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(54) Light-sensitive silver halide photographic material for rapid processing applications

(57) A light-sensitive silver halide photographic material is disclosed comprising a support and on one or both sides thereof one or more gelatino silver halide emulsion layers spectrally sensitised in the wavelength region between 490 and 850 nm, characterised in that at least one of said spectrally sensitised silver halide emulsion layers comprises a synthetic clay having a fluorosilicate structure.

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Description

1. FIELD OF THE INVENTION

The invention is related to a light-sensitive silver halide photographic material comprising spectrally sensitised emulsions, said material being suitable for rapid processing applications.

2. BACKGROUND OF THE INVENTION

As is well known in the field of radiography, there is a general trend to enhance the speed of processing. Therefore interest has been focused on rapid access of radiographs, being vital in diagnosis. By the manufacturing of films suitable for rapid processing applications an ideal balance has to be sought concerning the thickness of the coated hydrophilic layers and the obtained sensitivity within a short processing time. E.g., thicker gelatin layers provide a sufficient absorption of processing chemicals in favour of the degree of development which is attainable within short development times of, e.g., about 12 seconds or less. An inevitable disadvantage however is the longer drying time required for thicker coatings as the water absorption is also enhanced in the rinsing stage of the processing cycle. On the other hand thinner, sufficiently hardened coatings may be dried within very short times.

Rapid processing conditions that can alternatively be applied are development processing at higher pH and higher temperatures of, e.g., 30 to 40°C, to accelerate the said processing.

However thin coated layers as well as high temperature processing or processing in a developer medium having a higher pH bring about deterioration of the photographic images obtained. Especially in automatic processors it frequently occurs that the pressure resistance of the photographic materials is insufficient. In that case so-called roller marks appear due to the uneven pressure of the carrying or conveying rollers in the processing machine. A solution therefor was found by providing a light-sensitive photographic silver halide material comprising a support and on one or both sides thereof at least one silver halide emulsion layer, characterised in that said silver halide emulsion layer(s) comprise(s) at least one synthetic clay, as in EP-A 0 644 455.

Silver halide emulsion crystals have an intrinsic sensitivity for near ultra-violet and blue radiation waves. The absorption spectrum may be different, depending on the silver halide composition of the emulsion crystals. For specific applications wherein a suitable sensitivity of the crystals is required for radiation of longer wavelenghts, it is common knowledge to spectrally sensitise the said emulsion crystals in order to get an absorption, matching the emission radiation of the exposure source. Especially for rapid processing applications, the presence of spectral sensitisers may pose a problem: due to the short development, fixing and rinsing times an unacceptable residual colour may be inevitable after processing as the said spectral sensitiser may not have left the material within such a short processing cycle. Moreover in the presence of certain synthetic clays an unacceptable desensibilisation has been observed.

3. OBJECTS OF THE INVENTION.

Therefor it is the main object of this invention to provide a light-sensitive silver halide photographic material comprising spectrally sensitised gelatino silver halide emulsions, wherein the presence of a synthetic clay in the said emulsions for their benificial effect on avoiding pressure marks does not cause speed desensitisation, the said material further allowing a rapid processing cycle in an automatic processor without the presence of dye stain after processing.

Other objects will become apparent from the description hereinafter.

4. SUMMARY OF THE INVENTION.

A solution therefor has been found by providing a light-sensitive silver halide photographic material comprising a support and on one or both sides thereof one or more gelatino silver halide emulsion layers, spectrally sensitised in the wavelength region between 490 and 850 nm, characterised in that at least one of said spectrally sensitized silver halide emulsion layers comprises a synthetic clay having a fluorosilicate composition.

5. DETAILED DESCRIPTION

Natural clays are essentially hydrous aluminum silicates, wherein alkali metals or alkaline-earth metals are present as principal constituents. Also in some clay minerals magnesium or iron or both replace the aluminum wholly or in part. The ultimate chemical constituents of the clay minerals vary not only in amounts, but also in the way in which they are combined or are present in various clay minerals.

From the natural clays smectite clays are well-known. For the said smectite clays some substitutions in both octahedral and tetrahedral layers of the crystal lattice occur, resulting in a small number of interlayer cations. Smectite clays form a group of "swelling" clays which take up water and organic liquids between the composite layers and which have marked cation exchange capacities.

So it is also possible to prepare synthetic clays, so that more degrees of freedom can lead to reproducible tailor made clay products for use in different applications.

Synthetic chemically pure clays have been produced having an analogous structure as smectite clays and are now available. So a preferred synthetic smectite clay additive for the purposes of this invention is LAPONITE JS, trade mark product of LAPORTE INDUSTRIES Limited, London. Organophilic clays and process for the production thereof have been described in EP-Patent 161 411 B1.

LAPONITE JS has been described as a synthetic layered hydrous sodium lithium magnesium fluoro-silicate incorporating an inorganic polyphoshate peptiser. The said fluoro-silicate appears as free flowing white powder and hydrates well in water to give virtually clear and colourless colloidal dispersions of low viscosity, also called "sols". On addition of small quantities of electrolyte highly thixotropic gels are formed rapidly. The said thixotropic gels can impart structure to aqueous systems without significantly changing viscosity. An improvement of gel strength, emulsion stability and suspending power can be observed by making use of it in the said aqueous systems. Further advantages are the large solid surface area of about 350 m^2/g which gives excellent adsorption characteristics, its stability over a wide range of temperatures, its unique capability to delay gel formation until desired and its synergistic behaviour in the presence of thickening agents. Further, its purity and small particle size ensures an excellent clarity. In aqueous solutions of many polar organic solvents it works as a very effective additive.

LAPONITE RD has been described as a synthetic layered hydrous sodium lithium magnesium silicate with analogous properties as LAPONITE JS.

Laponite clay as a synthetic inorganic gelling agent for aqueous solutions of polar organic compounds has been presented at the Symposium on "Gums and Thickeners", organised by the Society of Cosmetic Chemists of Great Britain, held at Oxford, October 14, 1969. In "Laporte Inorganics Laponite Technical Bulletin L104/90/A" a complete review about the structure, the chemistry and the relationship to natural clays is presented. Further in "Laporte Inorganics Laponite Technical Bulletin L106/90/c" properties. preparation of dispersions, applications and the product range are disclosed. A detailed description of "Laponite synthetic swelling clay, its chemistry, properties and application" is given by B.J.R. Mayes from Laporte Industries Limited.

In praxis the primary particles are platelets having a diameter of about 0.025 μm and a thickness of about 0.001 μm.

The light-sensitive silver halide material of the present invention comprises a support having on at least one side thereof at least one light-sensitive hydrophilic colloid silver halide emulsion layer wherein the synthetic swelling clays according to this invention are present as an extra binder or filler between the silver halide grains in addition to the hydrophilic colloid.

Quite unexpectedly, as has already been described in the cited reference EP-A 0 644 455, it has been found that in the presence of the clays according to that invention, roller mark defects as described hereinbefore are significantly reduced or are even absent if the said light-sensitive material is rapidly run in an automatic processor. Even if the amount of hydrophilic binder has been reduced to obtain thin coated, rapidly processable layers, the presence of the said synthetic swelling clays is working very efficiently against pressure marks that are induced by the conveying rollers in the processing of the said materials.

As the main hydrophilic binder in the hydrophilic layers of the photographic material conventional lime-treated or acid treated gelatin can be used. The preparation of such gelatin types has been described in e.g. "The Science and Technology of Gelatin", edited by A.G. Ward and A. Courts, Academic Press 1977, page 295 and next pages. The gelatin can also be an enzyme-treated gelatin as described in Bull. Soc. Sci. Phot. Japan, N° 16, page 30 (1966). Before and during the formation of the silver halide grains it is common practice to establish a gelatin concentration of from about 0.05 % to 5.0 % by weight in the dispersion medium so that gelatin is already brought into the emulsion layer(s) by incorporation of silver halide crystals that are prepared in gelatinous medium. To minimize the amount of gelatin, the silver halide crystals can alternatively be prepared in silica sol medium as has been described in EP-B 0 392 092. Additional gelatin can be added in a later stage of the emulsion preparation, e.g., during the flocculation procedure, after washing or by redispersing the flocculate, to establish optimal coating conditions and/or to establish the required thickness of the coated emulsion layer. Preferably a ratio by weight of gelatin to silver halide, expressed as the equivalent amount of silver nitrate, ranging from 0.2 to 1.0 is then obtained.

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

The gelatin binder of the photographic elements can be forehardened with appropriate hardening agents such as those of the epoxide type, those of the ethylenimine type, those of the vinylsulphone type e.g. 1,3-vinylsulphonyl-2-propanol, chromium salts e,g. chromium acetate and chromium alum, aldehydes, e.g. formaldehyde, glyoxal, and glutaraldehyde, N-methylol compounds, e.g., dimethylolurea and methyloldimethylhydantoin, dioxan derivatives, e.g., 2,3-dihydroxy-dioxan, active vinyl compounds, e.g., 1,3,5-triacryloyl-hexahydro-s-triazine, active halogen compounds, e.g., 2,4-dichloro-6-hydroxy-s-triazine, and mucohalogenic acids, e.g., mucochloric acid and mucophenoxychloric acid. These hardeners can be used alone or in combination. The binder can also be hardened with fast-reacting hardeners such as carbamoylpyridinium salts as disclosed in US Patent 4,063,952 and with the onium compounds as disclosed in EP-A 0 408 143.

The halide composition of the silver halide emulsions used in the silver halide photographic material according to the present invention is not specifically limited and may be any composition selected from, e.g., silver chloride, silver bromide, silver chlorobromide, silver bromoiodide, and silver chlorobromoiodide. The content of silver iodide is equal to or less than 20 mol%, preferably equal to or less than 5 mol%, even more preferably equal to or less than 3 mole %.

The photographic silver halide emulsions used in the photographic material according to the present invention can be prepared by mixing the halide and silver solutions in partially or fully controlled conditions of temperature, concentrations, sequence of addition, and rates of addition. The silver halide can be precipitated according to the single-jet method, the double-jet method, or the conversion method.

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

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

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

The average size of the silver halide grains may range from 0.1 to 2.0 μm, preferably from 0.1 to 1.0 μm and still more preferably from 0.2 to 0.6 μm.

The size distribution of the silver halide particles of the photographic emulsions to be used according to the present invention can be homodisperse or heterodisperse. A homodisperse size distribution is obtained when 95% of the grains have a size that does not deviate more than 30% from the average grain size.

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

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

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

The light-sensitive silver halide emulsion can be a so-called primitive emulsion, in other words an emulsion that has not been chemically sensitized. However, the light-sensitive silver halide emulsion can be chemically sensitized as described i.a. in the above-mentioned "Chimie et Physique Photographique" by P. Glafkides, in the above-mentioned "Photographic Emulsion Chemistry" by G.F. Duffin, in the above-mentioned "Making and Coating Photographic Emulsion" by V.L. Zelikman et al, and in "Die Grundlagen der Photographischen Prozesse mit Silberhalogeniden" edited by H. Frieser and published by Akademische Verlagsgesellschaft (1968). As described in said literature chemical sensitization can be carried out by effecting the ripening in the presence of small amounts of compounds containing sulphur, e.g., thiosulphate, thiocyanate, thioureas, sulphites, mercapto compounds, and rhodamines, but also the analogous selenium and tellurium compounds. The emulsions can be sensitized also by means of gold-sulphur ripeners, gold-selenium or gold-tellurium compounds or by means of reductors, e.g. tin compounds as described in GB-A 789,823, amines, hydrazine derivatives, formamidine-sulphinic acids, and silane compounds. Chemical sensitization can also be performed with small amounts of Ir, Rh, Ru, Pb, Cd, Hg, Tl, Pd, Pt, or Au. One of these chemical sensitization methods or a combination thereof can be used.

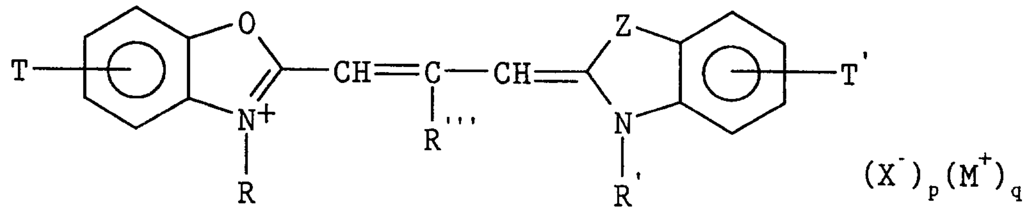
According to this invention the silver halide emulsions coated in the layers of the photographic material are sensitised to the green, to the red, to the near-infrared or to the infrared region of the wavelength spectrum. Preferred absorption maxima are situated around the wavelengths of 550 nm, 633 nm, 670 nm, 780 nm and 820 nm.

Therefor useful spectral sensitisers for the silver halide emulsions coated in the layers of the photographic material according to this invention are methine dyes such as those described by F.M, Hamer in "The Cyanine Dyes and Related Compounds", 1964. John Wiley & Sons, Further included are cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, homopolar cyanine dyes, hemicyanine dyes, styryl dyes and hemioxonol dyes. Particularly valuable dyes are those belonging to the cyanine dyes, merocyanine dyes, complex merocyanine dyes.

It has surprisingly been found now that there is no problem if synthetic clay, independant on its composition, is used in emulsion crystals having an intrinsic sensitivity or a(n) (enhanced) sensitivity after spectral sensitisation for near ultra-violet and blue incident radiation waves. A totally different situation is met if the emulsion crystals are spectrally sensitised in the green, the red or the (near) infrared region: a strong desensitisation occurs if synthetic clay is added, having a composition different from fluorosilicate.

Particularly, in accordance with this invention spectrally sensitised silver halide photographic emulsions are present wherein the silver halide emulsions are spectrally sensitised with at least one spectrally sensitising dye, the general structure of which is given hereinafter.

A dye corresponding to the general structure according to the formula (I) is



(I)

wherein

Z represents an oxygen or a nitrogen atom substituted with R'',
R, R' and R'' each independently represent at least one member selected from the group consiting of substituted or unsubstituted alkyl,
R''' represents hydrogen, substituted or unsubstituted alkyl or substituted or unsubstituted aryl,
T and T' each independently represent the usual substituents known in the art,
$(X^-)_p$ represents an negatively charged atom or group of atoms to compensate for the positive charge(s) present on the dye, and
$(M^+)_q$ represents a positively charged atom or group of atoms to compensate for the negative charge(s) present on the dye and wherein
p and q each represent an integer in order to get an electronically neutral compound.

Preferred spectral sensitisers suitable for use together with the emulsion crystals according to this invention are those of the type where R''' is $-C_2H_5$, Z is an oxygen atom, at least one of R and R' represents -a sulphoalkyl group, preferably corresponding to the one of the formulae

$-(CH_2)_nSO_3^-$ wherein n equals 2, 3 or 4,
$-(CH_2)_2-CH(CH_3)-SO_3^-$ and
$-CH_2-CHY-CH_2-SO_3^-$ wherein Y represents -OH or -Cl; -a sulphatoalkyl group, preferably corresponding to the formula
$-(CH_2)_nOSO_3^-$ wherein n equals 2, 3 or 4, -an acylsulphonamido group, preferably corresponding to the formulae
$-(CH_2)_n-C(O)-N(R'''')-SO_2-(CH_2)_mH$ wherein n equals 1, 2 or 3; m equals 1, 2, 3;
$-(CH_2)_r-SO_2-N(R'''')-SO_2-(CH_2)_sH$ wherein r equals 2, 3 or 4; s equals 1, 2, 3;
$-(CH_2)_v-SO_2-N(R'''')-C(O)-(CH_2)_wH$ wherein v equals 2, 3 or 4; w equals 1, 2, 3;

wherein R'''' represents H or alkyl;
and wherein T and T' each independantly represent hydrogen, 5-phenyl, 5-Cl, $5-OCH_3$ or $5-CH_3$.

In this context, EP-A 0 638 841 is incorporated herein by reference.

Another class of preferred spectral sensitisers suitable for use together with the emulsion crystals according to this invention are those of the type where R''' is hydrogen, Z is an nitrogen atom, substituted with R'', being a substituted or unsubstituted alkyl; wherein T represents 5-phenyl, 5-Cl, $5-OCH_3$ or $5-CH_3$ and wherein T' represents $5,6-(Cl)_2$; 5-CN-6-Cl; $5-CF_3$-6-Cl; 5-Cl: 5-CN, $5-CF_3$, $5-CHF_2$, $5-SO_2CH_3$, $5-SO_2R'''''$ or 5-COOR''''''(R''''' and R'''''' each representing a fluoro-subsituted or non-fluoro-substituted alkylgroup); and $5-SO_2-N(R^x)(R^y)$ or $5-CO-N(R^x)(R^y)$, wherein R^x and R^y each independently represent substituted or unsubstited alkyl groups, or independantly or together form a ring with the N-atom to which they are attached.

Especially preferred structures of the type wherein Z represents oxygen are those wherein T and T' each represent Cl or T represents 5-Cl and T' represents 5-Phenyl or vice versa and wherein R and R' each independantly represent one of the combinations of the formulae

$-(CH_2)_nSO_3^-$ wherein n equals 2, 3 or 4,

$-(CH_2)_2-CH(CH_3)-SO_3^-$ and

$-CH_2-CHY-CH_2-SO_3^-$ wherein Y represents -OH or -Cl; or wherein R, represents one of the formulae given above and R'corresponds to one of the formulae

$-(CH_2)_pH$ wherein p equals 1, 2, 3 or 4;

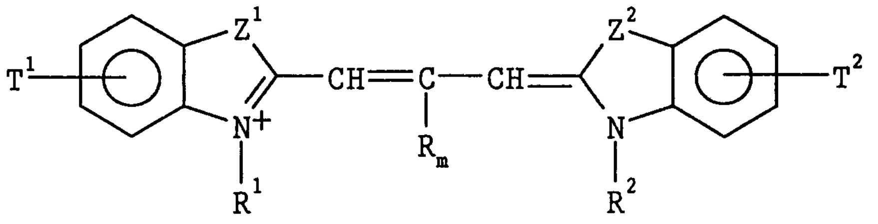
$-CH_2-Phen-SO_3^-$ wherein Phen = phenyl;

$-(CH_2)_q-Phen-COOH$ wherein q equals 1, 2 or 3.

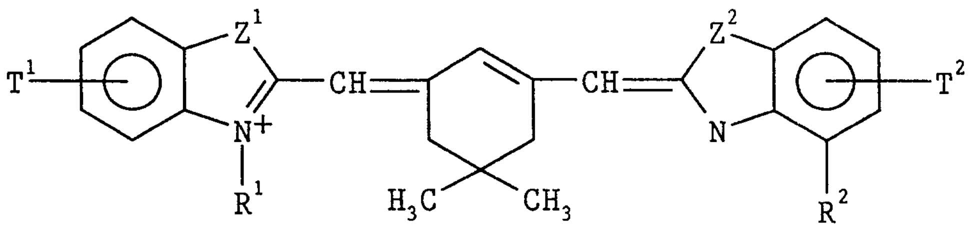
An example of a useful spectral sensitizer according to the general formula given above is anhydro-5,5'-dichloro-3,3'-bis(n-sulphobutyl)-9-ethyloxacarbo-cyanine hydroxide or anhydro-5,5'-dichloro-3,3'-bis(n-sulphopropyl)-9-ethyl-oxacarbo-cyanine hydroxide.

A suitable mixture of spectral sensitizers that can be applied is anhydro-5,5'-dichloro-3,3'-bis(n-sulphobutyl)-9-ethyl oxacarbocyanine hydroxide or anhydro-5,5'-dichloro-3,3'-bis(n-sulphopro pyl)-9-ethyloxacarbo-cyanine hydroxide and anhydro-5,5'-dicyano-1,1'-diethyl-3,3'-di(2-acetoxyethyl)ethyl-imidacarbocyanine bromide.

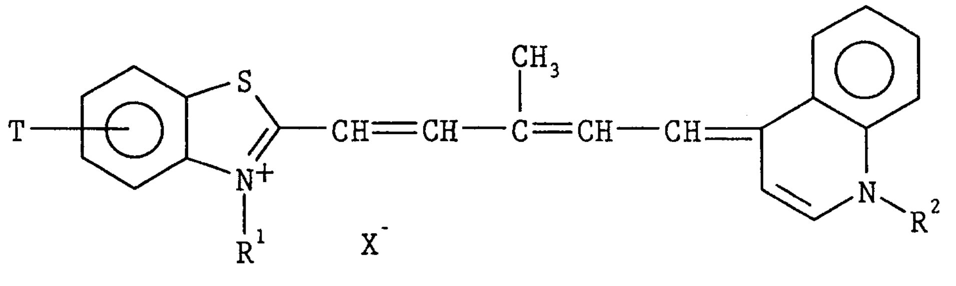
Especially suitable sensitising dyes in the red part of the visible spectrum are trimethinecyanines corresponding to the general formula (II), pentamethines corresponding to the general formula (III) absorbing more bathochromically and to the general formula (IV) absorbing in the infrared regio



(II)



(III)



(IV)

In formula (II)

R_m represents hydrogen, methyl, ethyl, phenyl or

$-S-CH_3$ when Z^1 and Z^2 each represent sulphur (and wherein the structure can be symmetrical or asymmetrical); wherein methyl, ethyl and $-S-CH_3$ are most preferred;

R_m represents hydrogen, methyl, ethyl, isopropyl, phenyl or

-S-CH_3 when Z^1 represents sulphur and Z^2 represents oxygen; wherein ethyl is most preferred;

R_m represents hydrogen and R represents ethyl when Z^1 represents sulphur and Z^2 represents -NR;

R^1 and R^2 each independantly represent

-$(CH_2)_nSO_3^-$ wherein n= 2, 3, 4 or iso-4;
-$(CH_2)_mCOO^-$ wherein m= 1, 2 or
-$(CH_2)_m$-CO-NH-SO_2CH_3 wherein m equals 1; eventually 2.

T^1 and T^2 represent
-hydrogen, 5-Cl, 5-Phenyl, 5-CH_3, 4,5-benzo, 5,6-benzo if T_1 or T_2 is present on a benzoxazole nucleus;
-5,6-dichloro; 5-CN; 5-SO_2R if T_1 or T_2 is present on a benzimidazole nucleus;

T^1 and T^2 each independantly represent
-hydrogen, 5-Cl, 5-CH_3, 5-OCH_3, 4,5-benzo, 5,6-benzo, 6-CH_3, 6-OCH_3, 5,6-$(CH_3)_2$, 5,6-$(OCH_3)_2$, 5-CH_3/6-OCH_3 if T_1 and/or T_2 is(are) present on a benzthiazole nucleus;

In the patent literature specific structures corresponding with the general formula (II) have been described in US-P 3,282,933; in BP-A 0 467 370; in JP-A 05 040 324; in SU 01 645 270; in DE 01 028 718 and in GB 2,267,287.

Structures having a meso -S-CH_3 substitution have been described in US-P's 2,557,806 and 3,460,947 and in GB's 1,207,006 and 2,048,888.

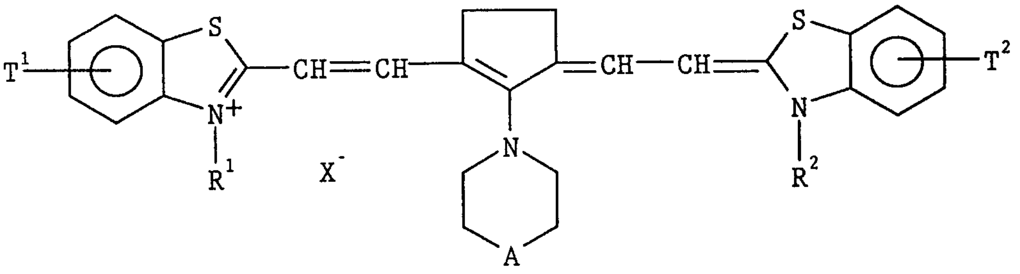
In formula (III) the structure can be symmetrical or asymmetrical if Z^1 and Z^2 each represent sulphur. R^1 and R^2 further have the same meaning as in formula (II), which can give rise to a symmetrical or an asymmetrical structure. The presence of an oxygen atom instead of sulphur for Z^2 only appears rarely.

In the patent literature specific structures corresponding with the general formula (III) have been described in US-P's 3,615,632 and 3,669,672; in DE 03 216 568; in JP-A's 50 000 503: 53 142 223; 62 191 846; 62 194 252; 62 254 139; 62 262 853; 63 100 448 and 63 264 743 and in JP-B's 85 057 583; 92 064 060; 93 058 176; 93 060 093; 93 220 339 and 94 058 536.

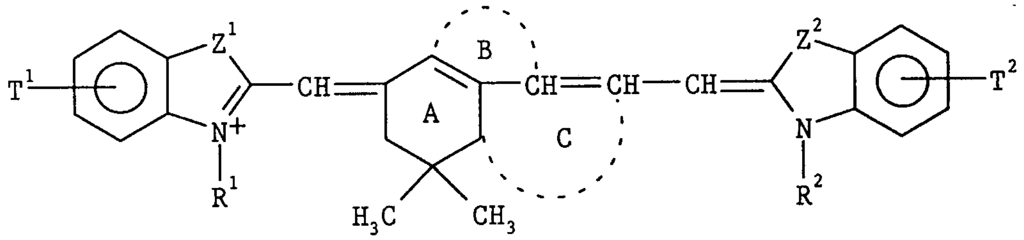
In the cationic structure corresponding to the formula (IV) the substituents have the same meaning as given hereinbefore. X^-represents a suitable anion.

In the patent literature specific structures corresponding with the general formula (IV) have been described in JP-A 02 071 257 and in Research Disclosure 00 289 052, May 1988, p. 301-303.

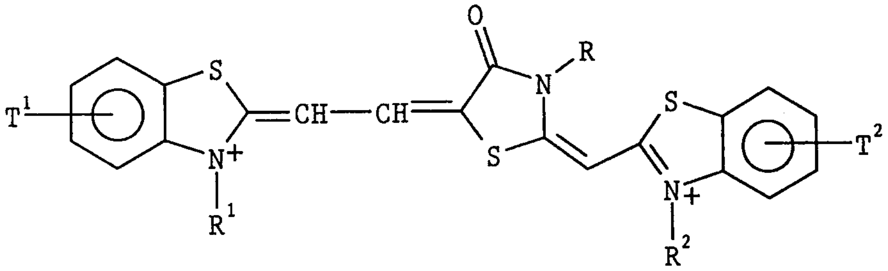
Other useful red absorbing spectral sensitisers are heptamethines, corresponding to the formulae (V) and (VI) and rhodacyanines, corresponding to the formulae (VII), (VIII) and (IX).


T1
S
N+
R1
X-
CH=CH
N
A
CH—CH
S
N
R2
T2

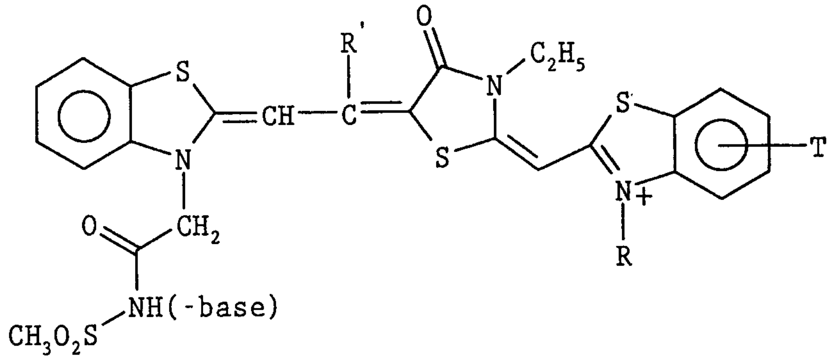
(V)


T1
Z1
N+
R1
CH
A
B
C
H3C
CH3
CH=CH—CH
Z2
N
R2
T2

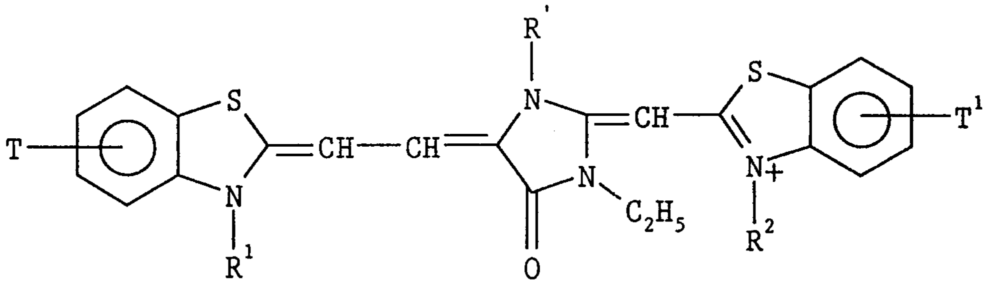
(VI)


T1
S
N+
R1
CH—CH
O
N
R
S
S
N+
R2
T2

(VII)


S
N
CH2
O
NH(-base)
CH3O2S
CH—C
R'
O
N
C2H5
S
S
N+
R
T

(VIII)

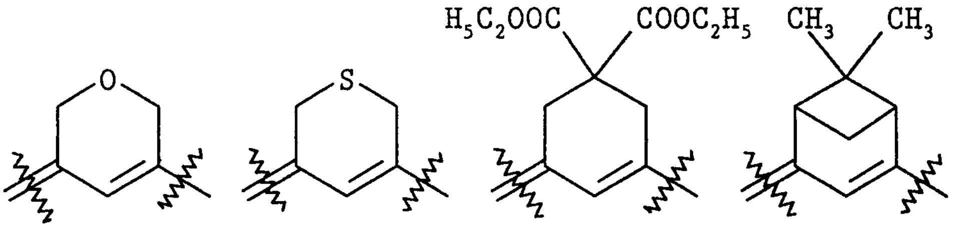


(IX)

In formula (V), representing a cationic heptamethine dye, T^1 and T^2 each represent hydrogen, 5-Cl, 5-CH_3, 5-OCH_3, 6-CH_3, 6-OCH_3, 5,6-$(CH_3)_2$, 5,6-$(OCH_3)_2$, if the structure is symmetrical; and T^2 preferably represents 4,5 benzo if the structure is asymmetrical, whereas T^1 has the same structure as has been given hereinbefore.

In formula (VI) Z^1=Z^2=S or Z^1=S and Z^2=O, whereas R^1 and R^2 can be different but are almost the same and are preferably both C_2H_5.

The closed ring B can be represented by the following structures:



The rhodacyanines represented in the formulae (VII), (VIII) and (IX) have the same benzthiazole substitution as given hereinbefore.

In formula (VII) R is preferably alkyl; R^1=R^2=C_2H_5 for a cationic rhodacyanine, having preferably an -O-Tosylate anion as a counterion and R^1=R^2=$C_4H_8SO_3^-$ for an anionic rhodacyanine having $(C_2H_5)_3N^+H$ as a counterion.

In formula (VIII) R can be hydrogen, but preferably represents phenyl, -S-CH_3 or

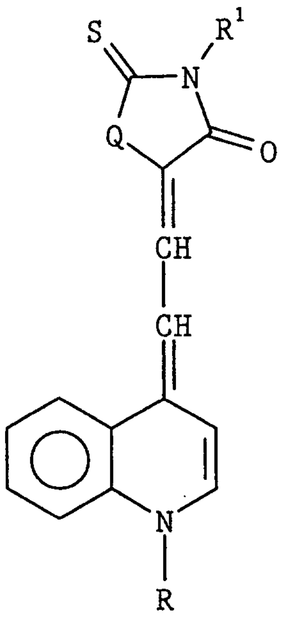
-$(CH_2)_nSO_3^-$ wherein n= 3 or (preferably) 4;
-$(CH_2)_mCOO^-$ wherein m= 1 or 2 or
-$(CH_2)_m$-CO-N^--SO_2CH_3 wherein m equals 1 or 2.

In formula (IX) R^1=R^2 represents $(CH_2)_4SO_3^-$ or (CH_2)-CO-N^--SO_2CH_3; or

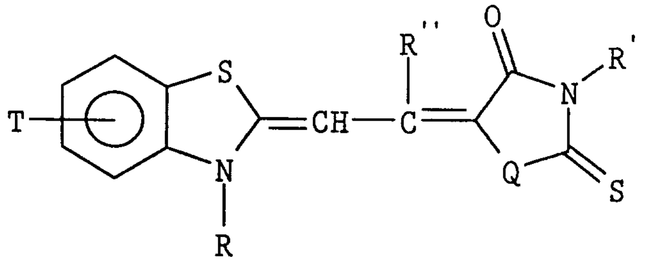
R^1 represents CH_2-CO-NH-SO_2CH_3 (.base) and R^2 represents $(CH_2)_4SO_3^-$; -(CH_2)-CO-N^--SO_2CH_3; or $(CH_2)_nCOO^-$. R'has the same meaning as in formula (VIII).

T further preferably represents hydrogen, whereas T^1 represents the common substituents for benzthiazol nuclei given hereinbefore or T and T^1 may be the same.

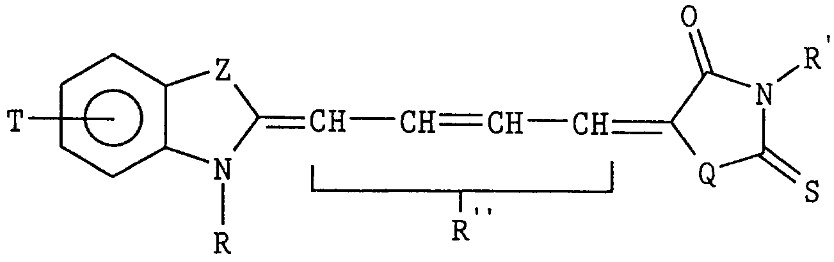
Dimethine merocyanines corresponding to the general formulae (X) and (XI) are also useful as red light absorbing spectral sensitisers, as well as tetramethine merocyanines corresponding to the formula (XII).



(X)



(XI)



(XII)

In formula (X) Q represents S or NR^3.

If Q=S, R and R^1 preferably represent sulpho- or carboxyalkyl; if $Q=NR^3$ R^1 preferably represents alkyl or phenyl, R^3 represents phenyl, CH_2COOR or isopropyl, with the proviso that at least one alkali soluble group is present in the dye structure.

In the patent literature specific structures corresponding with the general formula (X) have been described in US-P's 3,625,698 and 4,461,828; in EP-B 0 127 455; in JP-A 61 281 235; in JP-B 76 041 055 and in DE's 01 028 718 and 02 330 602.

In formula (XI) Q also represents S or NR^3.

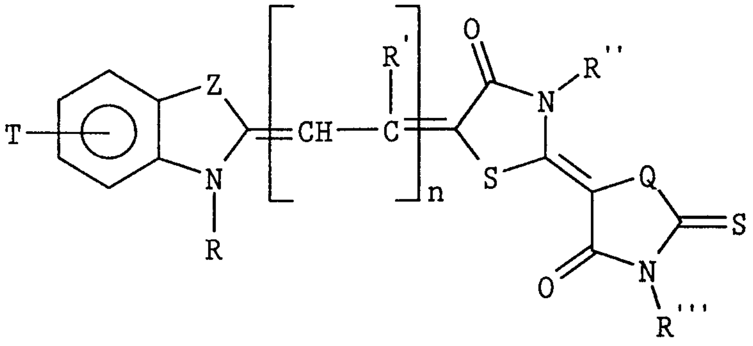
If Q=S, R and R^1 preferably represent sulpho-, carboxyalkyl or - CH_2CH_2OH with the proviso that at least one alkali soluble group is present and R" represents hydrogen, methyl, ethyl, isopropyl, phenyl or -SCH_3; if Q=NR^3 R^1 represents hydrogen, R^3 represents phenyl or isopropyl if R^1 represents alkyl; or R^3 represents -CH_2COOR if R^1 represents methyl or phenyl with the proviso that at least one alkali soluble group is present for R, R^1 and/or R^3 in the dye structure.

In the patent literature specific structures corresponding with the general formula (XI) have been described in US-P's 2,493,747; 2,497,876; 2,719,152; 2,947,631; 3,288,610; 3,385,707; 3,439,774; 3,519,430; 3,537,858; 3,567,458; 3,576,641; 3,579,348; 3,615,640; 3,642, 786; 3,660,102 and 3,854,956; in GB's 846,298; 1,078,227; 1,144,548 and 1,192,267; in SU 01 126 572; in JP-A's 51 059 881; 51 123 223; 62 073 251 and 62 208 043; and in JP-B's 65 014 112; 65 023 467; 67 023 573; 67 027 165; 67 027 166; 67 027 167; 70 015 894; 74 046 416; 76 041 055; 77 025 333; 79 036 852; 84 017 822; 91 007 930 and 93 003 570.

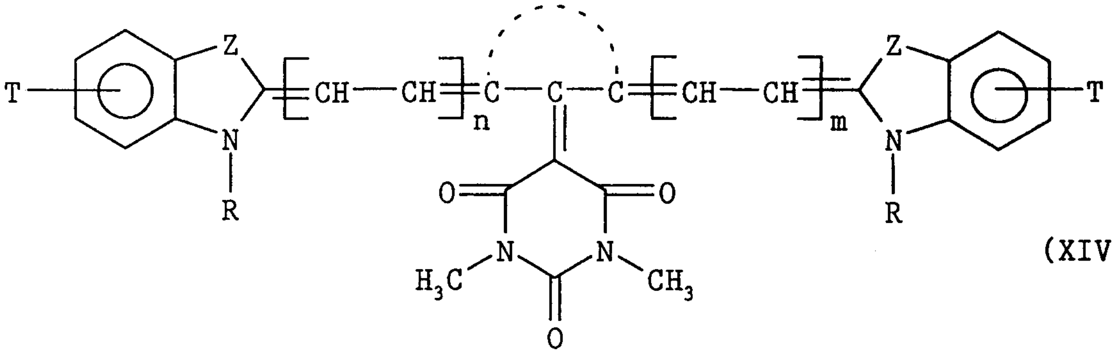
In formula (XII) Q also represents O or S. T has the same meaning as given hereinbefore, R" represents methyl or ethyl (present on positions differing from each other) and R and R^1 represent carboxy or sulphoalkyl with the proviso that at least one of them has a water soluble goup. Further Q represents S and NR and has the same meaning as just given hereinbefore.

In the patent literature specific structures corresponding with the general formula (XII) have been described in US-P's 2,719,152; 2,742,833; 3,519,430; 3,642,787; 3,658,522 and 4,113,496; in DE's 02 207 352 and 02 451 158; in GB's 1,192,267; 1,582,132; 2,065,314 and 2,162,855; in EP-B 0 412 851; in JP-A's 59 135 461; 60 131 533; 60 170 852; 60 192 937; 60 263 937; 61 174 540; 61 262 739; 61 282 832; 62 087 953; 62 089 038; 62 174 740; 62 254 147; 62 275 239; 63 104 234; 02 124 561; 02 262 653; 02 269 334 and 03 110 545; in JP-B's 76 041 055; 80 015 013 and 83 004 335; in Research Disclosure 160058 and in J. Imag. Sci. Technol. Vol, 57 (6), p. 589-597 (1993).

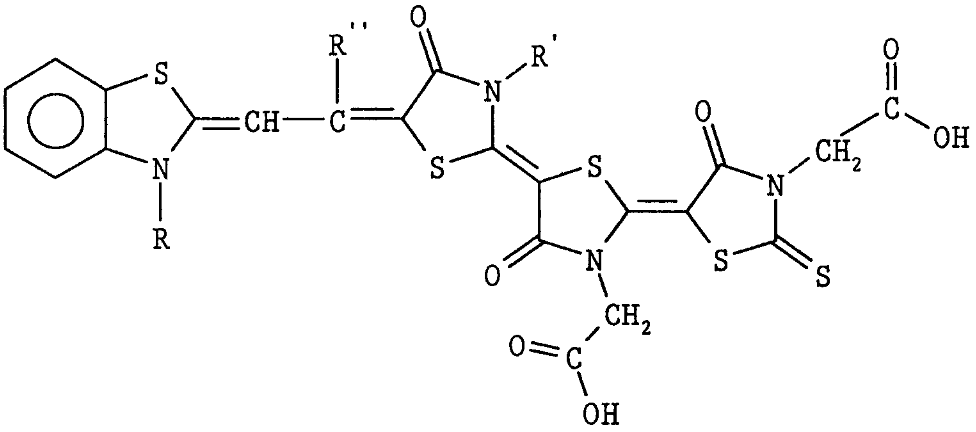
Polynuclear merocyanines according to the general formula (XIII) are further absorbing more bathochromically for n=1 (green sensitising for n=0) as well as the polynuclear merocyanines corresponding to the general formulae (XIV), (XV) and (XVI).



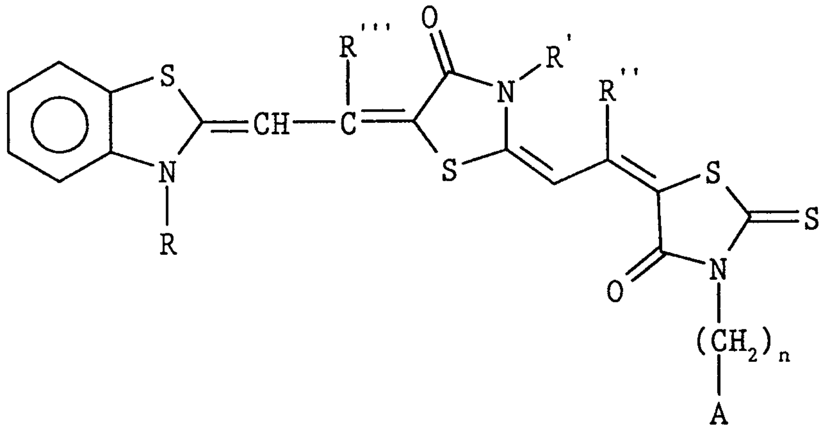
(XIII)



(XIV)



(XV)


(XVI)

In formula (XIII) for Z=S, R^1 represents one member selected from the group consisting of hydrogen, methyl, ethyl, isopropyl, phenyl, $-SCH_3$ and $-CH_2CH_2COOH$, whereas for Z=O, R^1 represents hydrogen.

At least two alkali soluble groups are present in R, R" and R'''. For Q=S, R" and/or R''' preferably represent by CH_2CH_2COOH. R''' can however also represent $CH_2CH_2SO_3H$. R preferably represents methyl, ethyl, $CH_2CONHSO_2CH_3$, $(CH_2)_nSO_3H$ (wherein n preferably equals 3). If $Q=NR^3$, R''' preferably represents methyl or phenyl whereas R^3 represents CH_2COOH; or R''' preferably represents ethyl whereas R^3 represents phenyl or isopropyl.

In formula (XIII) T corresponds with Z and has the meaning as given hereinbefore. In the case that Z equals 0, Q represents sulphur. If each of Z and Q represent sulphur n equals 0; in all other cases n equals 1.

In the patent literature specific structures corresponding with the general formula (XIII) but with a benzthiazine nucleus have been described in US-P 4,228,232; in DE's 02 140 539 and 02 917 483; in GB 2,020,297 and in JP-B 80 002 613.

Specific structures corresponding with the general formula (XIII) but with a benzoxazol nucleus have been described in US-P 2,493,748 and 3,110,591; in ES 00 374 301; in JP-A's 61 077 843 and 02 519 001 and in JP-B's 76 041 055; 79 034 331 and 91 007 091.

In formula (XIV) m normally equals 1, but can be 0. Z can represent O, but normally Z represents sulphur (and in that case T has the same meaning as given hereinbefore) or $C(CH_3)_2$ (and in that case T represents hydrogen). R preferably represents $(CH_2)_nSO_3H$.base wherein n equals 2 or 4.

In the patent literature specific structures corresponding with the general formula (XIV) have been described in WO's 95 007822 and 95 007950; in JP-A 05 119 425 and in JP-B 89 038 299.

In formula (XV) R preferably represents methyl or ethyl, R' preferably represents ethyl or allyl and R" preferably represents phenyl, isopropyl or $S(CH_3)$.

In formula (XVI) R and R' have the same meaning as in formula (XIV), whereas R''' has the same meaning as R". Preferably R" represents hydrogen, methyl or ethyl; n equals 1 or 2 and A equals COOH.base or SO_3H.base.

In the patent literature specific structures corresponding with the general formula (XVI) have been described in BE 00 508 677; in CH 00 677 409; in DE 00 958 684; in FR 01 103 384; in GB 789,077; in EP-A's 0 467 370 and 0 614 114; in EP-B 0 427 892; in JP-A 05 313 285 and in JP-B 86 045 548.

Other dyes, which per se do not have any spectral sensitization activity, or certain other compounds, which do not substantially absorb visible radiation, can have a supersensitization effect when they are incorporated together with said spectral sensitizing agents into the emulsion. Suitable supersensitizers are i.a. heterocyclic mercapto compounds containing at least one electronegative substituent as described, e.g., in US-P 3,457,078, nitrogen-containing heterocyclic ring-substituted aminostilbene compounds as described, e.g., in US-P 2,933,390 and in US-P 3,635,721, aromatic organic acid/formaldehyde condensation products as described e.g. in US-P 3,743,510, cadmium salts, and azaindene compounds.

The silver halide emulsion for use in accordance with the present invention may comprise compounds preventing the formation of fog or stabilizing the photographic characteristics during the production or storage of photographic elements or during the photographic treatment thereof. Many known compounds can be added as fog-inhibiting agent or stabilizer to the silver halide emulsion. Suitable examples are, e.g., the heterocyclic nitrogen-containing compounds such as benzothiazolium salts, nitroimidazoles. nitrobenzimidazoles, chlorobenzimidazoles, bromobenzimidazoles, mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiadiazoles, aminotriazoles, benzotriazoles (preferably 5-methyl-benzotriazole), nitrobenzotriazoles, mercaptotetrazoles, in particular 1-phenyl-5-mercapto-tetrazole, mercaptopyrimidines, mercaptotriazines, benzothiazoline-2-thione, oxazoline-thione, triazaindenes, tetrazaindenes and pentazaindenes, especially those described by Birr in Z. Wiss. Phot. 47 (1952), pages 2-58, triazolopyrimidines such as those described in GB-A 1,203,757, GB-A 1,209,146, JA-Appl. 75-39537, and GB-A 1,500,278, and 7-hydroxy-s-triazolo-[1,5-a]-pyrimidines as described in US-P 4,727,017, and other compounds such as benzenethiosulphonic acid, benzenethiosulphinic acid, benzenethiosulphonic acid amide. Other compounds that can be used as fog-inhibiting compounds are metal salts such as, e.g., mercury or cadmium salts and the compounds described in Research Disclosure N° 17643 (1978), Chaptre VI. Fog-inhibiting agents or stabilizers can be added to the silver halide emulsion prior to, during, or after the ripening thereof and mixtures of two or more of these compounds can be used.

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

Development acceleration can be accomplished with the aid of various compounds, preferably polyalkylene derivatives having a molecular weight of at least 400 such as those described in, e.g., US-P's 3,038,805 - 4,038,075 - 4,292,400.

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

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

Suitable UV-absorbers are, e.g., aryl-substituted benzotriazole compounds as described in US-P 3,533,794, 4-thiazolidone compounds as described in US-P 3,314,794 and 3,352,681, benzophenone compounds as described in JP-A 2784/71, cinnamic ester compounds as described in US-P 3,705,805 and 3,707,375, butadiene compounds as described in US-P 4,045,229, and benzoxazole compounds as described in US-P 3,700,455 and suitable compounds summarised in Research Disclosure 36544, dated September 1994.

In general, the average particle size of spacing agents is comprised between 0.2 and 10 µm. Spacing agents can be soluble or insoluble in alkali. Alkali-insoluble spacing agents usually remain permanently in the photographic element, whereas alkali-soluble spacing agents usually are removed therefrom in an alkaline processing bath. Suitable spacing agents can be made, i.a., of polymethyl methacrylate, of copolymers of acrylic acid and methyl methacrylate, and of hydroxypropylmethyl cellulose hexahydrophthalate. Other suitable spacing agents have been desribed in US-P 4,614,708.

Further information about photographically useful compounds is summarised in Research Disclosure 36544, dated September 1994, and incorporated herein by reference inasfar as it is relevant for this invention.

It is further remarkable that, if synthetic clay is added to hydrophilic layers differing from the emulsion layer(s) comprising silver halide emulsions spectrally sensitized to the wavelength region between 490 and 850 nm, a synthetic clay having a fluorasilicate composition is also required, in order to avoid desensitisation of the spectrally sensitised emulsions coated in adjacent layers thereto.

According to this invention the said hydrophilic layer is an intermediate layer, adjacent to at least one gelatino silver halide emulsion layer or an outermost afterlayer of the material according to this invention. This means that the said hydrophilic layer is an intermediate layer between two emulsion layers, an undercoat layer between the subbing layer and the emulsion layer situated the more close to the support, a protective antistress layer coated on the emulsion layer farthest from the support or even an afterlayer coated on top thereof.

According to this invention an amount of synthetic clay present in the said silver halide emulsion layer or layers is from 0.05 to 0.75 g/m^2, and more preferably from 0.1 to 0.5 g/m^2. Further according to this invention, when the synthetic clay is present in a hydrophilic layer coated on top of the emulsion layer situated farthest from the support, called "protective antistress layer" or "afterlayer", the said clay is present therein in an amount of from 0.05 to 0.25 g/m^2.

According to this invention the said hydrophilic layer(s) coated on top of the silver halide layer(s) are containing gelatin in an amount of from 0.5 to 1.2 g/m^2. More preferably, if an afterlayer is coated on top of the protective antistress layer or layers, the said afterlayer is free from gelatin.

A preferred protective layer is further made from gelatin hardened up to a degree corresponding with a water absorption of less than 2.5 grams of water per m^2.

In admixture with the hardened gelatin the protective layer may contain friction-lowering substance(s) such as dispersed wax particles (carnaubawax or montanwax) or polyethylene particles, fluorinated polymer particles, silicon polymer particles etc.

According to a specific embodiment the said friction lowering substance(s) are present in an antistatic layer on top of the antistress layer serving as outermost layer.

According to this invention in a preferred embodiment colloidal silica is added to the antistress layer composition on top of the silver halide emulsion layer(s). Preferably the said colloidal silica has an average particle size not larger than 0.010 μm, a surface area of at least 300 m^2 per gram. A coverage in the range of 50 mg to 500 mg per m^2 is used. Particularly good results can be obtained if in the protective antistress coating at least 50 % by weight of colloidal silica versus the binder is present. Especially preferred colloidal silica particles have a surface area of 500 m2 per gram and an average grain size smaller than 0.007 μm. Such type of silica is sold under the name KIESELSOL 500 (KIESELSOL is a registered trade name of Bayer AG, Leverkusen, West-Germany).

Further by making use of a layer composition wherein antistatic agents as. e.g., polyoxyalkylenes and more preferably polyoxyethylenes are present in an outermost layer, the presence of at least one ionic or non-ionic polymer or copolymer latex or at least one synthetic clay as described hereinbefore contributes to the preservation of the antistatic characteristics of the material before processing as has been described in EP-A 0 644 454.

Moreover the said layer composition provides excellent surface characteristics as sufficient surface glare and the absence of water spot defects after processing, in addition to the improvement of pressure marks from the rollers in automatic processing machines as has also been mentioned in EP-A 0 644 455.

A common support of a photographic silver halide emulsion material is a hydrophobic resin support or hydrophobic resin coated paper support. Hydrophobic resin supports are well known to those skilled in the art and are made, e.g., of polyester, polystyrene. polyvinyl chloride, polycarbonate, preference being given to polyethylene terephthalate and polyethylene naphthalate. A preferred resin coated paper support is a poly-Alpha-olefin coated paper support such as a polyethylene coated paper support.

The hydrophobic resin support may be provided with one or more subbing layers known to those skilled in the art for adhering thereto a hydrophilic colloid layer. Suitable subbing layers for polyethylene terephthalate supports are described, e.g., in US-P's 3,397,988, 3,649,336, 4,123,278 and 4,478,907.

Photographic silver halide emulsion materials containing a silver halide emulsion layer according to the present invention may be of any type known to those skilled in the art. For example, the hydrophilic silver halide emulsion layer(s) is (are) useful in continuous tone or halftone photography, micrography and radiography, in black-and-white as well as colour photographic materials. In a preferred embodiment according to this invention, the photographic material containing emulsions spectrally sensitised to the wavelength region between 490 and 850 nm is a medical X-ray material or a laser material.

The said medical X-ray material may be single-side coated or double side coated, whereas the laser material is usually single-side coated.

By making use of a photographic recording material comprising (a) silver halide emulsion layer(s) with a composition wherein silver halide photographic materials have been spectrally sensitised in order to make them sensitive to green, red or near-infrared radiation and comprising synthetic clay having a fluorosilicate structure according to the present invention, even in rapid processing cycles in automatic processing machines an enhanced minimum density due to the presence of dye stain can be avoided. Moreover there is no problem of desensitisation anymore and even for thin coated layers there are no disturbing roller marks.

This invention will further be illustrated hereinafter in the Examples without however being limited thereto.

6. EXAMPLES

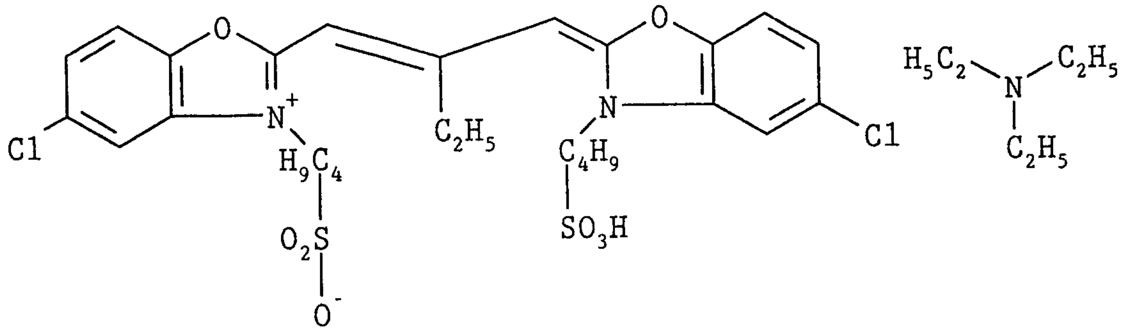
Example 1

A photographic silver iodobromide emulsion containing 2.0 mole % of silver iodide was prepared by a conventional single jet method in a vessel containing 42 g of phthaloyl gelatin. The ammoniacal silver nitrate solution was held at 40°C as well as the emulsion vessel, containing the halide salts. At a constant rate of 300 ml per minute the precipitation time was ended after 10 minutes and followed by a physical ripening time of 30 minutes. After that time an additional amount of 20 g of gelatin was added. The obtained emulsion was of an average grain size of 0.62 μm and contained an amount of silver halide corresponding to approximately 90 g of silver nitrate per kg of the dispersion after addition of 3 moles of silver nitrate.

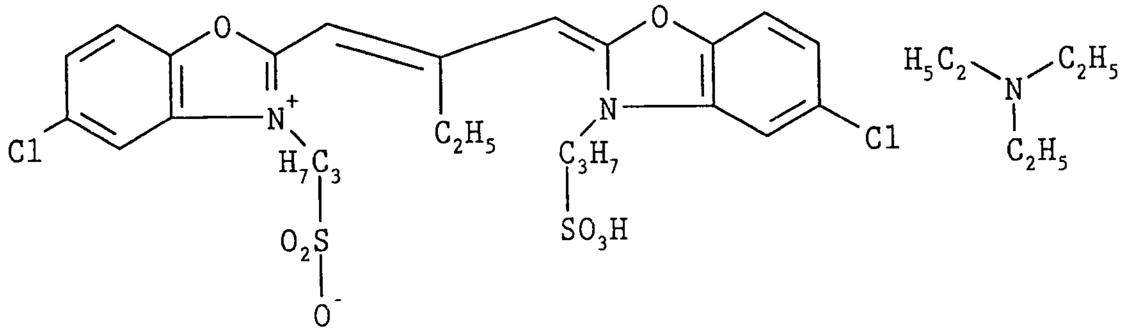
After addition of sulphuric acid to a pH value of 3.5 stirring was stopped and after sedimentation the supernatant liquid was removed. The washing procedure was started after a scrape-rudder was installed and after addition of polystyrene sulphonic acid in the first turn to get a quantitative flocculate without silver losses.

During the redispersion of the emulsion 150 g of gelatin were added so that the weight ratio of gelatin to silver halide expressed as silver nitrate was 0.40, the emulsion containing an amount of silver bromoiodide equivalent with 190 g of silver nitrate per kg.

The emulsion was chemically ripened with sulphur and gold compounds at 47°C for 4 hours to get an optimized relation between fog and sensitivity and was spectrally sensitised by succesively adding the spectral sensitisers according to the formulae SS-1 and SS-2.



SS-1



SS-2

Stabilisation was performed with 4-hydroxy-6-methyl-1,3,3a-tetrazaindene before coating the prepared layers on both sides of a polyester support of 175 μm thickness. A protective layer was coated thereover with a coating amount of 1.1 g of gelatin per m^2. Amounts of spectral sensitiser added to the emulsion were about 0.67 mmoles per mole of silver halide. For the different coatings the type of spectral sensitiser and the type of synthetic clay added has been given in Table 1.

Per side coating amounts of silver halide crystals, expressed as the equivalent amount of silver nitrate and of gelatin in the emulsion layer were: 4.41 g/m^2 and 1.05 g/m^2 respectively.

The film was exposed to light through a step wedge before processing to make the evaluation more realistic. The exposed radio-graphic materials were processed in the processing machine CURIX HT530 (Agfa-Gevaert trademarked name) with the following time (in seconds) and temperature (in °C) characteristics:

loading	0.2 sec.	
developing	9.3 sec.	35°C in developer I described below
cross-over	1.4 sec.	
rinsing	0.9 sec.	
cross-over	1.5 sec.	
fixing	6.6 sec.	35°C in fixer I described below
cross-over	2.0 sec.	
rinsing	4.4 sec.	20°C
cross-over	4.6 sec.	
drying	6.7 sec.	
total	37.6 sec.	

Composition of Developer I:

-concentrated part :	
water	200 ml
potassium bromide	12 grams
potassium sulphite (65% solution)	249 grams
ethylenediaminetetraacetic acid, sodium salt,trihydrate	9.6 grams
hydroquinone	106 grams
5-methylbenzotriazole	0.076 grams
1-phenyl-5-mercaptotetrazole	0.040 grams
sodiumtetraborate (decahydrate)	70 grams
potassium carbonate	38 grams
potassium hydroxide	49 grams
diethylene glycol	11 grams
potassium iodide	0.088 grams
4-hydroxymethyl-4methyl-1phenyl-3-pyrazolidinone	12 grams
Water to make 1 liter	
pH adjusted to 11.15 at 25°C with potassium hydroxide.	

For initiation of the processing one part of the concentrated developer was mixed with 3 parts of water.
No starter was added.
The pH of this mixture was 10.30 at 25°C.

Composition of the fixer:

-concentrated part :	
ammonium thiosulfate (78% solution)	661 grams
sodium sulphite	54 grams
boric acid	25 grams
sodium acetate-trihydrate	70 grams
acetic acid	40 grams
water to make 1 liter	
pH adjusted with acetic acid to 5.30 at 25°C	

To make this fixer ready for use one part of this concentrated part was mixed with 4 parts of water. A pH of 5.25 was measured at 25°C.

To reinforce the pressure mark defects the position of the conveying rollers was not optimized but made uneven. The following data are listed in Table 1:

-Coating No.
-Amounts (amt.) and type of LAPONITE additive expressed in g per m^2 in emulsion layer (Em. L.)
-Dye stain after processing: qualitatively indicated as "+++", "+", "-" ("-" is the objective)
-Fog measured at the processed material with the densitometer.
-Sensitivity: measured at a density value of 1 above fog.

For the Material No. 1 a reference value of 100 was taken.
Every changement with 0.30 log (exposure units) means a multiplication with or a division of this value by a factor of 2.

Table 1

Coating No.	Sensitiser	Clay t RDS	Clay t JS	Dye stain	Fog	Sensitivity
1	SS-1	0	0	-	0.011	100
2	SS-1	0.18	0	+++	0.030	---*
3	SS-1	0	0.19	+	0.032	102
4	SS-2	0	0	-	0.006	101
5	SS-2	0.18	0	+++	0.040	---*
6	SS-2	0	0.19	-	0.024	102

* not measurable due to a strong desensitisation (very unsensitive)

As can be derived from Table 1 the addition of the synthetic LAPONITE JS clay instead of Laponite RDS (having no fluorosilicate composition) brings about a substantial improvement: desensitisation is avoided and dye stain is at least reduced to an acceptable level or absent in critical rapid processing conditions.

Claims

1. A light-sensitive silver halide photographic material comprising a support and on one or both sides thereof one or more gelatino silver halide emulsion layer or layers spectrally sensitised in the wavelength region between 490 and 850 nm, characterised in that at least one of said spectrally sensitised silver halide emulsion layers comprises a synthetic clay having a fluorosilicate composition.

2. Material according to claim 1, wherein at least one hydrophilic layer different from the said gelatino silver halide emulsion layer(s) comprises a synthetic clay having a fluorosilicate composition.

3. Material according to claim 2, wherein the said hydrophilic layer is an intermediate layer, adjacent to at least one silver halide emulsion layer, a protective antistress layer or an outermost afterlayer.

4. Material according to any of claims 1 to 3, wherein the said synthetic clay is a synthetic fluorosilicate smectite clay.

5. Material according to any of claims 1 to 4, wherein an amount of synthetic clay present in the said gelatino silver halide emulsion layer or layers is from 0.05 to 0.75 g/m^2.

6. Material according to any of claims 1 to 5, wherein an amount of synthetic clay present in the silver halide emulsion layer(s) is from 0.1 to 0.5 g/m^2.

7. Material according to any of claims 1 to 5, wherein an amount of synthetic clay present in the protective antistress layer or in the afterlayer is from 0.05 to 0.25 g/m^2.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 20 2096

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
D,X	EP-A-0 644 455 (AGFA-GEVAERT) * page 3, line 6 - line 19 * * page 4, line 45 - line 50; claims * ---	1-7	G03C1/95 G03C5/16
Y	EP-A-0 644 454 (AGFA-GEVAERT) * claims * ---	1-7	
Y	EP-A-0 655 646 (MINNESOTA MINING AND MANUFACTURING COMPANY) * page 14, line 19 - line 32; example 1 * * claims * ---	1-7	
A	EP-A-0 444 326 (AGFA-GEVAERT) * page 3, line 21 - line 32 * * page 4, line 49 - line 57 * -----		

TECHNICAL FIELDS SEARCHED (Int.Cl.6)
G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	26 January 1996	Philosoph, L

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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