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(54) **Bright safe light handleable high contrast photographic materials**

Bei hellem Sicherheitslicht verarbeitbare hochkontrastreiche photographische Materialien

Matériaux photographiques à haut contraste utilisables à la lumière inactinique

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(56) References cited:
EP-A- 0 306 019 **JP-A-63 108 335**
US-A- 4 722 884

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Description

This invention relates to negative acting silver halide photographic materials capable of producing high contrast silver images. In particular the invention relates to high contrast photographic materials having a reduced propensity to formation of pepper fog which are also handleable under bright amber safelight conditions.

It is often desirable to produce black-and-white photographic images formed by a combination of maximum density areas and minimum density areas e.g. half tone imaging. For such imaging applications a contrast of at least 10 (herein referred to as high contrast) and more typically near or above 20 is employed. An example of high contrast photographic elements having white reflective supports are phototypesetting materials intended to produce black type character images on the white background. An example of high contrast photographic elements having transparent supports are lith films, so called because they are used as contact transparencies for exposing lithographic printing plates. The illusion that some areas of a printed image are of intermediate density is created by the viewer's inability to resolve tiny dots of maximum density and background areas of minimum density that separate them.

The use of hydrazines in the developer and/or photographic elements of high contrast systems to increase speed and contrast is well known and disclosed, for example, in British Patent No. 598108, United States Patents 2322027, 2419974, 2419975, 4166742, 4211857, 4224401, 4243739, 4272606, 4272614, 4311781 and 4323643 and in Research Disclosure, Vol. 235, November 1983, Item 23510.

In surface latent image forming silver halide emulsions the grains which are exposed to light are rendered developable while grains which are not exposed to light are not intended to be developed. Nevertheless, some of these unexposed grains develop spontaneously. In full-tone imaging the spontaneously developing grains raise minimum density more or less uniformly. Such minimum density levels are referred to as fog and, so long as they remain low, are not objectionable.

Pepper fog differs from ordinary fog in that it takes the form of small, maximum density areas randomly distributed on a substantially uniform minimum density background. When a photographic element exhibiting pepper fog is viewed under magnification the impression to the viewer is often that the magnified field of view has been sprinkled with grains of pepper.

Pepper fog is a well recognised problem in high contrast photographic systems and provides a serious problem to the photographic printing plate making process. These black spots are tiny black specks which appear in the area between dots that is not intended to be developed and tend to increase and grow on ageing of the photographic material and particularly during storage thereof under high temperature, high humidity conditions, or as the concentration of the sulphite ion used commonly as a preservative in the developer decreases or as the pH value of the solution increases. The formation of black peppers detracts considerably from the marketability of the product as a photographic material for manufacturing a photographic printing plate. Many efforts have been made to overcome this black pepper problem but improvement in black pepper is often accompanied by decreases in sensitivity and gamma (contrast), and there has been a strong demand for a photographic system conducive to an improvement in black pepper which does not entail losses of sensitivity and high contrast.

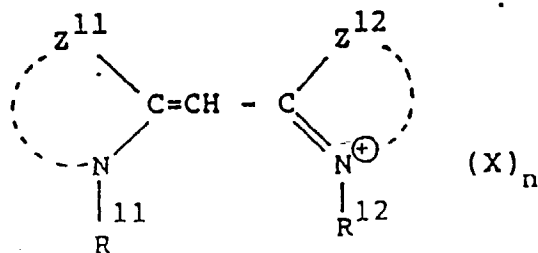
United States Patent Specification No. 4618574 discloses a negative working photographic element capable of producing a high contrast silver image. The element comprises surface latent image forming monodispersed silver halide grains having a mean diameter of less than 0.7 microns a contrast enhancing arylhydrazide, and, in an amount sufficient to reduce pepper fog while maintaining high contrast, a polyhydroxybenzene and a carboxyalkyl-3H-thiazoline-2-thione.

European Patent Publication No. 0196626 discloses a silver halide photographic material comprising a support, at least one silver halide emulsion layer and one or more light-insensitive hydrophilic colloid layers, wherein said silver halide emulsion layer or said light-insensitive hydrophilic colloid layer contains a hydrazine derivative, and the photographic material has a film surface pH not higher than 5.8 on the side of said emulsion layer inclusive of said light-insensitive hydrophilic colloid layer. The formation of pepper fog is reduced by maintaining the pH of the film surface on the side of the emulsion layer to not more than 5.8.

U.S. Patent Specification No. 4,272,606 discloses the construction of a photographic material having high contrast and lower pepper fog which contains a hydrazine together with a compound containing a thioamido moiety in the molecule, included within this class are molecules containing the rhodanine and thiohydantoin nucleus.

European Patent Publication No. 0285308 discloses the use of water-soluble bromide and chloride compounds e.g. alkali metal chlorides or bromides, added to a high contrast silver halide photographic emulsion in association with a hydrazine as a way of controlling pepper fog and increasing contrast.

EP-A-306019 which forms part of the state of the art by virtue of Article 54(3) EPC discloses a negative silver halide photographic material composed of a support having thereon at least one chemically sensitised silver halide emulsion layer at least one hydrophilic colloidal layer containing a hydrazine derivative and a compound having substantially all absorption maxima outside the visible light region represented by formula (I)

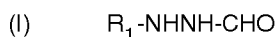


wherein:

Z¹¹ and Z¹² each represents a non-metallic atomic group necessary for completing a substituted or unsubstituted heterocyclic ring selected from benzoxazole, benzothiazole, benzoselenazole, naphthoxazole, naphthothiazole, naphthoselenazole, thiazole, thiazoline, oxazole, selenazole, selenazoline, pyridine, benzimidazole, and quinoline, R¹¹ and R¹² each represents a substituted or unsubstituted alkyl group, provided that at least one of them is substituted with an acid radical,

X represents a counter ion necessary for charge balance, and n is 0 or 1.

US-A-4722884 discloses a negative silver halide photographic light-sensitive material, having a silver halide emulsion layer, which layer comprises silver haloiodide grains prepared in the presence of an iridium salt in an amount of 1×10^{-8} to 1×10^{-5} mole per one mole of silver, wherein the silver iodide content in the surface part of said grain is larger than the average silver iodide content in said grains, and additionally containing in said emulsion layer or in some other hydrophilic colloid layer, a compound of formula (I):



wherein:

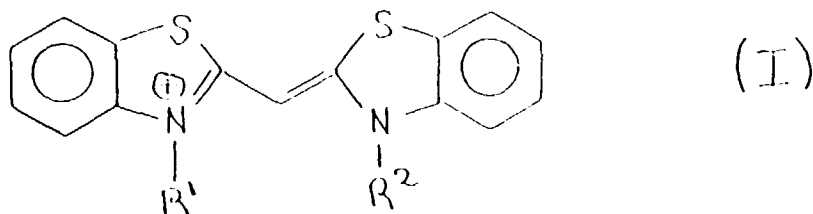
R₁ represents an aliphatic group or an aromatic group. The emulsion may optionally be spectrally sensitised and various kinds of sensitising dyes which are known in the technical field of photographic light-sensitive materials, for example, cyanine dyes or merocyanine dyes, may be used therefor.

JP-A-63 108335 discloses a high contrast photographic emulsion containing a contrast enhancing hydrazine compound, at least one cationic cyanine dye and at least one anionic dye which is added after the cationic dye.

It is highly desirable in modern photographic workshops to have a brightly lit environment and there is a trend towards photosensitive materials which can be handled under these conditions. The sensitivity of materials which are handleable in bright amber light conditions must be such that the sensitivity to electromagnetic radiation does not extend much beyond 540nm. The natural sensitivity of silver halide emulsions is such that they meet the criteria, for example silver chloride absorbs little radiation above 440nm, silver bromide above 500nm and a typical iodobromide emulsion shows little sensitivity to radiation above 540nm. However, when a material is constructed using spectrally-unsensitised silver halide emulsion in combination with a hydrazine, although the requirements of sensitivity and bright amber safelight handleability are met, there are serious problems with the formation of pepper fog.

It has now been found that the presence of certain monomethinebenzthiazole compounds provides high contrast silver halide photographic emulsions with amber safelight tolerance, and greatly reduced levels of pepper fog.

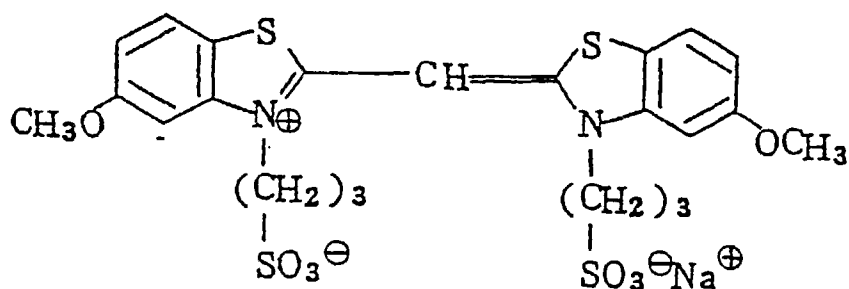
Therefore according to the present invention there is provided a photographic element capable of producing a high contrast silver image comprising a high contrast negative-acting silver halide photographic emulsion in association with a hydrazine characterised in that the emulsion is additionally associated with a monomethinebenzthiazole compound having a nucleus of the general formula:



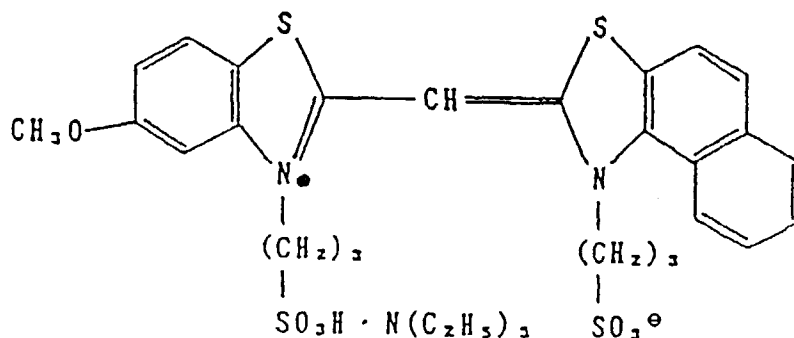
in which:

one of R¹ and R² represents an organic group containing an acid function and the other is selected from hydrogen, an optionally substituted alkyl group and an organic group containing an acid function, with the provisos that:

- (i) the emulsion is not associated with the combination of one or more anionic cyanine dyes and one or more cationic cyanine dyes,
- (ii) the silver halide grains were not prepared in the presence of an iridium salt, and
- (iii) the monomethinebenzthiazole compound is not



or



It has been surprisingly found that the addition of a monomethinebenzthiazole compound of formula (I) significantly reduces pepper fog formation in hydrazine-containing high contrast photographic emulsions. The compound is usually added in an amount 10^{-5} to 3×10^{-1} moles per mole of silver halide producing a dramatic reduction in pepper fog formation. Thus it is readily possible to provide high contrast photographic elements which are handleable under bright amber safelight conditions and have little propensity to formation of pepper fog.

Although benzthiazole cyanine dyes are well known as spectral sensitizers for silver chlorobromide or bromide emulsions, heretofore they have not been used as pepper fog controllers in hydrazine containing systems.

Canadian Patent No. 1146001 and U.S. Patent No. 4618574 disclose a list of useful spectral sensitizing compounds for high contrast hydrazine containing materials. The preferred compounds are said to be cationic cyanine and merocyanine dyes and are generally ortho and panchromatic sensitizers. There is no disclosure of the compounds of formula (I). U.S. Patent No. 2410690 relates to a combination of a hydrazine derivative and a cationic onium compound such as cyclammonium quaternary salts or sulphonium salts to give improved speed and contrast in photographic emulsion. This Patent gives examples of the ways in which such a system may be spectrally sensitized particularly to green light and the use of the monomethine dyes, 3,3'-diethyloxacyanine iodide, 3,3'-diethyl-4,5,4',5' dibenzothiacyanine iodide and 1,1'-diethyl 2,2'-cyanine iodide among others is disclosed in this connection. Although these compounds are structurally similar to the compounds of formula (I) they were added solely to increase the spectral sensitivity of the silver halide material and there is no indication they have any activity as pepper fog inhibitors. In the present invention spectral sensitization beyond about 500 nm is undesirable since the coating is intended for safe handling under bright orange lighting conditions.

Emulsions prepared in accordance with the invention show essentially no sensitivity at wavelengths beyond 540 nm, and a slightly enhanced sensitivity to the blue region. As a result, when imaged by a white-light source they display

a sensitivity that is only marginally less than that of a conventional green-sensitised lith emulsion, but their tolerance of amber safe-light is greatly improved. In addition, the emulsions show practically no pepper fog.

This desirable combination of effects appear to be restricted to the narrow range of compounds defined by formula (I). Thus monomethinebenzthiazoles similar to compounds of formula (I) but lacking an acidic group on R¹ and R² do not control pepper fog. Likewise, benzoxazole analogues of formula (I), with or without acid groups on R¹ or R², do not control pepper fog.

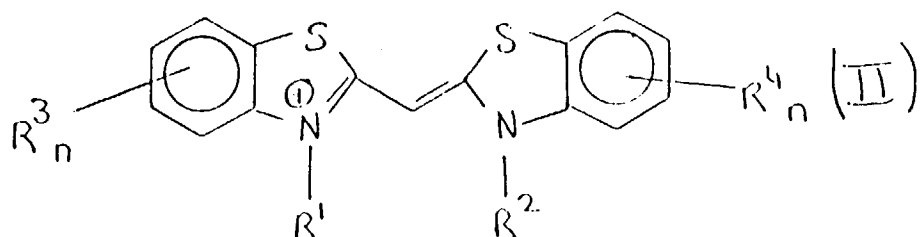
The compounds of formula (I) may be present in a silver halide photographic emulsion or may be incorporated in layers other than the silver halide photographic emulsion layer, such as a protective layer, interlayers, a filter layer, etc. adjacent to the emulsion layer. It is, however, preferred for the compound of formula (I) to be incorporated in a surface latent image type silver halide photographic emulsion layer together with the hydrazine compound.

The amount of the compound of formula (I) added is from 10⁻⁵ to 3 x 10⁻¹, generally from 10⁻⁵ to 5 x 10⁻² mole, per mole of silver contained in the silver halide photographic emulsion layer associated with the compound, but it is preferred to select the optimum content of the compound depending on the grain size of silver halide emulsion, the composition of the silver halide, the method and degree of chemical sensitisation employed and the type of hydrazine used. The method of testing for sensitisation is well known to one skilled in the art and can be easily accomplished.

To incorporate the dye of general formula (I) in a silver halide layer or other layer, various well known methods can be used. The compound may be added to an aqueous solution of a hydrophilic colloid as a solution in an organic solvent miscible with water, such as alcohols e.g. methanol, ethanol, etc, and ketones e.g. acetone, when the compound is oleophilic or as an aqueous solution when the compound is hydrophilic. In adding the compound it is sometimes convenient for dissolution to use an alkaline aqueous solution, alternatively combinations of solvent can be used.

In adding the compound of formula (I) to a silver halide photographic material, the compound may be added at any time between the start of chemical ripening and the start of the coating process, but it is preferred to add the compound after the end of the chemical ripening of the silver halide emulsion. It is particularly preferred to add the compound to the coating composition of a silver halide photographic emulsion prepared for coating.

The compound of formula (I) may possess one or more ring substituents of the type known in cyanine dyes. Thus the compounds may be represented by the general formula:



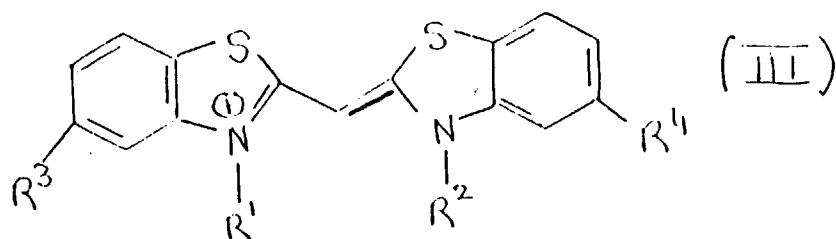
in which:

each n independently represents 0, 1, 2, 3 or 4,

each R³ and R⁴ may be the same or different and represent a substituent of the type known in cyanine dyes. Exemplary substituents include halogen, carboxyl, hydroxy, cyano, alkyl, alkoxy, alkylthio and alkoxy carbonyl. The carbon atom chains of these substituents generally contain up to 10 carbon atoms, preferably 1 to 5 carbon atoms. R³ and/or R⁴ may also represent the atoms necessary to complete a carbocyclic or heterocyclic ring, which itself may bear substituents selected from the above list.

At least one of R¹ and R² represents an organic group containing an acid function e.g. alkylsulphonate, alkylphosphate, alkyl carboxylate in which the alkyl groups generally contain 1 to 10 carbon atoms, preferably 1 to 5 carbon atoms. The other of R¹ and R² may additionally represent a hydrogen atom or an alkyl group, generally of up to 10 carbon atoms, preferably 1 to 5 carbon atoms. The alkyl group may be substituted e.g. with the substituents listed above with respect to R³ and R⁴.

Preferred compounds for use in the invention include those of the formula:

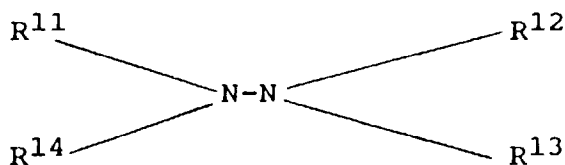


in which R¹ to R⁴ are defined above.

Specific examples of compounds of formula (III) are shown in the following Table. They are readily prepared by standard methods well-known in the cyanine dye art.

Compound No.	R ¹	R ²	R ³	R ⁴
1	(CH ₂) ₂ CHCH ₃ SO ₃ [⊖]	(CH ₂) ₂ CHCH ₃ SO ₃ (NH(C ₂ H ₅) ₃)	OCH ₃	OCH ₃
2	(CH ₂) ₂ CHCH ₃ SO ₃ [⊖]	(CH ₂) ₂ CHCH ₃ SO ₃ (NH(C ₂ H ₅) ₃)	Cl	Cl
3	(CH ₂) ₃ SO ₃ [⊖]	C ₂ H ₅	H	H
4	(CH ₂) ₄ SO ₃ [⊖]	C ₂ H ₅	H	H
5	(CH ₂) ₂ CHCH ₃ SO ₃ [⊖]	C ₂ H ₅	SCH ₃	SCH ₃

The hydrazine compound present in the photographic element may comprise hydrazine or any hydrazine derivative capable of increasing speed and/or contrast of photographic silver halide emulsions. Such compounds are well known in the photographic art. In general suitable hydrazines will have the general formula:



wherein:

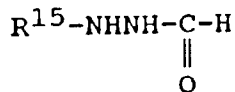
R¹¹ is an organic radical, and
R¹², R¹³ and R¹⁴ each are hydrogen or an organic radical.

Organic radicals represented by R¹¹, R¹², R¹³ and R¹⁴ include hydrocarbon groups, such as an alkyl group, an aryl group, an aralkyl group and an alicyclic group and such groups can be substituted with substituents such as alkoxy groups, carboxy groups, sulfonamido groups and halogen atoms.

Other examples of hydrazine derivatives are hydrazides, acyl hydrazines, semicarbazides, carbohydrazides and aminobiuret compounds.

Hydrazine compounds suitable to be incorporated into the photographic element according to the present invention are disclosed in GB Patent Specification 598108 and in US Patent Specification 2419974; they include the water soluble alkyl, aryl and heterocyclic hydrazine compounds as well as the hydrazide, semicarbazide and aminobiuret compounds.

A further class of hydrazine compounds, for use according to this invention incorporated in the photographic element, are the formylhydrazine compounds corresponding to the formula:

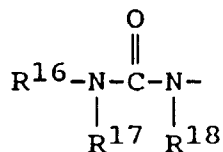


wherein:

R¹⁵ represents a substituted or unsubstituted aromatic group.

Examples of aromatic groups represented by R¹⁵ include a phenyl group and a naphthyl group. Such aromatic groups may be substituted with one or more substituents which are not electron attracting, such as straight or branched-chain alkyl groups (e.g. methyl, ethyl, propyl, isopropyl, n-butyl, n-octyl, n-hexyl, tert.-octyl, n-decyl, n-dodecyl, etc.), aralkyl groups (e.g. benzyl, phenethyl, etc.), alkoxy groups (e.g. methoxy, ethoxy, 2-methyl-propyloxy, etc.), amino

groups which are mono, or disubstituted with alkyl groups acylaminoaliphatic groups (e.g. acetylamino, benzoylamino etc.), as disclosed in US Patent 4168977 and in CA Patent 1146001. Such aromatic groups may also be substituted with a ureido group of formula:

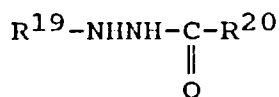


wherein:

R¹⁶ and R¹⁷ (which may be same or different) each represents hydrogen, an aliphatic group (such as a straight or branched-chain alkyl group, a cycloalkyl group, a substituted cycloalkyl group, an alkenyl group and an alkynyl group), an aromatic group (such as a phenyl group and a naphthyl group) or a heterocyclic group;

R¹⁸ represents hydrogen or an aliphatic group (such as those listed above as described in US Patent 4323643).

Other hydrazine compounds, for use according to this invention incorporated in the photographic element, are those represented by the formula:

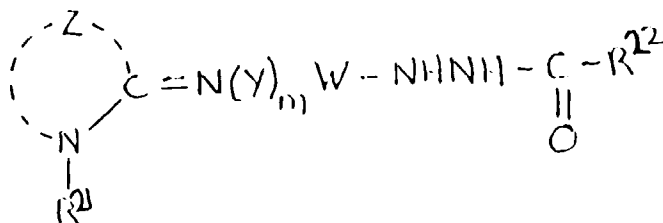


wherein:

R¹⁹ represents the same aromatic group of the formula above, and

R²⁰ represents an alkyl group having 1 to 3 carbon atoms, which may be a straight or branched-chain alkyl (e.g. methyl, ethyl, n-propyl and isopropyl) or a phenyl group. The phenyl group may be substituted with one or more substituents which preferably are electron attracting groups, such as halogen atoms (chlorine, bromine, etc.), a cyano group, a trifluoromethyl group, a carboxy group or a sulfo group, etc. Specific examples of hydrazine compounds represented by the formula above are disclosed in US Patent Specification 4224401.

Still other examples of hydrazine compounds, for use according to this invention incorporated in the photographic element, are those corresponding to the formula:



wherein:

R²¹ represents hydrogen, an aliphatic group which may be substituted;

Y represents a divalent linking group;

m represents 0 or 1,

W represents a divalent aromatic group (such as for example a phenylene group, a naphthylene group and the analogous substituted groups thereof);

R²² represents a hydrogen atom, an aliphatic group which may be substituted and Z represents the non-metallic atoms necessary to form a 5- or 6-membered heterocyclic ring. Specific examples of hydrazine compounds represented by the formula above are disclosed in US Patent 4272614.

In one particular form the hydrazine compound to be incorporated in the photographic element is substituted with ballasting groups, such as the ballasting groups of incorporated colour couplers and other non-diffusing photographic emulsion addenda. Said ballasting groups contain at least 8 carbon atoms and can be selected from the relatively non-reactive aliphatic and aromatic groups such as alkyl, alkoxy, alkylphenyl, phenoxy, alkylphenoxy groups and the like.

Such hydrazine compounds can be incorporated in the photographic element using various methods well-known

in the photographic art, the most common being the method of dissolving the hydrazine derivatives in a high boiling solvent and dispersing the mixtures in the emulsion, as described for example in US Patent 2322027.

A preferred class of hydrazines suitable for use in the invention as disclosed in European Patent Publication No. 253665 and are of the general formula:



in which:

R^{23} represents an aryl group,
 one of R^{24} and R^{25} is a hydrogen and the other is selected from hydrogen, arylsulphonyl and trifluoroacetyl,
 G represents carbonyl, sulphonyl, sulphony, phosphoryl, or an N-substituted or unsubstituted imino group and,
 X is hydrogen, alkyl, aryl or a moiety such that at a pH in the range of 9.5 to 12.5 in the presence of an oxidised hydroquinone a cyclisation reaction takes place cleaving the moiety -G-X from the remainder of the molecule and forming a cyclic structure comprising atoms of the moiety -G-X.

The hydrazine compound is incorporated in the photographic element, for example in a silver halide emulsion layer or in a hydrophilic colloidal layer, preferably a hydrophilic colloidal layer adjacent to the emulsion layer in which the effects of the hydrazine compound are desired. It can, of course, be present in the photographic element distributed between the emulsion and the hydrophilic colloidal layers, such as one or more of a subbing layer, interlayers and protective layers.

The hydrazines may be added to the silver halide photographic emulsion at any desired period from the initiation of chemical ripening to before coating, but it is preferred to add the compound after finishing chemical ripening. It is particularly preferred to add the compound to a coating composition prepared for coating.

Hydrazines of formula (IV) may be incorporated as microcrystalline dispersions as disclosed in European Patent Application No. 89300866.4. In these cases, no water-immiscible solvent is used in the preparation of the gelatin dispersions.

It is preferred that the hydrazine be incorporated in an amount of from 10^{-6} mol to 10^{-1} mol, and preferably from 10^{-5} mol to 5×10^{-2} mol per mol of silver halide but it is desirable to select the optimum amount of the compound according to the grain size of silver halide emulsion, the halogen composition, the manner and extent of chemical sensitization, and the kind of antifoggant compounds. The most appropriate compound and amount thereof for a particular use can be easily selected by general tests well known to persons skilled in the art.

It is preferred that silver halide grains used for at least one silver halide emulsion layer in this invention be of substantially surface latent image type.

The silver halide emulsion used in the invention may comprise any of silver chloride, silver chlorobromide, silver iodobromide, silver iodochlorobromide, etc., but preferably contains at least 60 mol% silver bromide. The iodide content is preferably not more than 10 mol% and more desirably is in the range of from 0.1 to 5 mol%.

In regard to the average grain size of silver halide used in accordance with this invention, fine grains (for example, 0.7 micron or less) are preferable, and very fine grains of average diameter not larger than 0.5 micron are particularly preferable. While the choice of grain size distribution is optional, a monodispersion is preferable. The term "monodispersion" as used herein means that, whether in weight or in number, at least 95% of grains are sized within $\pm 40\%$ of the mean grain size.

The silver halide grains in the photographic emulsion may be regular crystals such as cubes or octahedra, or irregular crystals such as spheres or plates (tabular grains), or composites.

Each of the silver halide grains may be made up of a uniform phase through its core and surface layer, or may be dissimilar in phase between the core and the surface. It is also possible to use two or more independently prepared silver halide emulsions as a mixture.

Gelatin is preferably used as the binder or protective colloid for the photographic emulsion, but other hydrophilic colloids can also be employed, for example, gelatin derivatives, graft copolymers of gelatin to other high polymers, proteins such as albumin and casein, cellulose derivatives such as hydroxyethyl cellulose, carboxymethyl cellulose, cellulose sulphate esters, etc., sugar derivatives such as sodium alginate, starch derivatives, etc., and synthetic homo- or copolymers such as polyvinyl alcohol, partially acetalized polyvinyl alcohol, poly-N-vinylpyrrolidone, polyacrylic acid, polymethacrylic acid, polyacrylamide, polyvinylimidazole and polyvinylpyrazole.

The silver halide emulsion may be chemically sensitized. Known methods of chemical sensitization of silver halide emulsions include sulphur sensitization, reduction sensitization and noble metal sensitization, and the chemical sensitization may be effected by any or a combination of such methods.

The usual method of the noble metal sensitization is gold sensitization and for this purpose a gold compound generally a complex salt of gold, is utilized. Complex salts of other noble metals such as platinum, palladium, rhodium,

etc., may be additionally contained. Examples of this method are described in U.S. Patent 2448060 and British Patent 618061.

Sulphur sensitizers include, in addition to sulphur compounds contained in gelatin, various sulphur compounds such as thiosulphates, thiourea compounds, thiazoles, and rhodanines.

Reduction sensitizers include stannous salts, amines, formamidinesulphonic acid, silane or borane compounds and the like.

The photographic elements may include a variety of compounds for the prevention of fog during production, storage or photographic processing or for the purpose of stabilising its photographic qualities. Thus, for example, there may be added the compounds referred to commonly as antifoggants or stabilizers, for example various azole compounds such as benzothiazolium salts, nitroimidazoles, chlorobenzimidazoles, bromo-benzimidazoles, mercaptothiazoles, mercaptobenzothiazoles, mercaptotetrazoles, mercaptothiadiazoles, aminotriazoles, benzothiazoles, nitrobenzothiazoles, etc.; mercaptopyrimidines, thioketo compounds such as oxazolythione, etc.; azaindenes such as triazaindene, teraazaindenes (particularly, 4-hydroxy-substituted-(1,3,3a,7)tetraazaindenes), pentaazaindenes, etc. benzenesulphonic acid, benzenesulphonamide, etc. Amongst these compounds, benzotriazoles (e.g., 5 methylbenzo triazole) and nitroindazoles (e.g., 5-nitroindazole) are preferred. These compounds may also be incorporated in the processing solution.

The photographic elements may contain inorganic or organic hardening agents in the photographic emulsion layer or other hydrophilic colloid layer. For this purpose, chromium salts (chrome alum, chromium acetate, etc.), aldehydes (formaldehyde, glyoxal, glutaraldehyde etc.), N-methylol compounds (dimethylolurea, methyloldimethylhydantoin, etc.), dioxane derivatives (2,3-dihydroxydioxane, etc.), active vinyl compounds (1,3,5 triacryloyl-hexahydro-s-triazines, 1,3,-vinylsulphonyl-2-propanol, etc.), active halogen compounds (2,4-dichloro-6-hydroxy-s-triazine, etc.), mucohalogenic acids (mucochloric acid, mucophenoxy-chloric acid, etc.), and the like may be used. These hardening agents may be incorporated alone or in combination.

In the photographic emulsion layer or other hydrophilic colloid layer in the photographic material produced in accordance with this invention, a variety of surface active agents may be incorporated for various purposes such as improvement of coating properties antistatic properties slipping properties, emulsion dispersibility, anti-adhesion properties, and photographic properties (for example, development acceleration, increase in contrast, sensitization, etc.).

Examples of nonionic surfactants are saponin, alkylene oxide derivatives e.g., polyethylene glycol, polyethylene glycol/polypropylene glycol condensate, polyethylene glycol alkyl ethers, polyethylene glycol alkyl aryl ethers, polyethylene glycol esters, polyethylene glycol sorbitan esters, polyalkylene glycol alkylamines or amides, silicone polyethylene oxide adducts), glycerol derivatives (e.g., alkenylsuccinic acid polyglyceride, alkylphenol polyglyceride), polyhydric alcohol-fatty acid esters, sugar alkyl esters, etc.. Anionic surfactants containing acid groups such as a carboxy group, a sulphy group, a phospho group, a sulphuric acid ester group, a phosphoric acid ester group, etc., for example alkyl-carboxylates, alkylsulphonates, alkylbenzenesulphonates, alkyl-naphthalenesulphonates, alkylsulphuric acid esters, alkylphosphoric acid esters N-acyl-N-alkyltaurines, sulphasuccinic acid esters, sulphonylalkylpolyoxyethylene alkylphenyl ether, polyoxyethylene alkylphosphoric acid esters, etc.; amphoteric surfactants such as amino acids, aminoalkylsulphonic acids, aminoalkylsulphuric or phosphoric acid esters, alkylbetaines, amine oxides etc., may also be used. Cationic surfactants such as alkylamines, aliphatic or aromatic quaternary ammonium salts, heterocyclic quaternary ammonium salts such as pyridinium salts, imidazolium salts, etc., aliphatic or heterocyclic ring-containing phosphonium or sulphonium salts, etc. may be included.

In the photographic emulsion layer or other hydrophilic colloid layer of the photographic material according to this invention, matting agents such as silica, magnesium oxide, polymethylmethacrylate, etc., may be incorporated for the purpose of preventing adhesion.

The support of the photographic element may be made of cellulose triacetate, cellulose diacetate, nitrocellulose, polystyrene, polyethylene terephthalate or the like. However, the use of polyethylene terephthalate is particularly useful.

Suitable developer compositions for use in the invention are any of those known in the art for development of hydrazine containing rapid access lith films and will generally have a pH in the range 9.5 to 12.5.

Thus, the silver halide photographic elements provide a sufficient ultra-high contrast negative image using a developer containing at least 0.15 mol/litre of sulphite ion as a preservative, and having a pH value in the range of from 10.5 to 12.3 and particularly preferably in the range of from 11.0 to 12.3.

There is no particular limitation on the developing agents than can be employed in the method of this invention. Thus, for example, dihydroxybenzenes (e.g., hydroquinone), 3-pyrazolidones (e.g., 1-phenyl-3-pyrazolidone, 4,4-dimethyl-1-phenyl-3-pyrazolidone), aminophenols (e.g., N-methyl-p-aminophenol), etc., can be used alone or in combination.

The silver halide photographic element is especially suitable for processing with a developer containing a dihydroxybenzene compound as the developing agent and a 3-pyrazolidone compound or an aminophenol compound as the auxiliary developing agent. The preferred concentrations of these compounds in the developer are from 0.05 to 0.5 mol/litre for the dihydroxybenzene, and 0.06 mol/litre or less for 3-pyrazolidone or aminophenol.

As described in US Patent 4269929, amine compounds may be added to the developer to thereby increase the rate of development thereby reducing development time.

In addition to the foregoing compounds, there may be added to the developer other additives including pH buffers such as sulphites, carbonates, borates, and phosphates of alkali metals, development restrainers or antifoggants such as bromides, iodides and organic antifoggants (preferably nitroindazoles and benzotriazoles). If desired, water softeners solubilizing agents or cosolvents, toners, development accelerators, surfactants (preferably aforesaid polyalkylene oxides), antifoams, hardeners, and silver stain inhibitors (e.g., 2-mercaptobenzimidazolesulphonic acids) may also be incorporated in the developer.

As a fixing bath, a solution of the conventional composition may be employed. Thiosulphates, thiocyanates, and those organic sulphur compounds which are generally known to be effective fixing agents can be used as fixing agents in the bath. The fixing bath may contain a water soluble salt of aluminium or the like as a hardener.

A stop bath e.g. 1% acetic acid solution, may be employed. The processing temperature is generally selected within the range of from 18°C to 50°C.

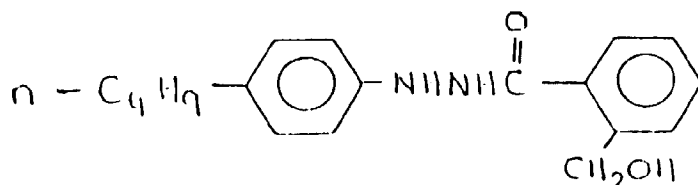
For photographic processing, an automatic developing machine is desirably used, and a sufficient ultrahigh contrast negative image can be obtained even with a processing time, i.e., the time for entry of the photographic material into the machine to exit from the machine of from 90 to 120 seconds.

The invention will now be illustrated by the following Example.

EXAMPLE

A silver halide emulsion having halide mole percentage ratio of 68:30:2 of Br:Cl:I was prepared by a conventional double jet technique under constant pAg conditions. The resulting emulsion had a narrow grain size distribution with an average size of 0.25 microns. The emulsion was then coagulated and washed being reconstituted to 95g gelatin per mole of silver.

The emulsion was chemically sensitised with sodium thiosulphate in the conventional fashion. Additions were also made before coating onto subbed polyester base, a monomethine benzothiazole as reported in the following Table, and then an anionic wetting agent (Hostapur SAS93) (10ml of 10% solution), polyoxyethylene cetyl ether (surfactant) (150ml of 1% solution), a contrast promoting agent (benzhydrol) (30ml of 5% solution in methanol) and a hydrazine derivative (3g):



(All quantities are per mole of silver).

The order of addition was not critical but preferably the monomethine benzothiazole was added first. The emulsion was coated at a silver coating weight of 3.5g per square metre.

A gelatin topcoat was applied comprising 50g gelatin per 1000g water, wetting agent, matting agent (silica), and a hardener (2-hydroxy-4,6-dichloro-1,3,5-triazine).

Samples of the film were then exposed in a sensitometer to light from a tungsten filament lamp attenuated by a 0 to 1.5 continuous neutral density wedge in contact with the coating. The coatings were then developed for 30 seconds at 38°C in a developer of the following composition:

Water	1800 g
Potassium hydroxide	195 g
Potassium metabisulphite	124 g
Diethylenetriaminepentaacetic acid 5Na	10 g
Pyruvic acid sodium salt	7.5 g
Hydroquinone	60 g
Metol	5.0 g
5-Methylbenzotriazole	0.2 g
Potassium bromide	9.25 g
Potassium chloride	2.7 g

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(continued)

Phosphoric acid (85%)	90 g
Final volume	2.0 litres pH 11.0

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After development the samples were fixed, washed and dried. Sensitometric characteristics are given below together with an assessment of pepper fog.

Dot quality was assessed by making an exposure using a tungsten filament lamp through a Kodak "Ultratec" contact halftone screen held in contact with the film sample by a vacuum frame, and processing as before.

10 Dot quality was measured microscopically on an evaluation scale of 1 (highest quality) to 5 (lowest quality). Scores of 2 or below indicate that the product has valuable commercial properties. A score of 3 indicates that the product is of moderate quality but is marginally usable. As score of 4 or higher indicates unacceptability.

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SAMPLE	COMPOUND	AMOUNT USED mol/mol of silver	RELATIVE ¹ SENSITIVITY	CONTRAST	MINIMUM DENSITY	MAXIMUM DENSITY	DOT QUALITY	SAFELIGHT TIME
1	-	-	100	TOO MUCH PEPPER FOG TO EVALUATE			-	-
2	1	6×10^{-4}	157	18	0.03	4.4	1	)
3	3	6×10^{-4}	138	23	0.04	4.8	1	) > 20mins ²
4	5	6×10^{-4}	135	18	0.04	4.5	1	)

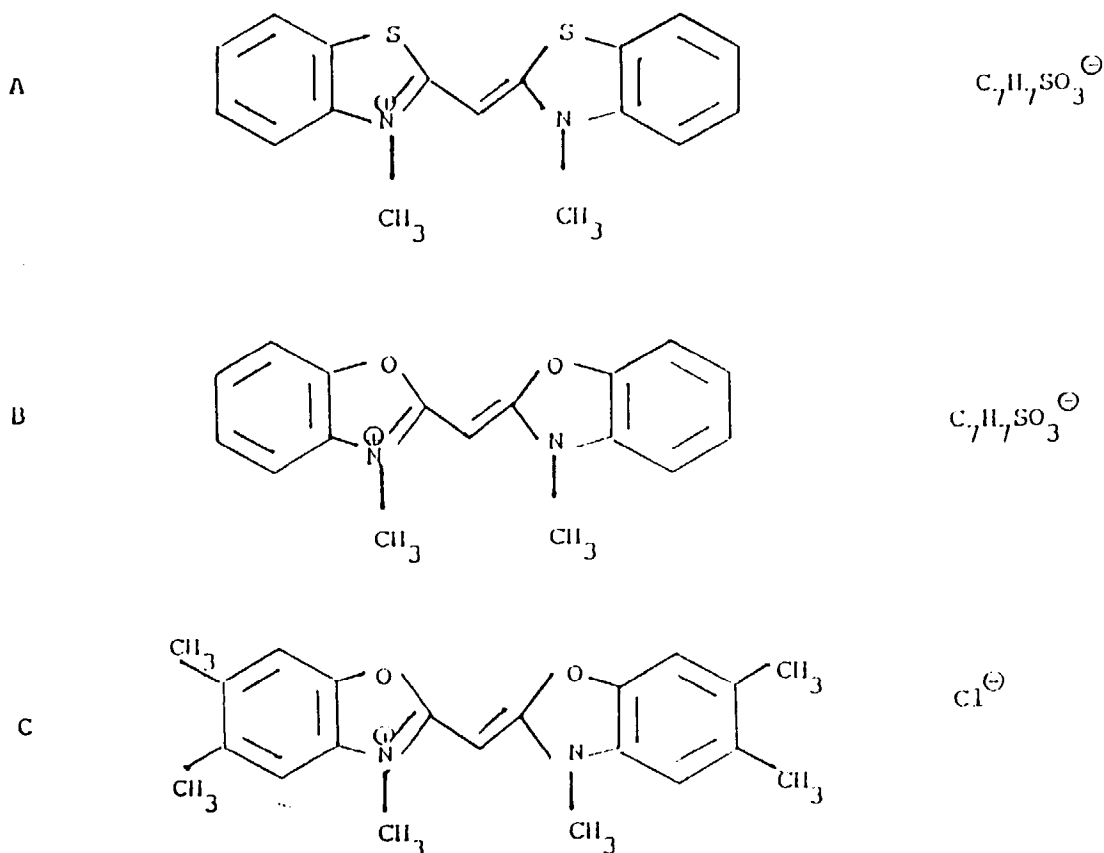
(1) Relative sensitivity with reference to sample (1) with no monomethine benzthiazole.

(2) Safelight time under 3M EDG Scanner Safelight conditions (light yellow).

It can be seen that the addition of the monomethine benzthiazole derivative in accordance with the invention gives

a high sensitivity high contrast film showing little sign of pepper fog.

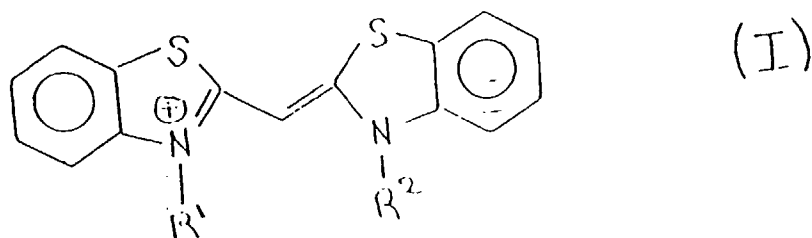
As comparative examples the following compounds were also separately incorporated into the system at the same concentration in place of the components of formula (I).



The addition of compounds A, B and C resulted in the level of pepper fog in the exposed and processed films to be so high that reliable sensitometric data could not be obtained. These examples illustrate the importance of nature of the groups R^1 and R^2 in the compounds of formula (I) and that benzoxazole compounds are not effective in limiting the amount of pepper fog obtained.

Claims

1. A photographic element capable of producing a high contrast silver image comprising a negative-acting high contrast silver halide photographic emulsion in association with a hydrazine characterised in that the emulsion is additionally associated with a monomethinebenzthiazole compound having a nucleus of the general formula:



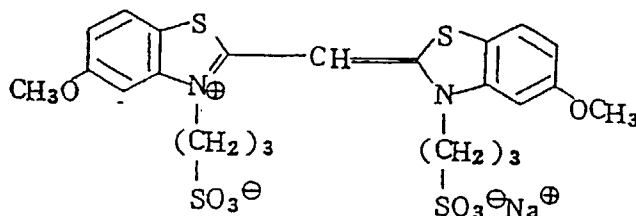
in which:

one of R^1 and R^2 represents an organic group containing an acid function and the other is selected from hydrogen, an optionally substituted alkyl group and an organic group containing an acid function, with the provisos that:

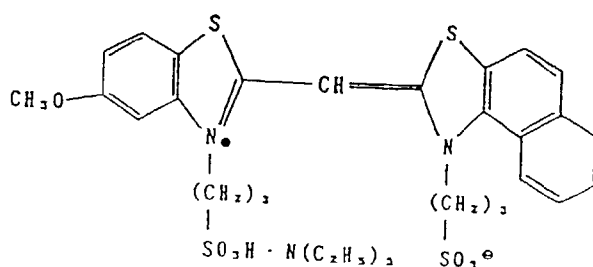
(i) the emulsion is not associated with the combination of one or more anionic cyanine dyes and one or more cationic cyanine dyes,

(ii) the silver halide grains were not prepared in the presence of an iridium salt, and

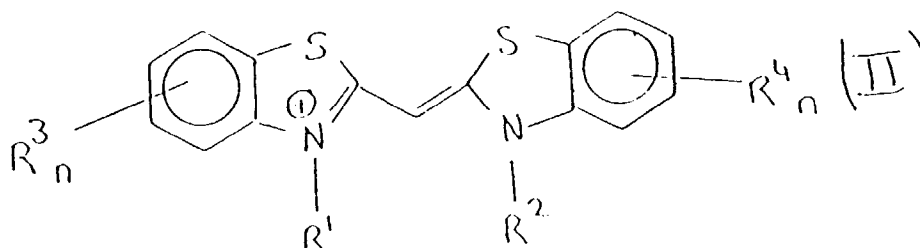
(iii) the monomethinebenzthiazole compound is not



or



2. A photographic element as claimed in Claim 1 characterised in that the monomethinebenzthiazole compound is of the formula:

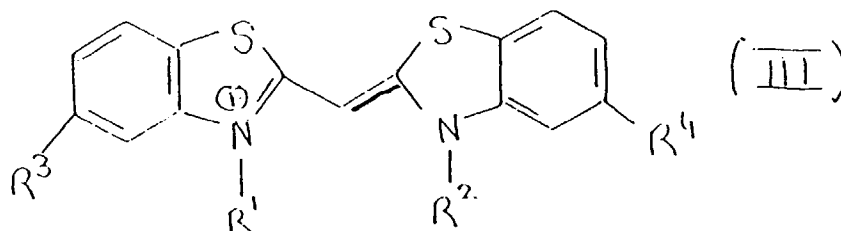


in which:

each n independently represents 0, 1, 2, 3 or 4,

each R³ and R⁴ may be the same or different and are selected from halogen, carboxyl, hydroxy, cyano, alkyl, alkoxy, alkylthio, alkoxycarbonyl and the atoms necessary to complete a carbocyclic or heterocyclic fused ring system.

3. A photographic element as claimed in Claim 1 characterised in that the monomethinebenzthiazole compound is of the formula:



in which:

R¹ to R⁴ are as defined in any one of Claim 1 or Claim 2.

4. A photographic element as claimed in any preceding claim characterised in that the monomethinebenzthiazole compound is present in an amount within the range 10⁻⁵ to 3 x 10⁻¹ mol per mol of silver halide.

5. A photographic element as claimed in Claim 4 characterised in that the monomethinebenzthiazole compound is present in an amount within the range 10⁻⁵ to 5 x 10⁻² mol per mol of silver halide.

6. A photographic element as claimed in any preceding claim in which the hydrazine is of the general formula:



in which:

R²³ represents an aryl group,

one of R²⁴ and R²⁵ is a hydrogen and the other is selected from hydrogen, arylsulphonyl and trifluoroacetyl, G represents carbonyl, sulphonyl, sulfoxy, phosphoryl, or an N-substituted or unsubstituted imino group and, X is hydrogen, alkyl, aryl or a moiety such that at a pH in the range of 9.5 to 12.5 in the presence of an oxidised hydroquinone a cyclisation reaction takes place cleaving the moiety -G-X from the remainder of the molecule and forming a cyclic structure comprising atoms of the moiety -G-X.

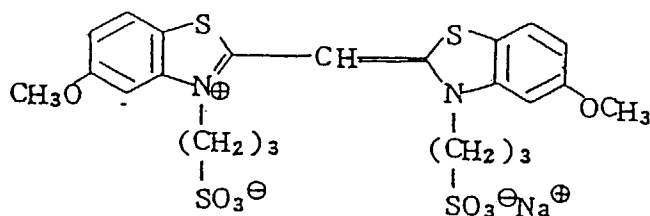
7. A photographic element as claimed in Claim 6 characterised in that the hydrazine is present as a microcrystalline dispersion.

8. A method of treating a high contrast photographic silver halide emulsion associated with a hydrazine to reduce the propensity of the emulsion to form pepper fog characterised in that the method comprises contacting the emulsion with a monomethinebenzthiazole as defined in any one of Claims 1 to 3, with the provisos that:

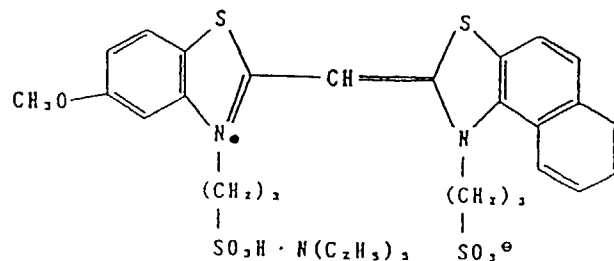
(a) the emulsion is not contacted with the combination of one or more anionic cyanine dyes and one or more cationic cyanine dyes,

(b) the silver halide grains were not prepared in the presence of an iridium salt, and

(c) the monomethinebenzthiazole compound is not



or



9. A method as claimed in Claim 8 characterised in that the monomethinebenzthiazole is added in an amount within the range 10⁻⁵ to 3 x 10⁻¹ mol per mol of silver halide.

10. A method as claimed in Claim 8 characterised in that the monomethinebenzthiazole is added in an amount within the range 10⁻⁵ to 5 x 10⁻² mol per mol of silver halide.

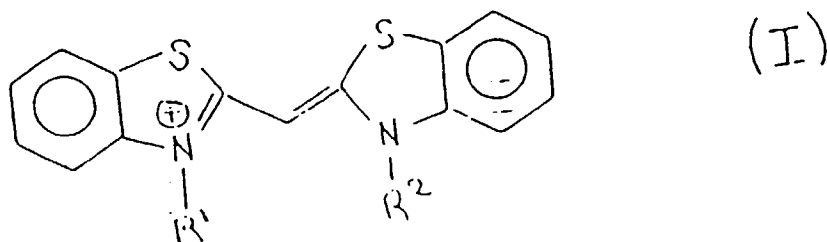
11. A method as claimed in any one of Claims 8 to 10 characterised in that the hydrazine is of the general formula:



in which R^{23} to R^{25} , G and X are as defined in Claim 6.

Patentansprüche

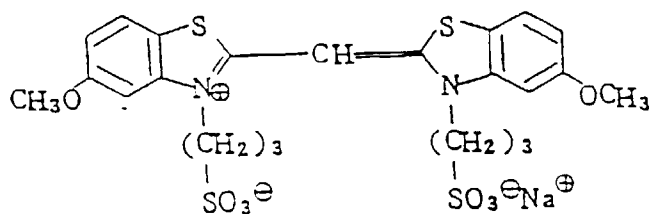
1. Photographisches Element, geeignet zur Erzeugung eines hochkontrastreichen Silberbildes, umfassend eine negativ arbeitende hochkontrastreiche photographische Silberhalogenidemulsion in Assoziation mit einem Hydrazin, dadurch gekennzeichnet, daß die Emulsion zusätzlich assoziiert ist mit einer Monomethinbenzthiazol-Verbindung mit einem Kern der allgemeinen Formel:



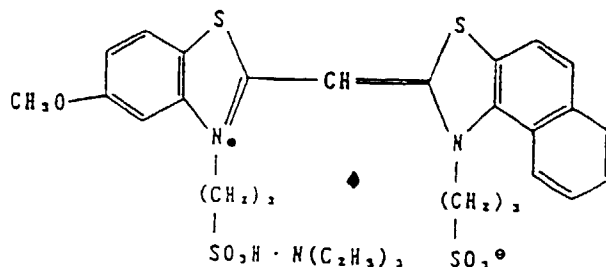
in der:

eines von R^1 und R^2 eine organische Gruppe ist, die eine Säurefunktion enthält, und das andere aus einem Wasserstoffatom, einem gegebenenfalls substituierten Alkylrest und einem organischen Rest, der eine Säurefunktion enthält, ausgewählt wird, mit den Maßgaben, daß

- (i) die Emulsion nicht mit der Kombination eines oder mehrerer anionischer Cyaninfarbstoffe und eines oder mehrerer kationischer Cyaninfarbstoffe assoziiert ist,
- (ii) die Silberhalogenidkörner nicht in Anwesenheit eines Iridiums Salzes hergestellt wurden und
- (iii) die Monomethinbenzthiazol-Verbindung nicht

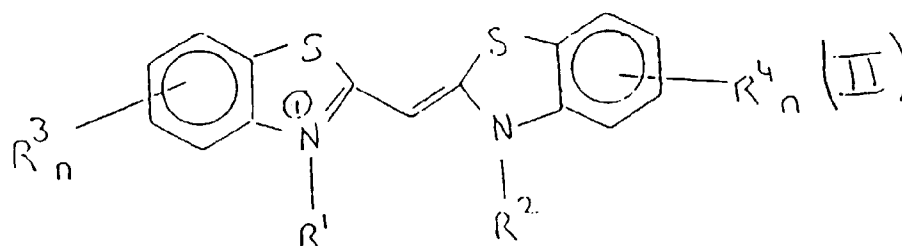


oder



ist.

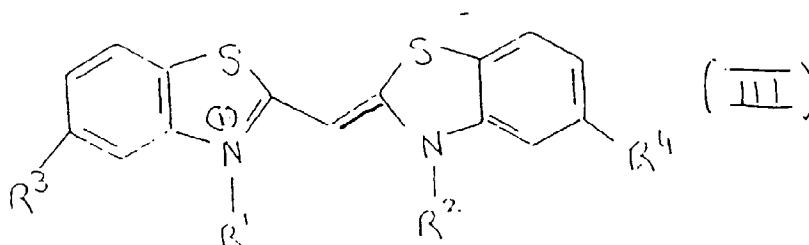
2. Photographisches Element nach Anspruch 1, dadurch gekennzeichnet, daß die Monomethinbenzthiazol-Verbindung die Formel:



hat, in der:

jedes n unabhängig 0, 1, 2, 3 oder 4 ist,
jedes R^3 und R^4 gleich oder verschieden sein kann und aus einem Halogenatom, einem Carboxyl-, Hydroxy-, Cyan-, Alkyl-, Alkoxy-, Alkylthio-, Alkoxy-carbonylrest und den Atomen, die notwendig sind, um ein carbocyclisches oder heterocyclisches kondensiertes Ringsystem zu vervollständigen, ausgewählt wird.

3. Photographisches Element nach Anspruch 1, dadurch gekennzeichnet, daß die Monomethinbenzthiazol-Verbindung die Formel:



hat, in der:

R^1 bis R^4 die in Anspruch 1 oder Anspruch 2 angegebene Bedeutung haben.

4. Photographisches Element nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, daß die Monomethinbenzthiazol-Verbindung in einer Menge innerhalb des Bereiches 10^{-5} bis 3×10^{-1} Mol pro Mol Silberhalogenid vorhanden ist.
5. Photographisches Element nach Anspruch 4, dadurch gekennzeichnet, daß die Monomethinbenzthiazol-Verbindung in einer Menge innerhalb des Bereiches 10^{-5} bis 5×10^{-2} Mol pro Mol Silberhalogenid vorhanden ist.
6. Photographisches Element nach einem der vorangehenden Ansprüche, in dem das Hydrazin die allgemeine Formel:



hat, in der:

R^{23} ein Arylrest ist,
eines von R^{24} und R^{25} ein Wasserstoffatom ist und das andere aus einem Wasserstoffatom, einer Arylsulfonyl- und einer Trifluoracetylgruppe ausgewählt wird,
G eine Carbonyl-, Sulfonyl-, Sulfoxy-, Phosphoryl- oder eine N-substituierte oder unsubstituierte Iminogruppe ist und.
X ein Wasserstoffatom, ein Alkylrest, ein Arylrest oder eine Einheit ist, derart, daß bei einem pH in dem Bereich von 9,5 bis 12,5 in Anwesenheit eines oxidierten Hydrochinons eine Ringschlußreaktion stattfindet, wobei die Einheit -G-X von dem verbleibenden Molekül abgespalten wird und eine die Atome der Einheit -G-X umfassende ringförmige Struktur gebildet wird.

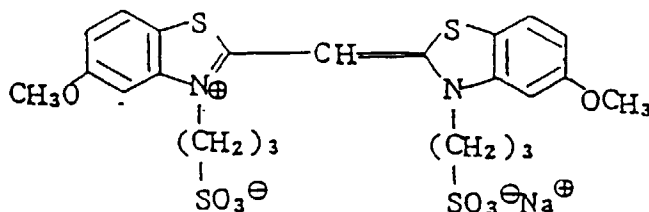
7. Photographisches Element nach Anspruch 6, dadurch gekennzeichnet, daß das Hydrazin als eine mikrokristalline Dispersion vorhanden ist.

8. Verfahren zur Behandlung einer hochkontrastreichen photographischen Silberhalogenidemulsion, assoziiert mit einem Hydrazin zur Verminderung der Neigung der Emulsion, Pfefferschleier zu bilden, dadurch gekennzeichnet, daß das Verfahren den Kontakt der Emulsion mit einem Monomethinbenzthiazol mit der in einem der Ansprüche 1-3 angegebenen Bedeutung umfaßt, unter den Maßgaben, daß:

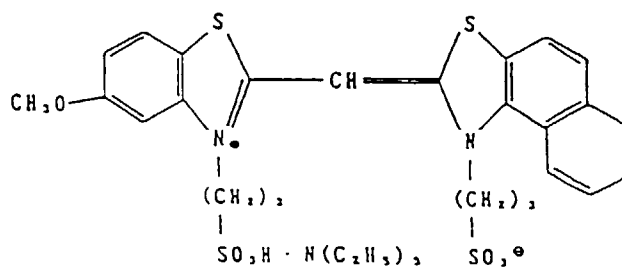
(a) die Emulsion nicht mit der Kombination eines oder mehrerer anionischer Cyaninfarbstoffe und eines oder mehrerer kationischer Cyaninfarbstoffe in Kontakt gebracht wird,

(b) die Silberhalogenidkörnchen nicht in Anwesenheit eines Iridiums Salzes hergestellt wurden, und

(c) die Monomethinbenzthiazol-Verbindung nicht



oder



ist.

9. Verfahren nach Anspruch 8, dadurch gekennzeichnet, daß das Monomethinbenzthiazol in einer Menge innerhalb des Bereiches 10^{-5} bis 3×10^{-1} Mol pro Mol Silberhalogenid zugefügt wird.

10. Verfahren nach Anspruch 8, dadurch gekennzeichnet, daß das Monomethinbenzthiazol in einer Menge innerhalb des Bereiches 10^{-5} bis 5×10^{-2} Mol pro Mol Silberhalogenid zugefügt wird.

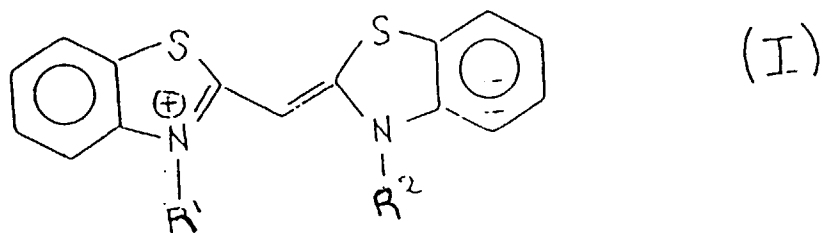
11. Verfahren nach einem der Ansprüche 8 bis 10, dadurch gekennzeichnet, daß das Hydrazin die allgemeine Formel:



hat, in der R^{23} bis R^{25} , G und X die in Anspruch 6 angegebenen Bedeutungen haben.

Revendications

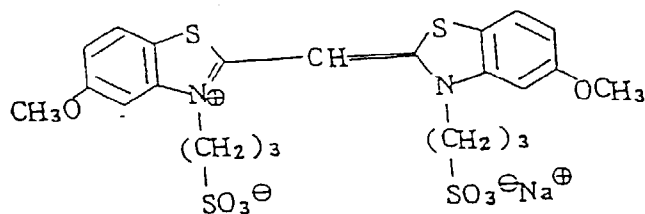
1. Élément photographique pouvant produire une image argentique à contraste élevé comprenant une émulsion photographique d'halogénure d'argent à contraste élevé de caractère négatif en association avec une hydrazine, caractérisé en ce que l'émulsion est de plus associée à un composé de monométhinebenzothiazole ayant un noyau de la formule générale :



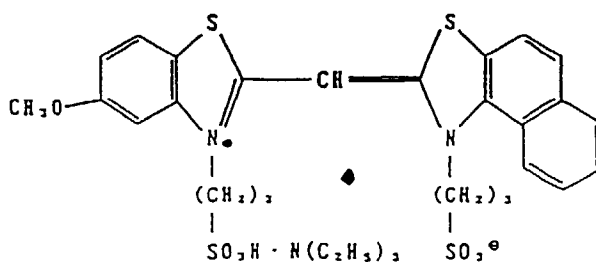
dans laquelle :

l'un des R^1 et R^2 représente un groupe organique contenant une fonction acide et l'autre est choisi parmi l'hydrogène, un groupe alkyle éventuellement substitué et un groupe organique contenant une fonction acide, aux conditions que :

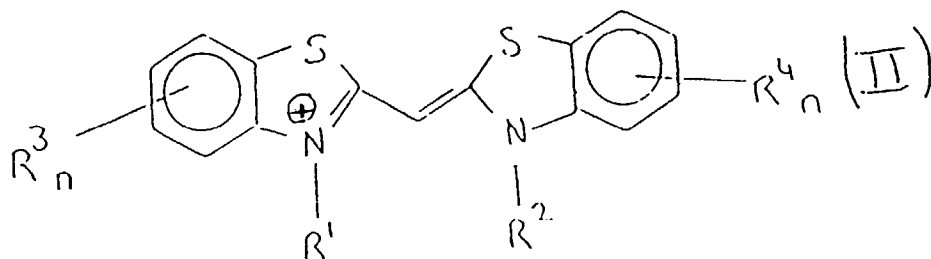
- (i) l'émulsion ne soit pas associée à la combinaison d'un ou plusieurs colorants de cyanine anioniques et d'un ou plusieurs colorants de cyanine cationiques,
- (ii) les grains d'halogénure d'argent n'aient pas été préparés en présence d'un sel d'iridium, et
- (iii) le composé de monométhinebenzothiazole ne soit pas le



ou le



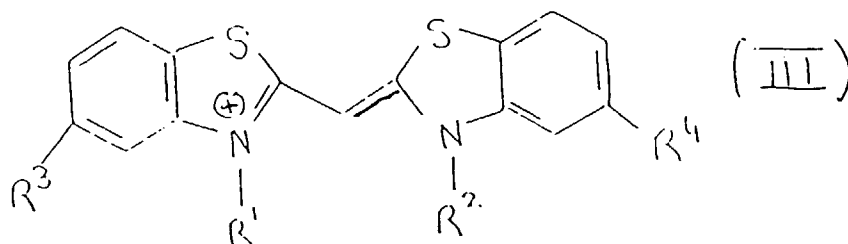
2. Élément photographique suivant la revendication 1, caractérisé en ce que le composé de monométhinebenzothiazole est de la formule :



dans laquelle :

chaque n représente indépendamment 0, 1, 2, 3 ou 4, R^3 et R^4 peuvent être chacun identiques ou différents et sont choisis parmi les groupes halogène, carboxyle, hydroxy, cyano, alkyle, alcoxy, alkylthio, alcoxycarbonyle et les atomes nécessaires pour former un système à noyaux condensés carbocyclique ou hétérocyclique.

3. Elément photographique suivant la revendication 1, caractérisé en ce que le composé de monométhinebenzothiazole est de la formule :



dans laquelle :

R^1 à R^4 sont tels que définis suivant l'une ou l'autre des revendications 1 et 2.

4. Elément photographique suivant l'une quelconque des revendications précédentes, caractérisé en ce que le composé de monométhinebenzothiazole se trouve en une quantité allant de 10^{-5} à 3×10^{-1} mole par mole d'halogénure d'argent.
5. Elément photographique suivant la revendication 4, caractérisé en ce que le composé de monométhinebenzothiazole se trouve en une quantité de 10^{-5} à 5×10^{-2} mole par mole d'halogénure d'argent.
6. Elément photographique suivant l'une quelconque des revendications précédentes, dans lequel l'hydrazine est de la formule générale :



dans laquelle :

R^{23} représente un groupe aryle,

l'un des R^{24} et R^{25} est l'hydrogène tandis que l'autre est choisi parmi l'hydrogène, un groupe arylsulfonyl et un groupe trifluoroacétyl,

G représente un groupe carbonyle, sulfonyl, sulfoxy, phosphoryl ou un groupe imino N-substitué ou non substitué et,

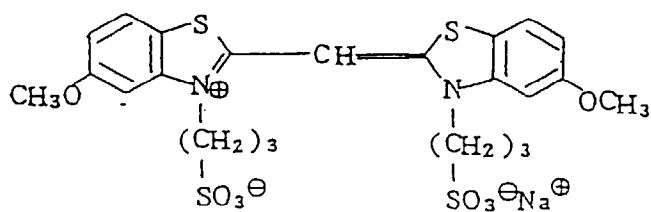
X est l'hydrogène, un groupe alkyle, un groupe aryle ou un fragment tel qu'à un pH de l'ordre de 9,5 à 12,5, en présence d'une hydroquinone oxydée, il se développe une réaction de cyclisation séparant le fragment -G-X du reste de la molécule et formant une structure cyclique comprenant des atomes du fragment -G-X.

7. Elément photographique suivant la revendication 6, caractérisé en ce que l'hydrazine est présente sous la forme d'une dispersion microcristalline.
8. Procédé de traitement d'une émulsion d'halogénure d'argent photographique à contraste élevé associée à une hydrazine pour réduire la tendance de l'émulsion à former un voile de poivre, caractérisé en ce que le procédé consiste à mettre en contact l'émulsion avec une monométhinebenzothiazole telle que définie dans l'une quelconque des revendications 1 à 3, aux conditions que :

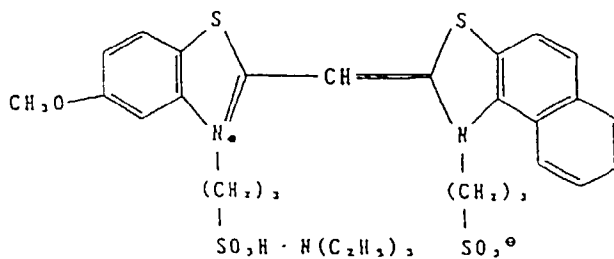
(a) l'émulsion ne soit pas au contact de la combinaison d'un ou plusieurs colorants de cyanine anioniques et d'un ou plusieurs colorants de cyanine cationiques,

(b) les grains d'halogénure d'argent n'aient pas été préparés en présence d'un sel d'iridium, et

(c) le composé de monométhinebenzothiazole ne soit pas le



ou le



9. Procédé suivant la revendication 8, caractérisé en ce que la monométhinebenzothiazole est ajoutée en une quantité allant de 10^{-5} à 3×10^{-1} mole par mole d'halogénure d'argent.
10. Procédé suivant la revendication 8, caractérisé en ce que la monométhinebenzothiazole est ajoutée en une quantité allant de 10^{-5} à 5×10^{-2} mole par mole d'halogénure d'argent.
11. Procédé suivant l'une quelconque des revendications 8 à 10, caractérisé en ce que l'hydrazine est de la formule générale :



dans laquelle R^{23} à R^{25} , G et X sont tels que définis à la revendication 6.