⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number : **0 650 086 A2**

⑫ EUROPEAN PATENT APPLICATION

㉑ Application number : **94202729.3**

㉒ Date of filing : **22.09.94**

(51) Int. Cl.^{6} : **G03C 1/06**, G03C 1/26, G03C 1/09

㉚ Priority : **24.09.93 GB 9319792**

㊸ Date of publication of application :
26.04.95 Bulletin 95/17

㊹ Designated Contracting States :
BE CH DE FR GB IT LI NL

㉑ Applicant : **KODAK LIMITED**
Headstone Drive
Harrow, Middlesex HA1 4TY (GB)
㊹ **GB**

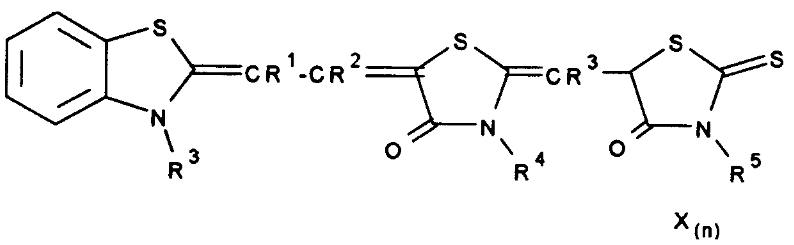
㉑ Applicant : **EASTMAN KODAK COMPANY**
343 State Street
Rochester, New York 14650-2201 (US)
㊹ **BE CH DE FR IT LI NL**

㉒ Inventor : **Pich, Julia, c/o Kodak Limited**
Patent Department,
Headstone Drive
Harrow, Middlesex, HA1 4TY (GB)
Inventor : **Baker, Julie, c/o Kodak Limited**
Patent Department,
Headstone Drive
Harrow, Middlesex, HA1 4TY (GB)
Inventor : **Pightling, Nicholas, c/o Kodak Limited**
Patent Department,
Headstone Drive
Harrow, Middlesex, HA1 4TY (GB)

㉔ Representative : **Baron, Paul Alexander Clifford**
Kodak Limited
Patent Department
Headstone Drive
Harrow Middlesex HA1 4TY (GB)

㊹ Photographic silver halide materials.

㊼ A method of improving abrasion resistance and sensitivity to variations in development time of a photographic material comprising a support bearing a silver halide emulsion layer comprising at least 50% silver chloride which contains in or adjacent the emulsion layer a hydrazide nucleating agent and an amine booster, the combination of which is capable of providing high contrast images, sensitised to radiation having a wavelength from 600 to 700 nm characterised by sensitising the emulsion wih a tricyclic merocyanine dye of the general formula :



wherein R^1, and R^2 are each hydrogen or a substituted or unsubstituted alkyl group of 1-5 carbon atoms, and

R^3, R^4 and R^5 are each a substituted or unsubstituted alkyl group of 1-5 carbon atoms, and wherein at least one of R^3, R^4 and R^5 contain a water-solubilising group,

X is a counter-ion, and

n is 0-3.

Jouve, 18, rue Saint-Denis, 75001 PARIS

Field of the Invention

The present invention relates to photographic silver halide materials having improved abrasion resistance, particularly to materials intended for exposure to radiation having a wavelength of from 600-690 nm, eg radiation from a Helium-Neon laser or laser diode exposing source, and especially to materials intended for exposure in graphic arts equipment.

Background of the Invention

Classes of sensitising dyes have previously been proposed for preparing silver halide materials that are both sensitive to red radiation having a wavelength of from 600-690 nm and relatively non-sensitive to safelight illumination. For example, British specification 1 471 701 and European specification 0 363 104 describe the use of triheterocyclic dyes for this purpose.

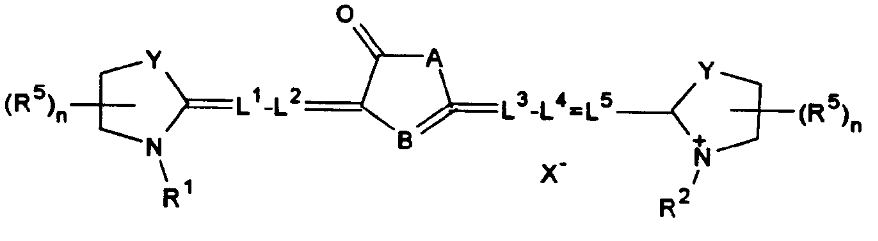
For many years the very high contrast photographic images needed in the graphic arts and printing industries were obtained by developing a 'lith' emulsion (usually high in silver chloride content) in a hydroquinone, low sulphite, 'lith' developer by the process known as infectious development. However, such low sulphite developers are inherently unstable and are particularly inappropriate for machine processing.

Recently emulsions containing hydrazide nucleating agents have been used and processed in a developer with conventional amounts of sulphite, hydroquinone and possibly metol or a pyrazolidone. Such developers also essentially contain an amine additive as described in US Patent 4,269,929. Other developers containing amines are described in US Patents 4,668,605 and 4,740,452.

Many hydrazides have been proposed for use in such materials, for example in US Patents 4,323,643, 4,278,748, 4,031,127, 4,030,925 and 4,323,643 and in European Patent 0,333,435.

More recently it has been proposed to incorporate amine boosters in high contrast materials with the advantage that it is not necessary to have a special developer in order to obtain the very high contrast that is demanded by much graphic arts work. Such amine boosters are described in Japanese Patent Publications 140340/85 and 222241/87 and in US Patent 4975354 (European Patent 0,364,166).

Classes of sensitising dyes have previously been proposed for preparing silver halide materials that are both sensitive to radiation having a wavelength of from 600-700 nm, eg radiation from a Helium-Neon laser or laser diode exposing source, and especially to materials intended for exposure in graphic arts equipment. For example, US Patent 5 079 139 describes the use of tri-heterocyclic dyes for this purpose which have the general formula:



wherein

Y is S or Se,

L^1, L^2, L^3, L^4 and L^5 are each independently substituted or unsubstituted methine groups,

A is N-R^3, O or S,

B is N-R^4 when A is O, or N-R^4, S, or O when A is N-R^3,

R^1, R^2, R^3 and R^4 are each a substituted or unsubstituted alkyl or a substituted or unsubstituted aryl group,

R^5 is an alkyl group of 1-4 carbon atoms,

n is 0, 1 or 2, and

X is a counterion,

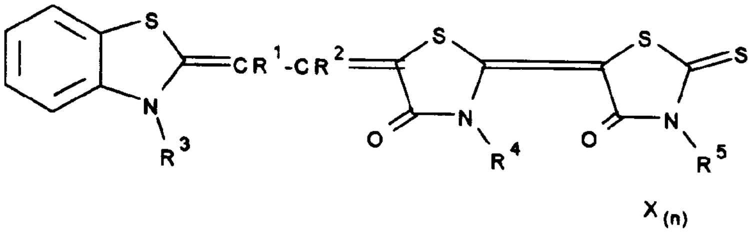
and wherein at least two of R^1, R^2, R^3 and R^4 are substituted with an acid or acid salt substituent.

Problem to be Solved by the Invention

A problem with such materials is that they do not have the desired resistance to abrasion when being handled. Another problem is that the materials have a considerable sensitivity to variations in development time.

Summary of the Invention

According to the present invention, therefore, there is provided a method of improving abrasion resistance and sensitivity to variations in development time of a photographic material comprising a support bearing a silver halide emulsion layer comprising at least 50% silver chloride which contains in or adjacent the emulsion layer a hydrazide nucleating agent and an amine booster, the combination of which is capable of providing high contrast images, sensitised to radiation having a wavelength from 600 to 700 nm characterised by sensitising the emulsion with a tricyclic merocyanine dye of the general formula:



wherein R^1, and R^2 are each hydrogen or a substituted or unsubstituted alkyl group of 1-5 carbon atoms, and

R^3, R^4 and R^5 are each a substituted or unsubstituted alkyl group of 1-5 carbon atoms, and wherein at least one of R^3, R^4 and R^5 contain a water-solubilising group,

X is a counter-ion, and

n is 0-3.

Advantageous Effect of the Invention

The sensitising dyes defined above not only sensitise the emulsion to light of 600-700 nm, but also provide both improved resistance to abrasion and sensitivity to development time.

Detailed Description of the Invention

The water-solubilising groups on R^3, R^4 and R^5 may be hydroxyl or acid groups, for example -OH, -COOH or $-SO_3H$ groups. Preferably two of groups R^3, R^4 and R^5 contain a water-solubilising group.

Examples of alkyl groups which R^1 to R^6 may represent are methyl, ethyl, n-propyl, iso-propyl, n-butyl, t-butyl, n-pentyl or t-pentyl. The alkyl groups may be substituted with halogen atoms, alkyl, substituted alkyl, aryl or substituted aryl groups.

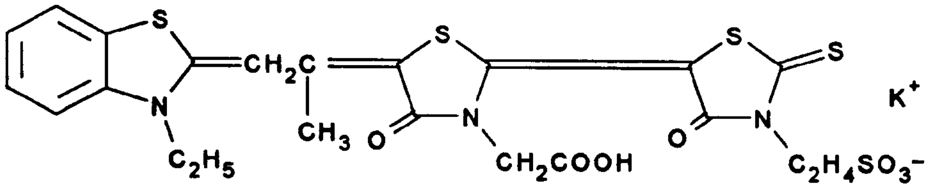
The counter-ion X is preferably ammonium or an alkali metal, eg. Na^+.

The dyes may be prepared by known methods, for example the dyes may be prepared by those methods described in "Cyanine Dyes and Related Compounds", by F M Hamer, Interscience, 1964. They may be incorporated into the silver halide emulsion as a solution in water or an alcohol in known manner.

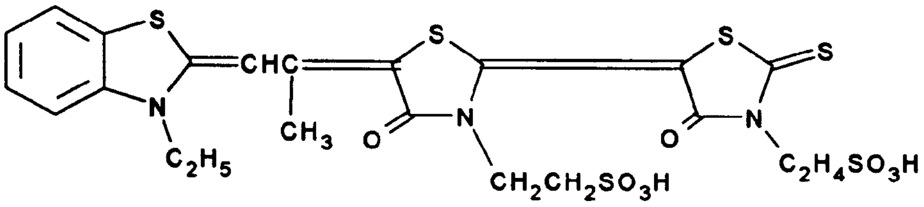
Examples of dyes to be used in the present invention have the following formulae:

TABLE 1

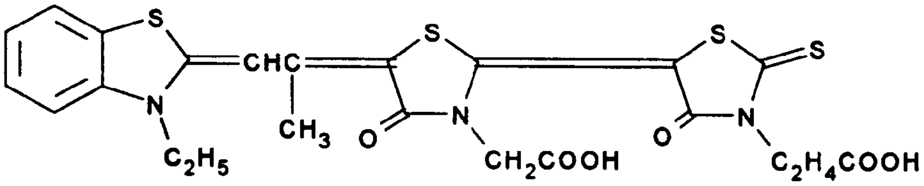
1.



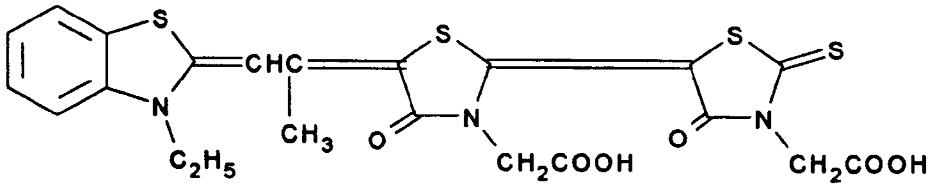
2.



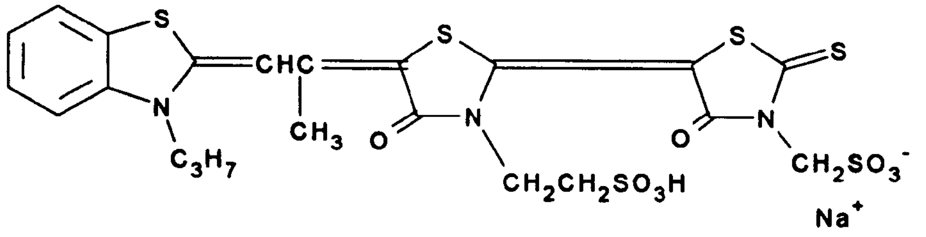
3.



4.

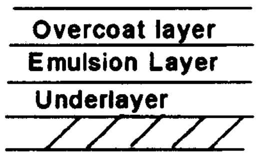


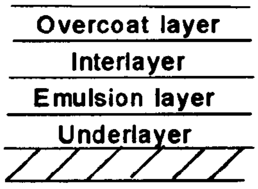
5.

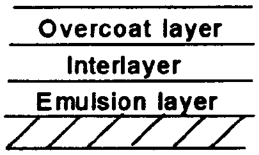


The dye may be present in the present materials in amounts of from 5 to 500, preferably from 50 to 250, more particularly from 100 to 200 mg per mole of silver halide in the emulsion layer.

The present photographic materials may be of a variety of structures. For example any of the following:







in which the underlayers and interlayers are preferably composed of a gelatin/polymer blend. The hydrazide and amine booster may be located in the emulsion layer, underlayer or interlayer. The emulsion layers may contain antifoggant.

The silver halide emulsion is preferably of the type that provides a high contrast image as required in graphic arts applications. Such emulsions are customarily high in silver chloride and low in silver iodide and may contain a hydrazide nucleating agent. Such emulsions are described in Research Disclosure Item 32410, November 1983 published by Kenneth Mason Publications, Emsworth, Hants, United Kingdom.

The preferred amine boosters to be used in the present invention are those described in the European Patent referred to above wherein they are defined as an amino compound which:

(1) comprises at least one secondary or tertiary amino group,

(2) contains within its structure a group comprised of at least three repeating ethyleneoxy units, and

(3) has an n-octanol/water partition coefficient (log P) of at least one, preferably at least three, and most preferably at least four,

log P being defined by the formula:

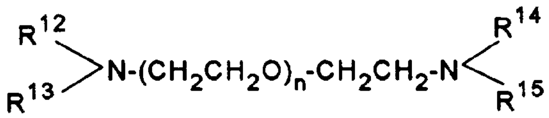
$$\log P = \log \frac{[X]_{octanol}}{[X]_{water}}$$

wherein X is the concentration of the amino compound.

Included within the scope of the amino compounds utilised in this invention are monoamines, diamines and polyamines. The amines can be aliphatic amines or they can include aromatic or heterocyclic moieties. Aliphatic, aromatic and heterocyclic groups present in the amines can be substituted or unsubstituted groups. Preferably, the amino compounds employed in this invention as "incorporated boosters" are compounds of at least 20 carbon atoms. It is also preferred that the ethyleneoxy units are directly attached to the nitrogen atom of a tertiary amino group.

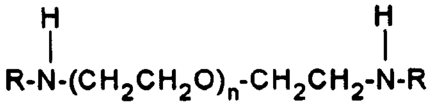
Preferably the partition coefficient is at least three, most preferably at least 4.

Preferred amino compounds for the purposes of this invention are bis-tertiary-amines which have a partition coefficient of at least three and a structure represented by the formula:



wherein n is an integer with a value of 3 to 50, and more preferably 10 to 50, R_{12}, R_{13}, R_{14} and R_{15} are, independently, alkyl groups of 1 to 8 carbon atoms, R_{12} and R_{13} taken together represent the atoms necessary to complete a heterocyclic ring, and R_{14} and R_{15} taken together represent the atoms necessary to complete a heterocyclic ring.

Another preferred group of amino compounds are bis-secondary amines which have a partition coefficient of at least three and a structure represented by the formula:



$$R\text{-}\overset{H}{\overset{|}{N}}\text{-}(CH_2CH_2O)_n\text{-}CH_2CH_2\text{-}\overset{H}{\overset{|}{N}}\text{-}R$$

wherein n is an integer with a value of 3 to 50, and more preferably 10 to 50, and each R is, independently, a linear or branched, substituted or unsubstituted, alkyl group of at least 4 carbon atoms.

Particular amine boosters are listed in European Specification 0,364,166.

The amine booster may be present in amounts of from 1 to 25, preferably 1 to 10, and particularly from 1 to 3 g per mole of silver halide in the emulsion.

Any hydrazine compound that functions as a nucleator and is capable of providing jointly with the amine booster high contrast can be used in the practice of this invention.

The hydrazine compound is incorporated in the photographic element, for example, it can be incorporated in a silver halide emulsion layer. Alternatively, the hydrazine compound can be present in a hydrophilic colloid layer of the photographic element, preferably a hydrophilic colloid layer which is coated to be 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 or among emulsion and hydrophilic colloid layers, such as undercoating layers, interlayers and overcoating layers.

Such hydrazine compounds may have the formula:

$R^7\text{-NHNHCHO}$

wherein R^7 is a phenyl nucleus having a Hammett sigma value-derived electron withdrawing characteristic of less than +0.30.

In the above formula, R^7 can take the form of a phenyl nucleus which is either electron donating (electropositive) or electron withdrawing (electronegative); however, phenyl nuclei which are highly electron withdrawing produce inferior nucleating agents. The electron withdrawing or electron donating characteristic of a specific phenyl nucleus can be assessed by reference to Hammett sigma values.

Preferred phenyl group substituents are those which are not electron withdrawing. For example, the phenyl groups can be substituted with straight or branched chain alkyl groups (e.g., methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, n-hexyl, n-octyl, tert-octyl, n-decyl, n-dodecyl and similar groups). The phenyl groups can be substituted with alkoxy groups wherein the alkyl moieties thereof can be chosen from among the alkyl groups described above.

The phenyl groups can also be substituted with acylamino groups. Illustrative acylamino groups include acetylamino, propanoylamino, butanoylamino, octanoylamino, benzoylamino, and similar groups.

In one particularly preferred form the alkyl, alkoxy and/or acylamino groups are in turn substituted with a conventional photographic ballast, such as the ballasting moieties of incorporated couplers and other immobile photographic emulsion addenda. The ballast groups typically contain at least eight carbon atoms and can be selected from both aliphatic and aromatic relatively unreactive groups, such as alkyl, alkoxy, phenyl, alkylphenyl, phenoxy, alkylphenoxy and similar groups.

The alkyl and alkoxy groups, including ballasting groups, if any, preferably contain from 1 to 20 carbon atoms, and the acylamino groups, including ballasting groups, if any, preferably contain from 2 to 21 carbon atoms. Generally, up to about 30 or more carbon atoms in these groups are contemplated in their ballasted form. Methoxyphenyl, tolyl (e.g., p-tolyl and m-tolyl) and ballasted butyramidophenyl nuclei are specifically preferred.

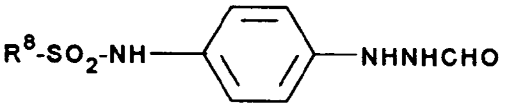
Examples of the specifically preferred hydrazine compounds are the following:

1-Formyl-2-(4-[2-(2,4-di-*tert*-pentylphenoxy)-butyramido]phenyl)hydrazine,
1-Formyl-2-phenylhydrazine,
1-Formyl-2-(4-methoxylphenyl)hydrazine,
1-Formyl-2-(4-chlorophenyl)hydrazine,
1-Formyl-2-(4-fluorophenyl)hydrazine,
1-Formyl-2-(2-chlorophenyl)hydrazine, and
1-Formyl-2-(p-tolyl)hydrazine.

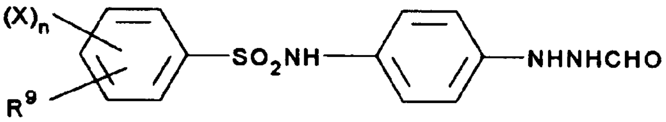
The hydrazide may also comprise an adsorption promoting moiety. Hydrazides of this type contain an unsubstituted or mono-substituted divalent hydrazo moiety and an acyl moiety. The adsorption promoting moiety can be chosen from among those known to promote adsorption of photographic addenda to silver halide grain surfaces. Typically, such moieties contain a sulphur or nitrogen atom capable of complexing with silver or otherwise exhibiting an affinity for the silver halide grain surface. Examples of preferred adsorption promoting moieties include thioureas, heterocyclic thioamides and triazoles. Exemplary hydrazides containing an adsorption promoting moiety include:

1-[4-(2-formylhydrazino)phenyl]-3-methyl thiourea,
3-[4-(2-formylhydrazino)phenyl-5-(3-methyl-2-benzoxazolinylidene)rhodanine-6-([4-(2-formylhydrazino)phenyl]ureylene)-2-methylbenzothiazole,
N-(benzotriazol-5-yl)-4-(2-formylhydrazino)-phenylacetamide, and
N-(benzotriazol-5-yl)-3-(5-formylhydrazino-2-methoxyphenyl)propionamide and N-2-(5,5-dimethyl-2-thiomidazol-4-yl-idenimino)ethyl-3-[5-(formylhydrazino)-2-methoxyphenyl]propionamide.

An especially preferred class of hydrazine compounds for use in the elements of this invention are sulphonamido-substituted hydrazines having one of the following structural formulae:



or



wherein:

R^8 is alkyl having from 6 to 18 carbon atoms or a heterocylic ring having 5 or 6 ring atoms, including ring atoms of sulphur or oxygen;

R^9 is alkyl or alkoxy having from 1 to 12 carbon atoms;

X is alkyl, thioalkyl or alkoxy having from 1 to about 5 carbon atoms; halogen; or $-NHCOR^{10}$, $-NHSO_2R^{10}$, $-CONR^{10}R^{11}$ or $-SO_2R^{10}R^{11}$ where R^{10} and R^{11}, which can be the same or different, are hydrogen or alkyl having from 1 to about 4 carbon atoms; and

n is 0, 1 or 2.

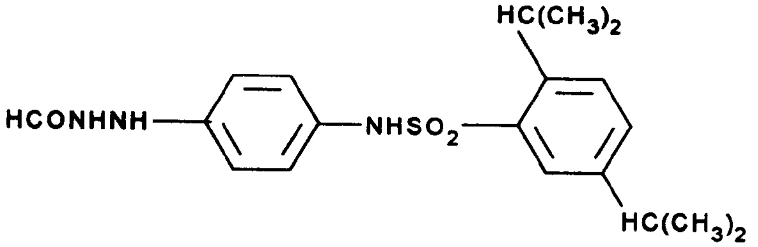
Alkyl groups represented by R^9 can be straight or branched chain and can be substituted or unsubstituted. Substituents include alkoxy having from 1 to 4 carbon atoms, halogen atoms (e.g. chlorine and fluorine), or $-NHCOR^{10}-$ or $-NHSO_2R^{10}-$ where R^{10} is as defined above. Preferred R alkyl groups contain from 8 to 16 carbon atoms since alkyl groups of this size impart a greater degree of insolubility to the hydrazide nucleating agents and thereby reduce the tendency of these agents to be leached during development from the layers in which they are coated into developer solutions.

Heterocyclic groups represented by R include thienyl and furyl, which groups can be substituted with alkyl having from 1 to 4 carbon atoms or with halogen atoms, such as chlorine.

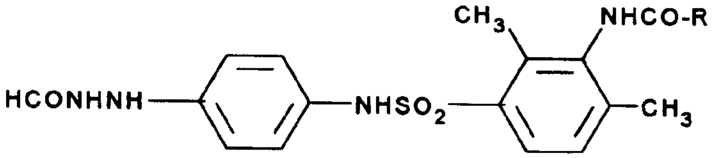
Alkyl or alkoxy groups represented by R^1 can be straight or branched chain and can be substituted or unsubstituted. Substituents on these groups can be alkoxy having from 1 to 4 carbon atoms, halogen atoms (e.g. chlorine or fluorine); or $-NHCOR^{10}$ or $-NHSO_2R^{10}$ where R^{10} is as defined above. Preferred alkyl or alkoxy groups contain from 1 to 5 carbon atoms in order to impart sufficient insolubility to the hydrazide nucleating agents to reduce their tendency to being leached out of the layers in which they are coated by developer solution.

Alkyl, thioalkyl and alkoxy groups which are represented by X contain from 1 to 5 carbon atoms and can be straight or branched chain. When X is halogen, it may be chlorine, fluorine, bromine or iodine. Where more than one X is present, such substituents can be the same or different.

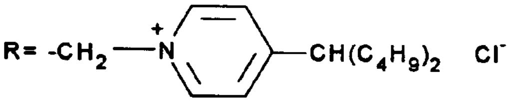
Particularly preferred nucleators have the following formulae:

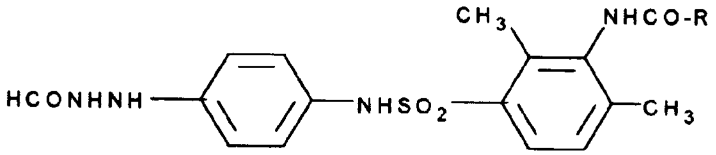


N1



N2





N3

R = $-CH_2S-(CH_2CH_2O)_4-C_8H_{17}$

The hydrazide nucleator may be present in amounts of from 40 to 350, preferably 60 to 350, and particularly from 90 to 270 mg per mole of silver halide in the emulsion.

The photosensitive silver halide emulsions employed in the present materials may contain both silver bromide and silver iodide in addition to the silver chloride. Preferably the iodide content is less than 10 mole percent. Substantially pure silver chloride emulsions may be used although the preferred emulsions comprise 70 mole % chloride and 30 mole % bromide. As is known in the graphic arts field the grains may be doped with Rhodium, Ruthenium, Iridium or other Group VIII metals. The emulsions may be negative or direct positive emulsions, mono- or poly-disperse.

Preferably the silver halide grains are doped with Group VIII metal at levels in the range 10^{-9} to 10^{-3}, preferably 10^{-6} to 10^{-3}, mole metal per mole of silver. The preferred Group VIII metal is Rhodium.

The emulsions employed and the addenda added thereto, the binders, supports, etc may be as described in Research Disclosure Item 308119, December 1989 published by Kenneth Mason Publications, Emsworth, Hants, United Kingdom.

The light-sensitive silver halide contained in the photographic elements can be processed following exposure to form a visible image by associating the silver halide with an aqueous alkaline medium in the presence of a developing agent contained in the medium or the element. It is a distinct advantage of the present invention that the described photographic elements can be processed in conventional developers as opposed to specialised developers conventionally employed in conjunction with lithographic photographic elements to obtain very high contrast images. When the photographic elements contain incorporated developing agents, the elements can be processed in the presence of an activator, which can be identical to the developer in composition, but otherwise lacking a developing agent.

Very high contrast images can be obtained at pH values in the range of from 11 to 12.3, but preferably lower pH values, for example below 11 and most preferably in the range of 10.3 to 10.5 are preferably employed for processing the photographic recording materials as described herein.

The developers are typically aqueous solutions, although organic solvents, such as diethylene glycol, can also be included to facilitate the solvency of organic components. The developers contain one or a combination of conventional developing agents, such as a polyhydroxybenzene, aminophenol, paraphenylenediamine, ascorbic acid, pyrazolidone, pyrazolone, pyrimidine, dithionite, hydroxylamine or other conventional developing agents.

It is preferred to employ hydroquinone and 3-pyrazolidone developing agents in combination. The pH of the developers can be adjusted with alkali metal hydroxides and carbonates, borax and other basic salts. To reduce gelatin swelling during development, compounds such as sodium sulphate can be incorporated into the developer. Also, compounds such as sodium thiocyanate can be present to reduce granularity. Chelating and sequestering agents, such as ethylenediaminetetraacetic acid or its sodium salt, can be present. Generally, any conventional developer composition can be employed in the practice of this invention. Specific illustrative photographic developers are disclosed in the Handbook of Chemistry and Physics, 36th Edition, under the title "Photographic Formulae" at page 3001 et seq. and in Processing Chemicals and Formulas, 6th Edition, published by Eastman Kodak Company (1963). The photographic elements can, of course, be processed with conventional developers for lithographic photographic elements, as illustrated by US Patent No. 3,573,914 and UK Patent No. 376,600.

The support may be any photographic support, for example, transparent film or reflective paper support, eg. polyethylene coated paper.

For paper materials, it is customary to employ a fluorescent brightening agent. These may be incorporated into the materials by known techniques, for example by dissolving a water-soluble brightener in the gelatin supercoat (the layer most remote from the support). In one embodiment a water-insoluble brightener may be used. It may be imbibed onto particles of a polymer dispersion as described in British Patent Specification 1,504,949 or 1,504,950 or dissolved in droplets of coupler solvents prior to incorporation in a layer of the material, e.g. in the supercoat. In each case the residual dye stain is either absent or acceptable.

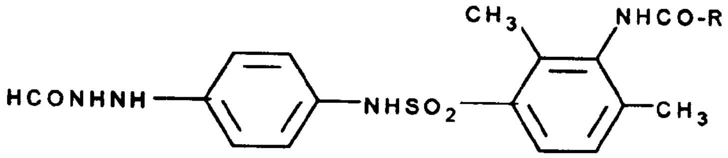
The following Examples are included for a better understanding of the invention.

EXAMPLE 1

The photosensitive materials used in this Example consist of a gel underlayer, a light sensitive layer and a gel overcoat; coated on a polyethylene terephthalate base with an antihalation pelloid layer designed to absorb red light.

The light sensitive layer consists of a 70:30 chlorobromide cubic monodispersed emulsion (0.22μ edge length) doped with ammonium hexachlororhodate and coated at 3.3g Ag/sq.m. Total gel laydown is 3.83g/sq.m. Addenda included in the emulsion layer are the sensitising dyes, 2-methylmercapto-5-carboxy-6-methyl tetraazaindene at 7.287mg/sq.m, 1-(3-acetamidophenyl)-5-mercaptotetrazole at 0.711mg/sq.m, 4-carboxy-methyl-4-thiazoline-2-thione at 2.137mg/sqm and copolymer (C1) of methyl acrylate, 2-acrylamido-2-methylpropane sulphonic acid and the sodium salt of 2-acetoxyethyl-methacrylic acid (88:5:7 by weight) at 22g per silver mole.

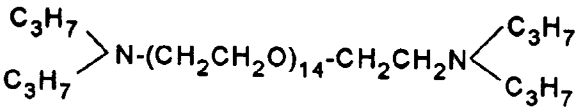
Other addenda coated in either in the emulsion layer or the underlayer include 3,5-disulphocatechol, disodium salt at 97.7mg/sq.m, nucleator N3 of the formula:



N3

$R = -CH_2S-(CH_2CH_2O)_4-C_8H_{17}$

at 6.147mg/sq.m, amine booster B1 of the formula:



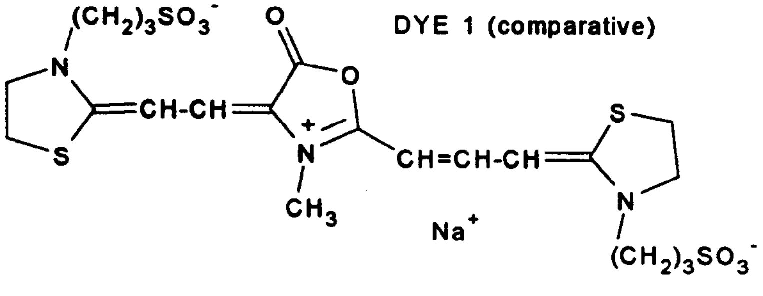
$$(C_3H_7)_2N-(CH_2CH_2O)_{14}-CH_2CH_2N(C_3H_7)_2$$

at 61.42mg/sq.m and hydroquinone at 222.8mg/sq.m. plus copolymer C1 at a rate of 0.20 mg/m^2.

The overcoat consists of gel at 0.5g/sq.m, with surfactants to aid coating, plus matting beads and colloidal silica to aid film handling. The layers are hardened with bis-vinylsulphonylmethyl ether at 3.5% of the total gel.

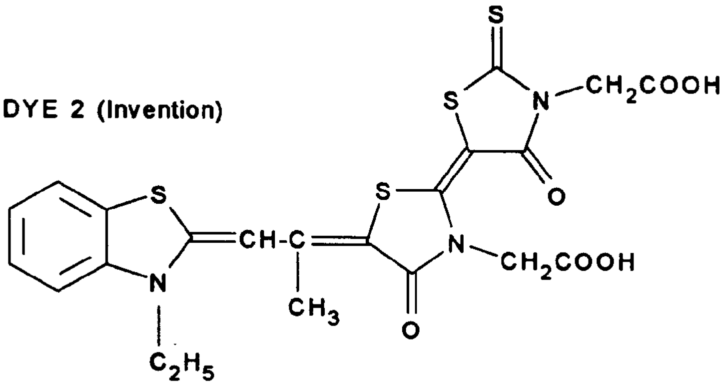
For photographic evaluation the coatings were exposed through a 0.1 increment step tablet on a Broad band Flash (BBF) sensitometer at 10^{-6}s with a filter to simulate a broad red exposure. The coating was then processed through Kodak® RA2000 developer, diluted 1+2 with water. Unless otherwise stated, all coatings were developed at 35°C for 30s, fixed washed and dried through an Interpro 20RA-s processor. For sensitivity to pressure, the coatings were abraded with a diamond stylus, weighted with a 100g weight, and processed unexposed. The level of pressure is determined by the increase in density produced by the stylus.

The dyes used in the examples were as follows:

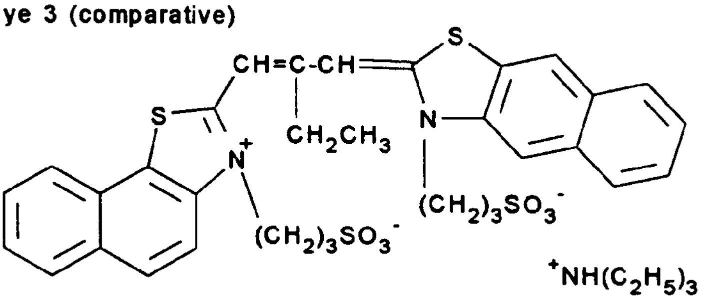


DYE 1 (comparative)

DYE 2 (Invention)



Dye 3 (comparative)



Three coatings were tested for pressure sensitivity. The dyes in the coatings were as follows:

Coating 1	Dye 1 at 200mg/Agmole
Coating 2	Dye 2 at 150mg/Agmole
Coating 3	Dye 1 at 200mg/Agmole plus Dye 2 at 150mg/Agmole

TABLE 1:

EFFECT OF DYE ON PRESSURE SENSITIVITY			
Coating	Dmin	ABRADED Dmin	DELTA
1	0.026	0.057	0.031
2	0.026	0.026	0.000
3	0.026	0.053	0.027

Only Coating 2 show no increase in Abraded Dmin.

EXAMPLE 2

All the coatings in example 1 contained hydroquinone. To eliminate any influence this may have on the results, two further coatings were made omitting this compound from the formulation. The coatings were:

Coating 4:	Dye 1 at 200mg/Ag mole
Coating 5:	Dye 2 at 150mg/Ag mole

TABLE 2:

Coating	Dmin	ABRADED Dmin	DELTA
4	0.026	0.306	0.28
5	0.026	0.058	0.032

As can be seen from these results, the coating containing Dye 2 alone showed little sensitivity to pressure whereas that containing Dye 1 showed a high sensitivity.

Explanation of terms used:

Dmin	Density of base plus fog
ABRADED Dmin	Density of base plus fog after abrasion
DELTA	ABRADED Dmin - Dmin

EXAMPLE 3

The photosensitive materials used in this example was either 2-layer, consisting of an emulsion layer and gel supercoat, or 3-layer, consisting of a gel underlayer, emulsion layer and gel supercoat. Both formats were coated on an polyethylene terephthalate base with a standard graphic arts anti-halation pelloid designed to absorb red light.

The light sensitive layer consists of a 70:30 chlorobromide cubic monodispersed emulsion (0.22μ edge length) doped with ammonium hexachlororhodate and coated at 3.3g Ag/sq.m. Total gel laydown in the 2-layer format is 3.1g/sq.m and for the 3-layer format 3.83g/sq.m. Other addenda included in the light sensitive layer are sensitising dye(s), 2-methylmercapto-5-carboxy-6-methyl tetraazaindene at 7.287mg/sq.m, 1-(3-acetamidophenyl)-5-mercaptotetrazole at 0.711mg/sq.m, 4-carboxy-methyl-4-thiazoline-2-thione at 2.137mg/sqm and copolymer (C1) at 22g per silver mole.

Other addenda which could be either in the emulsion or underlayer include 3,5-disulphocatechol, disodium salt at 97.7mg/sq.m, nucleator N1 at 6.147mg/sq.m, incorporated booster B1 at 61.42mg/sq.m and hydroquinone at 222.8mg/sq.m. In the 3-layer format, copolymer C1 is present in the underlayer at 20 g/sq.m.

The overcoat consists of gel at 0.5g/sq.m, with surfactants to aid coating, plus matting beads and colloidal silica to aid film handling. The layers are hardened with BVSM at 3.5% of the total gel.

For photographic evaluation the coatings were exposed through a 0.1 increment step tablet on a Broad band Flash (BBF) sensitometer at 10^{-6}s with a filter to simulate a broad red exposure. The coatings were then processed through Kodak® RA2000 developer, diluted 1+2 with water. Unless otherwise stated, all coatings were developed at 35°C for 30s, fixed, washed and dried through an Interpro 20RA-s processor.

Three coatings were tested for development latitude at 35°C. The dyes in the coatings were as follows:

Coating 1	Dye 1 (comp) at 200mg/Agmole
Coating 2	Dye 2 (inv) at 150mg/Agmole
Coating 3	Dye 1 at 200mg/Agmole plus Dye 2 at 150mg/Agmole

The processor used for the time and temperature tests was an Interpro 20RA-s. This processor gives good agitation during development. In addition, work was carried out in a Kodamatic 65A processor, which does not recirculate the developer in the same manner. All the coatings were given step tablet exposures and the Practical Density Point (PDP) is measured as the density at 0.4 logE less than the speed at 0.6 above fog.

Table 1:

Effect of Development Time on PDP			
Development Time (s)	Coating 1	Coating 2	Coating 3
20	3.44	5.09	3.79
25	4.13	5.28	4.59
30	4.74	5.53	4.95
35	5.27	5.59	5.16
40	5.50	5.56	5.30

Table 2:

Effect of Development Temperature at 30s Development Time on PDP			
Development Temp (°C)	Coating 1	Coating 2	Coating 3
32	3.94	5.36	4.42
35	4.74	5.53	4.95
38	4.9	5.42	4.92

Table 3:

Effect of Processor on PDP			
PROCESSOR	Coating 1	Coating 2	Coating 3
20RA-s	4.74	5.53	4.95
65A	3.12	4.73	4.23

Example 4

Using the same basic coating used in Example 3, the effect bromide build up has on the sensitometry of coatings was investigated. Samples of Kodak® RA2000 developer were spiked with increasing levels of KBr and the coatings processed at 35°C for 30s and the change in PDP compared.

Five coatings were tested for development latitude at 35°C. The dyes in the coatings were:

Coating 1	Dye 1 at 200mg/Agmole
Coating 2	Dye 2 (Inv) at 150mg/Agmole
Coating 3	Dye 1 at 200mg/Agmole plus Dye 2 (Inv) at 150mg/Agmole
Coating 4	Dye 1 at 200mg/Agmole plus Dye 3 at 25mg/Agmole

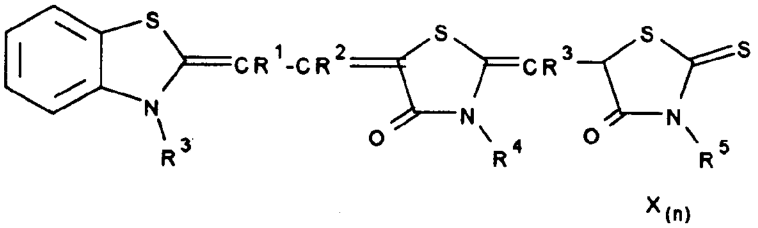
Table 4:

Effect of bromide level on PDP				
KBr level (g/l)	Coating 1	Coating 2	Coating 3	Coating 4
0	0.00	0.00	0.00	0.00
1	-0.72	-0.02	-0.04	
2	-1.67	-0.06	-0.26	
3	-2.08	-0.08	-0.26	-0.22
4	-2.21	-0.79	-0.41	
5	-2.63	-1.43	-1.06	-1.55

As can be seen from these examples, dyes of the invention such as Dye 2 offer similar spectral sensitivity, when coated in a nucleated format, compared to dyes such as Dye 1 but are not so sensitive to fluctuations in the processing cycle.

Claims

1. A method of improving abrasion resistance and sensitivity to variations in development time of photographic material comprising a support bearing a silver halide emulsion layer comprising at least 50% silver chloride which contains in or adjacent the emulsion layer a hydrazide nucleating agent and an amine booster, the combination of which is capable of providing high contrast images, sensitised to radiation having a wavelength from 600 to 700 nm characterised by sensitising the emulsion with a tricyclic merocyanine dye of the general formula.



wherein R^1, and

R^2 are each hydrogen or a substituted or unsubstituted alkyl group of 1-5 carbon atoms, and

R^3, R^4 and R^5 are each a substituted or unsubstituted alkyl group of 1-5 carbon atoms, and wherein at least one of R^3, R^4 and R^5 contain a water-solubilising group,

X is a counter-ion, and

n is 0-3.

2. A method as claimed in claim 1 in which the silver halide emulsion is a high contrast silver chlorobromide emulsion.

3. A photographic material as claimed in clain 1 or 2 in which the amine booster is an amine compour which:
   (1) comprises at least one secondary or tertiary amino group,
   (2) contains within its structure a group comprised of at least three repeating ethyleneoxy units, and
   (3) has an n-octanol/water partition coefficient (log P) of at least one, preferably at least three, and most preferably at least four,

   log P being defined by the formula:

$$\log P = \log \frac{[X]_{octanol}}{[X]_{water}}$$

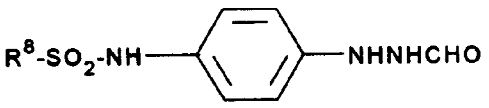
   wherein X is the concentration of the amino compound.

4. A photographic material as claimed in any of claims 1 to 3 in which the hydrazide nucleating agent has the formula:

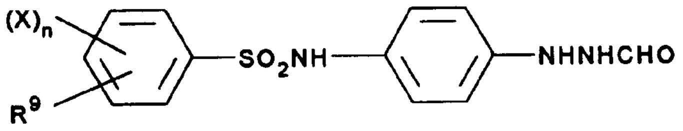
$$R^7\text{-NHNHCHO}$$

wherein R^7 is a phenyl nucleus having a Hammett sigma value-derived electron withdrawing characteristic of less than +0.30.

5. A photographic material as claimed in any of claims 1 to 4 in which the hydrazide nucleating agent is a sulphonamido-substituted hydrazine having one of the following structural formulae:



or



wherein:

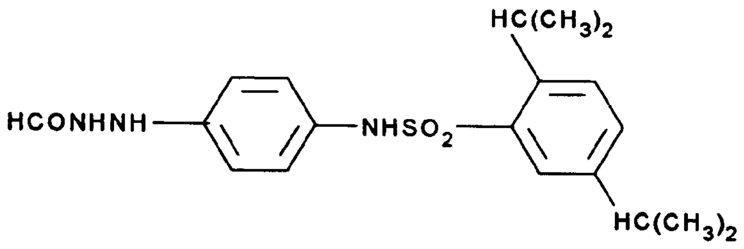
R^8 is alkyl having from 6 to 18 carbon atoms or a heterocylic ring having 5 or 6 ring atoms, including ring atoms of sulphur or oxygen;

R^9 is alkyl or alkoxy having from 1 to 12 carbon atoms;

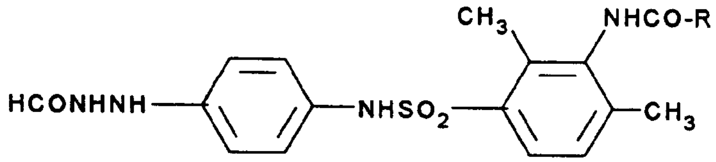
X is alkyl, thioalkyl or alkoxy having from 1 to about 5 carbon atoms; halogen; or $-NHCOR^{10}$, $-NHSO_2R^{10}$, $-CONR^{10}R^{11}$ or $-SO_2R^{10}R^{11}$ where R^{10} and R^{11}, which can be the same or different, are hydrogen or alkyl having from 1 to about 4 carbon atoms; and

n is 0, 1 or 2.

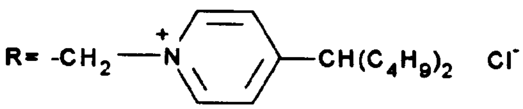
6. A photographic material as claimed in any of claims 1 to 5 in which the hydrazide nucleating agent is any one of the compounds having the following formulae:

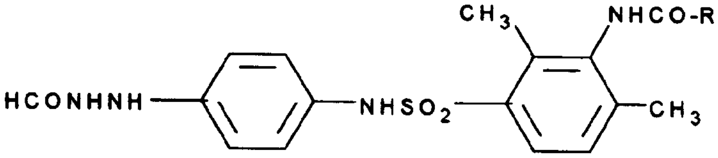


N1



N2





N3

$R = -CH_2S-(CH_2CH_2O)_4-C_8H_{17}$

7. A photographic material as claimed in any of claims 1 to 6 in which the silver halide emulsion comprises at least 70% chloride and less than 10% iodide.

8. A photographic material as claimed in any of claims 1 to 7 in which the silver halide emulsion is doped with Rhodium, Ruthenium, Iridium or other Group VIII metals.

9. A photographic material as claimed in claim 8 in which the Group VIII metal dopant is present in amounts in the range 10^{-9} to 10^{-3}, preferably 10^{-6} to 10^{-3}, mole Group VIII metal per mole of silver.