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(71) Applicant: **AGFA-GEVAERT**
2640 Mortsel (BE)

(72) Inventors:
• **Elst, Kathy c/o Agfa-Gevaert**
2640 Mortsel (BE)
• **Loccufier, Johan c/o Agfa-Gevaert**
2640 Mortsel (BE)
• **Henderickx, Freddy c/o Agfa-Gevaert**
2640 Mortsel (BE)

(54) **Film material exhibiting a "colder" blue-black image tone and suitable developability**

(57) A light-sensitive silver halide film material has been provided, comprising at least one light-sensitive silver halide emulsion layer overcoated with a protective antistress layer, said emulsion layer(s) having {111} tabular grains or crystals in an amount covering at least 50 % of the total projective grain surface of all grains, characterized in that at least one of said protective layer

or said emulsion layer(s) comprises a mercapto thiadiazole or a mercapto oxadiazole compound according to the general formula (I) or a mercapto triazole compound according to the formula (II), presented in the claims and in the detailed description.

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Description**FIELD OF THE INVENTION**

[0001] The present invention relates to a light-sensitive silver halide photographic film material, and, more particularly a material suitable for use in combination with one or two intensifying screens having luminescent phosphors, wherein said film material comprises, in the light-sensitive emulsion layers, tabular hexagonal {111} silver halide grains.

BACKGROUND OF THE INVENTION

[0002] Since the early eighties practical use of light-sensitive tabular silver halide grains or crystals has become common knowledge for anyone skilled in the art of photography. From Eastman Kodak's basic patents relied thereupon those related with the preparation of {111} tabular silver halide grains, sensitivity increase by spectral and chemical sensitization, and coating in a light-sensitive silver halide photographic material, more particularly in a forehardened duplitized radiographic material showing improved covering power for tabular grains having a thickness of less than 0.20 μm as described in US-A 4,414,304 and in the patents corresponding therewith in Japan and in the European countries, it becomes clear that problems encountered by making use of such grains are related with image tone and developability as has also been set forth in US-A 5,595,864.

[0003] In radiographic applications the film materials are coated with relatively high amounts of silver, in order to provide a suitable sensitometry even if a low radiation dose is applied to the patient as is always desirable. Although the use of {111} tabular silver halide grains permits coating of lower amounts of silver, if compared e.g. with grains having a more globular shape as applied before practical application of said tabular grains, there remains the need to provide an acceptable image tone after development of materials having light-sensitive silver halide layers containing said tabular grains. Reduction of thickness of the {111} tabular grains coated in a radiographic film material hitherto, although providing a higher covering power, remains unambiguously related indeed with the occurrence, after processing of such materials, of diagnostic images having an unacceptable reddish-brown image tone for radiologists as image tone and image quality are closely related with each other in the specific context of examination of diagnostic images.

[0004] Measures taken in order to get a shift in image tone from reddish-brown to the desired bluish-black colour of the developed silver, well-known from the state-of-the-art are hitherto unsatisfactory. Coating light-sensitive emulsion layers on a blue base as in US-A 5,800,976 makes increase minimum density, a phenomenon which is interpreted by the radiologist as an undesired increase of "fog density". Incorporation in the other layers of the film material of such dyes or dye precursors providing blue colour directly or indirectly (by processing and oxidative coupling reactions) are e.g. known from US-A's 5,716,769 and 5,811,229 and EP-A 0 844 520, and JP-A 10-274 824 respectively and causes the same problems as set forth hereinbefore, moreover showing, in the worst cases, staining of the screens with blue dyes diffusing from the material onto the screen, with residual colour of dyes due to uncomplete removal of said dyes in, nowadays desired, rapid processing steps and problems related with criticality of generation of imagewise developed blue coloured silver and preservation characteristics of the material.

[0005] Radiographic elements exhibiting increased covering power and colder image tones have been published in US-P's 5,795,795; 5,800,976 and 5,955,249.

[0006] More recently very effective measures in order to improve image tone have been described in EP-Applications Nos. 00203914, 00203916, 00203917, 00203918, simultaneously filed November 7, 2000.

[0007] Apart for an improved speed-image tone relationship it has always been an important goal to have materials with good developability characteristics, even in developers having lower activities or in exhausted stronger developers.

[0008] To summarize: the stringent demand remains to get a desired blue-black image tone of a diagnostic image without disturbing residual color obtained after rapid processing of the radiographic light-sensitive silver halide film material, wherein the said material moreover show very good developability characteristics.

OBJECTS OF THE INVENTION

[0009] It is a first object of the present invention to provide a better image tone after processing of a light-sensitive silver halide film material having tabular grain emulsions.

[0010] It is a second object of the present invention to provide a high speed and very good developability characteristics, even in developers having a lower activity.

[0011] Further objects will become apparent from the description hereinafter.

SUMMARY OF THE INVENTION

[0012] The above mentioned objects to improve speed/developability characteristics and image tone of the proc-

essed material after exposure have, unexpectedly, simultaneously been realized both by providing a light-sensitive silver halide film material, comprising at least one light-sensitive silver halide emulsion layer overcoated with a protective antistress layer, said light-sensitive emulsion layer(s) having {111} tabular grains or crystals in an amount covering at least 50 % of the total projective grain surface of all grains, characterized in that said protective layer, said light-sensitive layer(s) or both said protective layer and said light-sensitive layer(s) comprise, in an amount of at least 0.5 mmole per mole of silver halide coated, a mercapto thiadiazole compound or a mercapto oxadiazole compound according to the general formula (I) or a mercapto triazole compound according to the general formula (II), presented hereinafter in the claims and in the detailed description. More particularly presence of said compound in high amounts of from 1 up to 5 mmole per mole of silver halide coated in a radiographic film material is preferred.

[0013] Specific features for preferred embodiments of the invention are set out in the dependent claims.

[0014] Further advantages and embodiments of the present invention will become apparent from the following description.

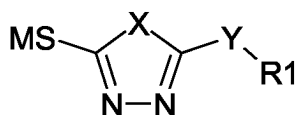
DETAILED DESCRIPTION OF THE INVENTION

[0015] A silver halide photographic film material has thus been provided, wherein said material comprises a transparent film support having first and second major surfaces coated on each of the major surfaces of the support, with a light-sensitive emulsion layer having {111} tabular hexagonal silver halide emulsions on at least one side of said support, wherein said layer is overcoated with a protective antistress layer at one or both sides of the film support, leading to a single-side coated or double-side coated (duplitized) material.

[0016] In a preferred embodiment said film material is a radiographic material suitable for use in a screen/film combination with one intensifying screen (for a single-side coated material) in contact with the film side coated with the photosensitive emulsion layer(s) or sandwiched between two intensifying screens (for a double-side coated material) in contact with both film sides.

[0017] Optionally the light-sensitive layer(s) is (are) in contact with a hydrophilic undercoat layer, e.g. a hydrophilic layer containing antihalation dyes and therefore called a "antihalation undercoat" instead of directly contacting the subbing layer, providing good adhesion between support and layer coated thereupon.

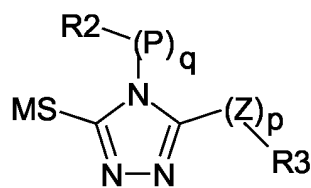
[0018] It is an essential feature of the present invention to add to that(those) protective antistress layer(s) and/or said optionally present hydrophilic undercoat layer(s), besides the normally added components as illustrated in the Examples hereinafter, in an amount of at least 0.5 mmole per mole of coated silver halide, a hetero aromatic compound according to the general formula (I) or (II) represented hereinafter



(I)

wherein :

X	represents O or S,
M	represents hydrogen or a monovalent counterion,
Y	represents a divalent linking group,
R1	represents $-\{O(CH_2)_n\}_m-OH$, wherein
n	represents an integer from 2 to 5 and
m	represents an integer from 1 to 5;



(II)

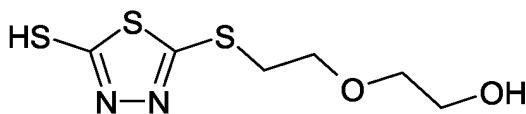
wherein :

- M represents hydrogen or a monovalent counterion,
 Z and P each independently represents a divalent linking group, so that Z and P may be the same or different,
 R2 is selected from the group consisting of hydrogen, a substituted or unsubstituted aliphatic group, a substituted or unsubstituted aromatic group, a substituted or unsubstituted heteroaromatic group, and $-\{O(CH_2)_n\}_m-OR_4$,
 R3 is selected from the group consisting of hydrogen, a substituted or unsubstituted aliphatic group, a substituted or unsubstituted aromatic group, a substituted or unsubstituted heteroaromatic group, and $-\{O(CH_2)_n\}_m-OR_5$, provided that at least one of R2 and R3 represents $-\{O(CH_2)_n\}_m-OR_4$ or $-\{O(CH_2)_n\}_m-OR_5$ respectively,
 p and q each independently represent 0 or 1,
 R4 and R5 are each independently selected from the group consisting of hydrogen, a substituted or unsubstituted aliphatic group, a substituted or unsubstituted aromatic group and a substituted or unsubstituted heteroaromatic group, so that R4 and R5 may be the same or different,
 n represents an integer having a value from 2 to 5 and
 m represents an integer having a value from 1 to 5.

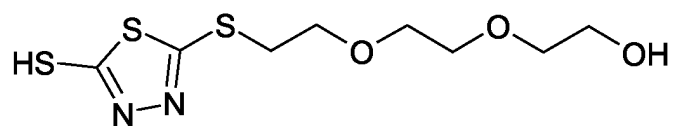
[0019] In a more preferred embodiment, the compounds according to general formula (I) are 1,2,4-thiadiazoles. In an even more preferred embodiment, R1, in said 1,2,4-thiadiazoles, represents $-\{O(CH_2)_2\}_m-OH$, where m is an integer from 1 to 5.

[0020] In a more preferred embodiment according to general formula (II), the divalent linking groups are aliphatic divalent linking groups, and even more preferably the compound according to general formula (II) has as aliphatic divalent linking group $-\{O(CH_2)_n\}_m-OR_4$, wherein n is 2 and R4 represents hydrogen.

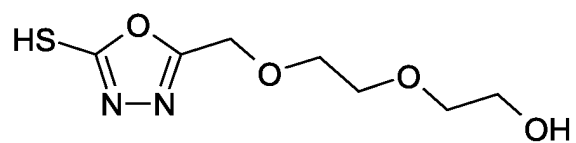
[0021] Specific examples of compounds according to general formula (I) are those presented hereinafter as compounds I-1 to I-11, without being however limited thereto.



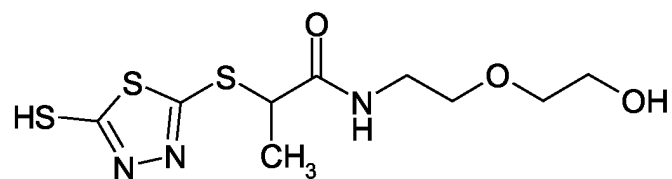
I-1



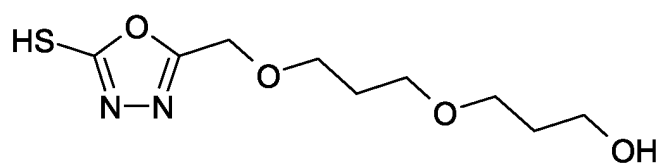
I-2



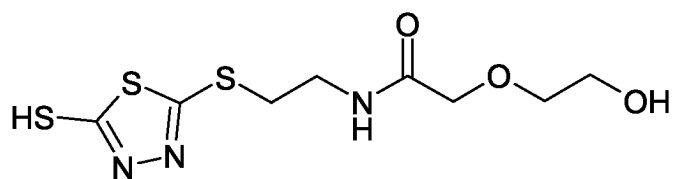
I-3



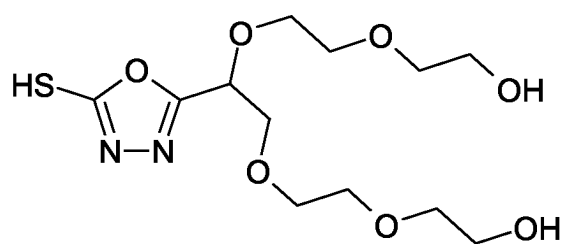
I-4



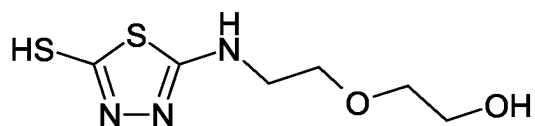
I-5



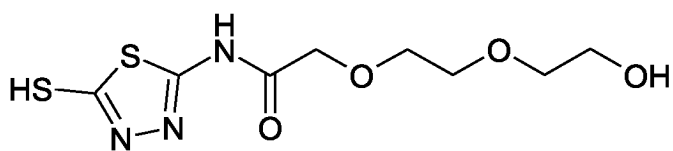
I-6



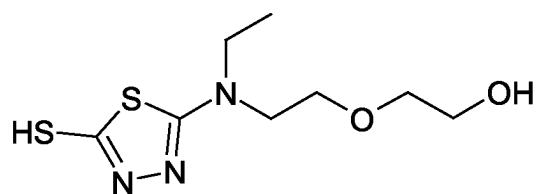
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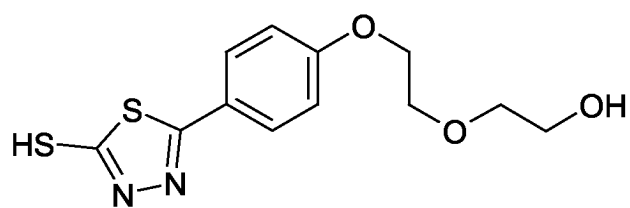
I-8



I-9

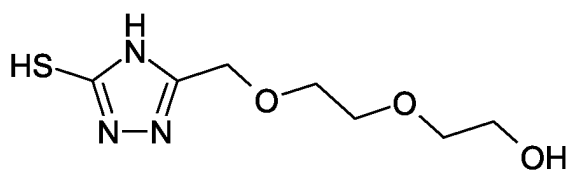


I-10

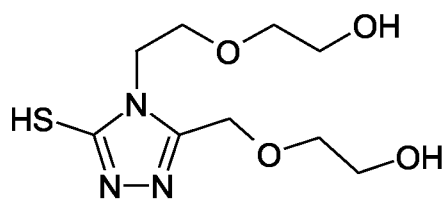


I-11

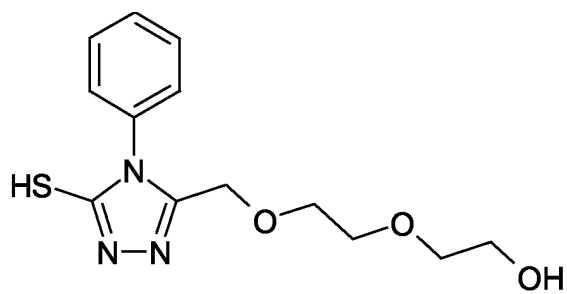
[0022] Specific examples of compounds according to general formula (II) are summarized hereinafter as compounds (II-1) to (II-12), again without being limited thereto.



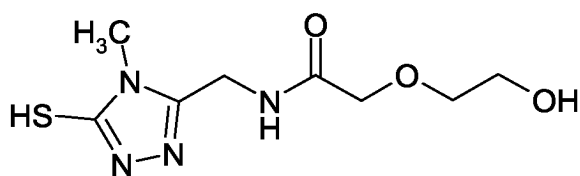
II-1



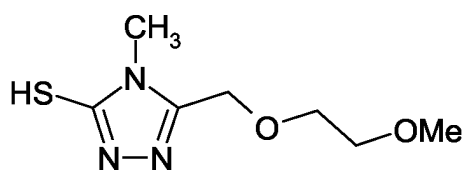
II-2



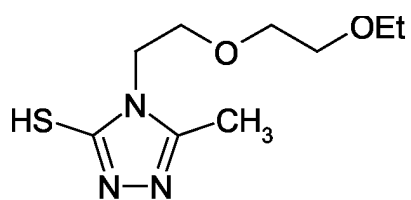
II-3



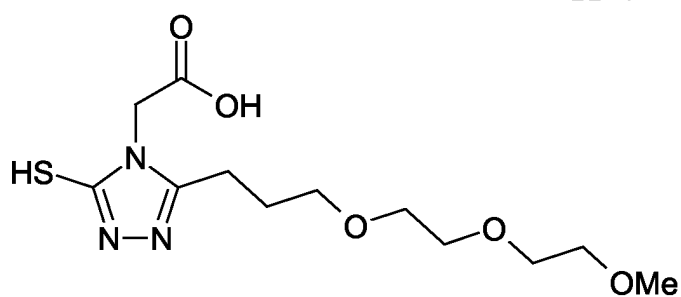
II-4



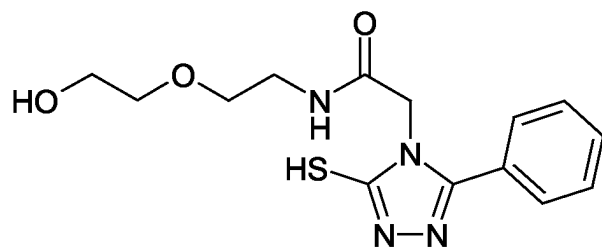
II-5



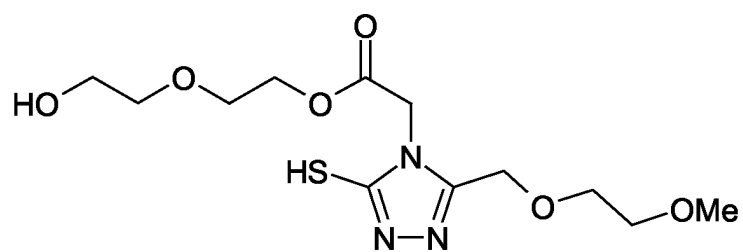
II-6



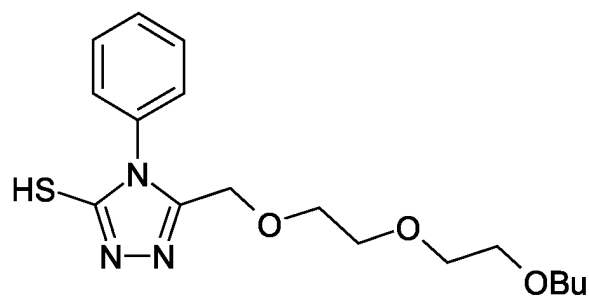
II-7



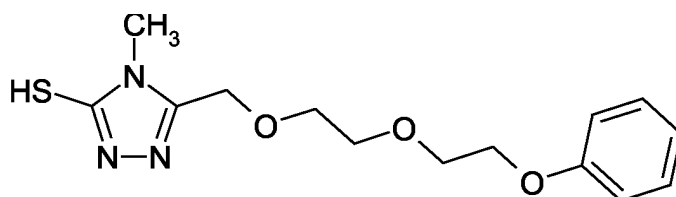
II-8



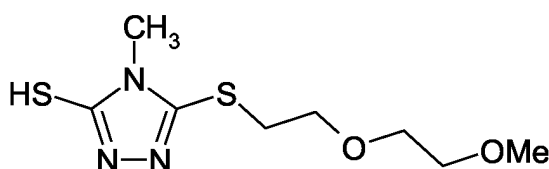
II-9



II-10



II-11



II-12

[0023] It has now unexpectedly been observed that, when examining the black-and-white silver image obtained after processing of the exposed material according to the present invention, that the presence of the hetero aromatic compounds according to the general formulae (I) or (II), when present in at least one non-light-sensitive hydrophilic coating layer as the protective antistress layer(s) and/or the optionally present hydrophilic undercoat layer(s) between subbing layer(s) and light-sensitive layer(s) of the said material, a further improved image tone is observed, in that a "colder" blue-black image is obtained for at least an equal and even an increased covering power, and that moreover a good developability is preserved, even in developers having a lower activity than the normally used more active ones (e.g. due to the use of lower amounts of developing agent in order to reduce costs, due to low replenishing amounts for the same reason or exhaustion of the developer, which may also be due to the use of low replenishing amounts).

[0024] According to the present invention the compound(s) according to the formulae set forth hereinbefore are present in an amount of at least 1 mmole up to 5 mmole per mole of coated silver halide.

[0025] The protective antistress layers of the silver halide photographic material according to the present invention may be the outermost layers of the material but an outermost afterlayer may be optionally present as has been disclosed e.g. in EP-A's 0 644 454 and 0 644 456, wherein a synthetic clay is present in favour of pressure resistance. Protective antistress layers, besides their function as protection layer may include compounds providing better antistatic properties as disclosed e.g. in EP-A 0 644 454 (with polyoxyalkylene compounds as antistatic agents), in EP-A's 0 505 626, 0 534 006 and 0 644 456. As said layers are in most cases outermost layers their contribution to satisfactory surface characteristics of the processed film material is very important, e.g. from the point of view of an excellent surface glare as desired by examining medecins, as has been described in EP-A 0 806 705 and in EP-A 0 992 845.

[0026] In a preferred embodiment according to the present invention a black-and-white silver halide photographic film material (especially for use in radiography) has been provided, wherein said material comprises a transparent film

support having first and second major surfaces coated with a subbing layer, further coated adjacent thereto on one side (for a single-side coated material) or on both sides (for a duplitized material) of said film support, optionally in contact with a hydrophilic undercoat layer and overcoated with a protective antistress layer, a light-sensitive silver halide emulsion layer having chemically and spectrally sensitized {111} tabular hexagonal grains, covering at least 50 %, more preferably at least 70 % and still more preferably at least 90 % of the total projective surface of all grains, with a mean or average equivalent volume diameter of from 0.3 μm up to 1.0 μm and an average grain thickness of less than 0.30 μm , wherein said film material is coated with a total amount of silver, expressed as an equivalent amount of silver nitrate of less than 7 g/m², characterized in that said protective antistress layer(s) and/or said hydrophilic undercoat layer comprise(s) a hetero aromatic compound according to general formulae (I) or (II) in an amount of at least 0.5 mmole, more preferably, at least 1 mmole and up to 5 mmole per mole of coated silver halide. Said general formulae (I) and (II) and other more specific formulae related with more specifically preferred compounds as presented in the Tables 1 and 2 hereinbefore and as demonstrated in the Examples given hereinafter.

[0027] The film material of the present invention, besides the protective antistress layer(s) and/or undercoat layer(s) containing a hetero aromatic compound according to the general formulae (I) or (II), thus further comprises a photosensitive layer at one or both sides of the transparent film support, said layer containing in an amount covering at least 50 %, preferably at least 70% and even more preferably at least 90 % of the total projective surface of all grains a {111} tabular grain emulsion containing chemically and spectrally sensitized hexagonal grains having a mean equivalent volume diameter of from 0.3 μm up to 1.0 μm and an average grain thickness of less than 0.30 μm , preferably from 0.05 μm up to 0.25 μm and wherein said film material is coated with a total amount of silver, expressed as an equivalent amount of silver nitrate of less than 7 g/m², more preferably from 3.0 up to at most 6.0.

[0028] Average grain volumes can be determined from calculations, after measurement for each individual grain of its volume determined after having applied electrochemical reduction techniques, wherein electrical signals thus obtained are related with silver halide grain volumes after total reduction thereof to metallic silver at the cathode of an electrochemical cell. The percentage of the total projective area of all tabular grains with respect to the total projective area of all grains present in the emulsion is calculated from electron microscopic photographs. Average grain diameters and thicknesses of the tabular grains are calculated after determination of individual grain thickness and diameter, calculated as equivalent circular diameter of the hexagonal surface, from shadowed electron microscopic photographs or scanning electron microscopic photographs. From the average ratios of (equivalent circular) diameter to thickness for each individual tabular grain aspect ratios are determined in order to get ability to further calculate the mean aspect ratio of the tabular grains in the emulsion distribution.

[0029] The film material may comprise light-sensitive layers, wherein presence of more than one light-sensitive layer per side is not excluded, at one (single-side coated) or both (double-side coated or duplitized) sides of the film support. According to the present invention, in favour of developability, said {111} tabular hexagonal silver halide grains are preferably silver halide grains, containing silver iodide in limited amounts: the film material should contain chemically and spectrally sensitized {111} tabular hexagonal grains having a composition wherein silver iodide is present in an amount of less than 3.0 mole %; preferably less than 1.0 mole % and even more preferably from 0.05 up to 0.5 mole % of iodide based on silver, without further restrictions with respect to the halide composition. An amount of at most 10 mole % of silver chloride may be present in the silver halide composition of the emulsion, but in a preferred embodiment the silver halide grains are composed of silver bromiodide. The said {111} hexagonal tabular grains having such a preferred silver bromiodide composition preferably have an average aspect ratio of 2 or more, preferably in the range from 5 to 20, with an average grain thickness of less than 0.30 μm , more preferably from 0.05 up to 0.15 μm , and account for a coverage of at least 50 %, more preferably at least 70 % and still more preferably at least 90 % of the total projective area of all grains. In a further preferred embodiment the {111} tabular grain population with hexagonal geometry for the flat tabular grains, make part of a light-sensitive emulsion which is homogeneous, i.e., has a variation coefficient of less and 0.40 and more preferably even from 0.10 up to 0.30, based on the equivalent circular diameters calculated for the individual {111} tabular hexagonal grains.

[0030] According to the present invention the chemically and spectrally sensitized {111} tabular hexagonal grains present in at least one light-sensitive layer of the material of the present invention thus have an average grain thickness of from 0.05 up to 0.15 μm .

[0031] Preparation methods for {111} tabular grain emulsions rich in silver bromide which are advantageously used in light-sensitive layers of materials of the present invention can be found in Research Disclosure No. 389057, p. 591-639 (1996), more particularly in Chapter I; No. 375042, published July 1, 1995; No. 391021, published November 1, 1996; No. 394023, published February 1, 1997. A very useful method has been described in EP-A 0 843 208. Iodide ions may be divided homogeneously or heterogeneously over the grain volume. When divided heterogeneously silver iodide may be present in one or more shells, divided over the grain volume.

[0032] In a preferred embodiment of the present invention however, all silver iodide is present at the surface of the {111} tabular hexagonal grains in an amount order to provide an average amount of silver iodide an average amount of silver iodide over the whole grain volume, based on silver, in the range from 0.05 up to 0.50 mole%. Iodide ions can

be provided in the preparation method by addition of such grains by adding an inorganic iodide salt as potassium iodide to the reaction vessel. More preferred as providing slower liberation of iodide in the reaction vessel are organic agents releasing iodide ions in order to provide the low silver iodide concentrations, not being equal or exceeding 3 mole %, more preferably not being equal or exceeding 1 mole % and even more preferably not exceeding the range from 0.05 mole % up to 0.5 mole % based on silver over the whole grain volume. Addition of iodide by organic agents releasing iodide ions can thus be applied within the context of the present invention as has been described e.g. in EP-A's 0 561 415, 0 563 701, 0 563 708 and 0 651 284 and in US-A's 5,482,826 and 5,736,312. In an alternative method iodide ions can be released from iodate as has been described in US-A 5,736,312. Release of iodide in the presence of a compound adjusting the rate of iodide release can be applied as described in US-A 5,807,663. In another embodiment addition of iodide to growing or already grown emulsion grains rich in silver bromide and/or chloride is performed by adding fine preformed grains of silver iodide, whether or not including bromide and/or chloride in minor amounts, said grains having a grain diameter of not more than 100 nm, and, more preferably, even not more than 50 nm. Such fine grains are so-called "Lippmann" emulsions. Addition of iodide making use from such fine grains rich in silver iodide can thus be applied as has been described for the preparation of {111} tabular grains in JP-A's 04251241 and 08029904 and in EP-A's 0 662 632 and 0 658 805, wherein an outermost phase rich in silver iodide has been added to {111} tabular grains rich in silver bromide (optionally comprising up to less than 10 mole % of silver chloride). Addition of said fine silver iodide "Lippmann emulsions" to the surface of the silver halide crystals in order to get a global iodide content of less than 3 mole %, preferably less than 1 mole %, and even more preferred from 0.1 mole % up to at most 0.4 mole % based on silver, in the grain may advantageously proceed as disclosed in EP-A 0 475 191, wherein an excellent speed/fog ratio and a high covering power are attained. Not only in favour of image tone as set forth in the objects of the present invention but also in favour of developability it is recommended for said tabular grains, when iodide is present, that all silver iodide is present on the grain surface thereof in an amount in order to get an average amount of iodide over the whole grain volume of less than 1 mole % and most preferably in the range from 0.05 up to 0.5 mole %, based on silver.

[0033] Preparation of {111} tabular grain emulsions is commonly, as is known by anyone skilled in the art, performed in the presence of gelatin. In one embodiment the precipitation of the hexagonal {111} tabular silver halide crystals according to the present invention is performed in the presence of a protective, hydrophilic colloid, e.g. conventional lime-treated or acid treated gelatin but also oxidized gelatin (see e.g. EP-A 0 843 208) but even a synthetic peptiser may be used. The preparation of such modified gelatin types, when use would be made thereof, can be found 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, No. 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.

[0034] In another embodiment tabular silver halide grains used in emulsions for the materials according to the present invention are precipitated in the absence of gelatin by using colloidal silica sol as a protective colloid in the presence of an onium compound, preferably a phosphonium compound, as has been described in EP-A 677 773. Colloidal silica sol as a binder providing colloidal stability during all preparation steps can indeed be applied as a valuable alternative.

[0035] In order to control the grain size, beside dyes (even spectral sensitizing dyes e.g.) or crystal habit modifiers, other grain growth restrainers or accelerators may also be used during the precipitation, together with flow rate variations and/or concentration variations of the silver and halide salt solutions, the temperature, pAg, physical ripening time, etc.. Silver halide solvents such as ammonia, a thioether compound, thiazolidine-2-thione, tetra-substituted thiourea, potassium or ammonium rhodanide and an amine compound may be present during grain precipitation in order to further adjust the average grain size.

[0036] At the end of the precipitation the emulsion can be made free from excess of soluble inorganic salts by a conventional washing technique e.g. flocculation by ammonium sulphate or polystyrene sulphonate, followed by one or more washing and redispersion steps. Another well-known washing technique is diafiltration or ultrafiltration. Finally extra gelatin is added to the emulsion in order to obtain a gelatin to silver ratio which is optimized with respect to the coating conditions and/or in order to establish the required thickness of the coated emulsion layer. Preferably a gelatin to silver halide weight ratio ranging from 0.3 to 1.0, and more preferably around 0.5, may be envisaged in order to provide low amounts of gelatin to be coated in favour of e.g. rapid processing applicability for the coated materials.

[0037] It is clear that {111} tabular silver halide emulsion grains, present in light-sensitive emulsion layers of materials according to the present invention, should, besides being spectrally sensitized, also be chemically sensitized. Said chemical sensitization, preferably following spectral sensitization, preferably proceeds at least with a combination of labile sulphur compounds and gold compounds and more preferably with compounds providing sulphur, selenium or even tellurium and gold in favour of attainable sensitivity, also called speed. Chemical sensitization methods for {111} tabular grain emulsions which can be applied herein can be found in Research Disclosure No. 389057, p. 591-639 (1996), more particularly in Chapter IV. Very useful methods related therewith have been disclosed in EP-A's 0 443 453, 0 454 069, 0 541 104 and in US-A's 5,112,733 and 5,654,134. Useful labile selenium compounds suitable for use

in the present invention have been disclosed in EP-A's 0 831 363, 0 889 354 and 0 895 121. Said labile selenium compounds are commonly applied in combination with sulphur and gold, and so are labile tellurium compounds as has been disclosed in EP-A 1 070 986.

[0038] The {111} tabular silver halide emulsion grains, present in light-sensitive emulsion layers of materials according to the present invention, are spectrally sensitized in the blue to near ultraviolet wavelength range and/or green wavelength range, depending on the requirements as set forth by medecins examining radiological images as especially sharpness (low cross-over percentage), but also contrast (which should be a "dedicated contrast" depending on the density range wherein image details should be discernable), speed and density range.

[0039] Preparation of spectrally and chemically sensitized tabular grains as may be applied to emulsion grains to be coated light-sensitive layers of a radiographic material according to the present invention has been described in US-A 4,439,520, wherein it has been established to perform spectral sensitization before chemical sensitization, so that the spectral sensitizer acts as a site-director for the sensitivity specks, generated during chemical sensitization. A broad review about spectral sensitization can be found in Research Disclosure No. 389057, p. 591-639 (1996), more particularly in Chapter V. Further useful information about additives which may be used in order to prepare emulsions to be coated in a material according to the present invention can be found in Research Disclosure No. 389057, p. 591-639 (1996), as in Chapter VII about antifoggants and stabilizers, in Chapter VIII about coating physical property modifying addenda, in Chapter XI about layer arrangements and in Chapter XV about supports.

[0040] In one embodiment according to the present invention the duplitzed film material comprises light-sensitive emulsion layers coated on both sides of a subbed support (i.e. a support coated with good adhesion providing subbing layers) with, optionally, inbetween said subbing layers and the light-sensitive layers coated thereupon, a hydrophilic non-light-sensitive layer, e.g. comprising antihalation dyes providing less cross-over and thus a better sharpness as described e.g. in US-A's 5,344,749; 5,478,708; 5,811,545 and 5,811,546. Said light-sensitive layers present in the material according to the present invention further comprise, in one embodiment, an emulsion having {111} hexagonal tabular grains rich in silver bromide, spectrally sensitive to irradiation in the wavelength range shorter than 420 nm by the presence of at least one J-aggregating zeromethine blue spectral sensitizer (preferred sensitizers have been given in EP-A's 0 712 034 and 1 045 282). Moreover at least one dye selected from the group consisting of azacyanine dyes and monomethine cyanine dyes, as further disclosed in the already cited EP-A 1 045 282 is preferably present. So the material according to the present invention has grains which have thus been made sensitive to the ultraviolet and/or blue range of the wavelength spectrum, wherein the blue/ultraviolet absorbing dye combination of zeromethine dyes with monomethine or azacyanine sensitizing dyes absorbing blue/UV-radiation as described in EP-A 1 045 282 is particularly preferred and suitable for use when the radiographic material according to the present invention is applied in combination with a blue/UV-intensifying screen. Besides the favourable diagnostic value with respect to image quality thanks to a low fog level, a high overall contrast, an enhanced sharpness (low cross-over percentage) and absence of residual colour, even in rapid processing cycles, as described therein, a particularly good image tone is provided offering cold black-bluish images as desired by the examiners, according to the objects of the present invention. Said blue-sensitizing dye or dyes are added as first dye during the chemical ripening procedure, before addition of the chemical ripening compounds or agents. Mixtures of blue sensitizing dyes are particularly interesting from the point of view of an increased spectral response in form of speed, which can be achieved at lower total amounts of dyes as becomes clear from US-A 5,707,794.

[0041] In another embodiment the material according to the present invention has grains which have been made sensitive to visible light in the range of the wavelength spectrum absorbing green light, more particularly in the wavelength range from 530 to 580 nm, and even more preferred in the range from 540 up to 570 nm. The radiographic film material as claimed thus has at least one emulsion comprising hexagonal {111} tabular silver halide grains rich in silver bromide (silver bromoiodide, optionally containing chloride in amounts of less than 10 mole % based on silver), spectrally sensitive to irradiation in the green wavelength range by the presence of at least one J-aggregating spectrally sensitizing tri-methine cyanine dye according to the general formula given in EP-A 0 678 772 and 0 953 867, wherein e.g. trimethine benzoxazoles and imidazoles are used apart or in combination, and of at least one dye selected from the group consisting of monomethine cyanine dyes and azacyanine dyes mentioned hereinafore.

[0042] Therefore in a preferred embodiment radiation-sensitive emulsions having silver bromoiodide grains, as in the present invention, sensitive to irradiation in the wavelength range between 530 and 580 nm, are made sensitive thereto by the presence of a J-aggregating spectrally sensitizing cyanine dye as the particularly preferred J-aggregating orthochromatic oxacarbocyanine dyes anhydro-5,5'-dichloro-3,3'-bis(n-sulpho-butyl)-9-ethyloxacarbocyanine hydroxide and anhydro-5,5'-dichloro-3,3'-bis(n-sulphopropyl)-9-ethyloxa-carbocyanine hydroxide. Furthermore green-light absorbing spectral sensitizers according to the formulae given in JP-A's 06,035,104; 06,035,101; 06,035,102; 62,191,847; 63,249,839; 01,312,536; 03,200,246; US-A 4,777,125 and DE 3,819,241 may be used. The right choice of said sensitizers or combinations thereof is always related with the purpose of obtaining the highest possible photographic speed while reducing possible dye stain, due to the use of huge amounts of dyes after processing, especially in rapid processing cycles.

[0043] As it is a particularly favourable aspect for materials coated from emulsions having tabular grains in general, and more specifically for materials according to the present invention coated from emulsions having tabular hexagonal {111} tabular grains to be coated with lower amounts of silver without loss of covering power in the material, the total amount of silver halide coated in said film material, expressed as an equivalent amount of silver nitrate, is less than 7.0 g/m², preferably in the range from 3.0 to 6.6 g/m².

[0044] Said duplitized film materials for use in radiographic applications are irradiated by the light emitted imagewise by X-ray intensifying screens after conversion of X-ray radiation to the said light by luminescent phosphors coated in the said screens or panels, in intimate contact therewith at both sides of the coated film support during X-ray exposure of part of a patient. A diagnostic silver image, in conformity with the X-ray image, is obtained after processing of the said film material. For use in common medical radiography (projection radiography) the X-ray film material comprises a transparent film support, coated on both sides with at least one silver halide emulsion layer, further overcoated with at least one protective antistress layer and, optionally, an afterlayer as disclosed e.g. in EP-A's 0 644 454 and 0 644 456. Optionally to the protective antistress layer(s), besides the normally added components a substituted 1-phenyl 5-mercaptotetrazole compound can be added. It has been established that the presence of such compound(s) in the protective antistress layer(s) further improves image tone in that a "colder" blue-black image is obtained for at least the same and even an increased covering power, with the remark that use of tetrazoles in the protective antistress layer is more effective when lower amounts of silver iodide are present at the grain surface of the {111} tabular grains.

[0045] During X-ray irradiation said film is arranged in a cassette between two X-ray intensifying screens each of them making contact with its corresponding light-sensitive side, thus forming a film/screen system or said film is in contact with one single X-ray intensifying screen in case of a single-side coated radiographic material. According to the present invention a radiographic screen/film combination or system is thus provided, said system comprising a radiographic film material as disclosed in the present invention in contact with one supported or self-supporting X-ray intensifying screen or sandwiched between a pair of said screens, wherein said intensifying screen or screens comprise (s) luminescent phosphor particles emitting at least 50 % of their emitted radiation in the wavelength range for which said material has been made spectrally sensitive.

[0046] In one embodiment according to the present invention a radiographic screen/film combination or system has been provided comprising a duplitized film material, sandwiched between a pair of supported or self-supporting X-ray intensifying screens, characterized in that

i) said pair of supported or self-supporting X-ray intensifying screens essentially consists of luminescent phosphor particles emitting at least 50 % and more preferably at least 80 % of their emitted radiation in the wavelength range shorter than 420 nm, as e.g. a niobium and gadolinium doped, monoclinic M, yttriumtantalate (MYT) phosphor or a calcium tungstate phosphor;

ii) said film comprises {111} tabular silver halide grains rich in silver bromide, spectrally sensitive to irradiation in the said wavelength range shorter than 420 nm by the presence of at least one J-aggregating blue spectral sensitizer (e.g. a zeromethine sensitizer as disclosed in EP-A 0 712 034) and of at least one of the non-J-aggregate forming dyes selected from the group consisting of azacyanine dyes and monomethine cyanine dyes (as disclosed in EP-A 1 045 282) respectively, mentioned hereinbefore in the description, wherein said emulsion is present in at least one light-sensitive emulsion layer on at least one side of the film support of the radiographic material of the present invention.

[0047] As the radiographic film material as claimed has as least one silver bromoiodide emulsion comprising {111} tabular grains, spectrally sensitive to irradiation in the wavelength range shorter than 420 nm by the presence of at least one spectrally sensitizing zeromethine dye and of at least one dye selected from the group consisting of monomethine cyanine dyes and azacyanine dyes respectively, the film perfectly matches with the screen emitting said radiation in the wavelength range shorter than 420 nm as in a preferred embodiment of the present invention absorption of radiation in the said wavelength range shorter than 420 nm by the {111} tabular silver bromoiodide grains is corresponding with at least 50 % and more preferably at least 80 % of the total radiation absorption by the said grains.

[0048] Luminescent phosphors suitable for use in a conventional intensifying screen of a radiographic film/screen system as the one according to the present invention must have a high prompt emission of fluorescent light on X-ray irradiation and low afterglow in favour of image sharpness. The relationship between resolution and speed of X-ray intensifying screens is described e.g. in Med. Phys. 5(3), 205 (1978). Specific intensifying screens emitting ultraviolet-blue radiation have e.g. been disclosed in US-A's 4,225,653; 4,387,141; 4,710,637; 5,112,700; 5,173,611 and 5,432,351; in EP-A's 0 650 089; 0 658 613; in PCT-Applications WO 93/11457 and WO 95/15514. Typical blue-UV emitting phosphors therein are tantalates as described in PCT-Applications WO 93/1521 and 93/1522, hafnates as described in US-A 5,173,611 and fluorohalides (fluorobromides) of barium and strontium as in WO 91/1357 and US-A 5,629,125, doped with europium and co-doped with samarium as in US-A's 5,422,220 and 5,547,807 and even mixtures of tantalates and fluorohalides as in US-A 5,077,145 and EP-A 0 533 234, replacing CaWO₄ as representative for an

older well-known generation of luminescent phosphors. Very useful phosphor particles have e.g. been disclosed in EP-A 0 820 069 wherein particles of niobium doped, monoclinic M, yttriumtantalate phosphor and particles of an europium doped bariumfluorohalide phosphor are composing the screen.

[0049] In the film/screen system according to the present invention preferred phosphor particles are niobium and gadolinium doped, monoclinic M, yttriumtantalate (MYT) phosphor corresponding to formula (III):



[0050] In another embodiment the radiographic film material has {111} tabular silver bromiodide emulsions spectrally sensitized with spectrally sensitizing dyes absorbing light in the green wavelength range.

[0051] In another embodiment according to the present invention a radiographic screen/film combination or system is thus provided comprising a duplitized film material, sandwiched between a pair of supported or self-supporting X-ray intensifying screens, characterized in that

i) said pair of supported or self-supporting X-ray intensifying screens essentially consists of luminescent phosphor particles emitting at least 50 % and more preferably at least 80 % of their emitted radiation in the green wavelength range from 500 nm to 550 nm, as e.g. a terbium doped gadolinium oxisulfide phosphor;

ii) said film comprises {111} tabular silver halide grains rich in silver bromide, spectrally sensitive to irradiation in the said wavelength range from 500 to 550 nm by the presence of at least one J-aggregating green spectral sensitizer and of at least one the non-J-aggregating dyes selected from the group consisting of azacyanine dyes and monomethine cyanine dyes, as mentioned hereinbefore respectively, wherein said emulsion is present in at least one light-sensitive emulsion layer on at least one side of the film support.

[0052] In the context of the present invention, more particularly with respect to the purposes to get reduced dye stain besides an excellent image tone, said reduced dye stain delivering an indispensable asset thereto, azacyanine dyes are advantageously used in the preparation of {111} tabular grain emulsions as the presence of said dyes permits further addition of J-aggregating spectral sensitizers in lower amounts, without loss in speed, thereby providing better decolouration in the processing. A survey of other useful chemical classes of J-aggregating spectral sensitizers suitable for use in spectrally sensitizing emulsions of the present invention has been described by F.M. Hamer in "The Cyanine Dyes and Related Compounds", 1964, John Wiley & Sons and other examples specifically useful for spectral sensitization of tabular grains have been given in Research Disclosure Item 22534 and in addition a more recent overview has been given in EP-A 0 757 285, wherefrom dyes forming J-aggregates on the flat surface of the preferred silver bromide or silver bromiodide crystals are particularly useful. It is moreover preferred that the radiation-sensitive emulsion used in the material according to the present invention has one or more azacyanine dye(s) and (a) J-aggregating spectrally sensitizing dye(s), whether providing spectral sensitivity in the blue/UV or in the green light range in a ratio amount of more than 1:4 for a grain coverage exceeding 50 %.

[0053] 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-A 3,457,078, nitrogen-containing heterocyclic ring-substituted aminostilbene compounds as described e.g. in US-A's 2,933,390 and 3,635,721, aromatic organic acid/formaldehyde condensation products as described e.g. in US-A 3,743,510 as well as cadmium salts and azaindene compounds.

[0054] At least one non-spectrally sensitizing dye can be added to an emulsion layer or to one or more non-light-sensitive hydrophilic layers such as an optionally present antihalation undercoat between the subbing layer and the emulsion layer as has e.g. been described in US-A's 5,077,184 and 5,693,370. The presence of such dye(s) in adapted amounts in an emulsion layer can even be recommended in order e.g. to adjust the sensitivity of the emulsion layer (s) or the required contrast, but also in order to reduce scattering of exposure radiation and thus to enhance sharpness. Preferred dyes are those that are removed easily from the photographic material during wet processing in order not to leave any residual colour. When said dyes are added to the emulsion side, it may be preferred that these dyes are non-diffusible during coating of the hydrophilic layers. Examples of such dyes, without being limited thereto, are the dyes that have been described in e.g. US-A's 3,560,214; 3,647,460; 4,288,534; 4,311,787 and 4,857,446. These dyes may be added to the coating solution as a solid particle dispersion of water insoluble dyes having a mean particle diameter of less than 10 µm, more preferably less than 1 µm and still more preferably less than 0.1 µm. Examples of such dyes are disclosed in EP-A's. 0 384 633; 0 351 593; 0 586 748; 0 587 230 and 0 656 401, EP-A's. 0 323 729; 0 274 723 and 0 276 566, and in US-A's 4,900,653; 4,904,565; 4,949,654; 4,940,654; 4,948,717; 4,988,611; 4,803,150 and 5,344,749. Said dyes can also be added in form of a solid silica particle dispersion as disclosed in EP-A 0 569

074. Still another technique applied in order to obtain ultra fine dye dispersions consists in acidifying a slightly alkaline coating composition "in situ" just before coating it onto the supporting layer. A more recent review of dispersion methods, useful in the context of the present application has been described in EP-A 0 756 201.

[0055] The silver halide emulsions used in light-sensitive layers of the material according to the present invention may also comprise compounds preventing the formation of a high minimum density or stabilizing the photographic properties during the production or storage of photographic materials 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 i.a. 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, JP-B 77/031738 and GB-A 1,500,278, and 7-hydroxy-s-triazolo-[1,5-a]-pyrimidines as described in US-A 4,727,017, and other compounds such as benzenethiosulphonic acid, benzenethio-sulphinic acid and benzenethiosulphonic acid amide.

[0056] Other compounds which can be used as fog-inhibiting compounds are those described in Research Disclosure No. 17643 (1978), Chapitre VI. These 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.

[0057] The binder of the layers, especially when gelatin is used as a binder, can be forehardened with appropriate hardening agents such as those of the epoxide type, those of the ethylenimine type, those of the vinylsulfone type, e.g. 1,3-vinylsulphonyl-2-propanol or di-(vinylsulphonyl)-methane, vinylsulphonyl-ether compounds, vinylsulphonyl compounds having soluble groups, chromium salts like e.g. chromium acetate and chromium alum, aldehydes as e.g. formaldehyde, glyoxal, and glutaraldehyde, N-methylol compounds as 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-A's 4,063,952 and with the onium compounds as disclosed in EP-A 0 408 143.

[0058] The photographic material according to the present invention may further comprise various kinds of surface-active agents in the light-sensitive emulsion layer(s) 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 carboxyl, sulfo, phospho, sulphuric or phosphoric ester group; ampholytic agents such as aminoacids, aminoalkyl sulphonic acids, aminoalkyl sulphates or phosphates, alkyl betaines, and amine-N-oxides; and cationic agents such as alkylamine salts, aliphatic, aromatic, or heterocyclic quaternary ammonium salts, aliphatic or heterocyclic ring-containing phosphonium or sulphonium salts. Such surface-active agents can be used for various purposes, e.g. as coating aids, as compounds preventing electric charges, as compounds improving film transport in automatic film handling equipment, as compounds facilitating dispersive emulsification, as compounds preventing or reducing adhesion, and as compounds improving photographic properties such as higher contrast, sensitization and development acceleration. Especially when rapid processing conditions are important, development acceleration may be useful, which can be accomplished with the aid of various compounds, preferably polyoxyalkylene derivatives having a molecular weight of at least 400 such as those described in e.g. US-A's 3,038,805; 4,038,075 and 4,292,400. Especially preferred developing accelerators are recurrent thioether groups containing polyoxyethylenes as described in DE 2,360,878, EP-A's 0 634 688 and 0 674 215. The same or different or a mixture of different developing accelerators may be added to at least one of the hydrophilic layers at the emulsion side. It may be advantageous to partially substitute the hydrophilic colloid binder, preferably gelatin, of the light-sensitive silver halide emulsion layer or of an hydrophilic colloid layer in water-permeable relationship therewith by suitable amounts of dextran or dextran derivatives to improve the covering power of the silver image formed and to provide a higher resistance to abrasion in wet condition.

[0059] The photographic material of the present invention may further comprise various other additives such as compounds improving the dimensional stability of the photographic material, UV-absorbers, spacing agents, lubricants, plasticizers, antistatic agents, etc. Suitable additives for improving the dimensional stability 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, α - β -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-A 3,533,794, 4-thiazolidone compounds as described in US-A's 3,314,794 and 3,352,681, benzophenone compounds as described in JP-A 2784/71, cinnamic ester compounds as described in US-A's 3,705,805 and 3,707,375, butadiene compounds as described in US-A 4,045,229, and benzoxazole compounds as described in US-A 3,700,455.

[0060] 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 material, whereas alkali-soluble spacing agents usually are removed 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 described in US-A 4,614,708.

[0061] Compounds which can be used as a plasticizer for the hydrophilic colloid layers are acetamide or polyols such as trimethylolpropane, pentanediol, butanediol, ethylene glycol and glycerine. Further, a polymer latex is preferably incorporated into the hydrophilic colloid layer for the purpose of improving the anti-pressure properties, e.g. a homopolymer of acrylic acid alkyl ester or a copolymer thereof with acrylic acid, a copolymer of styrene and butadiene, and a homopolymer or copolymer consisting of monomers having an active methylene group.

[0062] The photographic material according to the present invention may comprise an antistatic layer to avoid static discharges during coating, processing and other handling of the material. Such antistatic layer may be an outermost coating like the protective layer or an afterlayer or a stratum of one or more antistatic agents or a coating applied directly to the film support or other support and overcoated with a barrier or gelatin layer. Antistatic compounds suitable for use in such layers are e.g. vanadium pentoxide soles, tin oxide soles or conductive polymers such as polyethylene oxides (see e.g. EP-A 0 890 874) or a polymer latex and the like or polymers providing permanent antistatic properties as polyethylene dioxythiophenes (PEDT) described e.g. in US-A 5,312,681; 5,354,613 and 5,391,472; and in EP-A 1 031 875.

[0063] During X-ray irradiation of the radiographic film material of the present invention said film material (made sensitive to green or blue light by suitable spectral sensitization of its light-sensitive emulsion grains) is arranged in a cassette with one X-ray intensifying screen (emitting green or blue light by suitable luminescent phosphors) making contact with the silver halide emulsion layer. For chest radiography said cassette is provided with two X-ray intensifying screens making contact with two X-ray intensifying screens, being the same or different. When two intensifying screens are used it is thus possible to use two identical screens (having same radiation sensitivity), to use two screens emitting the same irradiation but differing in speed, e.g. due to different coating amounts of phosphors (coating thickness), or even to use two intensifying screens having a different light emission. So combination of an intensifying screen sensitive to blue/UV-irradiation and a screen sensitive to green light may be favourable in order to attain desired properties with respect to sensitometry (desired sensitometric curve from the point of diagnostic view) and/or image quality (granularity and/or image definition, particularly sharpness).

[0064] Specific intensifying screens or conversion screens emitting green or blue light for use in the diagnostic image forming method according to the present invention are the commercially available X-ray generating devices providing an exposure to X-rays (e.g. with a tube voltage from 70 kV up to 100 kV - as in chest radiography - without however being limitative).

[0065] A preferred luminescent phosphor coated in the X-ray conversion screen used in a film/screen system sensitive to green light is Gd₂O₂S:Tb, emitting light in the wavelength range from 540 to 555 nm. Said phosphor and its use in intensifying screens have been described extensively in patent literature, e.g. in US-A's 3,872,309; 4,130,429; 4,912,333; 4,925,594; 4,994,355; 5,021,327; 5,107,125 and 5,259,016 and in GB-Patent 1,489,398 and is suitable for use in the context of the film/screen system according to the present invention. The thickness of the phosphor layer therein depends on the amount of coated phosphor required in order to obtain the desired screen speed. X-ray intensifying screens used in the film/screen system according to the present invention can be self-supporting or supported. X-ray intensifying screens in the screen/film system according to the present invention generally comprise in order: a support (also called substrate), at least one layer comprising phosphor particles dispersed in a suitable binder and a protective coating coated over the phosphor containing layer to protect said layer during use. Further, a primer layer is sometimes provided between the phosphor containing layer and the substrate to closely bond said layer thereto.

[0066] X-ray intensifying screens according to the present invention can be self-supporting or supported. X-ray intensifying screens in accordance with the present invention generally comprise in order: a support (also called substrate), at least one layer comprising phosphor particles dispersed in a suitable binder and a protective coating coated over the phosphor containing layer to protect said layer during use. Further, a primer layer is sometimes provided between the phosphor containing layer and the substrate to closely bond said layer thereto. A plastic film is preferably employed as the support material. Depending on the speed class of the screens for which a synergistic effect should be attained in the relation between speed and sharpness, supports characterized by their reflectance properties, expressed as % reflectance over the wavelength range from 350 to 600 nm, are particularly used as described e.g. in US-A 5,381,015.

Such supports can be highly light reflecting as e.g. polyethylene terephthalate comprising a white pigment, e.g. BaSO₄, TiO₂, etc., or it can be light absorbing supports, e.g. polyethylene terephthalate comprising a black pigment, e.g. carbon black. Supports comprising dyes or pigments that absorb light of a specific wavelength can also be useful in the preparation of X-ray intensifying screens in the film/screen system according to the present invention. In most applications the phosphor layers contain sufficient binder to give structural coherence to the layer. A mixture of two or more of these binders may be used, e.g., a mixture of polyethyl acrylate and cellulose acetobutyrate. The weight ratio of phosphor to binder is generally within the range of from 50:50 to 89:11, preferably from 80:20 to 89:11. The screen used in a screen/film system according to the present invention may comprise a supported layer of phosphor particles dispersed in a binding medium comprising one or more rubbery and/or elastomeric polymers as described in EP-A's 0 647 258 and 0 648 254. In this way a ratio by weight of pigment to binding medium of more than 90:10 and more preferably of at least 93:7, e.g. 98:2 can be obtained providing besides an excellent image resolution a high ease of manipulation as a result of a good elasticity of the screen and good adhesion properties between the support and the phosphor layer. Problems concerning staining of screens comprising said rubbery binder(s) may be overcome by the addition of known rubber antioxidation compounds. Screen structure mottle can be reduced, further providing a good relation between speed and image definition as disclosed in EP-A 0 758 012 and in the corresponding US-A 5,663,005. Anti-static properties can be improved by addition of e.g. polyoxyethylene compounds to the surface layers of the screens.

[0067] According to the present invention a method of image formation is further obtained by consecutively performing the steps of

- exposing to X-rays the radiographic screen/film combination or system described hereinbefore; followed by
- processing the film according to the present invention by the steps of developing, fixing, rinsing and drying.

[0068] The said processing is preferably performed in an automatic processing machine. More in detail for processing the film material of the present invention, preferably an automatically operating apparatus is used provided with a system for automatic replenishment of the processing solutions. The processing dry-to-dry within a short processing time of from 30 to 90 seconds and more preferably from 30 seconds to less than 60 seconds of materials coated from low amounts of silver is made possible by the steps of developing said material in a developer (preferably) without hardening agent; fixing said material in a fixer, optionally without hardening agent; rinsing and drying said material.

[0069] A normally used configuration in the processing apparatus shows the following consecutive tank units corresponding with, as consecutive solutions: developer-fixer-rinse water. Recent developments however have shown, that from the viewpoint of ecology and especially with respect to reduction of replenishing amounts, as consecutive solutions the sequence developer-fixer-fixer-rinse water-rinse water is preferred. One washing step between developing and fixation and one at the end before drying may also be present. As ecology and low replenishing amounts are main topics with respect to the present invention use is made of concentrated hardener free processing solutions in one single package. Examples thereof have been disclosed e.g. in US-A's 5,187,050 and 5,296,342. Especially preferred developers comprising ecologically acceptable developing agents such as ascorbic acid and derivatives thereof have been described in EP-A 0 732 619 and in US-A's 5,593,817 and 5,604,082. Instead of or partially substituting (e.g. in a ratio by weight of from 1:1 up to 9:1) the ecologically questionable "hydroquinone" (iso)ascorbic acid, 1-ascorbic acid and tetramethyl reductic acid are preferred as main developing agent in the developer. Said developing agents have further been described in EP-A's 0 461 783, 0 498 968, 0 690 343, 0 696 759, 0 704 756, 0 732 619, 0 731 381 and 0 731 382; in US-A's 5,474,879 and 5,498,511 and in Research Disclosure No 371052, published March 1, 1995, wherein a more general formula covering the formula of said developing agents has been represented. In order to reduce "sludge formation" which is favored by solubilizing agents like sulphites, present in the developer as preservatives, a particularly suitable developer solution is the one comprising a reduced amount of sulphite and ascorbic acid which acts as a main developer and anti-oxidant as well and which is called "low-sludge" developer. Suitable measures taken therefore have recently been described in the EP-Applications Nos. 99201891 and 99201892, both filed simultaneously June 14, 1999. In favour of ecological fixation the presence of aluminum ions should be reduced, and more preferably, no aluminum ions should be present. This is moreover in favour of the absence of "sludge" formation, a phenomenon which leads to pi-line defects when high amounts of silver are coated in the light-sensitive layers. Measures in order to reduce "sludge-formation" have further been described in US-A's 5,447,817; 5,462,831 and 5,518,868. A particularly suitable fixer solution comprises an amount of less than 25 g of potassium sulphite per liter without the presence of acetic acid wherein said fixer has a pH value of at least 4.5, in order to make the fixer solution quasi odorless. If however aluminum ions are present in the fixer composition for whatever a reason, the presence of α -ketocarboxylic acid compounds is recommended as has been described in EP-A's 0 620 483 and 0 726 491 as well as in RD 16768, published March 1978. It is possible to use sodium thiosulphate as a fixing agent, thus avoiding the ecologically undesirable ammonium ions normally used. For low coating amounts of emulsion crystals rich in chloride a fixation time which is reduced to about 2 to 10 seconds can be attained. Moreover regeneration is kept to a minimum, especially in the processing of materials coated with reduced amounts of silver halide as in the present invention.

[0070] As already set forth hereinbefore single-side coated materials are also envisaged in the present invention, such as in combination with a single screen having luminescent phosphors with a high prompt emission of fluorescent light on X-ray irradiation and low afterglow in favour of image sharpness, suitable for use in mammography, wherefore the relationship between resolution and speed of X-ray intensifying screens has been described e.g. in Med. Phys. 5 (3), 205 (1978). Other single-side coated materials wherein the emulsions can advantageously be applied, e.g. with respect to preservation properties, developability, etc. are black-and-white silver halide material used e.g. in micrography, in aviation photography, in black-and-white cinefilms, in laserfilms or hardcopy films and in graphic or reprographic applications. Even use thereof in light-sensitive layers of multilayered colour materials may be useful.

[0071] While the present invention will hereinafter be described in connection with preferred embodiments thereof, it will be understood that it is not intended to limit the invention to those embodiments.

EXAMPLES

Emulsion E1

1.1. Emulsion preparation

[0072] To a solution of 7.5 g of oxidized gelatin, in 3 l of demineralized water at 25 °C, adjusted to a pH of 1.8 by adding H₂SO₄ and a pBr of 2.39 by adding a diluted solution of potassium bromide, stirred up to a rate of 700 r.p.m., were added by double jet. Aqueous solutions of 1 M AgNO₃ (hereinafter referred to as A1) and 1 M KBr (hereinafter referred to as B1): 25 ml of A1 and 25 ml of B1 were added in a time interval of 30 seconds. After a physical ripening time of 90 seconds the temperature was increased up to 70 °C over a period of 60 minutes. The pH was adjusted to a value of 5, followed by another 3 minutes during which the temperature was held at 70°C and after which a solution of 50 g of phthalated gelatin in 500 ml of demineralized water of 60°C was added.

[0073] 3 minutes later A1 was added at a rate of 7.0 ml/min during 120 seconds, while adding B1 at a rate in order to get a UAg of +40 mV at a temperature of 70°C.

[0074] In a double jet addition A1 and B1 were added during a growth step taking 47 min. at a linearly increasing rate going from 7 up to 21.1 ml/min., while adding B1 in order to maintain a constant UAg potential of +40 mV in the reaction vessel. 5 minutes after ending that double-jet addition period, a new double jet addition was started taking 83 min at a linearly increasing rate going from 10 ml up to 46 ml/min, while adding B1 in order to maintain a constant UAg potential of +30 mV in the reaction vessel.

[0075] An amount of an emulsion having ultrafine (ca. 0.040 µm) 100 % AgI crystals, was added to the reaction vessel in a time of 2 minutes in order to get a total AgI content at the end of precipitation of 0.1 mole % vs. silver precipitated.

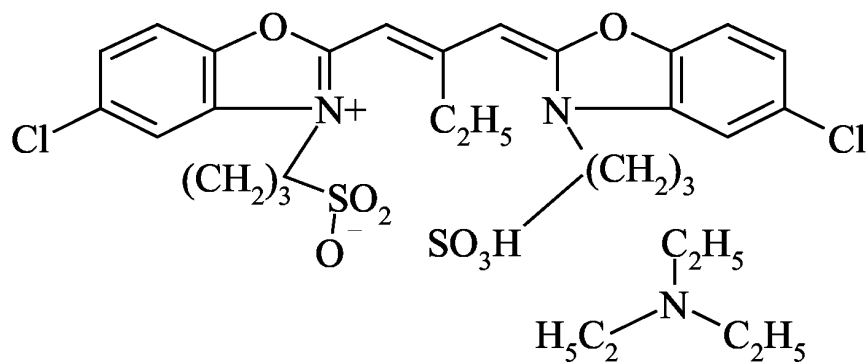
[0076] The average grain sizes of the silver bromiodide tabular {111} emulsion grains thus prepared, have been calculated as follows:

- * as average equivalent volume diameter - measured by Möller counting apparatus, expressing volume of each separate grain after electrochemical reduction - a value of 0.57 µm was obtained;
- * as average equivalent surface area - measured from electron microscopic photographs - a value of 1.1 µm was obtained;
- * as average thickness, measured from shadowed replicas obtained by electron microscopy, a value of 0.095 µm was obtained.

[0077] After addition of polystyrene sulphonic acid, followed by decrease of pH in order to flocculate the emulsion, a washing procedure followed by decanting supernatant liquid, and peptization after addition of gelatin, was leading to an emulsion having a weight ratio of gelatin to silver of 0.5 and silver, expressed as an equivalent amount of silver nitrate in an amount of 230 g/kg.

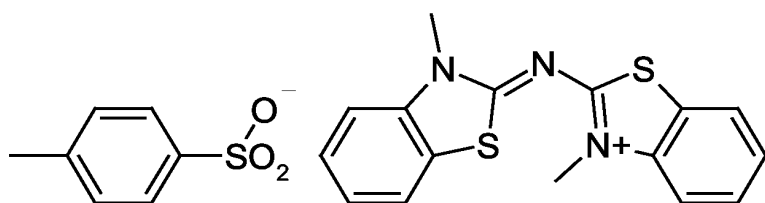
1.2. Chemical sensitization of emulsion E1

[0078] As spectral sensitizers following compounds 1 and 2 were added per 500 g AgNO₃/m²:



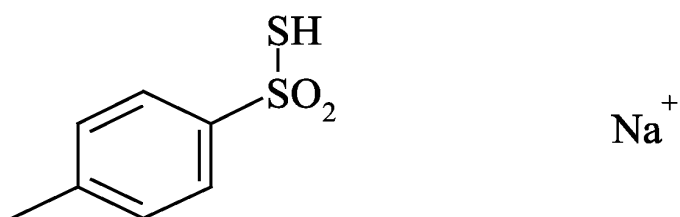
Compound 1

- 3 g of Compound 1 (as a main spectral sensitizer added in an aqueous solution).



Compound 2

- 0.5 g of Compound 2 (as an additional spectral sensitizer)



Compound 3

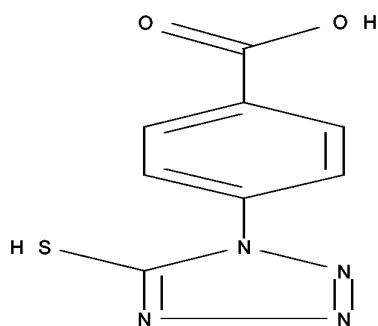
- Compound 3 as stabilizing agent was added in an amount of 1 μ mole per 500 g of AgNO_3 .

As chemical sensitizers were added

[0079]

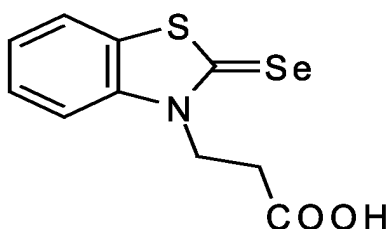
- 0.006 g of a sodium thiosulphate pentahydrate;
- 17.6 μ mole of ammonium gold thiocyanate;
- 0.4 mmole of KSCN;

- 0.75 mmole of compound 5, present as sodium salt,



compound 5

- 0.025 mmole of compound 6



Compound 6

Emulsion E2

2.1. Emulsion preparation

[0080] The emulsion was prepared in the same way as Emulsion A, except for the amount of an emulsion having ultrafine (ca. 0.040 μm) 100 % AgI crystals at the end of the preparation: the said emulsion was added to the reaction vessel in a time of 2 minutes in order to get a total AgI content at the end of precipitation of 0.3 mole % vs. silver precipitated.

2.2. Chemical sensitization of emulsion E2

[0081] As spectral sensitizers same compounds 1 and 2 were added per 500 g silver nitrate, in amounts of 3 g and 1 g respectively.

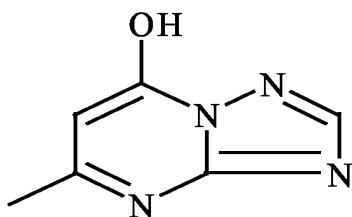
[0082] Compound 3 as stabilizing agent, was added in the same amount of 1 μmole per 500 g of AgNO_3 as to emulsion A.

- 0.008 g of a sodium thiosulphate pentahydrate;
- 11.7 μmole of ammonium gold thiocyanate;
- 0.4 mmole of KSCN;
- 0.75 mmole of compound 5, present as sodium salt and
- 0.025 mmole of compound 6

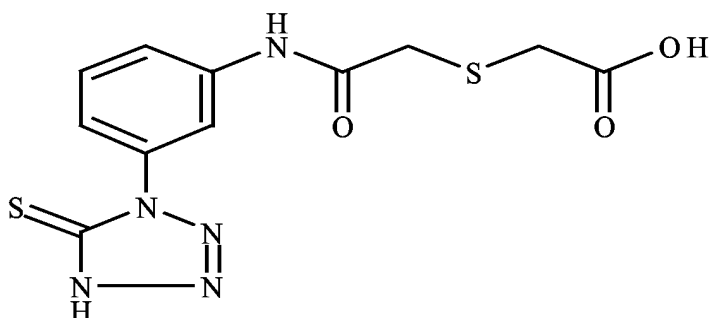
Coating of the materials

[0083] Per mole of silver nitrate, following compounds were added to the light-sensitive silver halide emulsion layer:

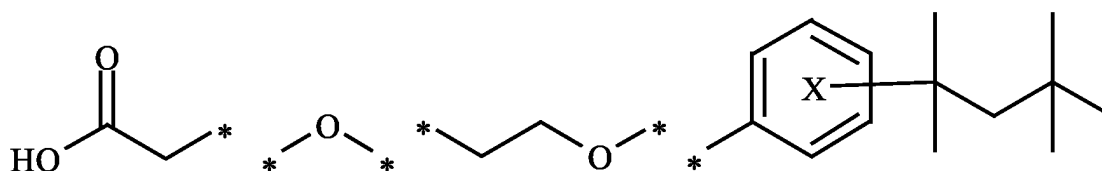
- 0.09 g of stabilizing compound 7, having following structure



- 33 mg of stabilizing compound 8, having following structure

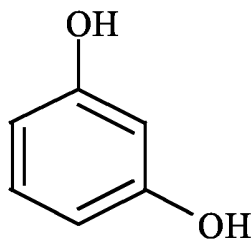


- 12.6 ml of sorbistol
- 47ml of antifoam latex (30% of silicone emulsion in water)
- 5 ml of surfactant compound 9 (45ml/l)



compound 9

- 2.8 g of resorcinol hardener - ses compound 10; having following structure,

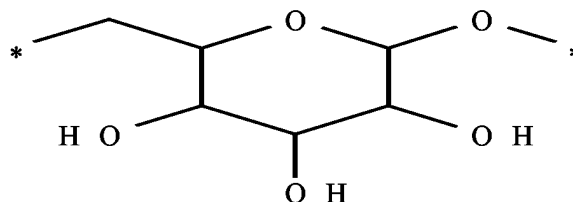


- 0.1 g of polyglycol - compound 11;

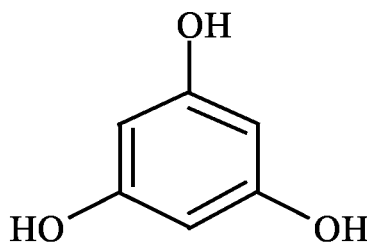


compound 11

- 14.8 ml of dextrane - compound 12 - (M.W.10.000)



- 0.2 g of fluoroglucinol - compound 13



Compound 13

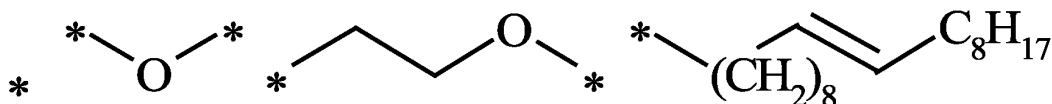
[0084] The emulsion coating solutions thus prepared were coated on a blue colored polyethylene terephthalate support (density of the support measured to be 0.200) in such an amount in order to give a coating weight of 2.25 g/m² per side in terms of AgNO₃ and 1.27 g of gelatin per m² per side.

[0085] The following protective layer was coated thereupon (pH value: 6.20) at both sides:

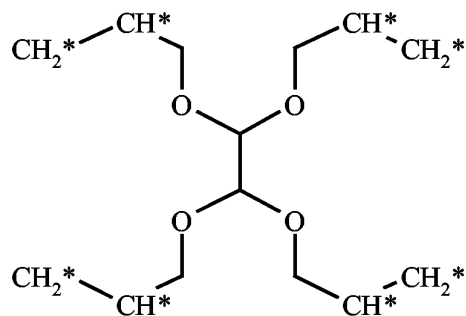
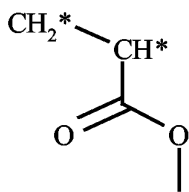
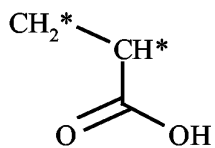
Composition of the protective antistress layer per m² :

[0086]

- 0.7 g of gelatin
- 56 mg of antistatic agent - compound 14

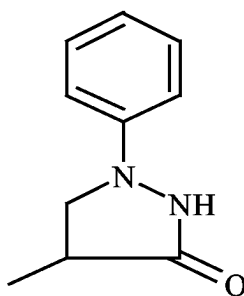


- 225 mg of latex - compound 15;



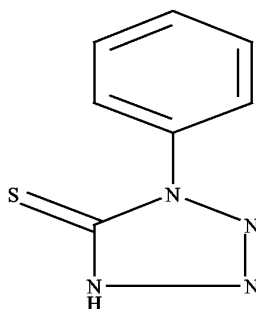
- 10 mg of surfactant - compound 16;
F₃C-(CF₂)₆-COOH NH₃ (Compound 16)
- 10 mg of stabilizing compound 7 (see above);
- 1.5 mg of stabilizing compound 17 (see hereinafter)

compound 17

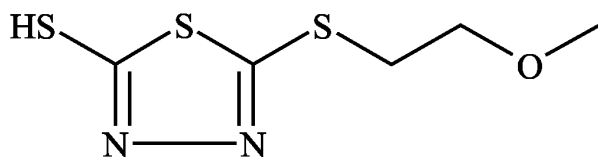


[0087] The following protective layer was coated thereupon (pH value: 6.20) at both sides:

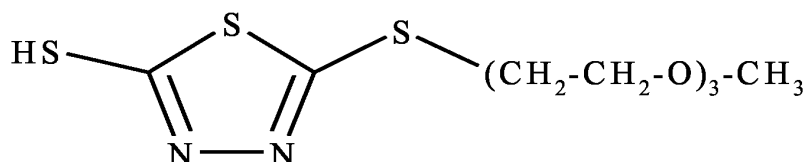
[0088] Image tone modifying compounds (see figures in the Table)



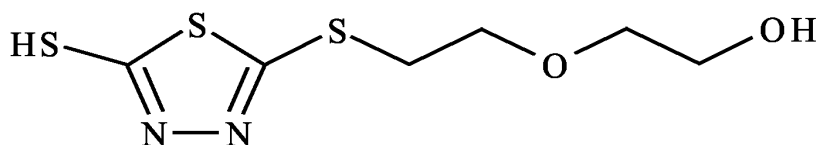
Compound A



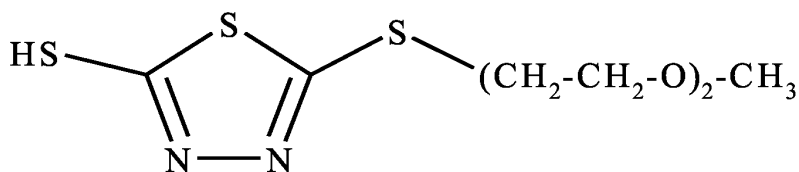
Compound B



Compound C



Compound D



Compound F

[0089] The coating layers of the material were hardened with bis vinyl sulfonyl methyl ether (BVSME) as a hardening agent in order to reduce the swelling degree up to a level of not more than 200 % (after swelling for 3 minutes in demineralized water of 20°C).

[0090] Film materials were numbered 1-11: Nos. 2-6 and 8-11 were coated in the presence of compounds added in favour of image tone of the processed material, while Nos. 1 and 7 were coated without such a compound in the protective antistress layer of the respective film materials. Samples of these coatings were exposed with green light of 540 nm during 0.1 seconds using a continuous wedge and were processed. The processing was run in the developer G138i, trademarked product from Agfa-Gevaert N.V., Mortsel, Belgium, followed by fixing in fixer G334i, trademarked product from Agfa-Gevaert N.V., Mortsel, Belgium, and rinsing at the indicated temperature of 33°C for a total processing time of 90 seconds. A comparison was made with a developing process in a weaker developer having following composition:

Potassium sulphite	23.0
Sodium sulphite	27.0

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(continued)

Boric acid	6.80
EDTA (tetra sodium salt)	1.40
HEDP	0.62
Hydroquinone	16.0
Potassium hydroxide	17.5
Phenidone	0.96
Nitro-6-Benzimidazole	0.06
Methyl benzotriazole	0.048
Acetic acid	9.54
Diethyleneglycole	14.5
Glutardialdehyde	3.50
Potassium metabisulphite	6.00
Potassium bromide	3.20
Potassium iodide	0.008

[0091] Following sensitometric data have been summarized in the Table 1:

- Fog "F", given as an integer after having multiplied the real fog density as measured with a factor of 1000;
- Speed "S", given as an integer after having multiplied the sensitivity measured at a density of 1.00 above minimum density as measured with a factor of 100; - an decrease of speed with a figure of 30 corresponding with a doubling in speed -;
- Image tone "IT", evaluated from figures corresponding with Dr, wherefore data are summarised with respect to the density Dr measured through a red filter at a blue density Db=2: the higher this value (figure multiplied by a factor of 100), the better (more desired blue-black instead of undesired red-brown) is the color of the developed silver.
- Differences in speed " ΔS ": loss in speed after development in a weaker developer vs. in stronger developer G138i.

Table 1

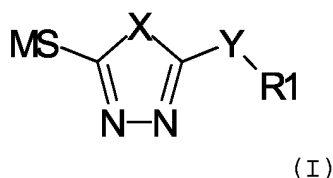
Matl. No. (cmpd)	Em.	Mmole/mole Of cmpd.	F	S	IT	ΔS
1 (No)	E2	-	201	170	1.89	-2
2 (A)	E2	3.36	200	182	1.93	-13
3 (B)	E2	3.36	200	184	1.91	-9
4 (C)	E2	3.36	204	178	1.93	-4
5 (D)	E2	3.36	204	179	1.92	-4
6 (F)	E2	3.36	203	171	1.93	-6
7 (No)	E1	-	199	167	1.90	-1
8 (A)	E1	3.36	200	171	1.95	-9
9 (B)	E1	3.36	199	186	1.94	-8
10 (D)	E1	3.36	198	182	1.94	-1
11 (F)	E1	3.36	203	167	1.95	-2

[0092] Presence of compound F in the inventive materials Nos 6 and 11 is clearly in favour of image tone with, moreover an increase in speed and better developability characteristics.

Claims

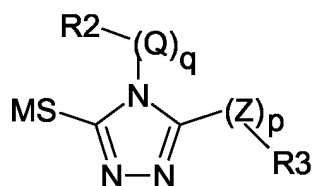
1. Light-sensitive silver halide photographic film material, comprising at least one light-sensitive silver halide emulsion layer overcoated with a protective antistress layer, said light-sensitive emulsion layer(s) having {111} tabular grains

or crystals in an amount covering at least 50 % of the total projective grain surface of all grains, **characterized in that** said protective layer, said light-sensitive layer(s) or both said protective layer and said light-sensitive layer(s) comprise, in an amount of at least 0.5 mmole per mole of silver halide coated, a heteroaromatic compound according to the general formula (I) or (II),



wherein :

X represents O or S,
 M represents hydrogen or a monovalent counterion,
 Y represents a divalent linking group,
 R1 represents $-\{O(CH_2)_n\}_m-OH$, wherein
 n represents an integer from 2 to 5 and
 m represents an integer from 1 to 5;



wherein :

M represents hydrogen or a monovalent counterion,
 Z and Q each independently represents a divalent linking group, so that Z and Q may be the same or different,
 R2 is selected from the group consisting of hydrogen, a substituted or unsubstituted aliphatic group, a substituted or unsubstituted aromatic group, a substituted or unsubstituted heteroaromatic group, and $-\{O(CH_2)_n\}_m-OR_4$,
 R3 is selected from the group consisting of hydrogen, a substituted or unsubstituted aliphatic group, a substituted or unsubstituted aromatic group, a substituted or unsubstituted heteroaromatic group, and $-\{O(CH_2)_n\}_m-OR_5$, provided that at least one of R2 and R3 represents $-\{O(CH_2)_n\}_m-OR_4$ or $-\{O(CH_2)_n\}_m-OR_5$ respectively,
 p and q each independently represent 0 or 1,
 R4 and R5 are each independently selected from the group consisting of hydrogen, a substituted or unsubstituted aliphatic group, a substituted or unsubstituted aromatic group and a substituted or unsubstituted heteroaromatic group, so that R4 and R5 may be the same or different,
 n represents an integer having a value from 2 to 5 and m represents an integer having a value from 1 to 5.

2. Material according to claim 1, wherein the compound according to general formula (I) is a 1,2,4-thiadiazole, wherein R1 stands for $-\{O(CH_2)_2\}_m-OH$, where m is an integer having a value of from 1 to 5.
3. Material according to claim 1, wherein the compound according to general formula (II) has as aliphatic divalent

linking group $-\{O(CH_2)_n\}_m-OR_4$, wherein n equals 2 and R4 represents hydrogen.

4. Material according to any one of claims 1 to 3, wherein said hetero aromatic compound is present in an amount between 1 and 5 mmole per mole of silver halide.
5. Material according to any one of claims 1 to 4, wherein the tabular grains have an average grain thickness from 0.05 up to 0.15 μm .
6. Material according to any one of claims 1 to 5, wherein said silver halide grains are composed of silver bromoiodide.
7. Material according to claim 6, wherein said silver bromoiodide grains have all silver iodide, present on the grain surface thereof, in an amount in order to provide an average amount of silver iodide over the whole grain volume, based on silver, in the range from 0.05 up to 0.50 mole%.
8. Material according to any one of claims 1 to 7, wherein said grains have been made sensitive to the ultraviolet and/or blue range of the wavelength spectrum.
9. Material according to any one of claims 1 to 7, wherein said grains have been made sensitive to visible light in the range from 540 up to 570 nm of the wavelength spectrum.
10. Screen/film combination or system comprising a film material according to claim 8 or 9, in contact with one supported or self-supporting X-ray intensifying screen or sandwiched between a pair of said screens, wherein said intensifying screen or screens comprise(s) luminescent phosphor particles emitting at least 50 % of their emitted radiation in the wavelength range for which said material has been made spectrally sensitive.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 01 00 0179

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.7)
A	US 5 229 249 A (KATOH ET AL) 20 July 1993 (1993-07-20) * column 1, line 6 - line 13 * * column 2, line 5 - line 17 * * column 2, line 40 - line 68 * * column 4, line 25 - line 37 * * column 6, line 16 - column 11, line 54 * * column 20, line 34 - line 58 * * claims 1,8,11 *	1-10	G03C1/76 G03C1/005 G03C5/17
A	US 5 994 037 A (TWIST ET AL) 30 November 1999 (1999-11-30) * column 1, line 13 - line 15 * * column 1, line 66 - column 2, line 31 * * column 3, line 1 - line 12 * * column 4, line 8 - column 13, line 50 * * claims 1,4-7,9-12,20 *	1-11	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			G03C
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 7 December 2001	Examiner Binder, R
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