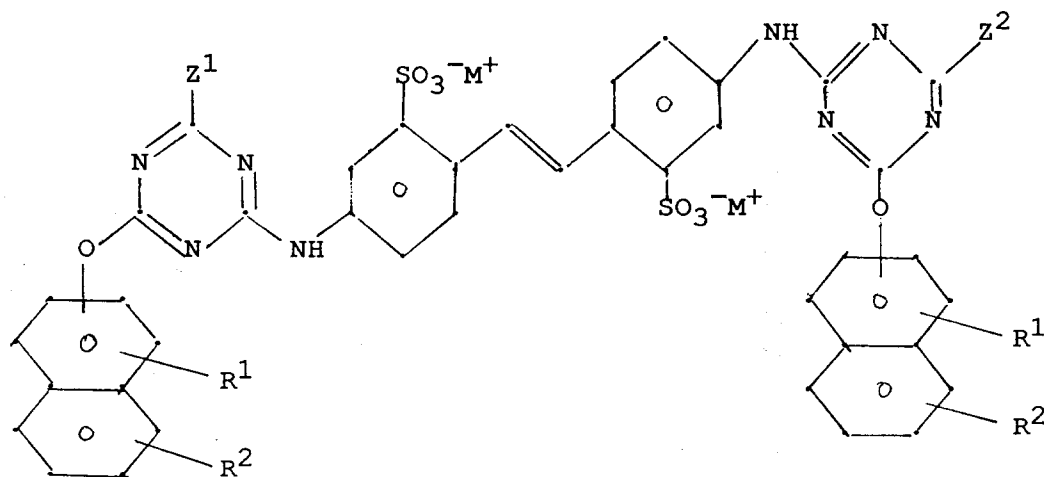
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B-2640 Mortsel (BE)**(54) **Stilbene compounds as supersensitizers in infrared sensitive photographic materials.**

(57) A photographic material is disclosed comprising a support and at least one emulsion layer containing a silver halide emulsion, an infra-red sensitizer and a stilbene compound corresponding to general formula (SS-Ia) :



(SS-Ia)

wherein M represents a hydrogen ion or a monovalent cation,

R¹ and R² each independently represent hydrogen, alkyl, alkoxy, NR³R⁴, SO₂R³, COOR³, CONR³R⁴, NR³COR⁴, or SO₃M, andZ¹ and Z² each independently represent Cl, OH, NR³R⁴, OR⁵ or SR⁵, and,R³, R⁴ and R⁵ each independently represent alkyl, aryl or hydrogen.

The most effective compounds bear in total four naphthoxy substituents on the triazine nuclei.

1. Field of the invention.

The present invention relates to infrared sensitized photographic emulsions and materials, and more particularly to a specific class of supersensitizers for the infra-red spectral region.

2. Background of the invention.

Infra-red sensitized photographic materials are known for quite some time in photographic technology. One of the well-known early applications was and still is in aerial photography. The most familiar classes of infra-red sensitizing substances are long-chain cyanine dyes. Suitable infra-red sensitizing dyes are disclosed in e.g. US-P Nos 2,095,854, 2,095,856, 2,955,939, 3,482,978, 3,552,974, 3,573,921, 3,582,344, 3,623,881 and 3,695,888.

In recent years new techniques of image recording have emerged wherein the exposure source of the recording apparatus is a laser unit. For instance, one application of lasers as exposure units is situated in the field of radiographic monitoring photography where a hard copy of radiographic information has to be produced. Other applications are situated in the pre-press field of phototype-setting and image-setting, where recorders are marketed which employ Ar ion lasers, He-Ne lasers or solid state semiconductor lasers, also called laserdiodes, as exposure source. The latter type of laser, the laserdiode, shows some advantages compared to other laser types such as low cost price, small size, long life time and no need for an acoustic-optical modulator. Generally the emission wavelength of these semiconductor laser beams is longer than 700 nm and mostly longer than 750 nm. So photographic materials appropriate for exposure by devices employing such laserdiodes must be sensitized for the near infra-red region of the radiation spectrum. Suitable photographic materials to be used with semiconductor laser device are disclosed in Japanese Unexamined Patent Publication (Kokai) No 61752/85 and US-P 4,784,933. Commercial infra-red sensitized film and paper were announced by Eastman Kodak Co in "Proceedings Lasers in Graphics, Electronic Publishing in the '80's, Vol 2 (sept. 1985) p. 508, and put on the market later on. Other manufacturers followed including Agfa-Gevaert N.V. and Fuji Photo Film Co. An example of an image-setter using a laserdiode exposure is the PROSET 9800 apparatus marketed by Miles Inc., Agfa division.

A permanent problem in the field of imaging by laserdiodes is the sensitivity level of the infra-red sensitized photographic material. A first reason for that is made up by the low energy output of the laserdiode which is in the order of a few milli-Watts. A second problem consists in the usually poor storage quality of emulsions sensitized with long-chain cyanine dyes unless considerable amounts of stabilizers are used ; however it is generally known that such a strong stabilization tends to reduce the original sensitivity level.

An at least partial remedy for the sensitivity problems in infra-red photographic materials was found in the use of so-called "supersensitizers".

Supersensitization can be achieved by a combination of at least two spectral sensitizers giving rise to a level of sensitization in some spectral region which is greater than that which would result from any concentration of either dye alone or from the mere additive effect of the dyes. Alternatively, supersensitization can be achieved with selected combinations of spectral sensitizing dyes and other addenda such as stabilizers, anti-foggants, development accelerators or inhibitors, coating aids, brighteners and antistatic agents. A general review on supersensitization is given in James, The Theory of the Photographic Process, Fourth Edition, 1977, pp. 259-265. Several possible mechanisms concerning supersensitization are discussed by Gilman, Photographic Science and Engineering, Vol. 18, 1974, pp. 418-430.

A class of effective supersensitizers, described in Research Disclosure Item 28952, published in May 1988, comprises water-soluble heterocyclic mercapto-compounds containing a thiazole, benzothiazole, naphthothiazole, or quinoline ring system, which ring system may be substituted or not, and also comprising at least one electronegative group e.g. halogen, sulfo, sulphonamide, carboxy and phenyl. These compounds are preferably combined with penta- or heptamethine cyanine dyes, or tetramethine merocyanine dyes sensitizing in the near infra-red spectral region.

Stilbene derivatives are known for a long time in the art as effective supersensitizers in combination with infra-red sensitizing dyes. For instance, US 3,695,888, issued 3 Oct. 1972, discloses sulphonated bis-(1,3,5-triazine-2-ylamino)-stilbene compounds in combination with some particular type of tricarbocyanine dyes. US 4,603,104 claims the combination of infra-red sensitized emulsions, bis(1,3,5-triazine-2-ylamino)-stilbene compounds and some particular stabilizers, e.g. arylmercaptotetrazoles. US 4,677,053 discloses infra-red sensitizers containing a quinoline nucleus in combination with bis(1,3,5-triazine-2-ylamino)-stilbenes. Unexamined Japanese Patent Publication 61-134755 describes the combination of benzopyrrolocyanine dye and a bis-triazinyl- or bis-pyrimidyl-iminostilbene. Unexamined Japanese Patent

Publications 62-035343 and 01-097947 disclose some hexamethine rhodanine type sensitizers in combination with stilbene derivatives.

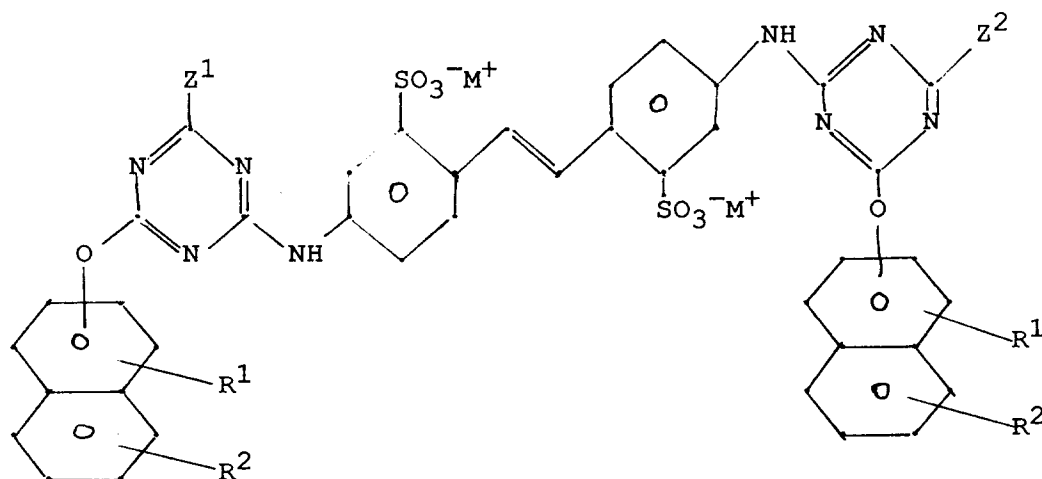
The present invention extends the teachings on stilbene compounds as useful supersensitizers for the near infra-red region.

Although the sensitivity of infra-red materials is greatly improved by the use of supersensitizers it can still be insufficient due to the low energy output of laserdiodes. So there is a permanent need for new ways or new compounds for enhancing the sensitivity. Several explicitly described stilbene derivatives proved to be still insufficiently effective supersensitizers.

It is the object of the present invention to provide photographic emulsions and materials containing supersensitizers which in combination with infra-red sensitizing dyes give rise to adequate sensitivity when exposed by a laserdiode.

3. Summary of the invention.

The objects of the present invention are realized by providing a photographic material comprising a support and at least one emulsion layer containing a silver halide emulsion, an infrared sensitizer and a stilbene compound corresponding to general formula (SS-Ia):



(SS-Ia)

wherein M represents a hydrogen ion or a monovalent cation,

R¹ and R² each independently represent hydrogen, alkyl, alkoxy, NR³R⁴, SO₂R³, COOR³, CONR³R⁴, NR³COR⁴, or SO₃M, and

Z¹ and Z² each independently represent Cl, OH, NR³R⁴, OR⁵ or SR⁵, and,

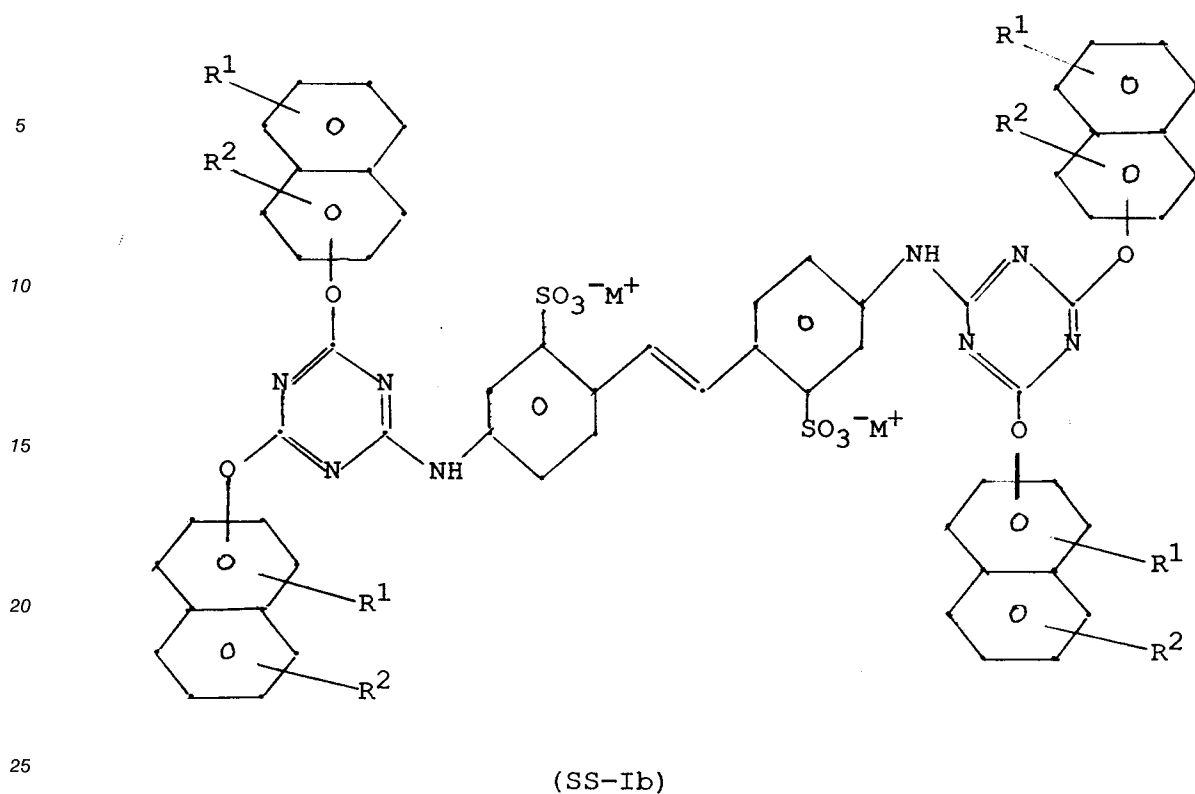
R³, R⁴ and R⁵ each independently represent alkyl, aryl or hydrogen.

The most effective supersensitizers are those where Z¹ and Z² represent naphthoxy groups too, thus making a total of four unsubstituted or substituted naphthoxy groups on the triazine nuclei.

Although the compounds represented by formule (SS-Ia) belong to a general class of stilbenes known from the cited prior art it was not recognized until now that substitution on the triazine nuclei by at least two and preferably four naphthoxy groups would give rise to a class of superior supersensitizers.

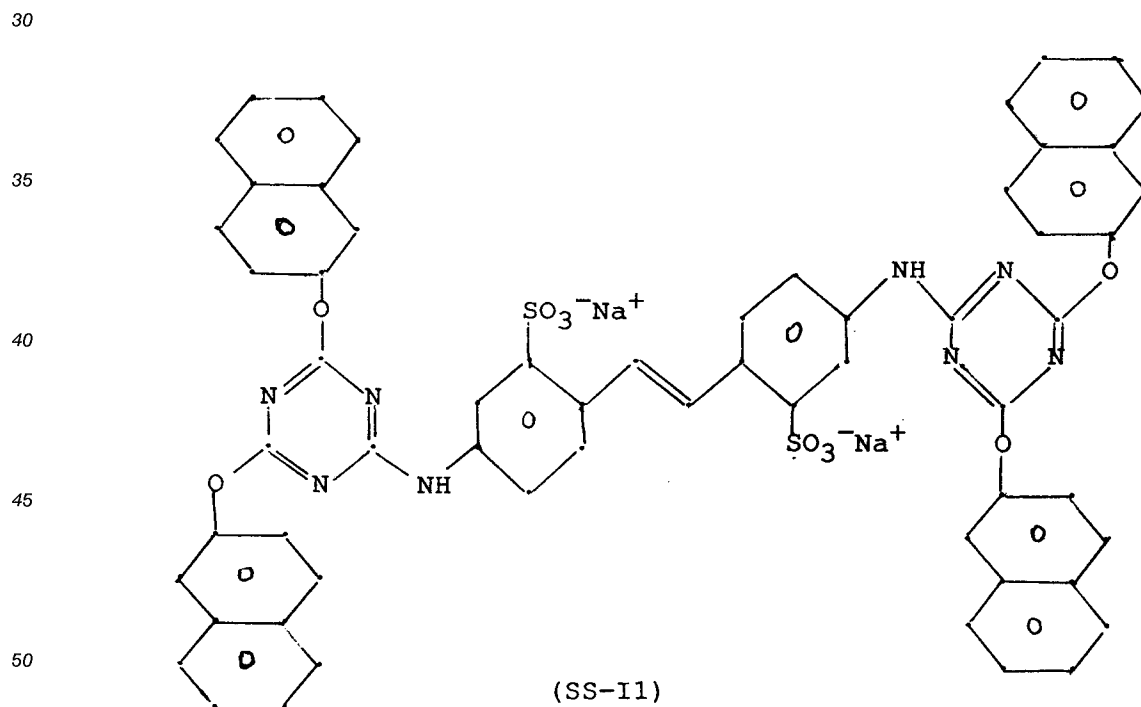
4. Detailed description of the invention.

As stated above a preferred class of stilbene derivatives is formed by those whose two triazine nuclei each bear two unsubstituted or substituted naphthoxy groups (four naphthoxy groups in total), given by general formula (SS-Ib):

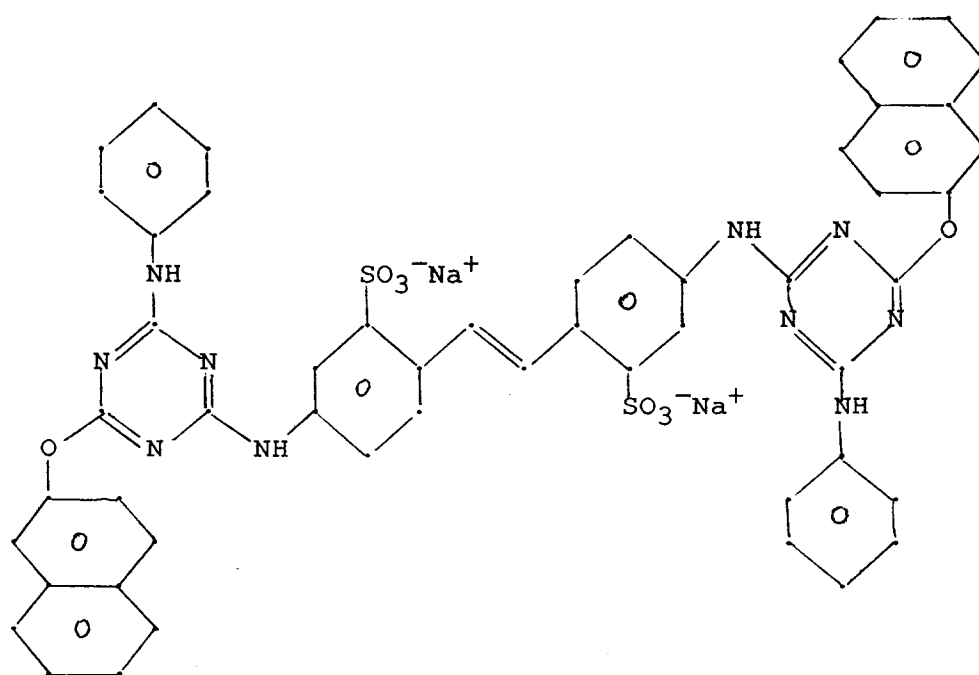


wherein the different R groups have the same meaning as in general formula (SS-Ia).

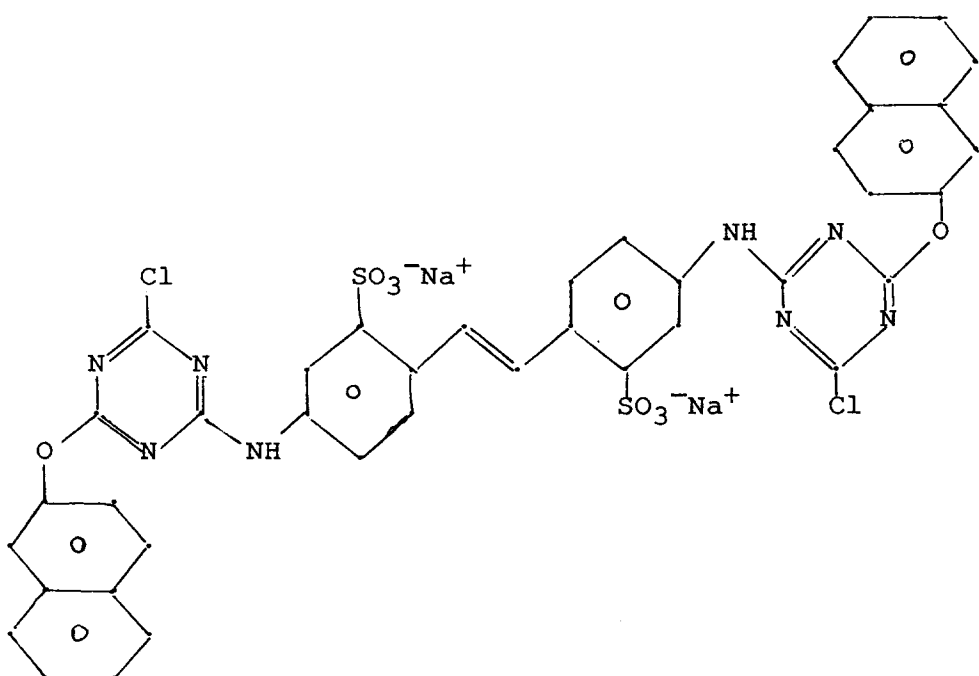
A most preferred supersensitizer according to general formula (SS-Ib) is represented by:



Other preferred stilbene supersensitizers for use in accordance with the present invention bearing only one naphthoxy group on each triazine nucleus are represented by following formulae SS-I2 and SS-I3 :



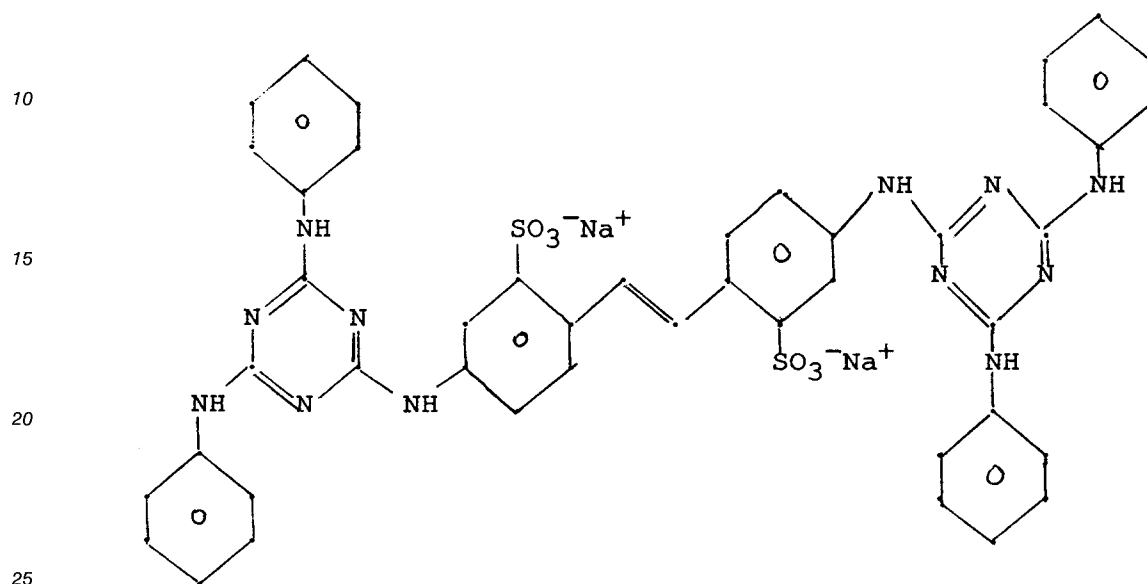
(SS-I2)



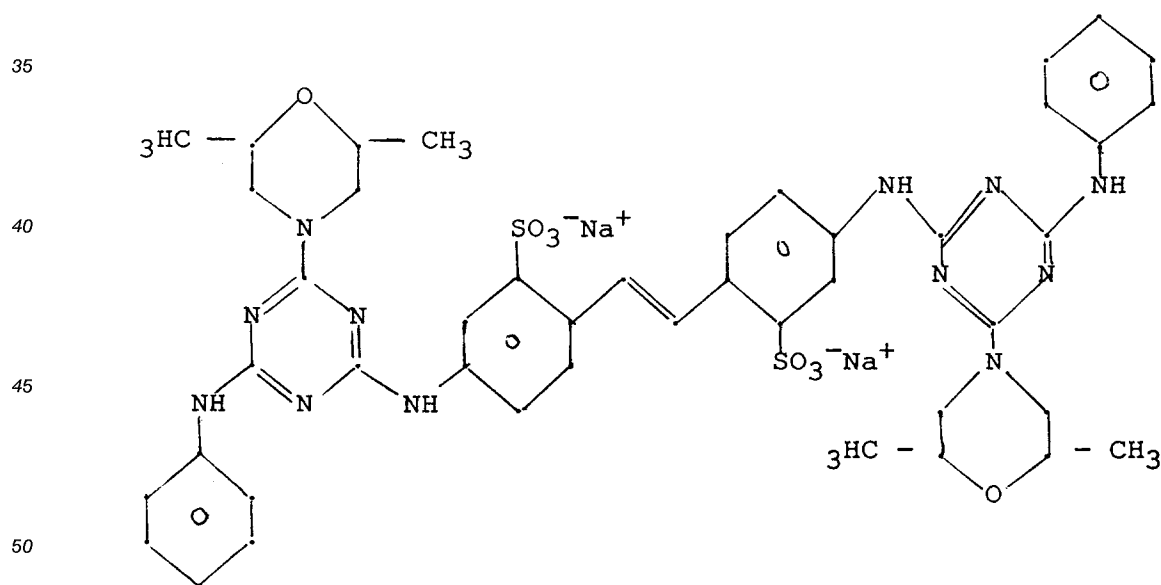
SS-I3

It will be easily recognized that the stilbene derivatives can exhibit cis-trans isomerism around the central double bond. It was experimentally found by us that for compounds SS-I1 and SS-I2 the actual isomeric form (cis, trans or a mixture of both) did not influence their photographic behavior.

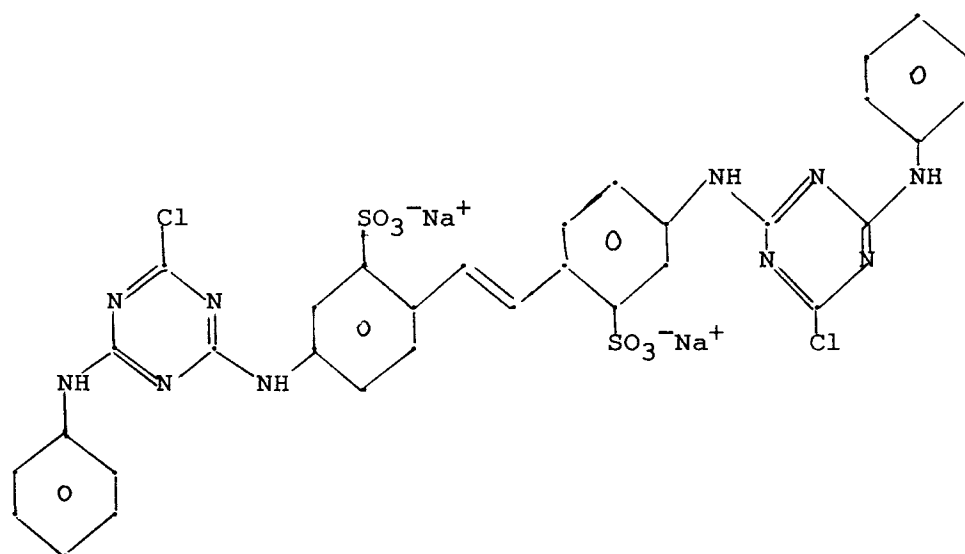
Stilbene compounds not belonging to the scope of the invention but useful as control compounds in
5 photographic examples (see later) are listed below :



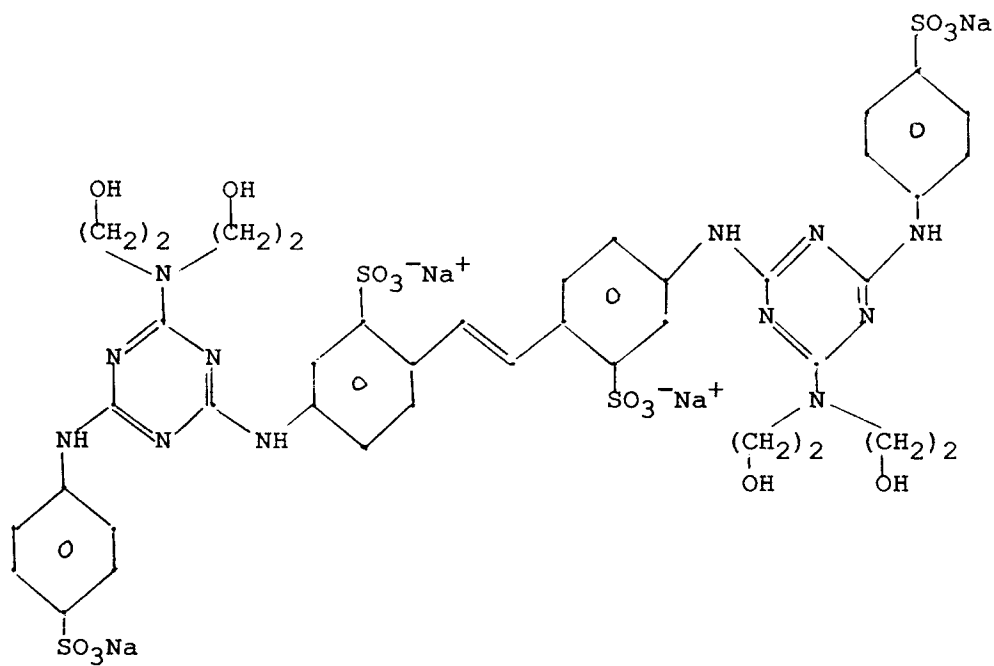
(SS-C1)



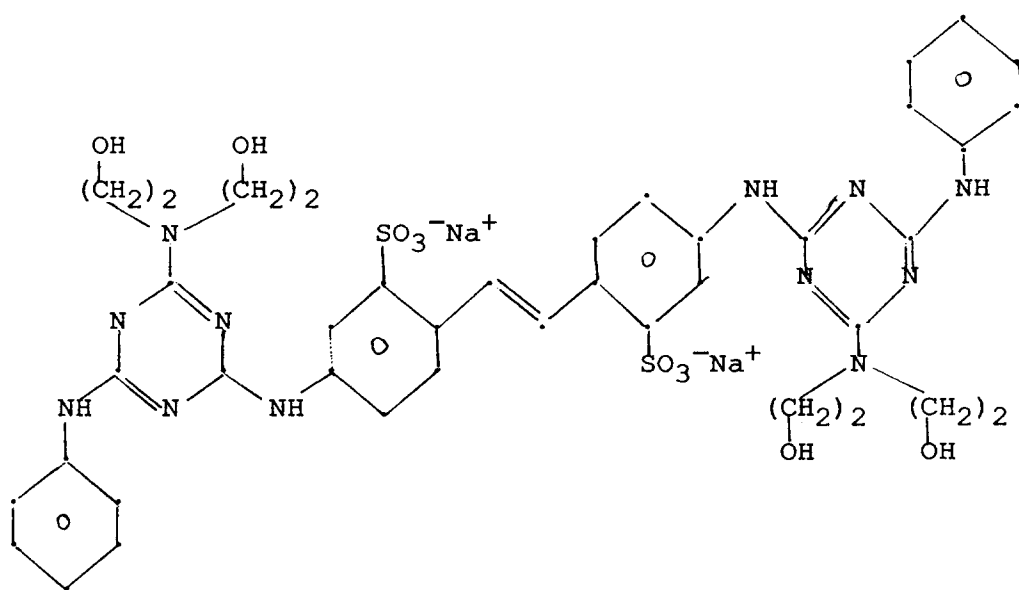
(SS-C2)



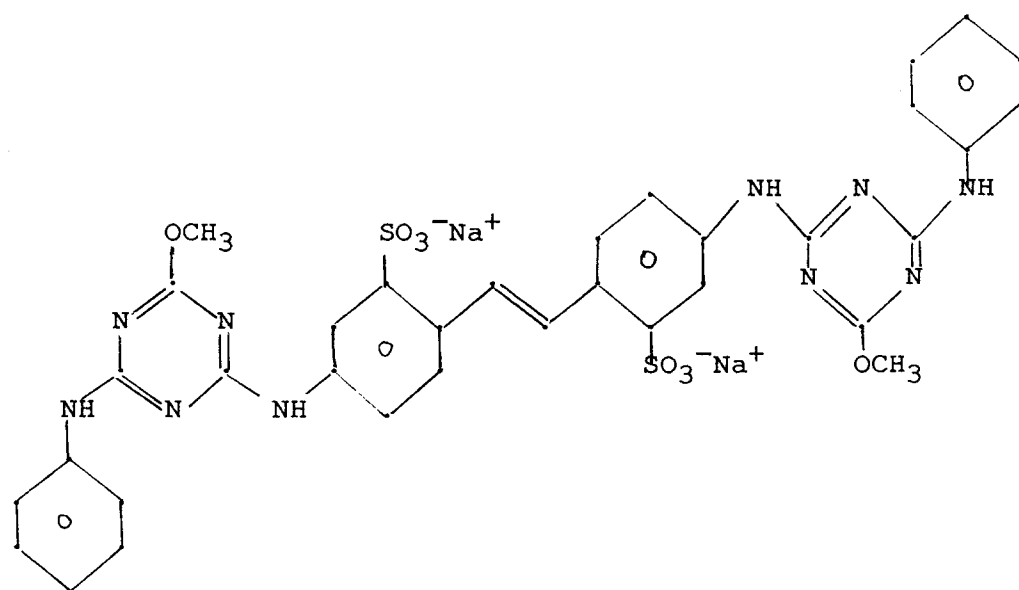
(SS-C3)



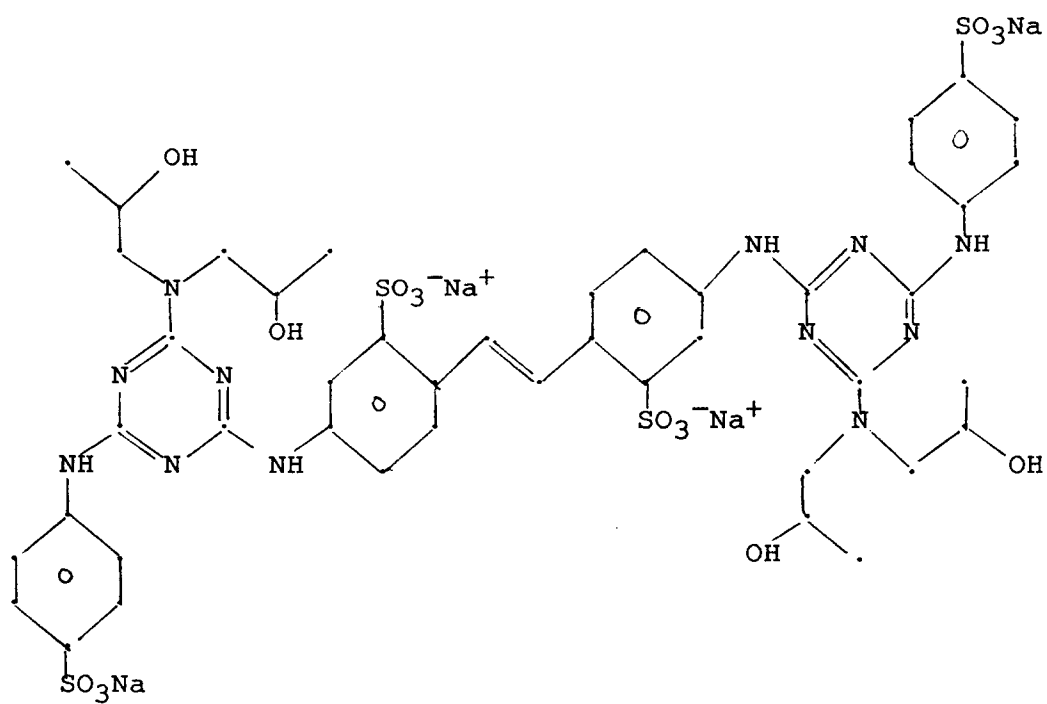
(SS-C4)



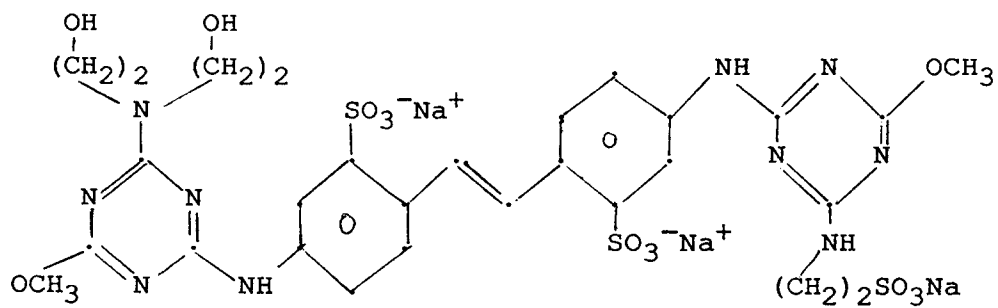
(SS-C5)



(SS-C6)



(SS-C7)



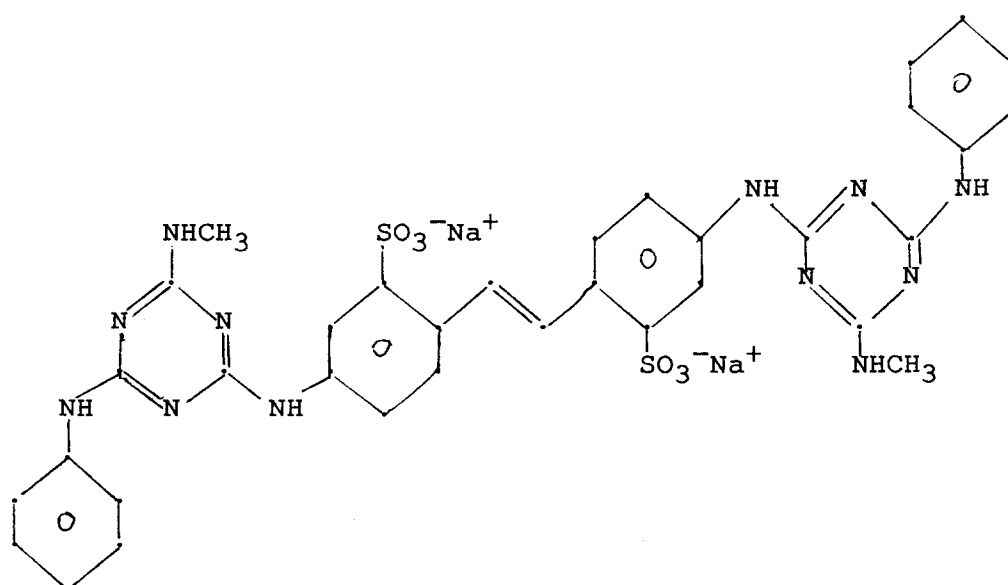
(SS-C8)

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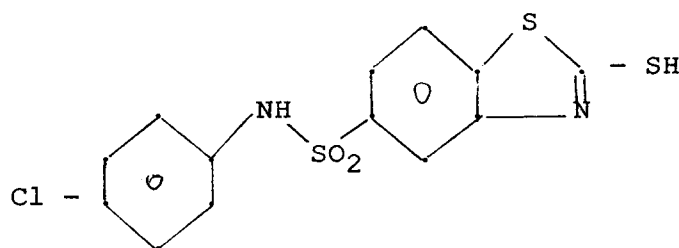
(SS-C9)

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A conventional non-stilbene control supersensitizer is compound SHM1 from Research Disclosure 28952, cited above. This compound is designated as SS-C10 furtheron in the photographic examples:

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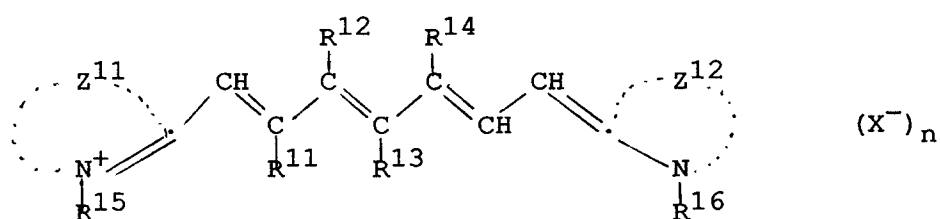
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(SS-C10)

Preferred infra-red sensitizing dyes used in accordance with the present invention are heptamethine chain containing infra-red sensitizers represented by general formula :

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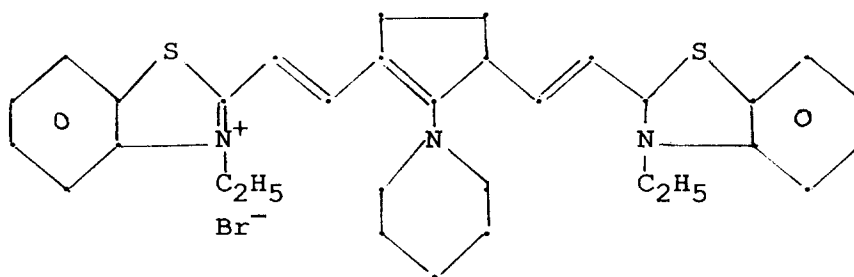
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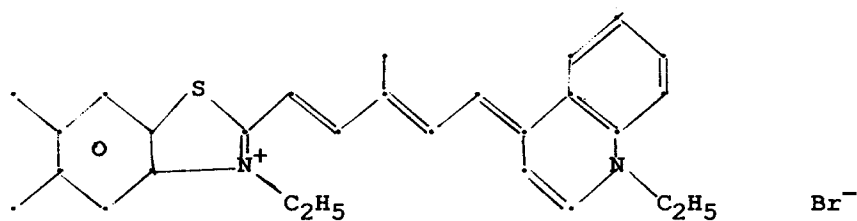
wherein,

- Z^{11} and Z^{12} each represent a non-metallic atomic group necessary to complete a benzothiazole, benzoxazole, naphthothiazole, naphthoxazole or quinoline nucleus; R^{15} and R^{16} each represent an alkyl or substituted alkyl group;
- R^{11} , R^{12} , R^{13} , and R^{14} each represent a hydrogen atom, a substituted or unsubstituted alkyl, alkoxy, amino, phenyl or benzyl group; R^{11} and R^{13} , or R^{12} and R^{14} respectively may combine with each other to form a substituted or unsubstituted 5- or 6-membered ring;
- X^- is an anion of the type commonly present in sensitizing dyes, e.g. bromide, chloride, iodide, methyl sulphate, p-tolyl sulphate; n is 0 or 1 (0 in case of an intramolecular salt via an anionic group in R^{15}).

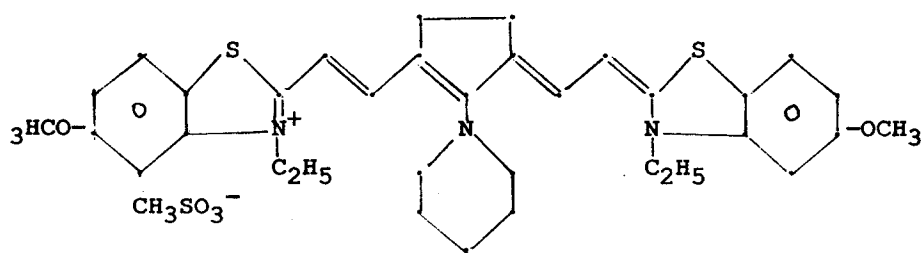
Useful specific examples of IR-sensitizers represented by this general formula are the following compounds :



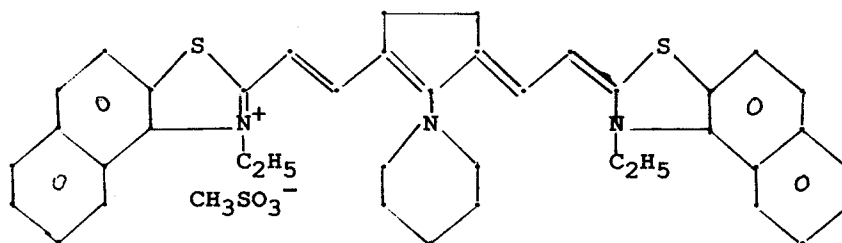
IRS-1



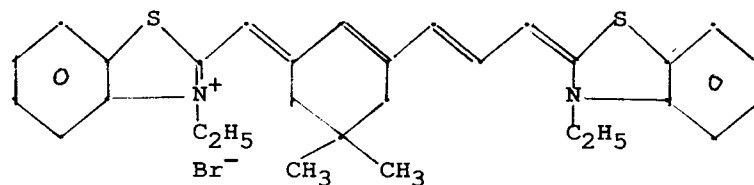
IRS-2



IRS-3



IRS-4



IRS-5

The infra-red sensitizing dyes and the supersensitizers in connection with the present invention are all incorporated in the emulsion layer(s) of the photographic material in order to exercise their photographic functions properly. The IR-sensitizers are usually added as solutions in an organic solvent. The supersensitizers are preferably added as methanolic solutions in a concentration ranging from about 0.1 % to about 1 %. The solubility in methanol depends on the cationic form. For instance, the lithium salt analogue of

compound (SS-I1) is better soluble (about 1 %) than the sodium salt (about 0.3 %). Once added to an aqueous photographic coating solution the supersensitizers used in accordance with the present invention remain dissolved without problems, which, for instance, is not the case with the compound, analogue to preferred compound (SS-I1) but bearing phenoxy substituents instead of naphthoxy ones.

5 The stilbene supersensitizers are preferably added to the silver halide emulsion in a concentration ranging from 0.01 mmole to 10 mmole per mole of silver halide. The infra-red sensitizing dyes are present in the emulsion preferably in a concentration between 0.01 mole and 1 mmole per mole of silver halide. The supersensitizers are added preferably before the infra-red sensitizing dyes, but they can be added also after the sensitizers or simultaneously. In normal practice only one effective supersensitizer is added but in
10 principle a mixture of more than one can be used.

For most purposes the emulsion layer of the photographic material consists of a single layer but principally a double or even a multiple emulsion layer can be present.

The halide composition of the silver halide emulsions used according to the present invention is not specifically limited and may be any composition selected from e.g. silver chloride, silver bromide, silver
15 iodide, silver chlorobromide, silver bromiodide, and silver chlorobromiodide.

The photographic emulsions can be prepared from soluble silver salts and soluble halides according to different methods as described e.g. by P. Glaucidès in "Chimie et Physique Photographique", Paul Montel, Paris (1967), by G.F. Duffin in "Photographic Emulsion Chemistry", The Focal Press, London (1966), and by V.L. Zelikman et al in "Making and Coating Photographic Emulsion", The Focal Press, London (1966).

20 They can be prepared by mixing the halide and silver solutions in partially or fully controlled conditions of temperature, concentrations, sequence of addition, and rates of addition. The silver halide can be precipitated according to the single-jet method, the double-jet method, the conversion method or an alternation of these different methods.

The silver halide particles of the photographic emulsions used according to the present invention may
25 have a regular crystalline form such as a cubic or octahedral form or they may have a transition form. They may also have an irregular crystalline form such as a spherical form or a tabular form, or may otherwise have a composite crystal form comprising a mixture of said regular and irregular crystalline forms.

The silver halide grains may have a multilayered grain structure. According to a simple embodiment the grains may comprise a core and a shell, which may have different halide compositions and/or may have
30 undergone different modifications such as the addition of dopes. Besides having a differently composed core and shell the silver halide grains may also comprise different phases inbetween.

Two or more types of silver halide emulsions that have been prepared differently can be mixed for forming a photographic emulsion for use in accordance with the present invention.

The average size of the silver halide grains may range from 0.05 to 1.0 micron, preferably from 0.2 to
35 0.5 micron. The size distribution of the silver halide particles can be homodisperse or heterodisperse.

The silver halide crystals can be doped with Rh^{3+} , Ir^{4+} , Cd^{2+} , Zn^{2+} or Pb^{2+} .

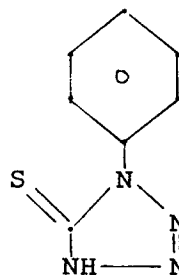
The emulsion can be desalted in the usual ways e.g. by dialysis, by flocculation and re-dispersing, or by ultrafiltration.

The light-sensitive silver halide emulsions are preferably chemically sensitized as described e.g. in the
40 above-mentioned "Chimie et Physique Photographique" by P. Glaucidès, in the above-mentioned "Photographic Emulsion Chemistry" by G.F. Duffin, in the above-mentioned "Making and Coating Photographic Emulsion" by V.L. Zelikman et al, and in "Die Grundlagen der Photographischen Prozesse mit Silberhalogeniden" edited by H. Frieser and published by Akademische Verlagsgesellschaft (1968). As described in said literature chemical sensitization can be carried out by effecting the ripening in the
45 presence of small amounts of compounds containing sulphur e.g. thiosulphate, thiocyanate, thioureas, sulphites, mercapto compounds, and rhodamines. The emulsions can be sensitized also by means of gold-sulphur ripeners or by means of reducers e.g. tin compounds as described in GB 789,823, amines, hydrazine derivatives, formamidine-sulphinic acids, and silane compounds. Chemical sensitization can also be performed with small amounts of Ir, Rh, Ru, Pb, Cd, Hg, Tl, Pd, Pt, or Au. One of these chemical
50 sensitization methods or a combination thereof can be used.

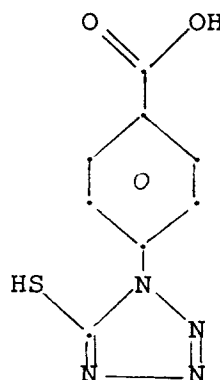
The silver halide emulsion(s) for use in accordance with the present invention may comprise compounds preventing the formation of fog or stabilizing the photographic characteristics during the production or storage of photographic elements or during the photographic treatment thereof. Many known compounds can be added as fog-inhibiting agent or stabilizer to the silver halide emulsion. Suitable examples are e.g.
55 the heterocyclic nitrogen-containing compounds such as benzothiazolium salts, nitroimidazoles, nitrobenzimidazoles, chlorobenzimidazoles, bromobenzimidazoles, mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiadiazoles, aminotriazoles, benzotriazoles, nitrobenzotriazoles, mercaptotetrazoles, mercaptopyrimidines, mercaptotriazines, benzothiazoline-2-thione, oxazoline-thione, triazin-

denes, tetrazindenes and pentazindenes, especially those described by Birr in Z. Wiss. Phot. 47 (1952), pages 2-58, triazolopyrimidines such as those described in GB 1,203,757, GB 1,209,146, JA-Appl. 75-39537, and GB 1,500,278, and 7-hydroxy-s-triazolo-[1,5-a]-pyrimidines as described in US 4,727,017, and other compounds such as benzenethiosulphonic acid, benzenethiosulphinic acid and benzenethiosulphonic acid amide. Other compounds that can be used as fog-inhibiting compounds are metal salts such as e.g. mercury or cadmium salts and the compounds described in Research Disclosure N° 17643 (1978), Chapter VI.

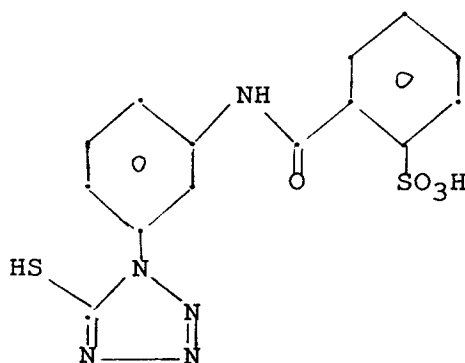
Particularly useful stabilizer compounds in the practice of this invention are substituted mercap-
totetrazoles, examples of which are listed below:



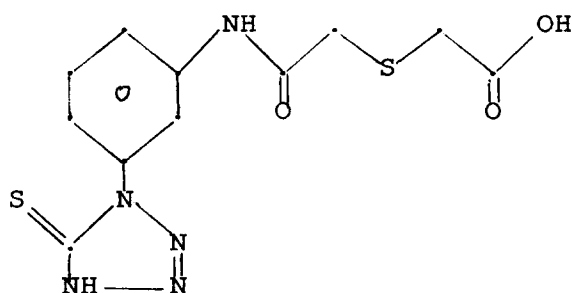
St-1



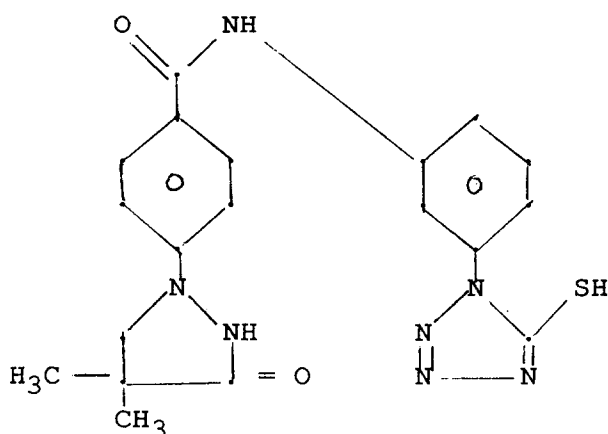
St-2



St-3



St-4



St-5

It was found by us that the nature and concentration of the mercaptotetrazole used played a crucial role in obtaining the maximally reachable sensitivity even when the optimal combination of infra-red sensitizer and supersensitizer was chosen. This will be illustrated with an example furtheron.

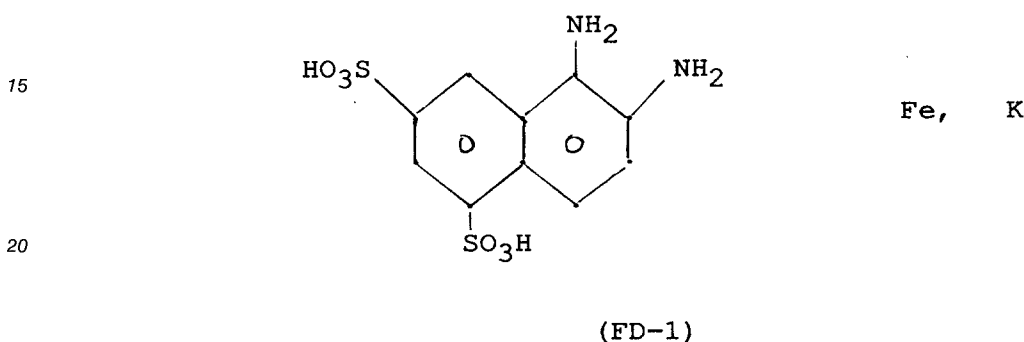
The fog-inhibiting agents or stabilizers can be added to the silver halide emulsion prior to, during, or after the ripening thereof and mixtures of two or more of these compounds can be used.

Besides the silver halide another essential component of a light-sensitive emulsion layer is the binder. The binder is a hydrophilic colloid, preferably gelatin. Gelatin can, however, be replaced in part or integrally by synthetic, semi-synthetic, or natural polymers. Synthetic substitutes for gelatin are e.g. polyvinyl alcohol, poly-N-vinyl pyrrolidone, polyvinyl imidazole, polyvinyl pyrazole, polyacrylamide, polyacrylic acid, and derivatives thereof, in particular copolymers thereof. Natural substitutes for gelatin are e.g. other proteins such as zein, albumin and casein, cellulose, saccharides, starch, and alginates. In general, the semi-synthetic substitutes for gelatin are modified natural products e.g. gelatin derivatives obtained by conversion of gelatin with alkylating or acylating agents or by grafting of polymerizable monomers on gelatin, and cellulose derivatives such as hydroxyalkyl cellulose, carboxymethyl cellulose, phthaloyl cellulose, and cellulose sulphates.

The binders of the photographic element, especially when the binder used is gelatin, can be hardened with appropriate hardening agents such as those of the epoxide type, those of the ethylenimine type, those of the vinylsulfone type e.g. 1,3-vinylsulphonyl-2-propanol, chromium salts e.g. chromium acetate and chromium alum, aldehydes e.g. formaldehyde, glyoxal, and glutaraldehyde, N-methylol compounds e.g. dimethylolurea and methyloldimethylhydantoin, dioxan derivatives e.g. 2,3-dihydroxy-dioxan, active vinyl compounds e.g. 1,3,5-triacryloyl-hexahydro-s-triazine, active halogen compounds e.g. 2,4-dichloro-6-hydroxy-s-triazine, and mucohalogenic acids e.g. mucochloric acid and mucophenoxychloric acid. These

hardeners can be used alone or in combination. The binders can also be hardened with fast-reacting hardeners such as carbamoylpyridinium salts as disclosed in US 4,063,952.

Beside the light sensitive emulsion layer(s) the photographic material can contain several non light sensitive layers, e.g. a protective top layer, one or more backing layers, and one or more intermediate layers which can contain light-absorbing dyes. Suitable light-absorbing dyes are described in e.g. US 4,092,168, US 4,311,787 and DE 2,453,217. Such light-absorbing dyes can exercise several photographic functions. They can be used as filter dyes. They can also function as so-called screening dyes in order to promote image sharpness. Very important is the use of light-absorbing dyes as antihalation dyes in order to reduce the reflection of light by a transparent support onto the light sensitive layer(s). A preferred infrared absorbing dye is represented by following formula (FD-1) :



The infra-red sensitized photographic materials of the present invention are preferably manufactured and treated in severe safelight conditions, e.g. faint cyan light, or in total darkness.

One or more backing layers can be provided at the non-light sensitive side of the support. These layers which can serve as anti-curl layer can contain e.g. lubricants, antistatic agents, light absorbing dyes, matting agents, silica, etc.

The photographic element of the present invention may further comprise various kinds of surface-active agents in the photographic emulsion layer or in at least one other hydrophilic colloid layer. Suitable surface-active agents include non-ionic agents such as saponins, alkylene oxides e.g. polyethylene glycol, polyethylene glycol/polypropylene glycol condensation products, polyethylene glycol alkyl ethers or polyethylene glycol alkylaryl ethers, polyethylene glycol esters, polyethylene glycol sorbitan esters, polyalkylene glycol alkylamines or alkylamides, silicone-polyethylene oxide adducts, glycidol derivatives, fatty acid esters of polyhydric alcohols and alkyl esters of saccharides; anionic agents comprising an acid group such as a carboxy, sulfo, phospho, sulphuric or phosphoric ester group; ampholytic agents such as aminoacids, aminoalkyl sulphonic acids, aminoalkyl sulphates or phosphates, alkyl betaines, and amine-N-oxides; and cationic agents such as alkylamine salts, aliphatic, aromatic, or heterocyclic quaternary ammonium salts, aliphatic or heterocyclic ring-containing phosphonium or sulphonium salts. Such surface-active agents can be used for various purposes e.g. as coating aids, as compounds preventing electric charges, as compounds improving slidability, as compounds facilitating dispersive emulsification, as compounds preventing or reducing adhesion, and as compounds improving the photographic characteristics e.g. higher contrast, sensitization, and development acceleration. Preferred surface-active coating agents are compounds containing perfluorinated alkyl groups.

The photographic elements in connection with the present invention may further comprise various other additives such as e.g. compounds improving the dimensional stability of the photographic element, UV-absorbers, spacing agents and plasticizers.

Suitable additives for improving the dimensional stability of the photographic elements are e.g. dispersions of a water-soluble or hardly soluble synthetic polymer e.g. polymers of alkyl(meth)acrylates, alkoxy(meth)acrylates, glycidyl (meth)acrylates, (meth)acrylamides, vinyl esters, acrylonitriles, olefins, and styrenes, or copolymers of the above with acrylic acids, methacrylic acids, Alpha-Beta-unsaturated dicarboxylic acids, hydroxyalkyl (meth)acrylates, sulphoalkyl (meth)acrylates, and styrene sulphonic acids.

Spacing agents can be present, preferably in the top protective layer; in general the average particle size of such spacing agents is comprised between 0.2 and 10 micron. They can be soluble or insoluble in alkali. Alkali-insoluble spacing agents usually remain permanently in the photographic element, whereas alkali-soluble spacing agents usually are removed therefrom in an alkaline processing bath. Suitable spacing

agents can be made e.g. of polymethyl methacrylate, of copolymers of acrylic acid and methyl methacrylate, and of hydroxypropylmethyl cellulose hexahydrophthalate. Other suitable spacing agents have been described in US 4,614,708.

The support of the photographic materials in connection with the present invention can be transparent base, preferably an organic resin support, e.g. cellulose nitrate film, cellulose acetate film, polyvinylacetal film, polystyrene film, polyethylene terephthalate film, polycarbonate film, polyvinylchloride film or poly-Alpha-olefin films such as polyethylene or polypropylene film. The thickness of such organic resin film is preferably comprised between 0.07 and 0.35 mm. These organic resin supports are preferably coated with a subbing layer. On the other hand the support of the photographic material can be a paper base preferably a polyethylene or polypropylene coated paper base.

The photographic materials according to the invention can be processed by any means or any chemicals known in the art depending on their particular application. In the case of infra-red sensitive elements in the field of graphic arts for phototype- or image-setting they are preferably processed in so-called "Rapid Access" chemicals, comprising a conventional Phenidone/hydrochinon developing solution and a conventional sodium or ammonium thiosulphate containing fixing solution. The development time is usually between 10 and 30 seconds at a temperature of about 35 °C. Alternatively they can be processed in so-called "hard dot Rapid Access" chemistry, e.g. the AGFASTAR system marketed by Agfa-Gevaert N.V.. Preferably an automatically operated processor provided with automatic regeneration is used, e.g. a RAPILINE device marketed by Agfa-Gevaert N.V..

The following examples illustrate the present invention without however limiting it thereto.

EXAMPLES

EXAMPLE 1

A high contrast sulfur plus gold sensitized cubic silver halide emulsion, doped with rhodium and iridium, was prepared, having an average grain size of 0.30 micron, and containing 0.4 % iodide, 16 % bromide and 83.4 % chloride. To 1 kg of emulsion, containing 1.10 moles of silver halide, was added a conventional substituted tetraazaindene and a conventional substituted mercaptotetrazole as antifoggant agents. A small amount of hydroquinone was added as an anti-oxidant. Supersensitizers and dyes were added as indicated in table 1. The pH was adjusted to 5.0.

The emulsion was coated at an amount of silver halide corresponding to 4.27 g Ag/m² and at 2.5 g/m² of gelatin. The photosensitive layer was overcoated with a layer containing 1 g/m² of gelatin, a matting agent and formaldehyde as gelatin hardener. Surfactants were added to both layers as coating aids.

In order to determine infrared speed the coated samples were exposed on a laser-sensitometer using a 780 nm laserdiode and a continuous wedge with a wedge constant of 0.10 log H/cm. The sensitivity, expressed as relative log H value, was measured at a density of 3.00 above fog. A higher number means more sensitive. So an increase by a value of 0.30 means a doubling of speed. The sensitivity of sample 1.2. was arbitrarily set at 1.00.

The samples were processed in an automatic processor using a conventional hydroquinone / Phenidone developer, a conventional fixer containing ammonium thiosulphate, and an aqueous rinsing solution. Finally the samples were dried. The total processing time was 45 sec dry to dry. The temperature of the developer was 35 C.

TABLE 1

No.	IR Dye	Supersensitizer		
		(mmoles/mole Ag)	(mmoles /mole Ag)	rel. speed
1.1	IRS-1	(0.039)	no supersensitizer	-
1.2	"	(0.039)	SS-C10 (0.529)	1.00
1.3	"	(0.039)	SS-C1 (0.103)	0.50
1.4	IRS-2	(0.039)	SS-C1 (0.103)	0.60
1.5	IRS-1	(0.051)	SS-C2 (0.211)	0.30
1.6	"	(0.051)	SS-C3 (0.211)	0.40
1.7	"	(0.051)	SS-C4 (0.157)	0.20
1.8	"	(0.051)	SS-C5 (0.157)	0.20
1.9	"	(0.051)	SS-C6 (0.157)	0.30
1.10	"	(0.051)	SS-C7 (0.157)	0.20
1.11	"	(0.051)	SS-C8 (0.157)	0.20
1.12	"	(0.051)	SS-C9 (0.157)	0.60
1.13	"	(0.039)	SS-I1 (0.103)	1.20
1.14	IRS-2	(0.039)	SS-I1 (0.103)	0.90
1.15	IRS-1	(0.051)	SS-I1 (0.211)	1.20
1.16	"	(0.051)	SS-I2 (0.211)	0.90

The data of table 1 show that preferred supersensitizer SS-I1 gives rise to higher sensitivity than a known non-stilbene type sensitizer like SS-C10 (compare ex. 1.2 and 1.13).

The data in Table 1 also show that the preferred supersensitizer SS-I1 of the invention gives much more sensitivity than other sulfonated stilbene derivatives not carrying four naphthoxy substituents. The sensitivity increases in the order : ex. 1.3 (4 anilino substituents, SS-C1), ex. 1.16 (2 anilino- and 2 naphthoxy substituents, SS-I2) and ex. 1.13 (4 naphthoxy substituents, SS-I1).

The data also show that supersensitizer SS-I1 of the invention acts in combination with different sensitizers (compare ex. 1.13 and 1.14).

EXAMPLE 2

A sulfur plus gold sensitized cubic silver halide emulsion was prepared consisting of 2 % iodide and 98 % bromide, and showing an average grain size of 0.24 micron. To 1 kg emulsion, containing 1.1 moles of silver halide, was added a conventional substituted tetraazaindene as antifoggant agent. Furtheron to this emulsion was added sensitizer IRS-1 and supersensitizer SS-I1 as shown in table 2. A small amount of hydroquinone was added as an anti-oxidant. The pH was adjusted to 6.00.

The emulsion was coated on a transparent support at a coverage of an amount of silver halide corresponding to 3.56 g Ag/m² and at 2.2 g/m² of gelatin. The photosensitive layer was overcoated with a layer containing 1 g/m² of gelatin, a matting agent and formaldehyde as gelatin hardener. Surfactants were added to both layers as coating aids.

A similar coated sample was prepared containing control supersensitizer SS-C10.

After exposure as in example 1 the samples were processed in an automatic processor using a so-called "hard dot Rapid Access" developer, a conventional fixer containing ammonium thiosulphate, and water as rinsing liquid. The development time was 40 s at 38 C.

The speed was determined as in example 1. The results are represented in table 2.

TABLE 2

	Dye	Supersensitizer		
		(mmoles/mole Ag)	(mmoles /mole Ag)	speed
2.1	IRS-1	(0.047)	no supersensitizer	-
2.2	"	(0.047)	SS-C10 (1.060)	1.20
2.3	"	(0.047)	SS-I1 (0.103)	2.00

The results of table 2 indicate a strong supersensitization effect of the supersensitizer SS-I1 according to the invention, compared with a conventional supersensitizer. Furtheron the results of table 2 compared with the results of table 1 (samples 2.3 and 1.13) show that on an emulsion with a high bromide concentration the supersensitization effect is even stronger than on an emulsion rich in chloride. A conventional supersensitizer shows this effect to a much less extent (compare samples 1.2 and 2.2).

EXAMPLE 3

A photographic element was coated on a opaque resin coated paper. The element consisted of three layers : an "undercoat", a photosensitive layer and a protective layer.

The "undercoat" contained 1.1 g/m² of TiO₂ (BAYERTITAN AN2, marketed by Bayer AG) and 1.0 g/m² of gelatin. The photosensitive layer contained the same emulsion and ingredients as in example 1. Supersensitizers and dyes were added as indicated in table 3. Furtheron, an infrared absorbing filter dye (FD-1) was added at 67 mg/m².

The emulsion was coated at an amount of silver halide corresponding to 1.43 g Ag/m² and at 1.32 g/m² of gelatin. The photosensitive layer was overcoated with a layer containing 1 g/m² of gelatin, a matting agent and formaldehyde as gelatin hardener. Surfactants were added to all three layers as coating aids.

The samples were exposed and processed as in example 1. The speed was measured at a density of 1.5 above fog. The results are summarized in table 3.

TABLE 3

	Dye	Supersensitizer		
		(mmoles/mole Ag)	(mmoles /mole Ag)	speed
3.1	IRS-1	(0.047)	no supersensitizer	-
3.2	"	(0.047)	SS-C10 (0.529)	1.20
3.3	"	(0.047)	SS-I1 (0.103)	1.60

The results show that the preferred supersensitizer SS-I1 of the invention gives rise to a very high sensitivity, compared with a conventional supersensitizer, even in the presence of a large amount of a filter dye, serving as a screening dye. The final result is a material with an excellent sharpness.

EXAMPLE 4

The same chlorobromoidide emulsion was prepared as example 1. To 1 kg emulsion, containing 1.10 moles of silver halide, was added a conventional substituted tetraazaindene as antifoggant agent each in an experimentally optimized concentration. Then various mercaptotetrazoles were added to aliquot portions of the emulsion as shown in table 4. A small amount of hydroquinone was added as an anti-oxidant. Supersensitizer SS-I1 and dye IRS-1 were added in an amount of 0.211 and 0.051 mmoles per mole of silver halide respectively.

The emulsion was coated at an amount of silver halide corresponding to 4.27 g Ag/m² and at 2.5 g/m² of gelatin. The photosensitive layer was overcoated with a layer containing 1 g/m² of gelatin, a matting agent and formaldehyde as gelatin hardener. Surfactants were added to both layers as coating aids.

The speed was determined as in example 1. To show the improvement in stability, the fog after a storage simulation test (3 days at 57 C and 34 % RH) is also given. The samples were processed as in example 1.

TABLE 4

Test no.	Mercaptotetrazole mmols/mole Ag	speed	fog after 3 d 57 °C-34% RH
4.1 St-1	(0.53)	1.02	0.048
4.2 St-2	(1.09)	1.20	0.048
4.3 St-3	(0.72)	0.62	0.048
4.4 St-4	(0.72)	0.98	0.413
4.5 St-5	(0.72)	0.88	0.075

The results show the importance of the nature and concentration of the mercaptotetrazole stabilizer used, when one tries to maximize the obtainable speed. Compound St-2 is far superior compared to the others. Especially sample 4.2 shows very good sensitivity and a perfect stability after storage of the material at a high temperature.

PREPARATIVE EXAMPLE 5

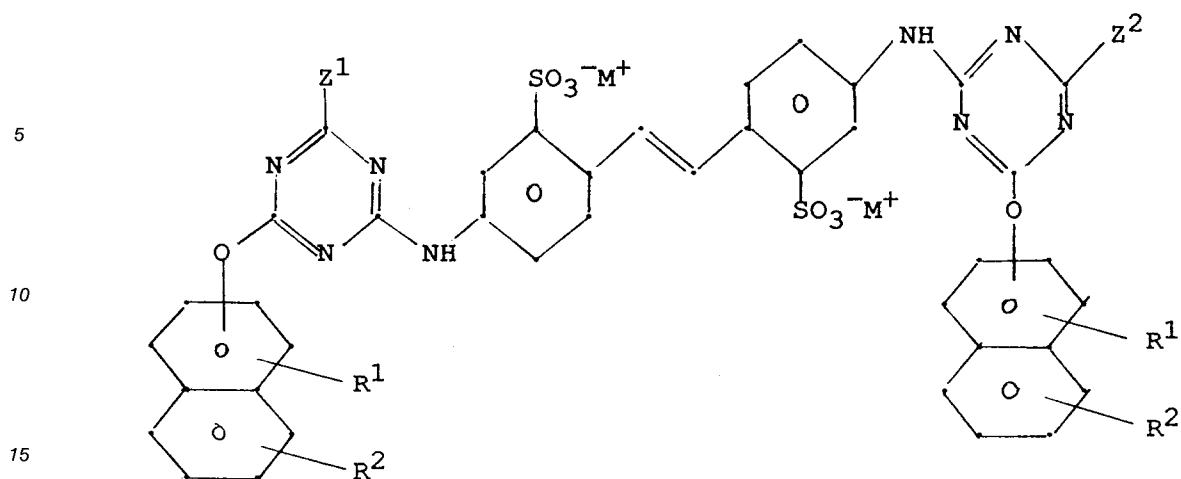
- Preparation of compounds SS-I3 and SS-I1

To a solution containing 20 g of sodium chloride, 2 g of an emulsifying agent of the polyethyleneoxy-carboxylic acid type (AKYPO OP80, Chemische Fabrik Chemy) and 50 ml of isoamylalcohol, 50 g (0.271 mole) of cyanuric chloride were added. To the resulting suspension an aqueous solution of 49.7 g (0.12 mole) of sodium flavonate and of 20.2 g (0.24 mole) of sodium bicarbonate was added dropwise at pH 4.2 and at a temperature between 18 °C and 22 °C. The resulting yellow suspension was adjusted to pH 7.35 with a 10 % sodium hydroxide solution and was then warmed up to 45 °C. Furtheron 38.5 g (0.267 mole) of 2-naphthol were added portionwise. The pH was kept at 7.35 by dropwise addition of sodium hydroxide solution. After fifty minutes the still warm suspension was filtered and washed with 900 ml of a 1 % sodium solution. The wet precipitate, being compound SS-I3, can be purified by recrystallization, or used immediately as intermediate for the preparation of compound SS-I1 as described hereafter.

To a suspension of 0.12 mole of this compound SS-I3 in water were added successively 34.3 g (0.327 mole) of sodium carbonate and 57.8 g (0.40 mole) of 2-naphthol. The reaction mixture was refluxed at 100 °C for 6 hours whilst stirring. After cooling to 85 °C a precipitate was formed which was filtered off on a BÜCHNER filter, and was washed with 900 ml of a 1 % sodium hydroxide solution and with 300 ml of water. The substance, being compound SS-I1, was dried in a ventilated oven until a constant weight was reached. The yield was 90 %.

Claims

1. Photographic material comprising a support and at least one emulsion layer containing a silver halide emulsion, an infra-red sensitizer and a stilbene supersensitizer corresponding to general formula (SS-Ia):



(SS-Ia)

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wherein M represents a hydrogen ion or a monovalent cation,
 R¹ and R² each independently represent hydrogen, alkyl, alkoxy, NR³R⁴, SO₂R³, COOR³, CONR³R⁴,
 NR³COR⁴, or SO₃M, and
 Z¹ and Z² each independently represent Cl, OH, NR³R⁴, OR⁵ or SR⁵, and,
 25 R³, R⁴ and R⁵ each independently represent alkyl, aryl or hydrogen.

2. Photographic material according to claim 1 wherein said stilbene compound is represented by general formula (SS-Ib) :

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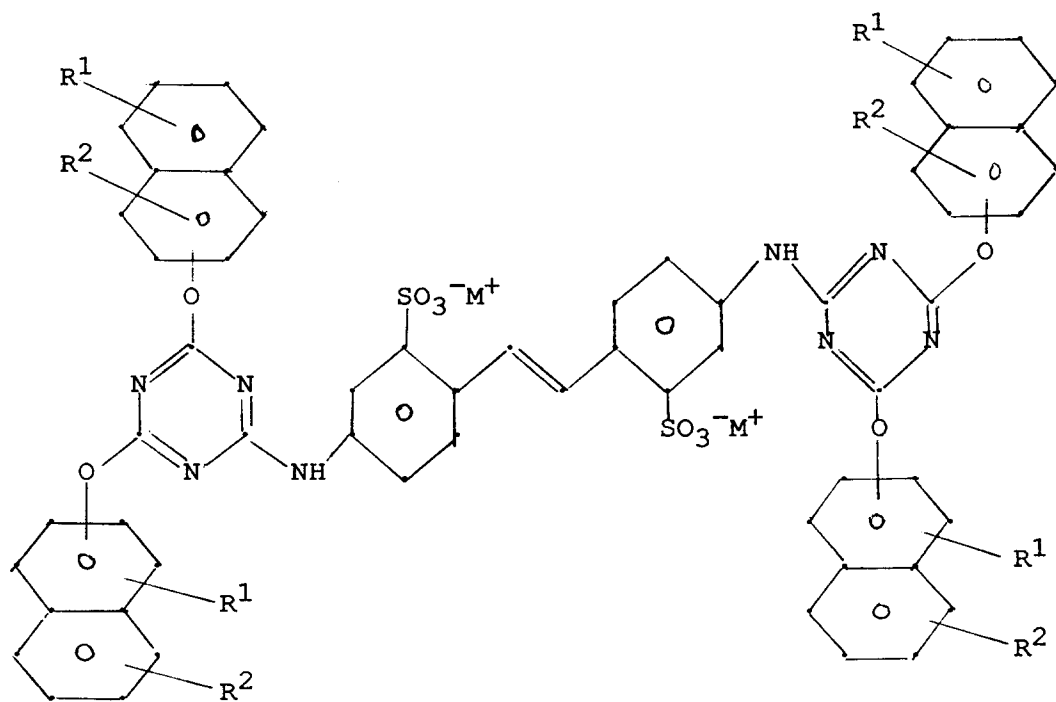
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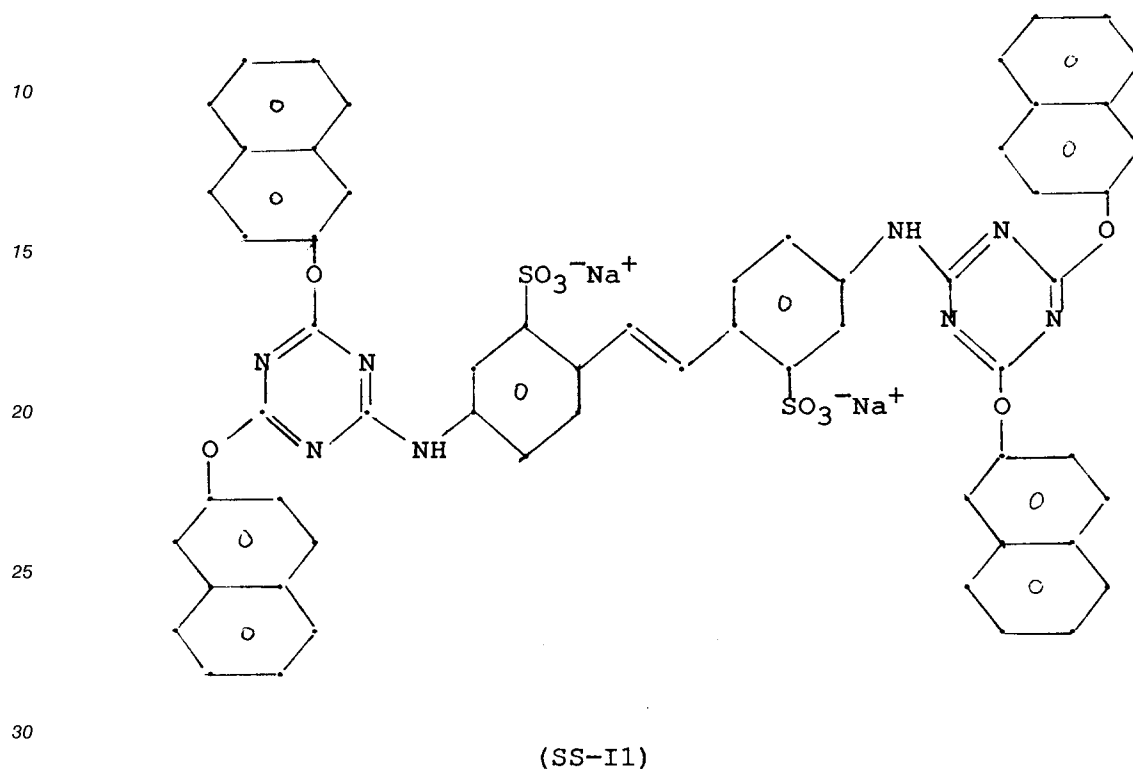
(SS-Ib)

wherein M represents a hydrogen ion or a monovalent cation,
 R¹ and R² each independently represent hydrogen, alkyl, alkoxy, NR³R⁴, SO₂R³, COOR³, CONR³R⁴,

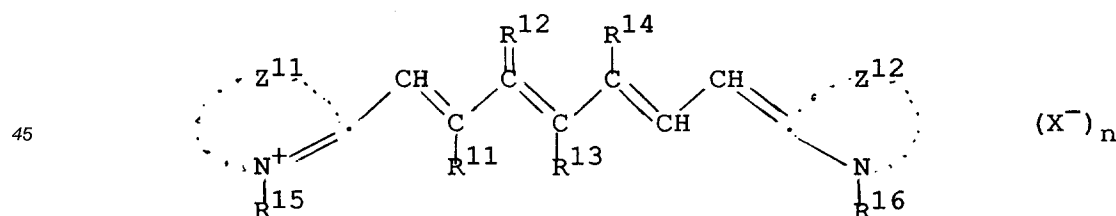
NR^3COR^4 , or SO_3M , and

R^3 and R^4 each independently represent alkyl, aryl or hydrogen.

3. Photographic material according to claim 1 or 2 wherein said stilbene compound corresponds to formula (SS-I1) :



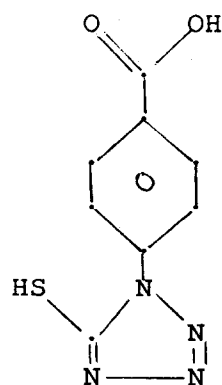
4. Photographic material according to any of claims 1 to 3 wherein said stilbene supersensitizer is present in the emulsion layer in a concentration between 0.10 mmole and 10 mmole per mole of silver halide.
5. Photographic material according to any of claims 1 to 4 wherein said infra-red sensitizer is represented by following general formula :



wherein,

- Z^{11} and Z^{12} each represent a non-metallic atomic group necessary to complete a benzothiazole, benzoxazole, naphthothiazole, naphthoxazole or quinoline nucleus; R^{15} and R^{16} each represent an alkyl or substituted alkyl group;
- R^{11} , R^{12} , R^{13} , and R^{14} each represent a hydrogen atom, a substituted or unsubstituted alkyl, alkoxy, amino, phenyl or benzyl group; R^{11} and R^{13} , or R^{12} and R^{14} respectively may combine with each other to form a substituted or unsubstituted 5- or 6-membered ring;
- X^- is an anion; n is 0 or 1 (0 in case of an intramolecular salt via an anionic group in R^{15}).

6. Photographic material according to any of claims 1 to 5 wherein said infra-red sensitizer is present in the emulsion layer in a concentration between 0.01 mmole and 1.0 mmole per mole of silver halide.
7. Photographic material according to any of claims 1 to 5 wherein said emulsion layer further contains a mercaptotetrazole type of stabilizer.
8. Photographic material according to claim 7 wherein said mercaptotetrazole type of stabilizer is following compound :





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 93 20 0249

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.5)
A	EP-A-0 126 455 (FUJI PHOTO FILM CO., LTD.) 28 November 1984 * See compound III-13 on page 59 * ---	1-8	G03C1/28 G03C5/16
D,A	US-A-4 677 053 (YUHI MIHARA, JAPAN) 30 June 1987 * See Claim 1 * -----	1-8	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G03C
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 06 APRIL 1993	Examiner GUILLEMOIS F. S.
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			