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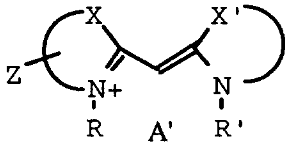
(54) Blue sensitized silver halide emulsions with particular addenda

(57) A silver halide photographic element comprising a silver halide emulsion sensitized by a blue dye of formula (I) below, the emulsion also containing a thiosulfonate, a sulfinate, and an alkynylamine;



(I)

wherein:

X and X' each independently represent the atoms necessary to complete a 5- or 6-membered heterocyclic nucleus, and X may be further substituted and X' is substituted or unsubstituted;

R and R' each independently represents substituted or unsubstituted aryl or substituted or unsubstituted alkyl,

Z represents a substituted or unsubstituted aryl or heteroaryl;

A' a counterion as needed to balance the charge of the molecule.

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Description

Field of the Invention

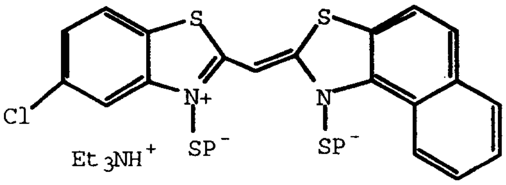
The present invention relates to a photographic element which has an emulsion sensitized by a particular class of sensitizing dyes and which also contains particular addenda, and which has good blue speed characteristics.

Background of the Invention

Advances in the art of photographic science have required silver halide emulsions be made such that high sensitivity is obtained. This has enabled the silver halide emulsion to respond faster to radiation without loss and distortion of the image captured. The use of silver chloride emulsions in particular also has made it possible to process the exposed silver halide emulsion rapidly, with the result that the output for developing photographic materials be increased to produce improvement in operational efficiency and productivity. Thus there has been a trend in the photofinishing industry towards using silver chloride emulsions in photographic elements, in particular for color paper, that have high photographic speed and that can be processed rapidly.

Photographic elements, particularly color printing papers, usually comprise at least three emulsions that are sensitized to blue, green and red light. Proper sensitization can be achieved by employing an appropriate sensitizing dye in each layer. Most common color photographic printing papers have a blue layer with a sensitizing dye that has a maximum sensitivity at about 480 nm.

Color photographic printing paper is intended to generate a print from a photographic color negative. An important quality characteristic of color paper is color reproduction, that is the ability to accurately portray the colors, or, more precisely, the hues of the original scene. Replacing a deep blue sensitizing dye, such as dye C (λ_{max} = 480 nm; wherein λ_{max} represents the wavelength of maximum sensitivity provided by the dye on the emulsion):



C

with a dye that sensitizes at a shorter wavelength can provide a color paper with improved color reproduction. The benefits of using a blue senstizing dye which senstizes at shorter wavelengths were described, for example, in Research Disclosure June 1994, p. 291 (Item 36216), published by Kenneth Mason Publications, Ltd., Dudley Annex, 12a North Street, Emsworth, Hampshire P010 7DQ, ENGLAND. However, using a shorter blue sensitizing dye results in a sensitivity (speed) loss with normal printer exposures. One reason for this is that the energy output of the exposing device in many color paper printers diminishes at wavelengths shorter than 480 nm.

It has been recognized in the art that photographic speed can be increased by adjusting the pH and/or the pAg of the emulsion. It is also known in the art that enhanced photographic speed can be obtained by the addition of emulsion adjuvants. These include alkyl ethers of polyethylene glycols, poly(thiodiethylene glutarate), azaindenes, mercaptoazoles and the like. Certain reducing agents such as stannous chloride, ascorbic acid, dimethylamineborane have also been used to increase sensitivity in silver halide emulsions. One problem with using these reducing agents is that these chemicals are, by their very nature, unstable materials, that is, they can be oxidized in the air during storage. As a result of this decomposition, these reducing agents lose their activity and give variable results which are also unacceptable. Another problem is an undesirable fog which results from an indiscriminate reduction of silver, particularly in the case of silver chloride emulsions.

In order to control the formation of this fog, it has been known to add to the emulsion chemicals known as antifoggants. Many antifoggants have been used in the art, they include mercaptotetrazoles, tetraazaindenes, benzothiazolium salts, thiosulfonates, etc. The latter, in particular, have been used in connection with reduction sensitization in order to obtain a high emulsion sensitivity without the above described fogging problems.

US 4,960,689 describes the use of thiosulfonates in the finish in high chloride emulsions. Aromatic thiosulfonic acids are disclosed in US 5,009,992 as supersensitizers in an IR-sensitive high Cl emulsion. In US 5,079,138, thiosulfonates are used for control of reduction sensitization in the growing of structured iodide emulsions. Similarly, US 5,061,614 teaches the control of reduction sensitization in tabular grains by using thiosulfonates. In EP 368,304 control of reduction sensitization in the grain formation step is alleged in the presence of thiosulfonates and palladium compounds. In EP 369,491, and EP 371,338 the control of reduction sensitization of BrI grains by using a combination of ascorbic acid or its derivative with thiosulfonates is described. EP 434,012, and EP 435,270 describe the use of thiosulfonates in the precipitation of bromoiodide emulsions. EP 435,355 describes the use of thiosulfonates during grain formation of AgX materials.

US 5,110,719 describes the use of the combination of thiosulfonates with sulfinates and nucleating agents in a direct positive internal latent image core/shell ClBr emulsion. A combination of iodate ions and sulfinates has also been described as useful in preventing yellow fog in silver halide materials. US 5,393,635 discloses the use of thiosulfonates and sulfinates in controlling speed change or both speed change and fog growth on incubation of color photographic materials. The combination of thiosulfonates with sulfinates has been alleged to be useful in the sensitization of chloride emulsions for color paper in JP 3,208,041. US 2,440,206 describes the use of the combination of sulfinates along with small amounts of polythionic acids to stabilize photographic emulsions against fog growth. US 2,440,110 teaches the use of the combination of sulfinates with aromatic or heterocyclic polysulfides in controlling fog growth. US 2,394,198 discloses the use of sulfinates with thiosulfonates in stabilizing silver halide emulsions. The use of sulfinates has been disclosed to reduce stain in photographic paper when used in combination with sulfonates in US Statutory Invention Registration H706, and in EP 305,926.

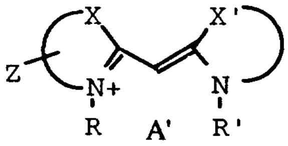
Alkyl and aryl disulfinates haven been disclosed for use in the formation pre-fogged direct positive silver halide emulsions in US 5,043,259. US 4,939,072 alleges the use of sulfinates as storage stability improving compounds in color photographs. US 4,770,987 describes sulfinates as anti-staining agents along with a magenta coupler in silver halide materials. EP 463,639 describes the use of sulfinic acid derivatives as dye stabilizers. The use of a paper base which has been treated with a sulfinic acid salt has been disclosed in US 4,410,619 to prevent discoloration of the photographic material. Aromatic sulfinates are alleged to be useful as stabilizers in a direct positive photographic material in US 3,466,173. In EP 267,483, sulfinates are added during the sensitization of silver bromide emulsions. Similarly, GB 1,308,938 alleges the use of sulfinates during processing of a silver halide photographic material to minimize discoloration of the image tone. Sulfinates are claimed to have fog-reducing properties in US 2,057,764.

Substituted alkynyl heterocycles have been claimed in US 4,378,426 and in US 4,451,557 to stabilize latent image and to increase speed of silver halide emulsions.

It would be desirable then, to find sensitizing dyes that have a maximum sensitization wavelength that is shorter than 480 nm for improved color reproduction but which can be used so as to provide a high speed. This would allow the advantage of good color reproduction without too much loss of speed over a dye which sensitizes at 480nm.

Summary of the Invention

The present invention then, provides a silver halide photographic element comprising a silver halide emulsion sensitized by a blue dye of formula (I) below. The emulsion also containing a thiosulfonate, a sulfinate, and an alkynylamine. Formula (I) is:



(I)

wherein:

X and X' each independently represent the atoms necessary to complete a 5- or 6-membered heterocyclic nucleus, and X may be further substituted and X' is substituted or unsubstituted;

R and R' each independently represents substituted or unsubstituted aryl or substituted or unsubstituted alkyl,

Z represents a substituted or unsubstituted aryl or heteroaryl;

A' a counterion as needed to balance the charge of the molecule.

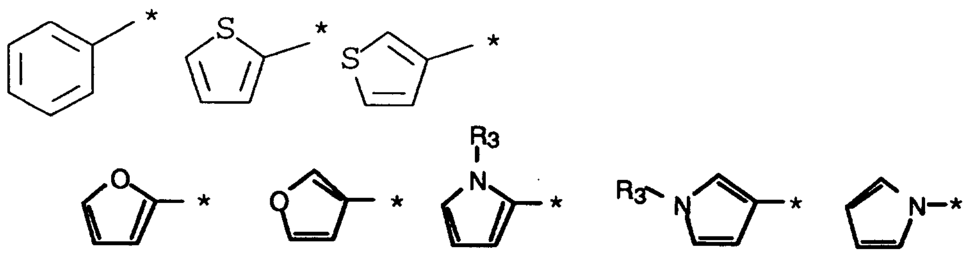
It has been found that such a combination can provide a short blue sensitivity (that is, the emulsion has a λ_{max} of less than 480nm) which is advantageous for good color reproduction, and yet have high speed. This allows a conventional blue sensitizing dye, which might sensitize at 480nm, to be replaced to obtain better color reproduction with little loss in speed.

Embodiments of the Invention

In the present application, the term "aromatic" refers to aromatic rings as described in J. March, Advanced Organic Chemistry, Chapter 2 (1985, publisher John Wiley & Sons, New York, NY). Further, the term "lower alkyl" refers to an alkyl group containing from 1 to 8 carbon atoms.

In formula (I), the 5- or 6-membered heterocyclic nucleus represented by X' or X" may be a benzo-naphtho- or other condensed nucleus. X' and X" may include a thiazole nucleus, benzothiazole nucleus, oxazole nucleus, benzoxazole nucleus, selenazole nucleus, benzoselenazole nucleus, naphthoselenazole nucleus, tellurazole nucleus, benzotellurazole nucleus, naphthotellurazole nucleus, quinoline nucleus, imidazole nucleus, benzimidazole nucleus, naphthimidazole nucleus, thiazoline nucleus, indoline nucleus, oxadiazole nucleus, thiadiazole nucleus. However, preferably, X and X' do not both simultaneously represent oxazole or benzoxazole rings. Preferably, X and X' do not both simultaneously represent napthothiazole or napthoselenazole rings. Preferably, X and X' do not represent the combination of thiazole, or benzothiazole, a selenazole or benzoselenazole ring and a naphthothiazole or naphthoselenazole ring.

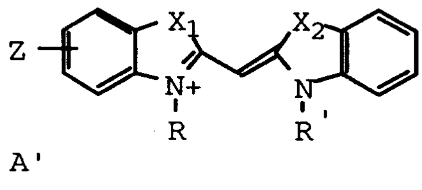
As mentioned, Z represents an aryl or heteroaryl, containing group, either of which may be substituted or unsubstituted. Examples of aryl include phenyl, naphthyl, and tolyl. Examples of heteroaryl include a thiophene, furan or pyrrole group. Preferably the aryl or heteroaryl ring of Z is directly appended to the nucleus which includes X and N (that is, linked to that nucleus by one single bond). By the "nucleus" in this context is meant the single ring which includes X and N, if only one ring is formed, or all of the rings together if X and N forms two or more fused rings. Thus, if X and N are part of a benzothiazole nucleus, for example, Z could be appended to the benzo ring. However, in reference to Z being an aryl or heteroaryl containing group, includes the possibility that the aryl or heteroaryl ring of Z may be linked to X through a linking chain of atoms which may, for example, be 4, 3, 2 or 1 atoms in length. However, if there is any such linking chain, such chain and any substituents on Z should preferably maintain the relatively planar shape of the Z-X group. Examples of Z include:



wherein * indicates the point of attachment of Z to X. In the foregoing formulas for Z, R3 is hydrogen, substituted or unsubstituted alkyl (such as methyl or ethyl or 2-hydroxyethyl), or substituted or unsubstituted aryl (such as phenyl or 4-hydroxyphenyl). The above heterocyclic rings for Z are unsubstituted (that is, they are as shown). In another embodiment though, the above examples of Z may be substituted, for example with a 1 to 8 carbon alkyl (particularly methyl, ethyl, or propyl) or with a halogen (for example, F or Cl).

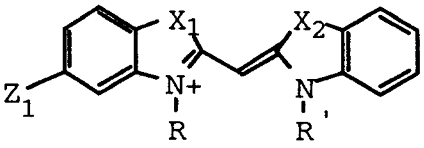
Examples of a counterion for A' include sodium, potassium, triethylammonium, and the like. However, it is preferred that the dye of formula (I) be anionic (that is, the dye molecule excluding A', has a net negative charge such that A' would be a positively charged counterion).

The dyes of formula (I) of the present invention may, in particular, be of formula (Ia) below:



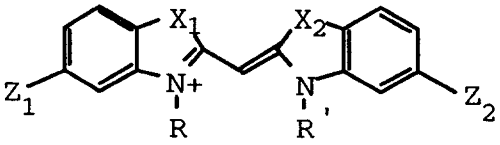
(Ia)

In formula (Ia), X_1 and X_2 are, independently, N, O, S or Se and the benzo rings may be further substituted or unsubstituted (including substituted with a fused ring). However, it is preferred that any two or more substituents do not together form a ring (that is, there is no ring fused to those shown in formula (Ia) so that such a preferred structure would not include naphtho-, anthracine, or other fused ring groups such as naphthoxazole, naphthiazole, or naphthoselenazole). Preferably, X_1 and X_2 are not both O. Further, the aryl or heteroaryl ring of Z is preferably directly appended to the benzo ring shown. Preferably, the aryl or heteroaryl ring of Z is directly appended to the 5-position of the benzo ring, that is the structure would be:



A'

Further, the only additional substituents on the benzo rings, if any, other than Z may be one substituent on the benzo ring attached to the ring which includes X_2. Particularly, such other substituent may be on the benzo ring 5-position, that is the dye with such substituents would then have the formula:



A'

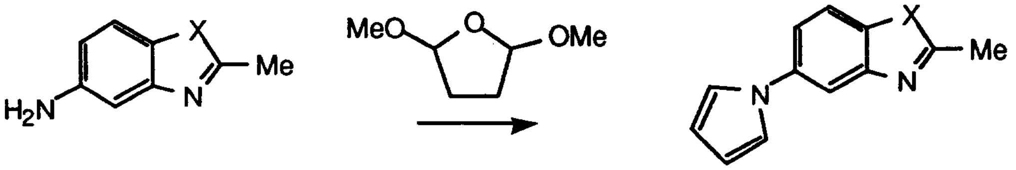
in which Z_1 can be any of those substituents represented by Z, and Z_2 can be any of those substituents represented by Z or any of the other benzo ring substituents described above, or Z_2 can be H.

X and/or X' or the benzene rings in any of formula (I) or (Ia) may be substituted with substituents including halogen (for example, chloro, fluoro, bromo), alkoxy (for example, methoxy, ethoxy), substituted or unsubstituted alkyl (particularly of 1 to 10 carbon atoms, for example, methyl, trifluoromethyl), amides, alkoxycarbonyl, and other known substituents, and substituted and unsubstituted aryl (for example, phenyl, 5-chlorophenyl), thioalkyl (for example, methylthio or ethylthio), hydroxy or alkenyl and others known in the art. All the substituents on the benzo rings of formula (Ia) may particularly be chosen such that no two form a ring (that is, so that there is no ring appended to the benzo rings shown in formula (Ia), such that compounds such as those with a naphtho group would be excluded). Additionally, all substituents on the benzo rings shown in formula (Ia), other than Z, may particularly be non-aromatic.

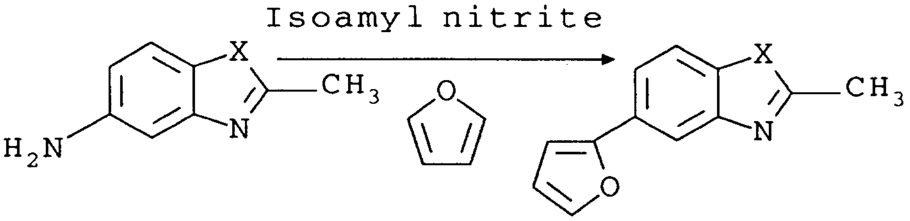
Although R and R' in each of formula (I) or (Ia) can represent a substituted or unsubstituted aryl group, it is preferred that such an aryl group have between 6 to 15 C atoms. More preferably, R and R' are alkyl groups (each preferably of from 1 to 6 carbon atoms). Examples of aryl include phenyl, tolyl, and the like, any of which may be substituted or unsubstituted. Examples of alkyl include methyl, ethyl, propyl, and the like, and substituted alkyl groups (preferably a substituted lower alkyl containing from 1 to 8 carbon atoms) such as hydroxyalkyl group (for example, 2-hydroxyethyl), a sulfoalkyl group, (for example, 4-sulfobutyl, 3-sulfopropyl) and the like. The alkyl or aryl group may also be substituted by one or more of the substituents on the above-described nuclei, X and X'. At least one (and optionally, both) of R and R' may particularly be substituted with an acid or acid salt group (for example, a sulfo group, carboxy group, or a sulfonamido group such as $-CH_2-CO-NH-SO_2-CH_3$). Other examples of such groups include 3-sulfobutyl, 3-sulfopropyl or 2-sulfoethyl and the like. In particular, R and R' may be sulfoalkyl such as 2-sulfoethyl or sulfopropyl. When any substituent on X or X' in formula (Ia), other than Z, is an aromatic substituent (including heteroaromatic), it is preferred that R and R' both be an acid or acid salt substituted alkyl, for example sulfopropyl, sulfoethyl, or sulfobutyl.

Dye precursors can be made by techniques that are well-known in the art. For a review of the synthesis of substituted pyrroles see, G. P. Bean, Pyrroles, R. A. Jones, Ed.,John Wiley & Sons, Inc., New York, 1990, Chapter 2. For a review of furan synthesis see, F. M. Dean, Advances in Heterocyclic Chemistry, A. R. Katritzky, Ed., vol .30, Academic Press, New York, 1982, p 167.

For example, a pyrrol-1-yl substituted base can be made by reaction of an amino base with 2,5-dimethoxytetrahydrofuran.



Preparation of a diazonium salt from an amino-substituted base followed by decomposition in the presence of furan results in formation of the furan-2-yl substituted base.

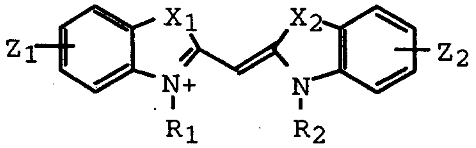


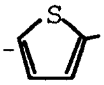
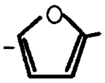
Dyes of the present invention can be prepared from the above dye precursers according to techniques that are well-known in the art, such as described in Hamer, Cyanine Dyes and Related Compounds, 1964 (publisher John Wiley & Sons, New York, NY) and James, The Theory of the Photographic Process 4th edition, 1977 (Eastman Kodak Company, Rochester, NY).

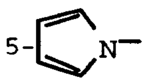
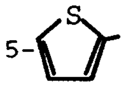
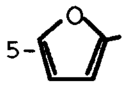
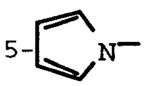
The amount of sensitizing dye that is useful in the invention is preferably in the range of 0.0001 to 4.0 millimoles per mole of silver halide and more preferably from 0.1 to 3 millimoles (or even to 3 or 2.2 millimoles) per mole of silver halide. Optimum dye concentrations can be determined by methods known in the art. As already mentioned, a dye of formula (I) is preferably chosen so as to provide the emulsion with a λ_{max} at less than 480nm (for example, at 478nm or less, 475nm or less, or even 470 or 460nm or less). Using such a dye which sensitizes at a wavelength shorter than 480nm can provide advantages in color reproduction as described above.

Examples of dyes of formula (I) of the present invention include those listed in Table I below:

Table I



Dye	X_1	X_2	Z_1	Z_2	R_1, R_2[a]
I-1	S	O	5- 	4,5-Benzo	SP, SP
I-2	O	S	5- 	"	"
I-3	O	S	"	5-Cl	"
I-4	S	S	"	"	"
I-5	S	S	"	=Z_1	"

I-6	S	O		5-Cl	"
I-7	O	O	"	"	"
I-8	S	S	"	"	"
I-9	S	S		"	3SB, SP
I-10	S	S	"	5-F	3SB, 3SB
I-11	S	S	"	$=Z_1$	"
I-12	S	S		"	SP, Et
I-13	O	S	"	"	"
I-14	S	O	"	5-Phenyl	"
I-15	S	S	"	5-F	"
I-16	S	S		"	"
I-17	O	S	"	4,5-Benzo	SP, SP
I-18	S	S	"	$=Z_1$	"
I-19	S	S	5-Cl	5-Phenyl	"
I-20	S	S	5-Phenyl	"	"

[a] SP is 3-sulfopropyl, 3SB is 3-sulfobutyl

The alkynylamine is preferably of formula (II) below:

$$Y\text{-}NHCH_2C\equiv CR'' \qquad \text{(II)}$$

In formula (II), R" represents an aliphatic, or carbocyclic substituent (including aromatic), any of which may be substituted or unsubstituted, or H. Preferably, R" is other than hydrogen. More preferably, it is an alkyl having 1 to 20 carbon atoms (and optimally, R" is a methyl group).

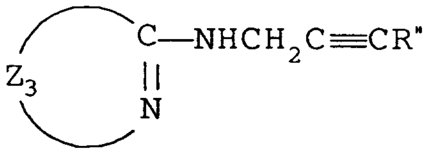
Examples of suitable aliphatic groups for R" include methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, ethylhexyl, decyl, dodecyl, hexadecyl, octadecyl, isopropyl, t-butyl, butenyl, propynyl, and butynyl. Examples of suitable carbocyclic groups are phenyl, tolyl, naphthyl, cyclohexyl, cycloheptatrienyl, cyclooctatrienyl, cyclononatrienyl, p-methoxyphenyl, and p-chlorophenyl.

Examples of suitable heterocyclic groups for R" are pyrrole, furan, tetrahydrofuran, pyridine, picoline, piperidine, morpholine, pyrrolidine, thiophene, oxazole, thiazole, imidazole, selenazole, tellurazole, triazole, tetrazole, and oxadiazole.

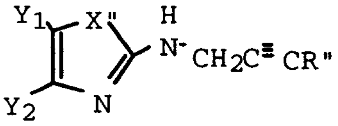
The substituent represented by Y in formula (II) above is preferably a nitrogen containing heterocycle (including a heterocyclic ring system of two or more fused rings). Thus, Y includes substituted and unsubstituted oxazoles, thiazoles, selenazoles, oxadiazoles, thiadiazoles, triazoles, tetrazoles, pyrimidines, pyrroles, pyridines, quinolines, and benzimidazoles. Preferably, Y is a nitrogen containing azole.

Groups suitable for substitution on Y (as well as R") include alkyl groups (for example, methyl, ethyl, hexyl), fluoroalkyl groups (for example, trifluoromethyl), alkoxy groups (for example, methoxy, ethoxy, octyloxy), aryl groups (for example, phenyl, naphthyl, tolyl), halogen groups, aryloxy groups (for example, phenoxy), alkylthio groups (for example, methylthio, butylthio), arylthio groups (for example, phenylthio), acyl groups (for example, acetyl, propionyl, butyryl, valeryl), sulfonyl groups, acylamino groups, sulfonylamino groups, cyano groups and acyloxy groups (for example, acetoxy, benzoxy).

Preferred alkynylamines of formula (II) are ones in which the alkynylamine is substituted on the carbon of a N=C moiety as shown in the following structure:

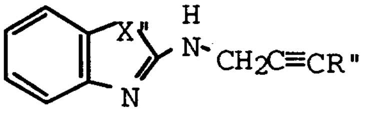


wherein Z_3 represents the atoms necessary to complete a five to nine-membered heterocyclic ring system, preferably a nine-membered fused heteroaromatic ring system such as a benzoxazole. R" in this structure is defined as above. Particular alkynlamines of formula (II) include those of formula (IIa) below:



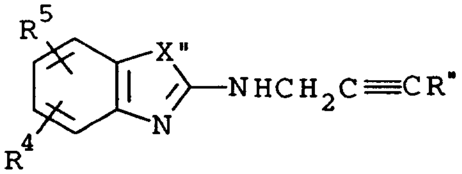
(IIa)

wherein: X" is O, S, Se, or -NH- or a substituted N (particularly NR_6 where R_6 can be any of those groups represented by R_3 above); and Y_1 and Y_2 are, independently, alkyl (such as 1 to 18, or 1 to 6 carbon atoms) or aryl (particularly of 6 to 18 or 6 to 12 carbon atoms) both of which may be substituted or unsubstituted, or together they may form a ring which may be substituted or unsubstituted. The most preferred compounds of formula (II) are those of formula (IIb) below, and particularly those of formula (IIc) :



(IIb)

wherein X" and R" are as previously defined, and the benzo ring may or may not be further substituted (such substituents can include rings fused to those shown; however in a particular embodiment such substituents do not together form a ring, that is, in such a case the compound would not for example be a naphthothiazole or the like);

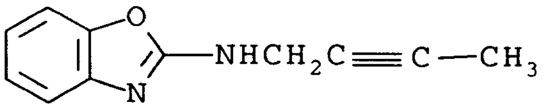


(IIc)

wherein X" is as already defined but is preferably oxygen; R" is as defined above; and R^5 and R^4 independently represent hydrogen, a halogen, or a substituted or unsubstituted alkyl or alkoxy group, preferably one having from 1 to 10 carbon atoms. In the alkynylamines described above, R^4 and R^5 are preferably in the 5 and 6 positions, respectively. It is also contemplated that the alkynylamines of the present invention be water soluble; that is, they further comprise a water solubilizing group. In this embodiment, the water solubilizing group can be substituted anywhere on the alkynylamine (for example, on R", R^4, or R^5), preferably not on the nitrogen atom of the amine group. Preferably, it should be sufficient to enable the alkynylamine to be soluble at 0.1 gram per liter of water. Representative solubilizing groups include carboxy, carboxyalkyl, sulfo, sulfoalkyl, phosphato, phosphatoalkyl, phosphono, phosphonoalkyl, carbonamido, sulfonamido, hydroxy, and salts thereof. Preferably, the water solubilizing group is a carboxy or sulfo group, or salt thereof. Optimally, it is the sodium or potassium salt of a carboxy group.

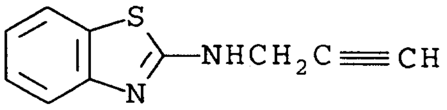
Specific compounds of formula (II) contemplated to be within the scope of the present invention include:

Compound IIA:

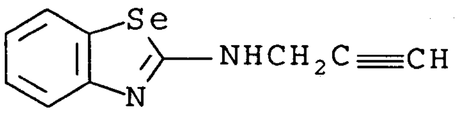


Compound IIB:

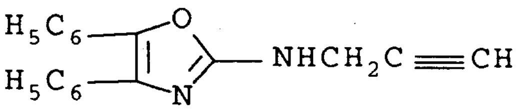
Compound IIC:



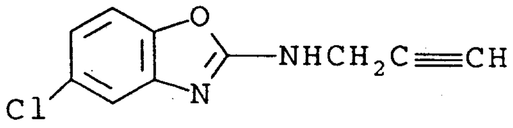
Compound IID:



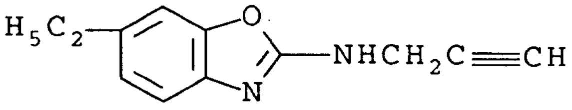
Compound IIE



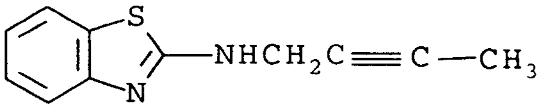
Compound IIF



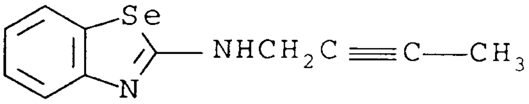
Compound IIG



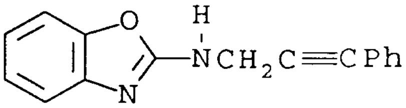
Compound IIH



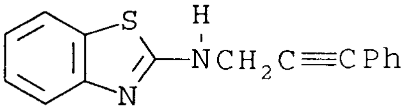
Compound IIJ



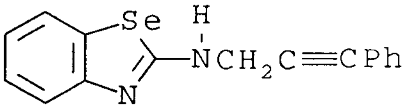
Compound IIK



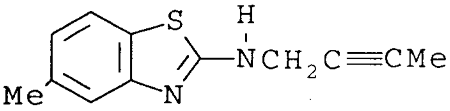
Compound IIL:



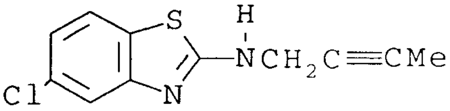
Compound IIM



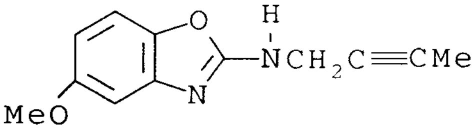
Compound IIN



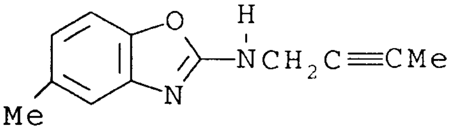
Compound IIO



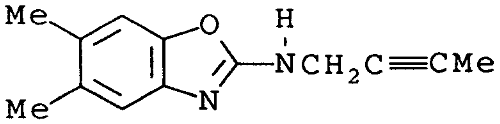
Compound IIP



Compound IIQ



Compound IIR



The alkynylamines are preferably incorporated into the emulsion in an amount between about 0.1 and about 1000 milligrams per mole of silver halide. A more preferred level of incorporated alkynylamine is between about 1 and about 500 milligrams per mole of silver halide.

Ideally, the alkynylamine of the present invention is butynylaminobenzoxazole (compound IIA). It is preferably incorporated into the emulsion in an amount between about 1 milligram per mole of silver halide and about 200 milligrams per mole of silver halide. More preferably, it is incorporated in an amount between about 5 and about 50 milligrams per mole of silver halide; and optimally, it is incorporated in an amount between about 5 and about 20 milligrams per mole of silver halide.

The alkynylamine of the invention may be prepared by any methods known in the art. Examples of such methods can be found in U.S. Patents 4,451,557 and 4,378,426, and in co-pending U.S. Patent Application Serial Number 93/00169833 filed December 16, 1993 by Lok et al., all of which are incorporated herein by reference.

The thiosulfonate and sulfinate compounds are preferable of Formula (III) and (IV), respectively, below:

$$Z_3\text{-}SO_2S\text{-}M^1 \qquad \text{(Formula III)}$$

$$Z_4\text{-}SO_2\text{-}M^2 \qquad \text{(Formula IV)}$$

For each compound of formula (III) or (IV), the Z substituent, whether Z_3 or Z_4, independently represents an aliphatic, carbocyclic (which includes an aryl), or heterocyclic group, which may be substituted or unsubstituted. Preferably, the Z substituents are independently selected from the group consisting of an unsubstituted or substituted alkyl of 1 to 22 (or even 1 to 10) carbon atoms, an unsubstituted or substituted aryl group having 6 to 20 carbon atoms, or an unsubstituted or substituted 3-membered to 15-membered heterocyclic group having one or two heteroatoms.

Examples of suitable aliphatic groups for formula (III) or (IV) compounds include methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, ethylhexyl, decyl, dodecyl, hexadecyl, octadecyl, isopropyl, t-butyl, butenyl, propynl, and butynyl. Examples of suitable carbocyclic groups are phenyl, tolyl, naphthyl, cyclohexyl, cycloheptatrienyl, cyclooctatrienyl, and cyclononatrienyl. Examples of suitable heterocyclic groups are pyrrole, furan, tetrahydrofuran, pyridine, picoline, piperidine, morpholine, pyrrolidine, thiophene, oxazole, thiazole, imidazole, selenazole, tellurazole, triazole, tetrazole, and oxadiazole.

Groups suitable for substitution on Z_3 and Z_4 include alkyl groups (for example, methyl, ethyl, hexyl), fluoroalkyl groups (for example, trifluoromethyl), alkoxy groups (for example, methoxy, ethoxy, octyloxy), aryl groups (for example, phenyl, naphthyl, tolyl), hydroxy groups, halogen (including Cl, F, and Br), aryloxy groups (for example, phenoxy), alkylthio groups (for example, methylthio, butylthio), arylthio groups (for example, phenylthio), acyl groups (for example, acetyl, propionyl, butyryl, valeryl), sulfonyl groups (for example, methylsulfonyl, phenylsulfonyl), acylamino groups, sulfonylamino groups, acyloxy groups (for example, acetoxy, benzoxy), carboxy groups, cyano groups, sulfo groups, and amino groups.

The Z substituents may further be associated with one or more divalent linking groups. The linking groups include an atom or group containing at least one atom of carbon, nitrogen, sulfur, or oxygen. Examples include alkylene, alkenylene, alkynylene, arylene, O, S, NH, CO, and SO_2. When such a linking group is present in the antifoggant/stabilizer compound, the compound is preferably a polymer.

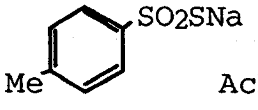
For each of the compounds represented by formulas (III) and (IV), M_1 and M_2 independently represent any cation, particularly a mono-, di-, or tri-valent cation. Thus, M_1 and M_2 include metal ions such as sodium ions, potassium ions, calcium ions, and lithium ions, as well as, ammonium ions and phosphonium ions. Preferably, M_1 and M_2 represent sodium ions.

Preferably. the emulsions contain a thiosulfonate (preferably of formula (III)) in an amount between about 20 to 20,000 milligrams per mole of silver halide (more preferably from 1 to 500 mg/mole of Ag). The amount of sulfinate (preferably of formula IV) is typically between 10^{-4} to 100 g per silver mol ("mol" = mole), and more preferably from 10^{-3} to 50 g, and most preferably from 10^{-2} to 10 g per silver mol. The ratio of thiosulfonate to sulfinate may vary from 1:0.1 to 1:10. The thiosulfonate and sulfinate could be premixed in a solution which is then added to a silver halide emulsion, or they may be added separately to the emulsion. The thiosulfonate and sulfinate compounds may be added to the silver halide emulsion layer or to a non-radiation sensitive layer or they may be added to a coupler containing dispersion. Further, the thiosulfonate and sulfinate may be added (separately or in combination) added during the emulsion precipitation process, the sensitization process or just prior to coating.

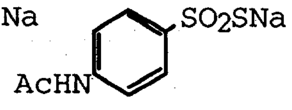
Optimally, the above-described thiosulfonate and sulfinate compounds are tolylthiosulfonate salts and tolylsulfinate salts, respectively.

Preparation of compounds of formula (III) have been described in the chemical literature such as in *Chem. Lett.* **1987**, *11*, 2161; *Organic Syntheses Collective* Volume VI, **1988**, p 1016; *Organic Syntheses*, **1974**, *54*, 33; *Journa of Organic Chemistry* **1986**, *51*(26), 5235; *Biochemical Preparations* **1963**, *10*, 72, or they may also be commercially available.

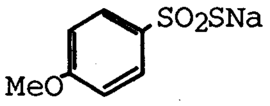
Examples of thiosulfonate compounds of the present invention include those of IIIA to IIID below:



IIIA



IIIC

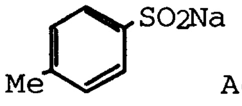


IIIB

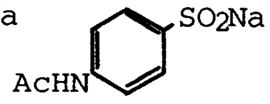
$EtSO_2SNa$

IIID

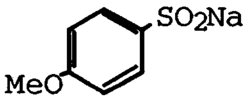
The sulfinates are also commercially available or they may be obtained by reduction of sulfonyl chlorides as taught in standard organic textbooks. Examples of particular sulfinates useful in the present invention are compounds IVA to IVD, below:



IVA



IVC



IVB

$EtSO_2Na$

IVD

The alkynylamine, as well as the thiosulfonate and sulfinate compounds, may be added to a black and white or color emulsion layer to which the blue sensitive dye of formula (I) is to be added, at any time during the preparation of the photographic element, including during the precipitation of the silver halide grains. It is preferred, though, that they be added post-precipitation and just prior to coating the emulsion on a support.

The combination of compounds selected from classes (I), (II), (III), and (IV) may also be used in addition to any conventional emulsion stabilizer or antifoggant as commonly practiced in the art.

Photographic materials of the present invention can be black and white photographic elements but are preferably color photographic elements. A color photographic element generally contains three silver emulsion layers or sets of layers (each set of layers often consisting of emulsions of the same spectral sensitivity but different speed): a blue-sensitive layer having a yellow dye-forming color coupler associated therewith; a green-sensitive layer having a magenta dye-forming color coupler associated therewith; and a red-sensitive layer having a cyan dye-forming color coupler associated therewith. Thus, in the foregoing elements the layers contain image forming couplers which form dyes which are the subtractive complement of the light to which the respective layers are sensitive. While this is preferred, it need not necessarily be the case and the layers may contain couplers which do not form such subtractive complements (that is, the image produced may be a false color image in which the processed element has colors which are not the same as those of the original image).

The layers of the element, including the layers of the image-forming units, can be arranged in various orders as known in the art. Typically, in a photographic element with a transparent support (such as a typical photographic color negative) the blue sensitive layer will be the lowest of the light sensitive layers, with the green sensitive layer above the blue sensitive layer, followed by the red sensitive layer above the green sensitive layer. The By "lower" and the like terms is meant that it will be furthest away from a light source during normal exposure of the element. The reverse order of the light-sensitive layers will typically be used on a reflective support (such as a typical photographic color paper). In a typical element having a support on which the various layers are coated, "lower" and the like will mean closer to the support.

In a alternative format, the emulsions sensitive to each of the different regions of the spectrum can be disposed as a single segmented layer.

The dye forming couplers are provided in the emulsion typically by first dissolving or dispersing them in a water immiscible, high boiling point organic solvent, the resulting mixture then being dispersed in the emulsion. Suitable solvents include those in European Patent Application 87119271.2. Dye-forming couplers are well-known in the art and are disclosed, for example, in Research Disclosure I referenced below. That reference and all patents and all other references cited in this application, are incorporated herein by reference.

The element can contain additional layers, such as filter layers, interlayers, overcoat layers, subbing layers, and the like. All of these can be coated on a support which can be transparent or reflective (for example, a paper support). Photographic elements of the present invention may also usefully include a magnetic recording material as described in Research Disclosure, Item 34390, November 1992, or a transparent magnetic recording layer such as a layer containing magnetic particles on the underside of a transparent support as in US 4,279,945 and US 4,302,523. The element typically will have a total thickness (excluding the support) of from 5 to 30 microns.

In the following discussion of suitable materials for use in elements of this invention, reference will be made to *Research Disclosure*, December 1989, Item 308119, published by Kenneth Mason Publications, Ltd., Dudley Annex, 12a North Street, Emsworth, Hampshire P010 7DQ, ENGLAND, which will be identified hereafter by the term "Research Disclosure I." The Sections hereafter referred to are Sections of the Research Disclosure I. The foregoing reference and any other reference cited herein are incorporated by reference in their entirety.

The silver halide emulsions employed in the elements of this invention can be either negative-working, such as surface-sensitive emulsions or unfogged internal latent image forming emulsions, or direct positive emulsions of the unfogged, internal latent image forming type which are positive working when development is conducted with uniform light exposure or in the presence of a nucleating agent. Suitable emulsions and their preparation as well as methods of chemical and spectral sensitization are described in Sections I through IV. Color materials and development modifiers are described in Sections V and XXI. Vehicles which can be used in the elements of the present invention are described in Section IX, and various additives such as brighteners, antifoggants, stabilizers, light absorbing and scattering materials, hardeners, coating aids, plasticizers, lubricants and matting agents are described , for example, in Sections V, VI, VIII, X, XI, XII, and XVI. Manufacturing methods are described in Sections XIV and XV, other layers and supports in Sections XIII and XVII, processing methods and agents in Sections XIX and XX, and exposure alternatives in Section XVIII.

With negative working silver halide a negative image can be formed. Optionally a positive (or reversal) image can be formed.

The photographic elements of the present invention may also use colored couplers (e.g. to adjust levels of interlayer correction) and masking couplers such as those described in EP 213.490; Japanese Published Application 58-172,647; U.S. Patent 2,983,608; German Application DE 2,706,117C; U.K. Patent 1,530,272; Japanese Application A-113935; U.S. Patent 4,070,191 and German Application DE 2,643,965. The masking couplers may be shifted or blocked.

The photographic elements may also contain materials that accelerate or otherwise modify the processing steps of bleaching or fixing to improve the quality of the image. Bleach accelerators described in EP 193,389; EP 301,477; U.S. 4,163,669; U.S. 4,865,956; and U.S. 4,923,784 are particularly useful. Also contemplated is the use of nucleating agents, development accelerators or their precursors (UK Patent 2,097,140; U.K. Patent 2,131,188); electron transfer agents (U.S. 4,859,578; U.S. 4,912,025); antifogging and anti color-mixing agents such as derivatives of hydroquinones, aminophenols, amines, gallic acid; catechol; ascorbic acid; hydrazides; sulfonamidophenols; and non color-forming couplers.

The elements may also contain filter dye layers comprising colloidal silver sol or yellow and/or magenta filter dyes, either as oil-in-water dispersions, latex dispersions or as solid particle dispersions. Additionally, they may be used with "smearing" couplers (e.g. as described in U.S. 4,366,237; EP 96,570; U.S. 4,420,556; and U.S. 4,543,323.) Also, the couplers may be blocked or coated in protected form as described, for example, in Japanese Application 61/258,249 or U.S. 5,019,492.

The photographic elements may further contain other image-modifying compounds such as "Developer Inhibitor-Releasing" compounds (DIR's). Useful additional DIR's for elements of the present invention, are known in the art and examples are described in U.S. Patent Nos. 3,137,578; 3,148,022; 3,148,062; 3,227,554; 3,384,657; 3,379,529; 3,615,506; 3,617,291; 3,620,746; 3,701,783; 3,733,201; 4,049,455; 4,095,984; 4,126,459; 4,149,886; 4,150,228; 4,211,562; 4,248,962; 4,259,437; 4,362,878; 4,409,323; 4,477,563; 4,782,012; 4,962,018; 4,500,634; 4,579,816; 4,607,004; 4,618,571; 4,678,739; 4,746,600; 4,746,601; 4,791,049; 4,857,447; 4,865,959; 4,880,342; 4,886,736; 4,937,179; 4,946,767; 4,948,716; 4,952,485; 4,956,269; 4,959,299; 4,966,835; 4,985,336 as well as in patent publications GB 1,560,240; GB 2,007,662; GB 2,032,914; GB 2,099,167; DE 2,842,063, DE 2,937,127; DE 3,636,824; DE 3,644,416 as well as the following European Patent Publications: 272,573; 335,319; 336,411; 346, 899; 362, 870; 365,252; 365,346; 373,382; 376,212; 377,463; 378,236; 384,670; 396,486; 401,612; 401,613.

DIR compounds are also disclosed in "Developer-Inhibitor-Releasing (DIR) Couplers for Color Photography," C.R. Barr, J.R. Thirtle and P.W. Vittum in *Photographic Science and Engineering*, Vol. 13, p. 174 (1969), incorporated herein by reference.

It is also contemplated that the concepts of the present invention may be employed to obtain reflection color prints as described in *Research Disclosure*, November 1979, Item 18716, available from Kenneth Mason Publications, Ltd, Dudley Annex, 12a North Street, Emsworth, Hampshire P0101 7DQ, England, incorporated herein by reference. The emulsions and materials to form elements of the present invention, may be coated on pH adjusted support as described in U.S. 4,917,994; with epoxy solvents (EP 0 164 961); with additional stabilizers (as described, for example, in U.S. 4,346,165; U.S. 4,540,653 and U.S. 4,906,559); with ballasted chelating agents such as those in U.S. 4,994,359 to reduce sensitivity to polyvalent cations such as calcium; and with stain reducing compounds such as described in U.S. 5,068,171 and U.S. 5,096,805. Other compounds useful in the elements of the invention are disclosed in Japanese Published Applications 83-09,959; 83-62,586; 90-072,629, 90-072,630; 90-072,632; 90-072,633; 90-072,634; 90-077,822; 90-078,229; 90-078,230; 90-079,336; 90-079,338; 90-079,690; 90-079,691; 90-080,487; 90-080,489; 90-080,490; 90-080,491; 90-080,492; 90-080,494; 90-085,928; 90-086,669; 90-086,670; 90-087,361; 90-087,362; 90-087,363; 90-087,364; 90-088,096; 90-088,097; 90-093,662; 90-093,663; 90-093,664; 90-093,665; 90-093,666; 90-093,668; 90-094,055; 90-094,056; 90-101,937; 90-103,409; 90-151,577.

The silver halide used in the photographic elements of the present invention may be silver iodobromide, silver bromide, silver chloride, silver chlorobromide, silver chloroiodobromide, and the like. Silver bromide and silver bromoiodide emulsions are particularly useful for the emulsions sensitized with a dye of formula (I). A high chloride silver halide emulsion is preferred though. In the case where a high chloride silver halide emulsion is used, the emulsion would contain at least 90% silver chloride or more (for example, at least 95%, 98%, 99% or 100% silver chloride). Some silver bromide may be present. Preferably if there is any iodide present in a high chloride emulsion it constitutes less than 2 mole% of all halide (although this may even be less than 1.5, 1, 0.5 or 0.1 mole%). In particular, the possibility is also contemplated that the silver chloride of a high chloride emulsion could be treated with a bromide source to increase its sensitivity, although the bulk concentration of bromide in the resulting emulsion will typically be no more than about 2 to 2.5% and preferably between about 0.5 to 1.5% (or even 0.5 to 1.0%) the remainder being silver chloride. The foregoing % figures are mole %.

The type of silver halide grains include polymorphic, cubic, octahedral or grains that are non-cubic. The grain size of the silver halide may have any distribution known to be useful in photographic compositions, and may be ether polydipersed or monodispersed. Tabular grain silver halide emulsions are also contemplated in the present invention.

Tabular grains are those with two parallel major faces each clearly larger than any remaining grain face and tabular grain emulsions are those in which the tabular grains account for at least 30 percent, more typically at least 50 percent, preferably >70 percent and optimally >90 percent of total grain projected area. The tabular grains can account for substantially all (>97 percent) of total grain projected area The tabular grain emulsions can be high aspect ratio tabular grain emulsions, that is emulsions wherein ECD/t >8, where ECD is the diameter of a circle having an area equal to grain projected area and t is tabular grain thickness; intermediate aspect ratio tabular grain emulsions, that is ECD/t = 5 to 8; or low aspect ratio tabular grain emulsions, that is ECD/t = 2 to 5. The emulsions typically exhibit high tabularity (T), where $T = ECD/t^2$, that is $ECD/t^2 > 25$, and ECD and t are both measured in micrometers (µm). The emulsion can further have a tabularity of > 40 or even >100 or >1000. The tabular silver halide emulsions for the blue sensitive layer preferably have a tabularity of from 25 to 4000, and more preferably from 100 to 1500).

The tabular grains can be of any thickness compatible with achieving an aim average aspect ratio and/or average tabularity of the tabular grain emulsion. Preferably the tabular grains satisfying projected area requirements are those having thicknesses of <0.3 µm, thin (<0.2 µm) tabular grains being specifically preferred and ultrathin (<0.07 µm) tabular grains being contemplated for maximum grain surface to volume ratios.

High iodide tabular grain emulsions are illustrated by House U.S. Patent 4,490,458, Maskasky U.S. Patent 4,459,353 and Yagi et al EPO 0 410 410.

Tabular grains formed of silver halide(s) that form a face centered cubic (rock salt type) crystal lattice structure can have either {100} or {111} major faces. Emulsions containing {111} major face tabular grains, including those with controlled grain dispersities, halide distributions, twin plane spacing, edge structures and grain dislocations as well as adsorbed {111} grain face stabilizers, are illustrated by Wey U.S. Patent 4,399,215, Maskasky U.S. Patents 4,400,463, 4,684,607, 4,713,320, 4,713,323, 5,061,617, 5,178,997, 5,178,998, 5,183,732, 5,185,239, 5,217,858 and 5,221,602, Wey et al U.S. Patent 4,414,306, Daubendiek et al U.S. Patents 4,414,310, 4,672,027, 4,693,964 and 4,914,014, Abbott et al U.S. Patent 4,425,426, Solberg et al U.S. Patent 4,433,048, Wilgus et al U.S. Patent 4,434,226, Kofron et al U.S. Patent 4,439,520, Sugimoto et al U.S. Patent 4,665,012, Yagi et al U.S. Patent 4,686,176, Hayashi U.S. Patent 4,748,106, Goda U.S. Patent 4,775,617, Takada et al U.S. Patent 4,783,398, Saitou et al U.S. Patents 4,797,354 and 4,977,074, Tufano U.S. Patent 4,801,523, Tufano et al U.S. Patent 4,804,621, Ikeda et al U.S. Patent 4,806,461 and EPO 0 485 946, Bando U.S. Patent 4,839,268, Makino et al U.S. Patent 4,853,322, Nishikawa et al U.S. Patent 4,952,491, Houle et al U.S. Patent 5,035,992, Piggin et al U.S. Patents 5,061,609 and 5,061,616, Nakamura et al U.S. Patent 5,096,806, Bell et al U.S. Patent 5,132,203, Tsaur et al U.S. Patents 5,147,771, '772, '773, 5,171,659, 5,210,013 and 5,252,453, Jones et al U.S. Patent 5,176,991, Maskasky et al U.S. Patent 5,176,992, Black et al U.S. Patent 5,219,720, Antoniades et al U.S. Patent 5,250,403, Zola et al EPO 0 362 699, Maruyama et al EPO 0 431 585, Urabe EPO 0 460 656, Verbeek EPO 0 481 133, 0 503 700 and 0 532 801, Jagannathan et al EPO 0 515 894 and Sekiya et al EPO 0 547 912. Emulsions containing {100} major face tabular grains are illustrated by Bogg U.S. Patent 4,063,951, Mignot U.S. Patent 4,386,156, Maskasky U.S. Patents 5,264,337 and 5,275,930, Brust et al EPO 0 534 395 and Saitou et al EPO 0 569 971.

The silver halide grains to be used in the invention may be prepared according to methods known in the art, such as those described in Research Disclosure I and James, The Theory of the Photographic Process, or US 4,439,520 for precipitation of iodobromide tabular grains (these references and all other references cited herein are incoporated in their entirety by reference to them). These include methods such as ammoniacal emulsion making, neutral or acid emulsion making, and others known in the art. These methods generally involve mixing a water soluble silver salt with a water soluble halide salt in the presence of a protective colloid, and controlling the temperature, pAg, pH values, etc, at suitable values during formation of the silver halide by precipitation.

The silver halide to be used in the invention may be advantageously subjected to chemical sensitization with noble metal (for example, gold) sensitizers, middle chalcogen (for example, sulfur) sensitizers, reduction sensitizers and others known in the art. Compounds and techniques useful for chemical sensitization of silver halide are known in the art and described in Research Disclosure I and the references cited therein.

The photographic elements of the present invention, as is typical, provide the silver halide in the form of an emulsion. Photographic emulsions generally include a vehicle for coating the emulsion as a layer of a photographic element. Useful vehicles include both naturally occurring substances such as proteins, protein derivatives, cellulose derivatives (e.g., cellulose esters), gelatin (e.g., alkali-treated gelatin such as cattle bone or hide gelatin, or acid treated gelatin such as pigskin gelatin), gelatin derivatives (e.g., acetylated gelatin, phthalated gelatin, and the like), and others as described in Research Disclosure I. Also useful as vehicles or vehicle extenders are hydrophilic water-permeable colloids. These include synthetic polymeric peptizers, carriers, and/or binders such as poly(vinyl alcohol), poly(vinyl lactams), acrylamide polymers, polyvinyl acetals, polymers of alkyl and sulfoalkyl acrylates and methacrylates, hydrolyzed polyvinyl acetates, polyamides, polyvinyl pyridine, methacrylamide copolymers, and the like, as described in Research Disclosure I. The vehicle can be present in the emulsion in any amount useful in photographic emulsions. The emulsion can also include any of the addenda known to be useful in photographic emulsions. These include chemical sensitizers, such as active gelatin, sulfur, selenium, tellurium, gold, platinum, palladium, iridium, osmium, rhenium, phosphorous, or combinations thereof. Chemical sensitization is generally carried out at pAg levels of from 5 to 10, pH levels of from 5 to 8, and temperatures of from 30 to 80°C, as illustrated in Research Disclosure, June 1975, item 13452 and U.S. Patent No. 3,772,031.

The silver halide may be sensitized by sensitizing dyes of formula I by any method known in the art, such as described in Research Disclosure I. Of course, various layers of photographic elements of the present invention may use sensitizing dyes other than those of formula I, but a dye of formula I will be present in at least one layer as a sensitizing dye. The dye may be added to an emulsion of the silver halide grains and a hydrophilic colloid at any time prior to (e.g., during or after chemical sensitization) or simultaneous with the coating of the emulsion on a photographic element. The dye/silver halide emulsion may be mixed with a dispersion of color image-forming coupler immediately before coating or in advance of coating (for example, 2 hours).

Photographic elements of the present invention are preferably imagewise exposed using any of the known techniques, including those described in Research Disclosure I, section XVIII. This typically involves exposure to light in the visible region of the spectrum (generally regarded as about 400 to 700nm) and includes exposure to a real-time image (that is, a live image) through a lens, or alternatively exposure to a stored image, such as a computer stored image, by exposure with light emitting devices such as light emitting diodes or lasers. Photographic elements of the present invention can be used in single use cameras (that is, so called "film with lens" units). Such cameras are manufactured and sold with film preloaded in them, and may or may not use plastic lenses.

Photographic elements comprising the composition of the invention can be processed in any of a number of well-known photographic processes utilizing any of a number of well-known processing compositions, described, for example, in Research Disclosure I, or in James, The Theory of the Photographic Process 4th, 1977. For example, in the case of processing a typical negative working element (such as a typical photographic color negative or photographic color paper), the element is treated with a color developer so that after processing is complete, an image which is the negative of that to which the element was exposed, is obtained. In the case of processing a reversal color element (which uses a negative working emulsion), the element is first treated with a black and white developer followed by fogging of the silver halide (chemically or by light), followed by treatment with a color developer. The resulting image after processing is complete is the reverse of that to which the element was exposed.

Preferred color developing agents are p-phenylenediamines. Especially preferred are:

4-amino N,N-diethylaniline hydrochloride,
4-amino-3-methyl-N,N-diethylaniline hydrochloride,
4-amino-3-methyl-N-ethyl-N-(β-(methanesulfonamido) ethylaniline sesquisulfate hydrate,
4-amino-3-methyl-N-ethyl-N-(β-hydroxyethyl)aniline sulfate,
4-amino-3-β-(methanesulfonamido)ethyl-N,N-diethylaniline hydrochloride and
4-amino-N-ethyl-N-(2-methoxyethyl)-m-toluidine di-p-toluene sulfonic acid.

Development is followed by bleach-fixing, to remove silver or silver halide, washing and drying.

The invention is described further in the following examples.

Example 1

An emulsion in accordance with the present invention was made by adding compounds of the formulas (I), (II), (III) and (IV) to a Au(I) sensitized 0.78μm monodisperse silver chloride negative emulsion having a dye coverage of 2.62 x 10^{-4} mol/Ag mol. Said emulsion containing yellow dye-forming coupler alpha-(4-(4-benzyloxy-phenyl-sulfonyl)phenoxy)-alpha(pivalyl)-2-chloro-5-(gamma-(2,4-di-5-amylphenoxy)butyramido)acetanilide (1.08 g/m^2) in di-n-butylphthalate coupler solvent (0.27 g/m^2) and gelatin (1.51 g/m^2). In addition, 0.104 g of 1-(3-acetamidophenyl)-5-mercaptotetrazole and 1.033 g of potassium bromide per silver mole were added. The emulsion (0.34 g Ag/m^2) was coated on a resin coated paper support and 1.076 g/m^2 gel overcoat was applied as a protective layer along with the hardener bis (vinylsulfonyl) methyl ether in an amount of 1.8% of the total gelatin weight.

The coatings were given a 0.1 second exposure, using a 0-3 step tablet (0.15 increments) with a tungsten lamp designed to simulate a color negative print exposure source. This lamp had a color temperature of 3000 K, log lux 2.95, and the coatings were exposed through a combination of magenta and yellow filters, a 0.3 ND (Neutral Density), and a UV filter. The processing consisted of a color development (45 s, 35 °C), bleach-fix (45 s, 35 °C) and stabilization or water wash (90 s, 35 °C) followed by drying (60 s, 60 °C). The chemistry used in the Colenta processor consisted of the following solutions:

Developer	
Lithium salt of sulfonated polystyrene	0.25 mL
Triethanolamine	11.0 mL
N,N-diethylhydroxylamine (85% by wt.)	6.0 mL
Potassium sulfite (45% by wt.)	0.5 mL
Color developing agent (4-(N-ethyl-N-2-methanesulfonyl aminoethyl)-2-methyl-phenylenediaminesesquisulfate monohydrate	5.0 g
Stilbene compound stain reducing agent	2.3 g
Lithium sulfate	2.7 g
Potassium chloride	2.3 g
Potassium bromide	0.025 g
Sequestering agent	0.8 mL
Potassium carbonate	25.0 g
Water to total of 1 liter, pH adjusted to 10.12	

Bleach-fix	
Ammonium sulfite	58 g
Sodium thiosulfate	8.7 g
Ethylenediaminetetracetic acid ferric ammonium salt	40 g
Acetic acid	9.0 mL
Water to total 1 liter, pH adjusted to 6.2	

Stabilizer	
Sodium citrate	1 g
Water to total 1 liter, pH adjusted to 7.2	

The speed at 1.0 density units was taken as a measure of the sensitivity of the emulsion.

Table II illustrates the effects of compound I-17 of the present invention in the presence of IIA (a compound of formula (II)), and IIIA. Compound I-17 provides the emulsion with a λ_{max} at about 10 nm shorter than the comparison dye C and the coating containing I-17 is clearly slower than that containing C (that is, sample 2 has a lower speed than sample 1). While the combination of dye I-17 with compound IIA improves the emulsion speed, the D-min position (fog) of the coating has significantly increased (sample 3 vs 2). The combination of IIIA with I-17 has little effect on speed even though D-min is improved (sample 4 vs 3). In sample 5 where the use of I-17 is combined with both IIA and IIIA, there is an increase in emulsion speed, with only a limited rise in fog (sample 5 vs 1, 2, and 3).

Table II

Dye	IIA	IIIA*	Sample #	Speed	D-min
	mg				
	Ag mole				
C	0	0	1 (comparison)	174	0.15
I-17	0	0	2 (comparison)	136	0.12
I-17	60	0	3 (comparison)	225	0.94
I-17	0	100	4 (comparison)	136	0.09
I-17	60	100	5 (invention)	165	0.39

*IIIA is co-mixed with IVA at 10X amount of IIIA.

Example 2

The same emulsion for this example is used as in Example 1, except that compound I-8 is combined with IIA and IIIA. Dye I-8 also provides the emulsion with a λ_{max} which is at 10 nm shorter than that provided by dye C. The emulsion sensitized with dye I-8, as expected, is slower than C (sample 6 vs 1 in Table III). Sample 7, which contains compound I-8 and IIA shows that there is a clear speed increase over sample 6 but is accompanied by high fog. The combination of the present invention (sample 9) matches the speed of the comparison dye (sample 1) with little increase in fog.

Table III

Dye	IIA	IIIA*	Sample #	Speed	D-min
	mg				
	Ag mole				
C	0	0	1 (comparison)	174	0.15
I-8	0	0	6 (comparison)	158	0.10
I-8	60	0	7 (comparison)	183	0.36
I-8	0	100	8 (comparison)	160	0.10
I-8	60	100	9 (invention)	175	0.17
IIIA is co-mixed with IVA at 10X amount of IIIA.					

Example 3

Another emulsion in accordance with the present invention was made by adding compounds I-19, IIA, and IIIA to an emulsion as in example 1 except mercuric chloride was used during the precipitation of the silver chloride emulsion.

The results in Table IV show that the sample of the present invention (sample 14) containing the combination has a higher speed and lower fog than the comparison samples (samples 11, 12, and 13).

Table IV

Dye	IIA	IIIA*	Sample #	Speed	D-min
	mg				
	Ag mole				
C	0	0	10 (comparison)	204	0.08
I-19	0	0	11 (comparison)	181	0.08
I-19	60	0	12 (comparison)	209	0.48
I-19	0	100	13 (comparison)	180	0.10
I-19	60	100	14 (invention)	198	0.16
IIIA is co-mixed with IVA at 10X amount of IIIA.					

Example 4

This example illustrates the keeping benefits of the emulsion containing the combination of I-20, IIA, IIIA and IVA of the present invention in an emulsion similarly sensitized as in example 3. After coating, the samples were stored for 4 and 6 weeks at 48.8°C. The changes in speed ("Δ Speed") and fog ("ΔD-min") were measured against those from samples that were kept as checks at -17.7°C . The data is tabulated in Table V below:

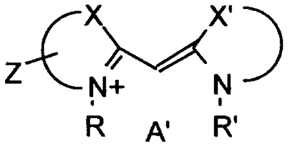
Table V

IIA	IIIA	Sample #	Fresh		4-week		6-week	
mg					48.8°C vs -17.7 °C		48.8°C vs -17.7 °C	
Ag mol			Speed	Δ-min	Δ Speed	Δ D-min	Δ Speed	Δ D-min
0	0	15 comparison	180	0.07	22	0.21	26	0.48
60	0	16 comparison	191	0.16	31	0.50	51	0.79
0	100	17 comparison	181	0.07	4	0.11	-2	0.21
60	100	18 invention	188	0.10	4	0.17	-5	0.29

As expected, the data in Table V shows that the invention coating (sample 18) has the advantage of higher fresh speed at a reasonable fog level than sample 15 which does not have the combinations of the classes of compounds represented by formulae II and III. Further, the keeping property of sample 18 is superior to sample 15 in that there is less change in speed and fog either in the 4 or the 6 weeks of storage.

Claims

1. A silver halide photographic element comprising a silver halide emulsion sensitized by a blue dye of formula (I) below, the emulsion also containing a thiosulfonate, a sulfinate, and an alkynylamine;



(I)

wherein:

X and X' each independently represent the atoms necessary to complete a 5- or 6-membered heterocyclic nucleus, and X may be further substituted and X' is substituted or unsubstituted;

R and R' each independently represents substituted or unsubstituted aryl or substituted or unsubstituted alkyl,

Z represents a substituted or unsubstituted aryl or heteroaryl containing group;

A' a counterion as needed to balance the charge of the molecule.

2. A photographic element according to claim 1 wherein the alkynylamine is of formula (II) below:

$$\text{Y-NHCH}_2\text{C}{\equiv}\text{CR''} \qquad \text{(II)}$$

wherein:

R" represents an aliphatic, carbocyclic, or heterocyclic group, any of which may be substituted or unsubstituted, or a hydrogen atom; and

Y represents a nitrogen containing heterocycle; the thiosulfonate is of formula (III) below

$$Z_3\text{-SO}_2\text{S-M}_1 \qquad \text{(III)}$$

wherein:

Z_3 represents an aliphatic, carbocyclic, or heterocyclic group any of which may be substituted or unsubstituted; and

M_1 represents a cation;

and/or

the sulfinate is of formula (IV) below:

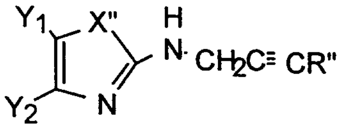
$$Z_4\text{-}SO_2\text{-}M_2 \qquad (IV)$$

wherein:

Z_4 represents an aliphatic, carbocyclic, or heterocyclic group, any of which may be substituted or unsubstituted; and

M_2 represents a cation.

3. A photographic element according to claim 1 or claim 2 wherein the alkynylamine is of formula (IIa) or formula (IIb):

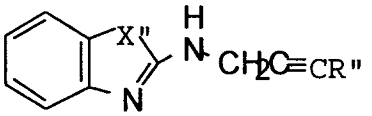


(IIa)

wherein:

X" is O, S or Se; and

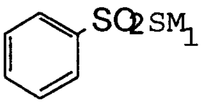
Y_1 and Y_2 are, independently, alkyl or aryl both of which may be substituted or unsubstituted, or together they may form a ring which may be substituted or unsubstituted;



(IIb)

wherein the benzo ring may be further substituted or unsubstituted, preferably, R" is methyl, X" is O and the benzo ring is unsubstituted;

the thiosulfonate is of formula (IIIA) below

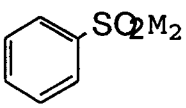


(IIIA)

wherein the phenyl ring may be further substituted or not further substituted;

and/or

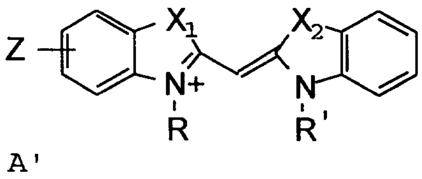
the sulfinate is of formula (IVa) below:



(IVA)

wherein the phenyl ring may be further substituted or not further substituted.

4. A photographic element according to any preceding claim, wherein the dye of formula (I) is of formula (Ia) below:

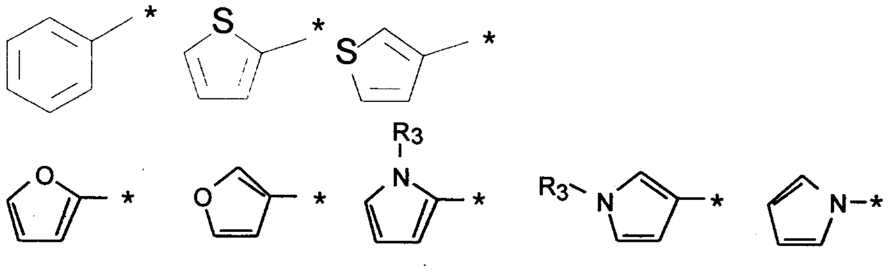


(Ia)

wherein: X_1 and X_2 are, independently, O, S or Se and the benzo rings may be further substituted or unsubstituted and the aryl or heteroaryl ring of Z is directly appended to the benzo ring shown.

5. A photographic element according to claim 4 wherein both R and R' of the dye of formula (Ia) are substituted or unsubstituted alkyl, with at least one of R or R' having an acid or acid salt substituent.

6. A photographic element according to any preceding claim wherein Z is any one of the following:



wherein each ring, when present, is directly appended to the nucleus which includes X and N and * indicates the point of attachment to that nucleus, R3 is hydrogen, substituted or unsubstituted alkyl, or substituted or unsubstituted aryl, and any of the rings shown can be substituted or unsubstituted.

7. A photographic element according to any preceding claim wherein the silver halide emulsion is a negative working emulsion.

8. A photographic element according to any preceding claim wherein the silver halide emulsion is 90 mole% silver chloride.

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 20 2906

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)
A	WO-A-92 12462 (EASTMAN KODAK COMPANY) 23 July 1992 * page 1, line 5 - page 1, line 11 * * page 4, line 20 - page 7, line 32 * ---	1-8	G03C1/10 G03C1/34
D,A D	EP-A-0 358 170 (FUJI PHOTO FILM CO.) 14 March 1990 * page 2, line 4 - page 4, line 11 * & US-A-5 110 179 5 May 1992 ---	1-8	
D,A	US-A-4 451 557 (R. LOK ET AL.) 29 May 1984 * column 1, line 10 - column 4, line 3 * ---	1-8	
D,A	RESEARCH DISCLOSURE, vol. 362, no. 16, June 1994 HAVANT GB, pages 291-303, DISCLOSED ANONYMOUSLY 'Photographic Multilayer Elements' * page 291, left hand column - page 291, right hand column, first paragraph * ---	1-8	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
P,A	US-A-5 399 479 (R. LOK) 21 March 1995 * column 1, line 5 - column 6, line 54 * -----	1-8	G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	4 January 1996	Markowski, V

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
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E : earlier patent document, but published on, or after the filing date
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& : member of the same patent family, corresponding document